

# Plastics, Rubber, and Paper Recycling

## A Pragmatic Approach

EDITORS

**Charles P. Rader**, *Advanced Elastomer Systems, L.P.*

**Sheryl D. Baldwin**, *Philip Morris Research Center*

**David D. Cornell**, *Eastman Chemical Company*

**George D. Sadler**, *National Center for Food Safety and Technology*

**Richard F. Stockel**, *Tosoh USA, Inc.*

Developed from a symposium sponsored by the divisions of Polymer Chemistry, Inc.; Polymeric Materials: Science and Engineering, Inc.; Cellulose, Paper, and Textile Chemistry; Agricultural and Food Chemistry; Environmental Chemistry, Inc.; Business Development and Management; Rubber, Inc.; and the Macromolecular Secretariat at the 208th National Meeting of the American Chemical Society, Washington, DC, August 21–25, 1994



American Chemical Society, Washington, DC 1995

# Plastics, rubber, and paper recycling



## Library of Congress Cataloging-in-Publication Data

Plastics, rubber, and paper recycling: a pragmatic approach / editors, Charles P. Rader... [et al.].

p. cm.—(ACS symposium series; 609)

“Developed from a symposium sponsored by the divisions of Polymer Chemistry... [et al.] at the 208th National Meeting of the American Chemical Society, Washington, D.C., August 21–25, 1994.”

Includes bibliographical references and indexes.

ISBN 0–8412–3225–X

1. Plastics—Recycling—Congresses. 2. Rubber, Reclaimed—Congresses. 3. Waste paper—Recycling—Congresses.

I. Rader, Charles P., 1935– . II. American Chemical Society. Division of Polymer Chemistry. III. Series.

TP1122.P566 1995  
338.4'76284458—dc20

95–37097  
CIP

This book is printed on acid-free, recycled paper.



Copyright © 1995

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each chapter in this volume indicates the copyright owner's consent that reprographic copies of the chapter may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per-copy fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating a new collective work, for resale, or for information storage and retrieval systems. The copying fee for each chapter is indicated in the code at the bottom of the first page of the chapter.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

American Chemical Society  
Library  
1155 16th St., N.W.  
Washington, D.C. 20036



# 1995 Advisory Board

## ACS Symposium Series

**Robert J. Alaimo**  
Procter & Gamble Pharmaceuticals

**Mark Arnold**  
University of Iowa

**David Baker**  
University of Tennessee

**Arindam Bose**  
Pfizer Central Research

**Robert F. Brady, Jr.**  
Naval Research Laboratory

**Mary E. Castellion**  
ChemEdit Company

**Margaret A. Cavanaugh**  
National Science Foundation

**Arthur B. Ellis**  
University of Wisconsin at Madison

**Gunda I. Georg**  
University of Kansas

**Madeleine M. Joullie**  
University of Pennsylvania

**Lawrence P. Klemann**  
Nabisco Foods Group

**Douglas R. Lloyd**  
The University of Texas at Austin

**Cynthia A. Maryanoff**  
R. W. Johnson Pharmaceutical  
Research Institute

**Roger A. Minear**  
University of Illinois  
at Urbana–Champaign

**Omkaram Nalamasu**  
AT&T Bell Laboratories

**Vincent Pecoraro**  
University of Michigan

**George W. Roberts**  
North Carolina State University

**John R. Shapley**  
University of Illinois  
at Urbana–Champaign

**Douglas A. Smith**  
Concurrent Technologies Corporation

**L. Somasundaram**  
DuPont

**Michael D. Taylor**  
Parke-Davis Pharmaceutical Research

**William C. Walker**  
DuPont

**Peter Willett**  
University of Sheffield (England)

# Foreword

**THE ACS SYMPOSIUM SERIES** was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually “snapshots in time” of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

# Preface

**PROPER DISPOSAL OF THE MATERIALS** from which thousands of different articles have been fabricated is a major problem facing our high-technology society. Prime attention is being given to the recovery of value from articles derived from polymers—paper, rubber, and plastics.

In the symposium upon which this book is based, seven American Chemical Society divisions participated under the aegis of the Macromolecular Secretariat. The purpose of the symposium was to provide authoritative updates on the technology, logistics, and economics of the recovery of value from discarded articles of paper, rubber, and plastics used in food packaging, automotive, and other application areas. The attendance and subsequent response to the symposium provided ample evidence that this task was accomplished.

In this volume, the status of the recycling of rubber, plastics, paper, and food packaging is reported and analyzed to early 1995 by a variety of experts from each of these areas of polymer technology. Introductory overview articles provide up-to-date summaries on the recycling of each of these polymeric materials. Concluding the volume is a look into the future research of polymer recycling.

The scope of the volume is quite broad by design. To adequately deal with this breadth, a team of five editors was assembled with expertise in paper, plastics, rubber, food packaging, and the business aspects of polymer recycling. This team selected the symposium papers for inclusion in the volume and secured additional invited papers to fill voids in the symposium coverage of the topic. The breadth of this volume is indicative of the many skills and backgrounds necessary to competently deal with the recycling of polymeric materials and make it commercially viable.

The variety of individuals to whom this volume should be of value is just as broad as that of those who collaborated in its creation. It is intended that the readership include researchers in numerous institutions and businesses, technologists in all polymer areas, managers and planners in existing and future businesses based on polymer recycling, individuals formulating and influencing government policy over materials disposal and recovery, and those seeking to derive value from discarded polymer articles that have given a useful lifetime of service.

The future of the emerging industry of polymer recycling will be influenced critically by the events of the next decade. It is hoped that the contents of this volume can provide guidance and information to those shaping these events. In recycling, as in life, we must focus on the future, for that is where all of us will spend the rest of our lives.

**CHARLES P. RADER**  
Advanced Elastomer Systems, L.P.  
388 South Main Street  
Akron, OH 44311-1058

**SHERYL D. BALDWIN**  
Packaging Design and Development  
Philip Morris Research Center  
P.O. Box 26603  
Richmond, VA 23261

**DAVID D. CORNELL**  
Eastman Chemical Company  
P.O. Box 1995  
Kingsport, TN 37762

**GEORGE D. SADLER**  
National Center for Food Safety and Technology  
Illinois Institute of Technology  
6502 South Archer Road  
Summit-Argo, IL 60501

**RICHARD F. STOCKEL**  
Tosoh USA, Inc.  
1952 Route 22 East  
Bound Brook, NJ 08805-1520

July 15, 1995

## Chapter 1

# Polymer Recycling: An Overview

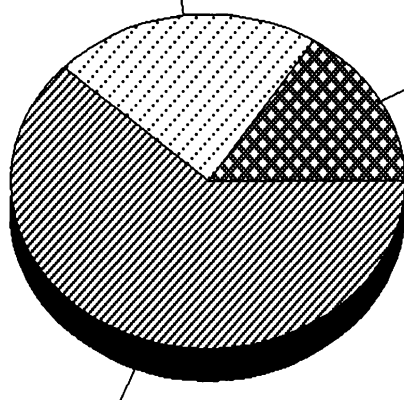
Charles P. Rader<sup>1</sup> and Richard F. Stockel<sup>2</sup>

<sup>1</sup>Advanced Elastomer Systems, L.P., 388 South Main Street,  
Akron, OH 44311-1058

<sup>2</sup>Tosoh USA, Inc., 1952 Route 22 East, Bound Brook, NJ 08805-1520

As the twentieth century nears its end, a perceived problem facing industrialized societies is the disposal of our solid wastes (1). Thus, the U.S. generates (2) 207 million tons of municipal solid waste each year. The great majority of this waste is destined for landfills (Figure 1), with significant but much smaller amounts incinerated or recycled.

**Recycling & Recovery 22.0%**



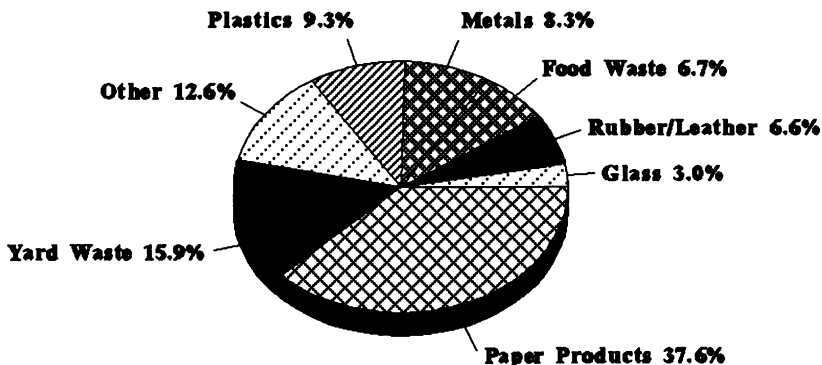
**Incineration 16.0%**

**Landfill 62.0%**

**Figure 1** *Disposal of municipal solid waste in USA, 1993.*

0097-6156/95/0609-0002\$12.00/0  
© 1995 American Chemical Society

In 1993 municipal solid waste had the composition given in Figure 2. An examination of these data finds a major fraction (paper, plastics, rubber/leather) of our solid wastes to be derived from polymeric materials of known composition. Thus, the solution of our solid waste disposal problem is intimately related to the recycle of polymers. All commercial polymers -- paper, plastics, rubber -- are subject to recycling.



**Figure 2** *Composition of municipal solid waste in USA, 1993.*

Some cardinal benefits of polymer recycling are a reduction of waste generation, less need for landfills, and a reduction in consumption of resources. Past benefits of polymer recycling have been modest, significant and progressively growing. Almost certainly, these benefits will grow markedly over the next decade. Yet, recycling is an industrial process and, therefore, subject to the constraints of technology and marketplace factors.

In 1988, there were about one thousand curbside recycling programs in the U.S. Today, there are more than seven thousand such programs gathering recyclables from over 100 million people. At present, (3) approximately 34.0 percent of paper, 22.0 percent of glass, 26.1 percent of steel, 3.5 percent of plastics and 5.9 percent of rubber and leather are recycled.

It is obvious by this low value for plastics recycle that there must be real economic hurdles. The many varieties of polymer fabrications are difficult to sort, clean and reformulate. These are just some of the inherent problems in polymer recycle which need improvement to lower operating costs. Lowering recycle costs and improving their quality are ongoing problems in polymer recycling.

Cellulose, our most abundant polymer, is also the most recycled one, in both the absolute quantity (26.5 million tons, 1993) and percentage (34%) of paper and paper products recovered from municipal solid waste (MSW). A series of papers in this monograph will cover the logistics, technology, engineering and applications of the recycle of paper products. Though a success story in itself, this recycle of paper has generally had a somewhat lower profile than the recycle of plastics, rubber or other industrially significant polymeric materials.

The recovery of polymeric materials from containers and packaging constitutes a highly significant recycle effort with polymer systems (2). A series of papers in this monograph is dedicated to the recycle of containers and packaging in contact with foods and beverages.

A major polymer application area is in the automotive industry, where the consumption of plastics is increasing due to the governmental push to lower gasoline usage by reducing the overall weight of the vehicle. Compared to the recycle of metals, polymer recycle is still in its infancy. Recently, the major car manufacturers have made (4) a commitment to cooperate with their polymer suppliers to enhance the recyclability of polymers utilized in automobiles. It is estimated that about 1.9 billion pounds of polymer are consumed annually in the manufacture of motor vehicles.

If the automobile is to truly become recyclable, this large stream of mixed polymers must be salvaged within reasonable economic bounds. The complexity of this recycle is apparent by virtue of the variety of materials -- thermoset polyurethanes, filled thermoplastics and a wide variety of rubber articles -- used in today's new motor vehicle.

It is possible that in the future, the marketer of a new motor vehicle (or other assembled device) will be legally obligated (4) to take it back from the consumer when the latter has ceased to use it. This will thus motivate the automotive companies and their suppliers to design for recycle, enabling the rapid dismantling of an exhausted vehicle and the removal of its component plastic, rubber, cellulose and metal parts. It will also provide impetus for the use of fewer different rubber and plastic materials, with a maximum amount of mutual compatibility.

A partial solution to the problem of polymer recycle in the automotive and appliance industries will be to increase the use of toughened polyolefins, particularly polypropylene. However, the recyclability of the specialized elastomers used in aggressive environments like under-the-hood applications poses a real technological challenge. Perhaps the standardization of a small number of different rubbers and plastics is the answer. This standardization would offer unique opportunities for the use of thermoplastic elastomers (TPEs) compatible with specific thermoplastics. These particular problems are discussed in this monograph and analyzed by scientists from a major automotive company. The recovery of materials from pneumatic tires is a unique and massive problem now receiving attention on a national scale.

Also included in this monograph section is a provocative article stating that the first and second laws of thermodynamics dictate that only 25 percent of existing polymer waste can be recycled economically. The article asserts that the remainder of polymeric materials should be incinerated, a conclusion which many at present would consider politically unacceptable. Perhaps it is time for all responsible parties to educate the public concerning this volatile issue.

Depolymerization of polymers to their monomers or other petrochemicals appears to offer only niche opportunities, such as the alcoholysis of polyethylene terephthalate (PETE). Yet, there is a significant effort, particularly in Europe, to pyrolyze commingled polymer waste to produce valued petrochemicals. The economic value of depolymerization should be viewed in the light of government requirements and subsidies, such as those in Germany in the mid-1990's.

### ***Conditions For Success Of Polymer Recycling***

While social and political forces can provide the motivation for polymer recycle, they cannot guarantee its ongoing success. This success can only come from satisfying a number of specific conditions, which include:

1. Recycle must make good business sense. It must obey the laws of economics, just as science and technology must obey the laws of thermodynamics. Those willing to venture their efforts and capital on recycling must ultimately be able to generate a viable business. Quite commonly, the polymer recycler is recurrently confronted with (1) an uncertain raw material supply with gross variation in quality, (2) difficult-to-predict governmental policies and regulations and (3) competitive products which are a commodity in nature and subject to broad shifts in the market place.
2. Recycle must be based on good science and good technology. If it is not, it will not make good business sense.
3. Its practice must be acceptable to a broad majority of consumers and voting citizens. They are the ones who pay its cost and expect to enjoy its benefits.
4. It must embrace a suitable compromise of the present with the future. Any reasonable chance of its success requires that at least a part of the present be sacrificed for the benefit of the future. Further, these benefits will likely be reaped, not by those foregoing the present, but by their posterity.
5. Recycle practice must be compatible with citizenry life style and population density. Thus, the practice in one community or region could be inappropriate for another. The recycling needs for New Jersey (population density 1042/square mile) will be markedly greater than those of Wyoming (population density 5/square mile). Further, these specific needs will be influenced by climate and physical geography.



***Economics Of Recycle***

Key parameters of the feasibility of recycling a polymeric material are the cost and quality of the recyclate relative to that of the corresponding virgin material (VM). If the quality is competitive with that of the VM, the recyclate is then competing head-on with the VM, and price becomes of paramount importance. Polymer recyclates are generally inferior to first-quality virgin resins. They commonly compete with broad-specification virgin resins, which sell at prices 40 to 80 percent of those of the first-quality resins.

Table I gives the price (\$) of several high-volume polymeric recyclates versus that of the respective VMs. A viable market for recyclate requires a price no higher than that of the VM, and preferably a price significantly lower since recyclate quality can, at best, be equal to or typically somewhat less than that of the VM.

**TABLE I**  
**RECENT YEAR-END U.S. DOLLAR PRICES\* PER POUND**  
**OF RECYCLED AND VIRGIN POLYMER MATERIALS**

<b><u>POLYMER MATERIAL</u></b>	<b><u>YEAR</u></b>			
	<b><u>1991</u></b>	<b><u>1992</u></b>	<b><u>1993</u></b>	<b><u>1994</u></b>
Paper pulp				
Recycle	--	--	--	0.07
Virgin	--	--	--	0.41
Polyethylene terephthalate (PETE)				
Recycle	0.48	0.49	0.52	0.52
Virgin	0.66	0.66	0.66	0.76
High density polyethylene (HDPE)				
Recycle	0.38	0.34	0.30	0.42
Virgin	0.38	0.36	0.36	0.50
Low density polyethylene (LDPE)				
Recycle	--	0.28	0.29	0.34
Virgin	0.30	0.39	0.37	0.53
Polystyrene (PS)				
Recycle	0.40	0.44	0.44	0.44
Virgin	0.44	0.47	0.49	0.65

\*Sources: Reference 5 for PETE, HDPE, LDPE, PS. Dr. Sheryl Baldwin for paper pulp. Prices are those at the end of 1994.

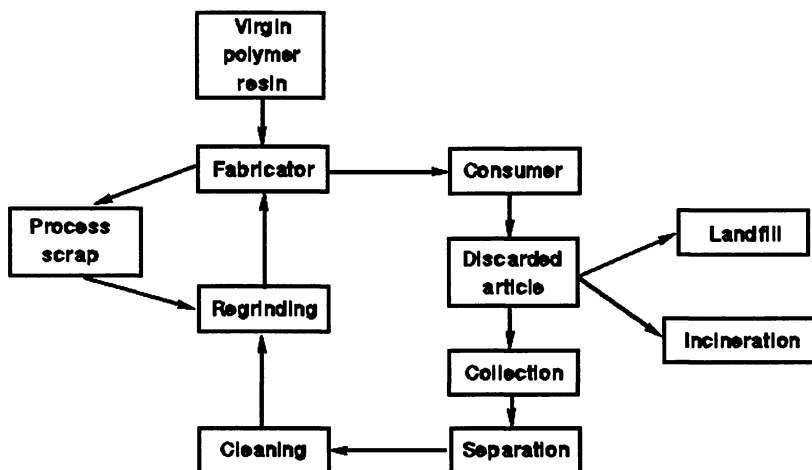
A major uncertainty for recyclate is the market price of the competitive VM. The immense price difference between recycled and virgin paper pulp indicates clearly the economic incentive for producing recycled paper. This has resulted in paper being the most widely recycled polymeric substance.

During 1994, the four plastic resins charted in Table I had a 15 to 43 percent increase in the price of the VMs, giving the recyclate a 16 to 46 percent cost advantage, which could be reversed in subsequent years, based on market conditions. This is an encouraging trend for the recyclates since their direct competition is their respective VMs. It is possible, and has been experienced during business recessions, that the price of recycle resin could exceed that of the corresponding virgin material.

The "wild card" in the economics of polymer recycling is the variety of mandates, regulations and economic incentives now emanating from all levels of government - local, state and federal. Though these government pressures reflect the values and desires of our citizenry, it is quite important that they be based on good science and technology, and sound economics. These pressures -- aimed to foster the success of recycling -- must be derived from good strategic planning and well-thought-out tactics, to produce meaningful motivation and give direction to the recycling effort.

### ***Logistics And Technology***

Much of the focus of the chapters in this monograph is on the technology of polymer recycle. Of comparable importance, however, are the mundane logistics surrounding the use of this technology. Figure 3 depicts the sequential steps in recycling a useful article fabricated from a macromolecular substance (6). A pronounced difficulty in any of these steps can make recycle impractical relative to some other disposal method (incineration, landfill).



**Figure 3** *Flow diagram for polymer recycle.*

The first step in the recycling process is collection of the used article -- be it a newspaper, beverage bottle, automobile tire or milk jug. Concurrently with and subsequent to collection is the separation of the articles by compositional similarity. The Society of the Plastics Industry (SPI) has developed (7) a simple coding system for designating the chemical nature of fabricated plastic bottles. This system is now widely used to mark for recycle a great variety of thermoplastic articles now fabricated in the U.S. A similar system for plastic and TPE automotive parts has been developed (8) by the Society of Automotive Engineers (SAE). Analogous systems for marking rubber articles are currently under development by the SAE Committee on Automotive Rubber Specifications and the International Standards Organization (ISO, Technical Committee 45). All of these codes simply designate the nature of the polymer in the fabricated article, and not its recyclability. These identification codes merely assist the recycling effort. They are not a certification of recyclability.

The separation step should result in all of the articles in a given category being compositionally compatible. These parts must now be cleaned to remove impurities, and then ground into pellets for drying (to remove troublesome moisture) and subsequent refabrication. Additives (for specific improvements in performance) may be compounded into the pellets prior to refabrication. It is also not uncommon for pellets of compatible polymer systems to be blended together.

The most desirable situation is for the recycle to have properties and performance essentially those of the virgin material. This has been attained (9) for TPEs but is not common. Some thermoplastics can be recycled to give a resin suitable for direct competition with the virgin material (such as PETE in food contact uses). A more likely prospect is for the recycled materials to have properties and appearance below those of the VMs, thus destining them for lower performance -- but still practical -- applications. Such is the case with the different plastic lumbers now in the consumer market as a replacement for wood. Properly employed, these synthetic lumbers can compete with natural wood on a performance/cost basis. Polymer recycle is often used in less demanding applications for the generic material.

Critical to the logistics of polymer recycle are the chemistry and morphology of the discarded article. The recycle of paper is thus the recycle of an aggregate of bonded cellulose fibers, with the reuse involving the removal of ink and other non-cellulose constituents of the paper. Composite materials -- pneumatic tires, drive belts, reinforced plastics, for example -- pose major obstacles to their recycle, to such a degree that it is often not practical or economically viable.

Thermoset articles -- conventional vulcanized rubber, melamine plastics, phenolic resins -- are far more difficult to recycle than thermoplastic materials (10). Their recycle must involve an irreversible chemical change of the material due to the necessity to cleave the crosslinks between the polymer chains. The recycle of a thermoplastic material, be it a rigid plastic or a rubber, involves a simple change of the physical state of the polymer -- that of melting, shaping the melt and subsequently cooling it below the melting point ( $T_m$ ) to enable resolidification. This

melting/resolidification cycle is reversible and may be carried out several times (up to 5 for PETE or a TPE) with little or no significant loss in properties. Thus, a thermoplastic article is capable of repeated recycling, being limited by thermal and oxidative degradation.

### ***Alternatives To Recycle***

The recycle of polymeric materials will likely never come close to 100 percent, as aptly pointed out in Stein's chapter of this monograph. Other means of disposal -- incineration, landfill -- will in many cases prove more practical and environmentally friendly than recycle. The best candidate polymers for generic resin recycle are those thermoplastic in nature, such as HDPE, PETE or a TPE. Major success stories in the recycle arena are PETE from soft drink bottles (42% recycle (2)) and high density polyethylene (HDPE) (24% recycle (2)) from milk and water jugs.)

The most difficult polymeric materials to recycle are those thermoset in nature -- especially reinforced composite materials where a rubber or plastic is reinforced with a textile cord or a metal. It is just not practical to separate the polymer matrix from the reinforcement to enable subsequent recycle of the materials. Serumgard and Eastman discuss in their chapter of this monograph the immense logistical and technological problems inherent in the proper disposal of pneumatic tires. A similar argument is valid for rubber drive belts and glass-reinforced plastics.

For these difficult-to-recycle polymer systems, incineration is an appealing alternative method of disposal. Approximately 90 percent of the gas and oil consumed in the world (11) is burned to generate energy -- thermal for warmth and mechanical for transportation. Safe, environmentally acceptable methods of incineration have been developed for most commercial polymeric materials. It offers a ready and reasonable means of disposing of the 3 to 4 billion scrap tires currently stockpiled in the U.S.

The least desirable method of discarding a polymeric material is landfilling, which totally fails to harness the utility of the polymer or even its inherent energy content. The undesirability of this method will progressively increase with population density and the cost of fossil fuels. For many communities, especially those in low population areas, landfilling will, by default, remain the most practical means of waste disposal.

### ***References***

1. *Rubber World*, Mar. 1991; *Plastics Engineering*, Sept. 1990, p. 29.
2. Franklin Associates Limited, *Characterization of Municipal Solid Waste in the United States, 1994 Update*, Report No. EPA 530-5-94-042, Nov. 1994.
3. *National Geographic*, July 1994.
4. Schultz, J., *Wards Auto World*, Dec. 1994, p. 21; Labana, S., *Wards Auto World*, Feb. 1995, p. 19.
5. *Plastics News*, Dec. 26, 1994, p. 102.

6. Purgly, E.P., Rader, C.P., and Gonzalez, E.A., *Rubber and Plastics News*, Aug. 31, **1992**, p. 15.
7. *The SPI Resin Identification Code*, Society of the Plastics Industry, Inc., Washington, D.C.
8. SAE J 1344, *Marking of Plastic Parts*, Society of Automotive Engineers, Warrendale, PA.
9. Alderson, M., and Payne, M.T., *Rubber World*, May **1993**, p. 22.
10. Purgly, E.P., Gonzalez, E.A., and Rader, C.P., *Society of Plastics Engineers*, ANTEC '92, Detroit, Michigan, May **1992**.
11. *Modern Plastics*, Sept. **1990**, p. 20.

RECEIVED May 2, 1995

## Chapter 2

# Curbside Recycling Infrastructure: A Pragmatic Approach

Raymond G. Saba<sup>1</sup> and Wayne E. Pearson<sup>2</sup>

<sup>1</sup>Center for Plastics Recycling Research, Rutgers, The State University  
of New Jersey, New Brunswick, NJ 08093

<sup>2</sup>Packaging Research Foundation, P.O. Box 189,  
Kennett Square, PA 19348

This chapter describes a pragmatic view of the current curbside recycling infrastructure for reclaiming polymers from the post-consumer solid waste stream. It concludes that the infrastructure is not economical, and it describes a future scenario by which technology improvements could achieve viable economics.

Plastics recycling is an important aspect of a much broader issue that our society is attempting to understand called "sustainable development", that is, the rate of growth of development in products and services that can be sustained by an environment and its resources. While innovation in products and services has created our high standard of living, it is prudent that we develop the necessary understanding to provide the environmentally sound management of the resources which sustain our society. Plastics recycling, through numerous technologies, is being investigated for its potential contribution to developing such an approach.

Polymers are a relatively new material to our product world when compared to glass, metal, paper and clay-based materials that have a history of several thousand years. The demands of the mid-20th century war operations accelerated the development and use of these relatively new materials because of their unique capability to be customized for specific end uses. Polymeric materials offered unique advantages through their inherent light weight, their broad range of properties related to strength, durability, moldability and colorability, as well as through their relatively low energy requirements in converting resin to manufactured product. Whether as virgin materials, blends, alloys or composites, polymeric materials provided a quantum leap forward in products and services to our society and the world. Every advanced culture in history is distinguished by the sophistication of both the materials and tools developed for its products and services. Polymeric materials, as the newcomer, has been able to greatly enhance that sophistication over a relatively short span of 50 plus years.

0097-6156/95/0609-0011\$12.00/0  
© 1995 American Chemical Society

The 1993 sales of virgin polymers were approximately 70 billion pounds. About one third of the material was used for packaging and transportation, relatively short-life products; the balance was used for construction, furniture, appliances, electrical and other longer-life products (1).

Interestingly, the recycling of plastics scrap is nearly as old as the manufacture of virgin polymers themselves, however the practice stems from the economic need to achieve maximum material utilization efficiencies. In large part, this is viable because approximately 90% of the virgin polymer production is thermoplastics (2), that is, capable of being molded or formed into a final product by the application of heat and pressure. As a consequence, rejected product (or related trim and scrap) in a molding operation has the potential to be recycled back into the molding process to produce a product that meets virgin specifications. The total quantity of in-plant recycling (pre-consumer), considering the polymer, intermediates and finished product, is estimated to be about 4 billion pounds per year (3). This recycling know-how provides a valuable technological cornerstone for the post-consumer recycling challenge.

Post-consumer plastics recycling, as an environmental issue, received recent national attention primarily from the public's concern about solid waste disposal. This concern was more focused on plastics through the public's everyday interaction with the plastics packaging discards entering the municipal solid waste (MSW) stream from consumer products. In 1993, over 34% by weight of the total MSW was containers and packaging materials, of which plastics represented 12% or 16 billion pounds (4).

A quite significant change has occurred in the management of MSW from 1985 to 1992 (5) (See Table 1). Although MSW has grown 24% from 164 million tons to 203 million tons, there has been a significant shift away from landfilling, the traditional means of waste disposal, to recycling and energy recovery. Recycling, including composting, has doubled to 21%, and energy recovery has tripled to 16%.

	1985	1992
Total MSW (Mil. Tons)	164	203
Recycling	10%	21%
Energy Recovery	5%	16%
Landfilling / Incineration	85%	63%

### Post-Consumer Polymer Recycling Process

Recycling post-consumer polymers is a tremendous challenge, economically as well as technically. Economically, the objective is to sell "trash" to someone, since post-consumer solid waste is "trash" from a general viewpoint. Technically, the challenge is to process the trash into quality raw materials that can be manufactured into products having acceptable value to a buyer. In total scope, from the processing of the

waste plastics to the development of markets for the recovered polymers, it is a challenge comparable to establishing a whole new industry.

The raw material source, municipal solid waste (MSW), contains literally thousands of potentially recyclable items, although few are being recycled. Currently, the ten most commonly recognized items commercially recycled today are newspapers, corrugated paperboard, aluminum and steel beverage cans, tin cans, three colors of glass bottles, PET soft drink bottles and HDPE milk, water and juice bottles. The aluminum and PET beverage containers were added to the list in the past two decades, and very recently, the HDPE beverage container has been included. However, with this embryonic recycling infrastructure, few other materials in the MSW have the economic viability for recycling.

Despite the fact that only the top ten items in the trash are technically and economically viable, a substantial infrastructure for recycling has arisen. There are two major reasons for this occurrence. First, the markets for the reclaimed post-consumer beverage containers and newspapers are huge and well established, so when the quality, availability and price of the reclaimed materials are acceptable, they can compete effectively either as substitutes for, or as complements to, virgin materials. The second reason is the willingness of homeowners to subsidize the recycling infrastructure by providing free labor through the cleaning, sorting and curbside set-out of the recyclable items from their trash. Although the curbside collections only amount to about 2.5 % by weight of the MSW (6), the uncrushed beverage containers and the newspapers make up half of the volume of their trash, when yard waste is excluded. Thus, homeowners are reinforced in their belief that, through recycling, they are making a worthwhile contribution to the environment.

Compared to newspapers and non-plastic beverage containers which have been recycled for decades, the recycling of plastic beverage containers has had significant growth in less than a decade. This is shown by the rapid increase in the number of collection programs,

<b>GROWTH IN INFRASTRUCTURE &amp; MARKET FOR RECLAIMED POLYMER</b>		
<b>Year</b>	<b>1985</b>	<b>1993</b>
<b># of Collection Programs</b>	0	9400
<b># of MRF's</b>	0	198
<b># of Reclamation Plants</b>	3	337
<b>PET (Mil. lbs)</b>	100	448
<b>HDPE (Mil. lbs)</b>	25	450
Source: American Plastics Council		

material recovery facilities (MRF's), plastics reclamation plants, and the end-use markets for the reclaimed polymers (See Table 2).

Adding to the legitimacy of the embryonic plastics recycling industry, a pilot project has been initiated to make recycled PET and HDPE two of the first recycled commodities electronically traded on the Chicago Board of Trade (7). In addition,



the Center for Plastics Recycling Research (CPRR) at Rutgers University is working with American Society for Testing and Materials (ASTM) to develop national standards for recycled resin (8).

Yet, when we consider that the one billion annual pounds of post-consumer plastics, principally beverage containers, being recycled today represents just 3.5% of the total amount of plastics in the MSW (9), we realize that we have successfully resolved only a small part of a much larger problem. Beyond beverage bottle recycling we see the problems as exponentially more complex, in technical content and in relation to broader environmental, economic and social issues. Beneath the top ten items are hundreds, thousands, and ten of thousands of other items: different types of paper, glass, metal, plastics, and combinations there of, that are even farther below the technological and economic thresholds. Yet, these problems are receiving increasing attention, and there are already numerous technologies and strategies being developed that show great promise. The remainder of the chapter will describe these problems and some of the potential solutions for recycling the balance of plastics in the MSW.

### Markets For Plastics Derived From Trash

Potentially, there is a large variety of polymeric products that can be reclaimed from the trash, and therefore, setting aside technical and economic considerations for the moment, the potential physical market opportunity is as large as the existing market for virgin polymers. The target markets for these materials depend on the types of products that can be derived from trash. Three general classifications could be described as: 1) chemically purified monomers and polymers, 2) mechanically separated polymers (such as PET, HDPE and PVC from beverage containers), and 3) commingled or mixed polymers.

**Chemically Purified Monomers And Polymers.** Such materials can be defined to a very high level of purity. Usually, any impurities will be measured at levels of less than 50 parts per million (99.995% pure). The markets for materials at the molecular level are huge and established. These are the markets that are already in place for virgin monomers and polymers. Therefore, there is little problem identifying the markets and the buyers for annual multi-billion pound quantities, i.e., for chemical monomers, such as ethylene and propylene. Performance can be judged by matching specifications. The only questions that must be answered for the buyer before there can be a commercial transaction, or sale, relate to price and availability.

**Mechanically Separated Polymers.** These polymers, on the other hand, will probably have a substantially higher level of contamination than the virgin competitive material. Therefore, specifications have to be changed before a sale or substitution for a generic virgin material can take place. This can be time consuming, and it usually requires a real-life performance test before a buyer will agree to begin negotiations on price and availability. Therefore, it will take more time to persuade a buyer to

purchase the generic polymer, and the selling expense associated with making the sale for this type of product will be higher than that associated with a monomer.

An example of a quality problem is the contamination of PET with PVC and, *visa versa*, the contamination of PVC with PET. Either polymer is difficult to fit into existing uses if the contamination with the other polymer exceeds 50 parts per million. The difficulty in selling contaminated polymers is a reflection of this phenomenon. The potential markets for clean generic polymers are huge because the markets for the virgin generic polymers exist and are huge. So, it is reasonable to expect that it will be possible to penetrate those markets in a reasonable period of time.

**Commingled Or Mixed Polymers.** Mixes are orders of magnitude more difficult to describe. The problem is that it is very difficult to define a mixed material in any terms except what it does. For example, "plastic lumber" could replace wood or concrete in certain applications, but it does not yet have the industry-accepted specifications as do wood and concrete. Therefore, it takes a very long time to prove to a potential buyer that such a new product will be a satisfactory replacement. Also, it can cost a considerable sum of money to run the experiments to prove the worth of the new product. In other words, the markets for mixed plastics do not exist *per se* as do the markets for monomers and generic polymers. These markets must be created. Consequently, there is much elapsed time from the initial contact with the potential buyer to when an actual sale is consummated. This greater time is reflected in higher selling expenses associated with the commingled product than with the generic polymer.

### The Problem: Current Recycling Technology Is Too Expensive

The issue that looms largest to restrict the amount of material that can be diverted from the trash through recycling is that the current systems in practice for collection, sorting and reclamation are too costly, mainly because they are small in scale and extremely labor intensive. About 59% of the cost of recycling is in the

collection and the sorting (10) prior to the reclamation of the polymers (See Table 3).

<b>COSTS TO RECLAIM POLYMERS IN FLAKE FORM<sup>(10)</sup></b>		
	<b>¢/lb</b>	<b>%</b>
Collection	10	(27)
Sorting	12	(32)
Subtotal	22	(59)
Grinding/ Cleaning	15	(41)
Total	37	(100)

An examination of the components of the recycling methodology in practice today will help to explain why it is so expensive. It will also be used to indicate where changes can and must be made to improve the efficiencies and the economics of the process.

There are four parts of the post-consumer recycling system, namely: collection, sorting, reclaiming and marketing. Recycling does not occur unless each of the four parts is completed. The typical recycling infrastructure in place today includes:

- ♦ Curbside Collection of Commingled Recyclables
- ♦ Sorting at a Materials Recovery Facility (MRF)
- ♦ Reclamation of the Polymers
- ♦ Marketing of Products

**Collection.** Collection options currently available to communities are voluntary drop-off, buy-back and curbside collection. Curbside programs are expensive, but they capture the most material (See Table 4). Typically, a municipality will have several recyclables picked up at the curbside. These include:

- ♦ Newspapers and Corrugated Cartons
- ♦ Aluminum and Steel Cans
- ♦ Glass Bottles and Jars

These containers are then emptied into a collection truck and transported (un-compacted) to the materials recovery facility.

Homeowners have shown a willingness to cooperate in these curbside recycling programs. However, the more convenient it is for them to separate the recyclables from the rest of the garbage, the greater their participation and the higher the recovery rate. Recognizing this, many communities are collecting all the recyclables commingled in a single container.

<b>TABLE 4</b>	
<b>Collection Methods/Recovery Rates</b>	
<b>Collection Methods</b>	<b>Recovery Rates (%)</b>
Voluntary Drop-Off	10-15
Buy-Back Centers	15-20
Curbside	70-90
Source: Center for Plastics Recycling Research	

<b>TABLE 5</b>	
<b>CAPTURE RATE BY PACKAGE TYPE</b>	
<b>Item</b>	<b>% Capture</b>
Beverage bottles	65
Detergent bottles	50
Other rigid containers	10
Film	5
Average of All Plastics	30
Source: Center For Plastics Recycling Research	

The public will deliver to curbside programs easy-to-identify, easy-to-clean plastics packaging materials such as beverage bottles and, possibly, detergent bottles (see Table 5). After that, the public's enthusiasm for digging deeper into the trash appears to wane, and the rate at which they deliver materials declines from a high of 65-70 percent for plastic beverage bottles to 5-10 percent of other containers and film packaging.

In other words, the "free" sorting labor in the home only captures 30 percent of the plastics, resulting in high collection costs (See Figure 1). By contrast, "conventional" trash collection captures 100 percent of the recyclables, and it is low cost. In short, the new curbside collection method to collect recyclables has a higher labor cost and captures only a fraction of the recyclables. In contrast, the conventional method of trash collection is very low in labor cost and captures all the recyclables.

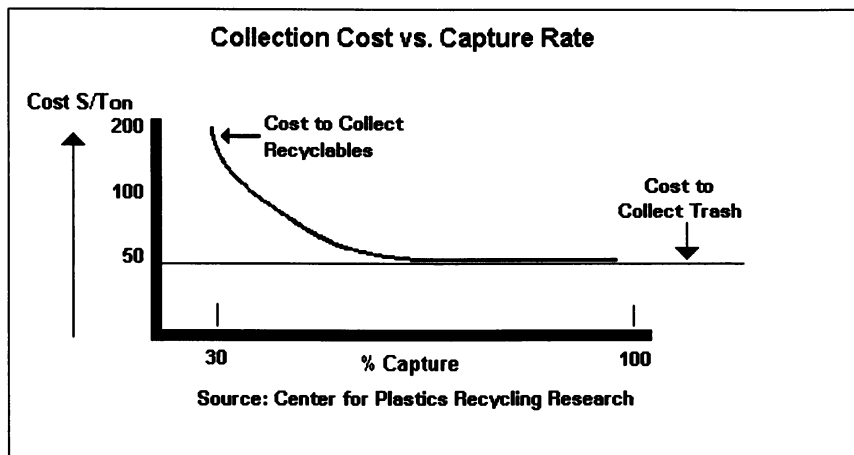


Figure 1. Collection Cost vs. Capture Rate.

**Sorting.** The second required component of the recycling system is the separation of the collected materials, which are subsequently processed to meet the purchasing requirements of the material reclaimer. Material recovery facilities (MRF's) are being built at the 100 to 500 ton per day capacity to take the commingled recyclables from curbside collection systems. On arrival at the MRF (Figure 2), the commingled materials are dumped onto the "tipping floor". There the newspapers are separated from the containers, and the containers are then pushed with a front-end loader onto a large conveyor belt. The steel and aluminum containers are removed from the glass and plastics by two different types of magnetic separators. Because of the density differences, the glass is easily separated from the plastic. From there, the glass containers are hand sorted by color (clear, brown and green) and the plastics are handsorted into

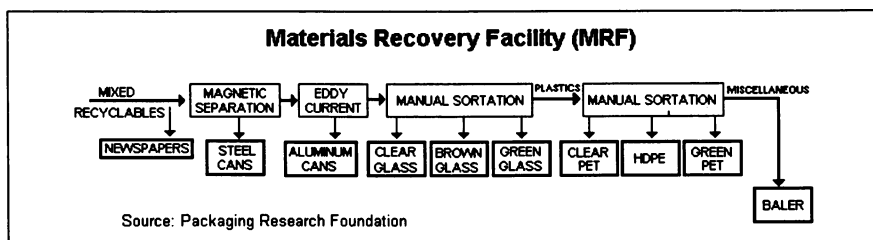


Figure 2. Materials Recovery Facility (MRF).

the different types of plastics bottles (PET soda, HDPE milk, water and juice, HDPE detergent, PVC water and PP ketchup, etc.). The separated materials are then baled and shipped to reclaimers.

**Reclamation (Plastics).** The bales of plastic bottles received by the reclaimer from the MRF are processed to a polymer resin through the following steps:

- ♦ Bale Breaking
- ♦ Sorting The Bottles
- ♦ Chopping and Grinding The Bottles To Flakes
- ♦ Washing The Flakes
- ♦ Separating Different Polymers As Flakes
- ♦ Melting the Flakes to Produce Pellets

The plastic bottles that may be separated include:

- ♦ Clear PET Soft Drink Bottles
- ♦ Green Soft Drink Bottles
- ♦ Translucent HDPE Milk, Water and Juice Bottles
- ♦ Pigmented HDPE Detergent Bottles
- ♦ PVC Water Bottles
- ♦ All Other Materials

Some reclamation PET plants are reclaiming non-soda PET bottles and containers, but many are not yet equipped to deal with either the slightly different polymer types or the content contaminants which usually have a higher chemical oxygen demand (COD) and biological oxygen demand (BOD) than the soft drink and juice residues left in discarded beverage bottles.

This extremely expensive recycling infrastructure, beginning with curbside collection, sorting at the MRF, and resorting at the reclamation plant, must compete with the well established, highly automated, large scale, capital intensive, minimum labor content technology for gathering virgin raw materials, for producing product from the virgin materials, for distribution of the products and for disposal of the products. The basic building block chemicals manufactured at the refinery are converted to polymers in enormous, capital intensive polymer plants ranging from 100 million to 1 billion pounds per year.

By contrast, the current technology for recycling the top ten items in municipal solid waste is inefficient and costly. It involves curbside pick-up in expensive trucks that require much labor to operate. This results in a cost of collection for recycling that can be 3 to 5 times higher than the cost to collect trash. Moreover, current curbside collection captures only about one third of the recyclables, and it is subsidized by the free sorting and handling of the households.

Moreover, the trash disposal system developed in the United States is very efficient and low cost because it, too, is capital intensive. Modern waste management has permitted the last human hand to be removed from touching garbage. The latest concepts use a single operator truck. A robotic arm on the truck picks up as much as 100 gallons of trash from the curbside and deposits the material into a compactor truck. The compactor truck densifies the material to maximize the number of collections per trip. Then, the truck drives to a landfill where the material is handled with large front end loaders and bull dozers, or it is deposited in an incinerator where a crane with a grapple gathers an enormous quantity and deposits it in the incinerator.

### Economic Realities

For recycling to be economically viable, the full cost of collecting, sorting and reclaiming must be recovered. The costs of collecting and sorting are generally borne by the community, or public sector. The costs of reclaiming are borne by the private sector. The costs to the community include the costs to collect, sort, package and ship the recyclables. These costs can be offset in part or in total by the costs avoided for the collection of the material as trash and the costs avoided for alternate disposal such as incineration or landfill. The sum of these costs would be the price the community should receive for material they would sell to a reclaimer. If the reclaimer paid that price as a raw material cost, the reclaimer would have to add the operating costs for refining the material, the cost for capital and the cost for paying dividends to stockholders.

With the technology that is being practiced today and with oil at \$20/barrel (See Figure 3), the sum of these costs to the public and private sectors is generally higher than the costs of comparable virgin materials. However, if the virgin material is expensive to manufacture in the first place, the high cost of recovering such a material from the waste stream may be competitive with the high cost to manufacture the virgin material. Some plastics have such a high value. The PET in soda bottles is one example. The polycarbonate in large water bottles is another, and there are some other materials used in automobiles, airplanes and houses which would have similar high value. However, the majority of plastic materials do not have this threshold value.

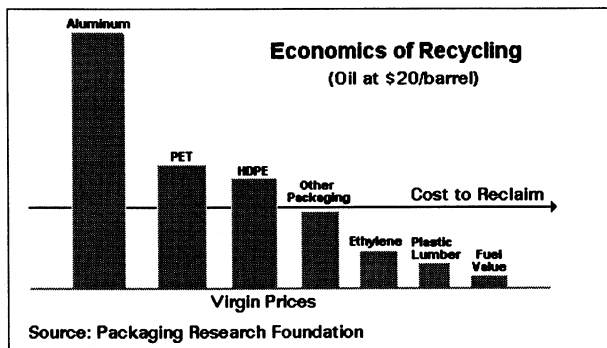


Figure 3. Economics of Recycling.  
(Oil at \$20/barrel)

### Economic Driving Forces.

**Higher Priced Oil.** An economic driving force that would make the economics of recycling more viable would be to have the price of oil increase significantly, to say, \$35 per barrel. The price of virgin materials would rise correspondingly, whereas the cost of recycled materials would not rise as abruptly (See Figure 4). Consequently, virtually all polymer recycling could become economically sound. However, there is no indication that oil prices will reach these levels in the foreseeable future.

**Higher Alternative Disposal Fees.** Another economic driving force that would make the current recycling technology become viable is if alternate disposal fees would increase. Since the avoided cost for alternate disposal can be legitimately applied as though it were revenue, it can be determined how high these fees need to be to make the lower price polymers become viable for recycling.

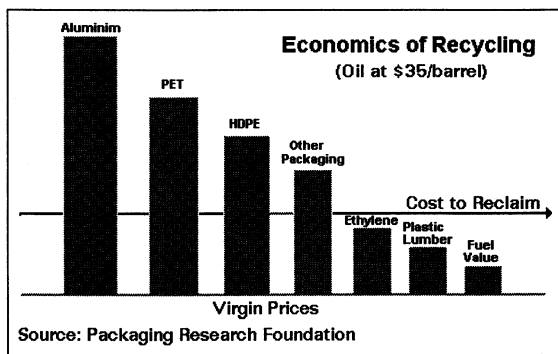


Figure 4. Economics of Recycling.  
(Oil at \$35/barrel)

It can be seen that high value items such as aluminum and PET require no offsetting subsidy in the form of an avoided tipping fee. However, a tipping fee of about \$200 per ton would be required to make the low price polymers, such as LDPE, PP and PVC, become viable, and a tipping fee of about \$400 per ton would be required to make it attractive to convert the polymers to the ethylene monomer. Realistically, the actual costs to build and safely operate a modern landfill or waste to energy plant are not nearly high enough to provide a driving force.

**Designing For Recycling.** A driving force that could make the current recycling technology become viable is to replace all the present materials with those that are economically viable to recycle with the current recycling technology. This logic is the basis of the simplistic form of the concept called "designing for recycling". It can be accomplished by product bans or by encouraging that products be switched from those materials that are not recycled to those that are.

Consumers often interpret the term "recyclable" to mean "what is recycled now in their own communities". For a consumer products company that wishes to respond to the wants of the consumer, this suggests changing to a material that is recycled now despite the fact that the material to be replaced is technically recyclable.

Some companies have chosen to switch from polyvinyl chloride or polypropylene to PET to have packages that are currently "recyclable". This option is both expensive and regressive. Since the replacement material is the one that usually costs the most as a virgin material, the package costs increase.

The biggest negative factor is that this approach causes a virtual abandonment of packaging innovation. New products and product concepts would be forced to fit the current recycling technology and infrastructure, which has not kept pace with the development of packaging technology.

**Legislation Mandating Recycle Content.** A fourth economic driving force that could make the current recycling technology become viable is to pass legislation that mandates products to use a prescribed percent of recycled material.

Companies would have to choose either to abandon the product or to pay whatever is required to incorporate the recycled material in their products. In this case, the supply and price of virgin material have no bearing on the decision. The price can be higher than virgin, and the substantial increase in price that would be permitted by this legislation would allow materials, which ordinarily could not compete with virgin materials, to become viable instantly. Many states and municipalities are passing or are considering passing such legislation. While this will accelerate recycling, it will be inflationary and will result in higher prices.

**Technology To Reduce the Cost Of Recycling.** The preferred economic driving force is one that reduces the cost of recycling plastics to make such materials competitive with their virgin counterparts (See Table 6). This will require a new research approach to achieve

the goal of recycling 25% - 50% of the plastic discards by the late 1990's. As goals, the cost to collect recyclables should not exceed the cost to collect trash, and the cost to sort should be offset by the revenue from the sale of high quality sorted materials plus the avoided cost of their disposal as trash. Under these conditions, the costs of collecting and sorting could be reduced by nearly 65%, which should make the recycled polymers competitive with virgin materials.

	Current	Goal
Collection	10	2.5
Sorting	12	5
Grinding/Cleaning	15	15
Subtotal	37	22.5
Landfill Avoidance <sup>1)</sup>	4	4
Total <sup>2)</sup>	33	18.5
<sup>1)</sup> \$80.00/ton		
<sup>2)</sup> Net with revenues		
Source: Packaging Research Foundation		



**Energy Savings.** The most widely used plastic in packaging is polyethylene, with an inherent (caloric) energy content of more than 23,000 Btu/lb. This is about the energy content of the crude oil from which it was produced. An additional amount of energy, used to rearrange the atomic structure of the molecules (monomer to polymer), can be called conformational energy. Recycling uses the already (con)formed polymer, rather than new crude oil, through technologies that require less energy than the original conformational energy, so that the inherent (caloric) energy content and some of the conformational energy can be saved.

### Emerging Technologies

As mentioned, collection and sorting costs are too high to meet the economic realities of the market place (See Table 7). Consequently, communities and reclaimers are experimenting with a number of technologies to reduce these high costs. Alternate methods of collection include: curbside co-collection of trash and recyclables (uncompacted), collection of all recyclables in a compactor truck, and collection of all trash in a compactor truck. Each of the collection methods has advantages and disadvantages.

<b>TABLE 7</b>		
<b>COLLECTION METHODS - ADVANTAGES &amp; DISADVANTAGES</b>		
<b>Method</b>	<b>Advantages</b>	<b>Disadvantages</b>
Curbside Recyclables	Easier for MRF	High cost Unasked for materials Low recovery rates
Co-collection	Lower cost	More difficult for MRF Unasked for materials Low recovery rate
Collect all trash	Lowest cost Highest recovery rate	Very difficult for MRF
Source: Packaging Research Foundation		

To reduce the cost of sorting, the MRF's and the reclaimers are experimenting with automated sorting technologies to replace expensive manual sorting. A few commercial installations are operating which can separate the major beverage containers, PET, HDPE and PVC, and the newest versions have the capability to separate plastic bottles and plastic chips by color. In effect, these new technologies replace labor with capital. It is too early to determine what the economic advantages are, and it is not clear whether the quality of separation per pass of either method is superior.

The challenge is to develop the lowest cost of collection that captures the maximum amount of clean recyclables while not making it impossible or uneconomical to separate the recyclables into marketable components at the MRF.

**Materials Recovery Facility (MRF) May Hold The Key.** Since the lowest collection costs and the highest recovery rates occur in the collection of raw trash, it follows that the most commercially viable recycling system could be one where the MRF has the capability of producing viable products from raw trash. Furthermore, a large scale MRF is required to make recycling become commercially viable. The appropriate technology at suitable processing volumes will have to be developed. Simultaneously, greater market efforts will be required to develop the customer base.

**The Future MRF.** A Future MRF must be designed to process "all" of the trash to obtain the maximum amount of suitable commodities for sale. This means that garbage will be the incoming feedstock. Foodstuff and product left in containers as residue or attached to films and paper will have to be acceptable to the MRF; and the MRF will have to operate with technologies that are acceptable to their neighbors. In addition, the residue from the MRF processing will be classed as garbage and, as such, must be disposed of as garbage. This strongly suggests that the MRF should be located adjacent to either a landfill or a waste-to-energy plant.

To deal with the question of how to process raw trash requires a fresh and bold approach. The goal should be to gather raw trash at the lowest cost, to transport it to a processing facility and to process raw trash into economically viable commodities in an environmentally sound manner. Research (11) suggests that ore processing technology may be applicable for the separation of the commodities in the raw trash. This technology is used in massive scale for the cleaning and separating of the minerals in ores, and it is used to clean coal. The feed for such a system is material ground into fine particles so that they can be separated in aqueous, froth flotation systems. It has been suggested by the investigator that raw trash could be comminuted and slurried in water, whereupon the recyclable resources could be separated from the non-recyclable material. The recyclables, slurried in water, could be transported by pipe lines literally hundreds of miles from the source of the trash to appropriately scaled processing facilities which could have the ore separation technology as a center piece of the material recovery process.

With such an approach in mind, one could imagine combining the collecting and transporting of municipal solid waste in aqueous form with the transporting of municipal sewage. The resources portion of the waste would be transported by pipeline to the processing facility ("Future MRF"), and the non-resource portion of the municipal solid waste could be combined with the sewage using the same large scale facilities and technologies that are in place for converting the organic portion of our waste to sludge. The sludge, in turn, could be converted to fertilizer and mulch.

**New Design For The Future MRF.** It is essential that the scale of the future MRF be large enough to justify automating as much of the sorting as possible to minimize costs, including transportation. The range in size of present day MRF's is only about one-tenth the size of the modern landfill and/or waste-to-energy plant (about 2000 tons per day).

It is also essential that the MRF be designed and operated to produce uniform and high quality products. This will require the development of a "vision" of the purpose of the MRF, and it will require a commitment on the part of the public and the MRF management to take a "long term" approach to the venture.

The future MRF and its management will need to insist upon separating high quality commodities from the trash, and the materials will have to be competitive in price. In addition, the MRF management will need to recognize that they must "create" the markets. To create markets, the MRF must produce new products and price them with incentives that will attract prospective buyers. All of the skills that the private sector employs to develop and sustain markets and customers must be used. Consequently, MRF management should be prepared to fund marketing development programs up front. This investment in the "business" to sell trash is as important, if not more important, than the investment in the hardware for collecting and sorting the trash.

In the scoping of a future MRF, it would seem wise to attempt to define the products that the MRF would ultimately sell. Therefore, the first task would be to assay the trash in terms of the types of materials that could ultimately be separated. From this breakdown, it would be possible to define some types of markets and potential customers for these materials. It would also be possible to assign some tentative specifications and market prices. Further, it would be possible to determine in what form the potential customers would want to receive the materials.

It would be highly desirable if the future MRF could include material chipping and then sorting of chips rather than whole items. This lends the system to automation, and it has the added advantage of producing a product that does not have to be baled to be shipped. A chipped product of plastic could be shipped by rail hopper car or by hopper truck, as virgin resins are handled today. The elimination of the bale will save money at the MRF and also at the reclamation plant. The giant challenge, of course, is that the MRF must have good enough technology and control to produce a high quality end product.

The future MRF could also implement some simple cleaning of dirty materials to remove food stuffs and/or contaminants that would create effluent problems for the reclaimer. By locating the MRF at a landfill or waste to energy plant, the effluent could be readily treated and disposed. On the other hand, disposing of the effluent from a reclamation plant that is located in an urban area can be very difficult. The COD and BOD levels of the contaminants may require the reclaimer to put in a secondary treatment facility at huge capital and operating expense. Often a reclaimer is forced to shutdown because the plant, as initially approved by the public, was not authorized to handle garbage.

Another potential for the future MRF is to mine materials from landfills (12). As old landfills are recycled to make room for new wastes, the mined materials could

be salvaged for feedstock or fuel. Once this is realized, it is a small step for the MRF, which would be located on a landfill, to begin to store materials for future sale when the markets are more fully developed or when the price is more propitious.

The technologies that must be developed and demonstrated for the future MRF's will include methods to:

- ♦ Optimize MRF sitings and the associated truck routings to the MRF
- ♦ Separate metals from the rest of the trash
- ♦ Separate different metals from each other
- ♦ Separate glass from the rest of the trash
- ♦ Separate different glasses from each other
- ♦ Separate paper from plastics
- ♦ Separate different papers from each other
- ♦ Separate different plastics from each other

New technology for MRF's and/or reclamation plants will be required. Such technology would include:

- ♦ The substitution of automated technology for manual sorting.
- ♦ The inclusion of flake sorting technology.
- ♦ The washing of recyclables and separation of them by hydrocyclone and froth flotation technologies.
- ♦ The separation of mixed polymers by dissolution in solvents

**Products The Future MRF Would Make.** Some examples of products the MRF might market would include, but not be limited to:

- ♦ Glass for cullet (like today)
- ♦ Glass for fiber glass or asphalt modification
- ♦ High quality aluminum (like today)
- ♦ High quality tin cans (like today)
- ♦ Bi-metal products separated for specific markets
- ♦ Paper fiber of high quality such as bleached kraft
- ♦ Other plastics in addition to PET and HDPE from beverage containers
- ♦ Various commingled plastics feed stocks:
  - as replacements for virgin material
  - as feedstocks for solvent separation processes
  - as raw materials for plastic lumber and for refined commingled use
- ♦ Various mixtures of plastics (free of chlorinated, and possibly, oxygenated compounds):
  - As refinery feedstocks
  - As hydrogen donors in coliquefaction with coal
- ♦ Combinations of paper and plastics for:
  - Refuse Derived Fuel (RDF)
  - Raw material for composite board for walls and furniture

### Acknowledgement

The authors wish to acknowledge the contributions of the faculty and staff at the Center for Plastics Recycling Research, Rutgers University, with a special thanks to Jose Fernandes.

### Literature Cited

- 1) *Modern Plastics*, Jan. 1994, vol 71 No.1 pp.73-78.
- 2) Reference (1).
- 3) Authors' estimate.
- 4) *Characterization of Municipal Solid Waste in the United States: 1994 Update*, United States Environmental Protection Agency, Municipal and Industrial Solid Waste Division, Office of Solid Waste, Nov. 7, 1994 (EPA 530-R-94-042), p.6.
- 5) *The Role of Recycling in Integrated Solid Waste Management to the Year 2000*, Franklin Associates, LTD Report (Prepared for Keep America Beautiful, Inc. Stanford, CT) Summary, Sep., 1994, p.6.
- 6) Reference (5), p.9.
- 7) *Recycling Times*, Aug. 9, 1994, p.1.
- 8) *Morphological and Rheological Characteristics of Commercially Produced Plastic Lumber*, Van Ness, K.E.; Hocking, S.E.; Washington and Lee University, Lexington, VA 24450; Nosker, T. J.; Renfree, R. W.; Sachan, R.D.; Center for Plastics Recycling Research, Rutgers University, Piscataway, NJ 08855. To be published in Proceedings of the Society of Plastics Engineers, Annual Technical Conference, May, 1955.
- 9) Reference (4), p.5.
- 10) Authors' estimate
- 11) *Technical Report #64 Froth Flootation Recovery of Post-Consumer Plastics For Recycling*, Center for Plastics Recycling Research Rutgers University, New Brunswick, N.J. (7/1/90 -6/60/92).
- 12) *Landfill Reclamation Strategies*, Nelson, H.; Biocycle, Oct. 1994, p. 40

RECEIVED September 22, 1995

## Chapter 3

# Polymer Recycling: Thermodynamics and Economics

Richard S. Stein

Polymer Research Institute, University of Massachusetts,  
Amherst, MA 01002

Polymer recycling must conform to thermodynamic laws and economic restrictions. The objective of polymer recycling is two-fold: (1) the reduction of rubbish and the burden of waste polymers on the environment, and (2) the conservation of resources. The environmental burden should be considered as part of the cost for employing polymers. Polymer input to landfills can be reduced by source reduction, materials substitution, recycling, incineration, and/or degradation or reduction to low molecular weight compounds. While the value of separated polymers is considerably greater than that of commingled ones, the separation is often difficult and requires an energy investment for "demixing". With present technology, this has not been justified for more than about 25% of the polymer waste feedstock. For the rest, energy recovery through incineration appears to be the thermodynamically and economically sensible route.

The use of polymers is increasing with a consequent impact on the environment. This occurs because of (a) the consumption of non-renewable feedstock, primarily petroleum, for their manufacture, (b) the release of undesirable materials to the environment in their manufacture, and (c) the problems arising from the disposal of waste polymers (1). Less than 4% of petroleum resources are used for polymer production, with the major portion being utilized as fuel. While this 4% is not insignificant, decisions need to be made concerning the most effective use of available funds and efforts. It seems that the payback of attempts to reduce petroleum use by increasing fuel efficiency through use of polymers for lighter vehicles and cargo may often be a better course than that of reducing polymer use.

The chemical industry, including the polymer component, is making notable

0097-6156/95/0609-0027\$12.00/0  
© 1995 American Chemical Society

efforts to develop "clean" processes. There are strong attempts to minimize the release of organic vapors and liquids into the environment. Processes involving organic solvents are being replaced by others, using, for example, aqueous emulsions and supercritical solvents such as CO<sub>2</sub>. Chlorofluorocarbons have largely been replaced with less harmful "blowing agents" for making plastic foams, reducing damage to the ozone layer. Much more care is taken to prevent plastic pellets used for molding polymers from entering the sewage system, where they may find their way to waterways and harm marine life (2). Preconsumer recycling has been found to be economically as well as environmentally desirable by industry, and, in most cases, scrap arising from polymer fabrication is recycled (*primary recycling*). This is usually easily done, since one usually deals with an easily identifiable polymer which is not mixed with other materials.

The employment of polymers often serves to reduce undesirable environmental effects in other areas. For example, metal oxide pigments in paints have often been replaced with aqueous polymer latexes. Lacquers for automobiles employing organic solvents have frequently been replaced by heating polymeric powders.

### Reduction of Polymer Waste

A principal problem is the esthetic damage, harm to wildlife, and occupancy of landfill space arising from polymer disposal. As polymers are estimated to occupy about 8% by weight or 20% by volume of landfills in the United States (3), they are a significant, but not principal, contributor. Reducing the amount of polymer entering the waste stream is desirable. The means for doing this include the reduction in use of polymers, their replacement by other materials, recycling, reduction to monomer or other low molecular weight materials, employing bio or photodegradable polymers, or burning with energy recovery.

The reduction of polymer use, as well as the use of all other materials, not only reduces waste accumulation but reduces the consumption of non-renewable resources. Packaging for products is often excessive. However, justification comes not only from the esthetic appeal of attractive packages but from their value in improving product security and in reducing spoilage and contamination of food products. For example, if the need for refrigeration can be reduced by packaging a food product in a manner so as to resist bacterial growth, the resulting energy savings may have a desirable environmental impact that may more than compensate for the negative impact of the polymer used. Of course, a highly desirable way to reduce polymer consumption and waste production is through reuse of articles. For example, a well made plastic shopping bag can often be reused fifty or more times. This is much more effective than providing a new bag for each use and then attempting to collect and recycle these. Bringing this about, however, is a sociological problem, and its promotion through educational efforts is desirable. It could be encouraged by voluntary or mandatory policies of charging customers for new plastic bags.

For replacement of polymers by other materials, the total environmental

consequences need to be considered. One estimate, for example, suggests that the abandonment of plastics in packaging would result in a 404% increase in the weight of waste, a 201% increase in energy consumption in making the alternatives, and a 212% increase in cost (4). A much discussed case is the replacement of polymer packaging by paper (5). The advantages often cited are (a) paper does not consume non-renewable resources, (b) paper waste is less harmful to the environment than plastic waste, and (c) the paper can be recycled more easily. Contrary views may be expressed relative to these three contentions. The growth of the trees necessary to produce paper occupies considerable land area that might otherwise be used. The processing of the wood to produce paper requires extensive use of water and energy. It has been estimated that 30% more energy is required to manufacture a cardboard container than to make an equivalent Styrofoam one, so that the total toll of cardboard use on petroleum resources may be greater than that of its plastic counterpart.

Disposal of wastes resulting from paper production is a problem. The manufacture of the Styrofoam container is estimated to produce 46% less air pollution and 42% less water pollution than does that of cardboard. While paper does biodegrade, the rate in most landfills is slower than the rate of arrival of new waste paper. It has recently been discovered that newspapers discarded in the 1950s were still readable when unearthed in some landfills 30 years later (6). Effective recycling of paper requires separation of paper types, removal of fillers and waterproofing additives and deinking if the paper has been used for printed material. As with plastics, the economic value of paper from recycled feedstock is often lower than that derived from virgin feedstock. Thus, if all these factors are considered, the choice of paper being ecologically superior is questionable. The properties of plastic in being waterproof, stronger, and thus usable in thinner form should be considered.

As I prepare my breakfast in Japan this morning, I'm taking my eggs from a container fashioned from thin, light-weight, vacuum-formed plastic. One might compare this with the cardboard containers prevalent in the United States. The plastic container is lighter, transparent, and appears to protect the eggs from breakage better than its cardboard counterpart. Furthermore, provided it can be sorted and collected, it is easier to recycle.

When I bought this at the local Kyoto supermarket, I was not asked the U.S. familiar question, "*paper or plastic?*". I was given a thin plastic bag. In resource-hungry Japan, paper was not an alternative. (I would have been happier to see the European practice of being expected to bring one's own shopping bag to the market.)

Other examples include the comparison of glass with plastic containers for beverages. The greater weight in shipping glass containers for recycling, the energy involved in washing, and problems in sorting are negative features of glass. The energy required to melt waste glass is comparable with that required to make new glass from sand, a raw material readily available.



## Recycling.- General Considerations

The recycling of plastics is the main emphasis of this article. In 1990, less than 2% of eight major commodity polymers were recycled (7). Environmentalists, legislators, and the public have come to believe that this is not a satisfactory situation, and regulations have arisen requiring, in some cases, up to 50% recycled feedstock in plastic products. Often, such rules are adopted without regard to scientific or economic limitations. Some of these will be considered in this chapter.

An important distinction is that between plastics, which are separated according to type, and those mixed with other plastics, referred to as "commingled". Random mixing of plastics usually leads to a deterioration of properties. For example, the mixing of a few percent of polypropylene with polyethylene leads to a significant reduction in tensile strength. The reason is that most plastics are immiscible and form two phase systems having interfaces between phases across which there is not strong adhesion (8). Thus, such interfaces are a locus for mechanical failure. One may improve interface adhesion by addition of materials such as block copolymers where molecular ends are each miscible in one of the components. However, these would be specific for particular polymer pairs, and they are relatively expensive. Applications of commingled plastics are limited to products like park benches, marine planking, and parking barriers where mechanical properties are not demanding. There is not enough demand for such products to meet the potential supply of commingled plastics (9).

The economic value of separated plastics is much greater. Many separated plastics can be reprocessed without serious decrease in properties (10). However, the problem of achieving sufficiently thorough separation is great. There is a very large number of kinds of plastics. They not only differ in chemical composition but also in molecular weight and in distribution, branching, tacticity and additives. The situation is further complicated by the increasing use of copolymers and blends. Many of these are not readily distinguishable from each other, and physical properties such as density are often not very different, making recognition by automatic sorting devices difficult.

## Thermodynamic Considerations

One may apply the concepts of thermodynamics to the recycling problem. The First Law is concerned with the conservation of energy and relates to the environmental goal of conserving energy resources and not damaging the environment by carrying out unessential polluting processes for energy production. Petroleum is a principal source of energy, usually generated by burning to give heat to produce steam to drive turbines and generators or to be burned directly in internal combustion engines or aircraft jet engines. As previously stated, a fraction of the petroleum, less than 10%, is used by the petrochemical industry as a feedstock for processes to make other organic molecules, and, of this, under 4% is used to make polymers. Petroleum can be regarded as a source of molecules having high energy content, or more

precisely, high *enthalpy* (designated by  $H$ ). The energy is recovered by their conversion to lower energy compounds, ultimately the combustion products of carbon dioxide and water. The conversion of the components of petroleum to polymers involves some enthalpy change, which is considerably smaller than that involved in its combustion. The major change is encountered in the combustion of the polymer. Hence, the polymer may be regarded as having "borrowed energy" from the petroleum which may be recovered when the polymer is burned. If the polymer is converted to carbon dioxide and water by alternate means such as degradation without energy recovery, this "borrowed energy" is lost. Thus, from a thermodynamic viewpoint, burning the polymer is the preferred route. Of course, other ecological aspects of burning must be considered.

A motivation in replacing conventional materials with plastic is weight saving. For vehicles, reducing weight leads to using less fuel, an ecologically desirable consequence. While petroleum is used to make plastic, if its use leads to the saving of more petroleum than that used for its manufacture, the environment gains. For example, consider the fate of a gallon of petroleum. If instead of being burned as fuel (as about 90% is), it were used to make plastic to replace metal components of an airplane to make it lighter, the fuel saving over the life of the plane will be many gallons.

At first, plastic was used primarily for interior, non-aerodynamic, parts of planes. Recently, it has been employed for external components as parts of wings, stabilizers and other non-load bearing components. It has now found its way to load bearing parts like rudders, ailerons, and even complete wings. The change has occurred to a greater extent in military than in civilian aircraft since for these, the high cost/performance ratio can be tolerated better. There are other advantages such as higher accelerations possible with lighter craft and avoiding radar detection with "stealth" technology. Completely plastic small aircraft have appeared on the civilian market.

While the fuel economy gained by weight saving is not as great for automobiles and trains, the larger number of these in use also motivates attempts to reduce weight. Furthermore, the atmospheric problems arising from excessive fuel use lead to imposing fuel efficiency standards and the replacement of internal combustion powered vehicles with electrically powered ones. For these, the limited driving range that is possible with a reasonable weight of batteries limits performance. Here, plastic may help, with the prospect of replacing heavy metal electrodes in batteries with lighter ones fashioned from conducting polymers. These have the additional advantage of not contributing heavy metal contaminants to the environment. Exotic batteries using molten alkali metals or salts have been proposed. For these, plastics may serve for corrosion resistant containment.

Recent articles (11,12) have proposed an *ultra light car, the "Hypercar"*, weighing 3-4 fold less than today's steel cars. It would use 86% more composites and polymers. Besides saving substantial fuel, even if every such car were landfilled, their contribution of polymer and composites to landfill would be less mass than that arising from the mass of shredder "fluff" from today's cars.

## The Second Law

The Second Law of Thermodynamics defines a quantity, the *entropy*,  $S$ , which is a measure of the disorder of a system.

$$S = k \ln W$$

Here,  $k$  is a constant, the Boltzmann constant, and  $W$  is the probability of a system being in a given state and is dependent on the number of arrangements available to the system for achieving that state. The law states that left by itself, the entropy of a system increases; that is, the change in entropy,  $\Delta S$  is positive. One must expend energy to make entropy decrease. Increasing  $S$  is the driving force, for example, for substances dissolving. A solution in which there are many different ways of arranging two different kinds of molecules has a greater  $W$  and a larger  $S$  than the pure components. The reason why some things do not dissolve is that the tendency for their molecules to dissolve is offset by forces tending to hold similar molecules or atoms together. Thus, a stone does not dissolve in water because the atoms constituting the stone attract each other sufficiently strongly so as to overcome the tendency for  $S$  to increase.

This is quantitatively expressed in terms of another quantity, the *free energy*,  $G$  defined by

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

Spontaneous processes occurring at constant temperature and pressure only occur if  $G$  decreases. An increase in  $S$  makes this happen, but only if it is not offset by an increase in  $H$ . The stone does not dissolve because doing so results in a positive  $\Delta H_{mix}$  which is greater than the  $T\Delta S_{mix}$  term arising because of its dissolution. The positive  $\Delta H_{mix}$  primarily expresses the energy required to separate the strongly attractive atomic (ionic) species constituting the stone from each other.

## Thermodynamics of Mixing

This consideration helps us understand why most different polymers are not soluble in each other to form homogeneous (one phase) solutions. Simple statistics shows that the gain in entropy depends on the *number* of molecules being mixed together. For a given weight of high molecular weight polymer, there are *fewer* molecules than for a corresponding weight of low molecular weight material. Therefore,  $\Delta S_{mix}$  is *less positive* so that this driving force is *less* and solubility is *more dependent upon*  $\Delta H_{mix}$ . If the positive  $\Delta H_{mix}$  exceeds the small value necessary to exceed the small  $T\Delta S_{mix}$ , the polymers will be insoluble. Unless there are specific interactions between polymer pairs such as hydrogen bonding,  $\Delta H_{mix}$  will be positive with a greater value, the more different the polymers from each other. In this case they become less

soluble the greater their difference and the larger the positive  $\Delta H_{mix}$  .. This is a quantitative expression of the familiar observation that *like dissolves like*. Thus, polystyrene and poly(methyl methacrylate) are insoluble just as oil and water are. However, similar polymers like linear and branched polyethylene do mix provided the degree of branching is not too great.

In cases where there are specific interactions between polymers,  $\Delta H_{mix}$  may become negative and solubility may ensue. This is the case for some miscible pairs like polystyrene/polyvinylmethyl ether (PS/PVME), polyvinylmethyl ether/poly(methyl methacrylate), and poly- $\epsilon$ - caprolactone/polyvinyl chloride. For low molecular weight materials, solubility usually increases with temperature because of the greater contribution of  $T\Delta S_{mix}$  at higher temperatures. Thus, sugar is more soluble in hot water than cold. When the temperature of such a solution is lowered, the solute may precipitate out at a particular temperature. Such mixtures are said to have an *upper critical solution temperature* (UCST). Many polymer mixtures show the opposite behavior with a *lower critical solution temperature* (LCST) above which the pair becomes immiscible. Thus, PS/PVME becomes immiscible at a temperature of about 150°C. The LCST depends upon molecular weight, becoming lower with higher molecular weight as  $\Delta S_{mix}$  becomes less. The reason for this inverse behavior with polymers relates to their change in volume upon mixing as they often achieve more free volume and become more "gas-like" and poorer solvents at higher temperatures.

Insoluble polymers may be rendered soluble by chemical modification so as to decrease  $\Delta H_{mix}$  by making polymers more similar or by introducing groups which will interact. Compatibilizers are third components which form three component systems which may be miscible, even though the two major components are not. For example, poly(methyl methacrylate) and poly(ethyl methacrylate) are immiscible but the three component system formed by adding poly (vinylidene fluoride) is miscible.

### Thermodynamics and Interfaces

Thermodynamic considerations help understand the interfacial adhesion between immiscible polymers. Polymers are held together by intermingling and entanglement of their molecules in the diffuse interfacial region. The width of this interfacial zone becomes less as  $\Delta H_{mix}$  becomes greater, and consequently, adhesion becomes less. Thus PS and PMMA adhere weakly whereas poly- $\epsilon$ -caprolactone and polycarbonate have a smaller  $\Delta H_{mix}$  and exhibit a broader interfacial region and adhere more strongly. Compatibilizers are often molecules which interact with both immiscible components and increase adhesion. Block copolymers serve in this way, but recently, the effect has been shown to occur with cheaper random copolymers.

### Environmental Implications of Thermodynamics

This concept can be applied to the environment. It is very apparent that, left to itself, the world becomes more disordered. The number of different atomic

species constituting the world remains constant, but left to themselves, they combine together in more random ways. The task of the synthetic chemist is to direct this combination to produce desired species in the form of molecules having specific structures. Thus, a polymer molecule is a more ordered and lower entropy entity than its constituent monomers, and polymer molecules will usually not assemble by themselves but require energy consuming processes to do so. A polymer molecule constitutes not only a storehouse of high energy, ( $H$ ), but of low entropy,  $S$ . In this sense, it possesses high free energy. Conservation can be considered as an uphill battle to minimize this natural tendency for free energy to decrease with the objectives to:

- a. Minimize the loss of energy,  $H$ .
- b. Minimize the increase in entropy,  $S$ .

A consequence of these goals is the conclusion that it is best to preserve the low entropy state of polymer molecules. The thermodynamic implications of remolding polymers into articles of other shape, preserving their molecular integrity, minimizes their gain in entropy without appreciably changing their enthalpy. This is a thermodynamic argument favoring recycling.

### Separated vs. Mixed Polymers

Without intervention, polymer articles of different sorts will tend to become mixed, increasing disorder and entropy. Thus, one needs to avoid mixing or devise efficient means for separation in order to convert them back to a lower entropy and higher free energy state. However, demixing to decrease entropy requires an expenditure of energy. Thus, the decision is necessary whether this energy expenditure is worthwhile as compared to alternative means whereby the free energy of the polymer may be used otherwise, say by burning and power generation. In cases where separation is easy, recycling is the best route, but when separation requires more elaborate means, it may not be. In this balance, one must consider all aspects of the separation process including that devoted to separate identifying and collecting polymers of differing types and transporting them to facilities where they might be further separated and reprocessed.

### Separation by Consumers

Separation can be carried out by the consumer who recognizes a given kind of polymer and places it in an appropriate receptacle (*secondary recycling*). Some polymers, like the polyethylene terephthalate (PET) in soft drink bottles or the polyethylene (PE) in milk and water jugs, are easily recognizable. Others, such as polyvinyl chloride (PVC), polycarbonate (PC), polybutylene terephthalate (PBT), etc. used in a variety of containers are more difficult to identify. The use of universal symbols helps, but this places an additional burden on the consumer with which he may or may not choose to deal. Machine readable bar codes are in use, but these must be read at some facility

equipped for this purpose. One approach is to have such devices at locations such as supermarkets, where consumers may return bottles. The practice may be encouraged by placing a deposit on the bottle which is returned when it is deposited in the collection device and properly identified. These "reverse deposit" (RD) devices can be programmed to recognize and reject bottles which are off-colored, dirty, or contain residual material.

When a given polymer article is identified and separated from others, there is then the problem of keeping it separated during transport to the recycling facility. If polymers are collected from residences, this requires collection vehicles having compartments for the various types. With the RD devices in supermarkets, this task is simplified.

Another problem is the bulkiness of many plastic articles such as bottles, leading to a decrease in the weight/volume ratio, and thus giving rise to increased shipping costs. This is dealt with in the RD device by grinding the bottle to a more compact mass of particles.

For some types of articles such as plastic bags, the value of their polymer does not justify the cost of identifying and shipping. Thus, for such articles, barring a technological breakthrough, alternatives to recycling appear reasonable. When articles are composed of more than one type of polymer, separation efforts are compounded. For example, it has been the practice to have high density PE (HDPE) base on PET soft drink bottles. Effective recycling then requires the separation of this base from the body of the bottle. A more recent practice is to design the bottle so that the base can also be PET. An environmentally desirable practice is to design articles so as to minimize combinations of difficultly separable polymers. At best, if different polymers are used for different parts of an article, these should readily come apart for separation. It is hoped that plastic producers will voluntarily adopt such practices. If necessary, they could be required through legislation.

In some cases, where consumers are users of large quantities of polymers or are institutions such as schools or hospitals, sorting and separation can be more efficient. For example, when McDonalds used Styrofoam hamburger clamshells, a large fraction of their plastic waste was polystyrene (PS) which could be readily separated from common contaminants such as paper and food waste by flotation and washing. Collection and recycling of this PS proved economical (13). Unfortunately, public pressure motivated them to abandon Styrofoam in favor of paper, an environmentally doubtful decision. School cafeterias often use plastic dishes and utensils in large enough volume that large amounts of a single type polymer can be accumulated. Furthermore, such efforts in schools has a positive educational value among the students. Another example is that of hospitals, where rather large amounts of single polymer articles, often of polypropylene, are used. Large ships, navy vessels, and submarines accumulate appreciable quantities of plastics during long periods at sea (2). Previous practices of dumping such material into the sea is no longer permitted under the MARPOL agreement. The problem of storage of such material on the vessel can be alleviated through use of compacting devices.

Often, the quantity of single polymer articles accumulated by large institutional users is great enough to consider on-site recycling to fashion

articles of value to the institution. If possible, this practice avoids transportation costs as well as the problem of finding a market for the recycled product.

### Separation Devices

An alternative to separation by the consumer is to transport mixed plastics to a central facility where separation occurs. This has two advantages. (a) The time and effort of the consumer in carrying out the separation is saved. This can be an important factor, for example, in households where wives are professionals, so that their time is valuable. (b) The necessity of keeping different types of plastics separated during transportation to the recycling facility is avoided.

At the central facility, separation may be carried out manually or by use of automatic devices. Manual separation can be advantageous where suitable labor is available. Some separation tasks do not require high skill and the practice offers employment in areas of low job opportunities. It has long been practiced in third world countries, where, for example, shoes and doormats are made from discarded tires. On the other hand, newer and more sophisticated polymer articles present a challenge for the less sophisticated sorter.

Automatic sorting can occur at various levels of sophistication. A simple procedure is that of flotation where polymers of different density may be separated. This works where density differences are appreciable, as in the case of PE and PET, but it is less satisfactory for other polymer pairs where densities are closer. The problem becomes more difficult with the increasing use of copolymers where the density depends upon composition.

Atomic analysis detection can be used where one of the polymers has a different atomic composition from the other. This can be used, for example, for separating PVC from polymers not containing chlorine, through detection of chlorine by means such as x-ray absorption.

Spectroscopic methods may be employed. A simple one is the detection of color by optical absorption. More sophisticated procedures may involve infrared or nuclear magnetic resonance techniques. These present the problem of dealing with objects having a variety of sizes and shapes. Often, multidetectors sensing several characteristics of the article must be employed and the results are then analyzed by computer to render the separation decision.

While in principle, instrumental techniques may be devised to distinguish different polymers, the problem is that the capital cost of the equipment, its operation, and maintenance rises with its degree of sophistication. Many efforts to use such means have not proved economical.

A difficulty is that the degree of separation necessary to produce a high quality polymer feedstock is great. As previously emphasized, small degrees of contamination can be quite detrimental to the quality of the product. Even if there is success in separating polymers by type, problems can arise from mixing materials of differing molecular weight, tacticity, branching, or copolymer composition. It is difficult to provide sorting techniques that will distinguish such variables.

## Overview

A conclusion is that sorting can be difficult and expensive. With current technology, sorting by polymer types, either by the manufacturer or fabricator, the consumer, or by a central facility is not likely to be economical for other than a few kinds of polymer articles, such as soft drink bottles, or when carried out by large volume consumers. Thus, the fraction of the waste polymer feedstock that can be processed in this manner is limited to perhaps 25-35% of the total.

The utilization of products formed from recycled polymers is often regulated. For example, FDA has strict requirements for polymeric containers used for food applications. This limits the market for such products.

## Thermosets, Composites, and Laminates

An increasing fraction of used polymers are not readily recyclable by conventional means. Thermosets, such as tires and epoxies, are crosslinked polymers in which molecules are connected together by chemical bonds. These find growing use in automobiles, aircraft, housing, and many consumer products. They cannot be reshaped or remolded without breaking these bonds. Thus, some degree of chemical degradation is required.

Many polymer articles contain fillers. Tires contain significant amounts of carbon black and tire cord. Nylon molded articles often contain mineral filler. Separation of the filler from the polymer is usually not possible because its high viscosity renders operations like filtering impossible, so the recycling of such articles is restricted to making products that tolerate this filler content (14).

There are ways in which some such articles may be directly discarded without harming the environment. The dumping of used tires into the sea is frowned on by environmentalists. However, they are quite stable under water and do not lead to appreciable amounts of undesired decomposition products. Furthermore, it has been found that these underwater tires can serve as nesting areas for fish, and in certain circumstances, can be environmentally beneficial.

Federal law requires that asphalt for roads contain a certain fraction of ground-up discarded tires. The motivation here is that this serves as a "sink" for the discarded material. They replace lower cost fillers, so there is an economic price. Furthermore, a conventional practice is to use a certain fraction of recycled asphalt mixed with virgin asphalt in road construction. The presence of rubber fragments in the recycled asphalt can lead to excessive smoke production during mixing and paving, so there are environmental disadvantages.

Composites usually contain fibers of glass, Kevlar, or similar material, either as continuous or chopped filaments. Again, recycling requires difficult, if possible, separation, or restriction to appropriate products. It is usually not worthwhile to recover these fibers and fillers. However, if high cost fibers such as graphite are extensively employed in products such as the proposed "hypercars" (11, 12), this may be worth doing.

Laminates, consisting of multilayer materials in which polymers are combined with other polymers or else with other kinds of materials such as



metals, are increasingly used. These often have desirable barrier or mechanical properties. Recycling of articles composed of these presents formidable separation problems. While environmentalists have sometimes proposed legislation to restrict their use, their superior properties will offer support for continued utilization

There is a variety of polymeric products which are not susceptible to conventional recycling techniques and require alternative means for dealing with them.

### Tertiary Recycling

*Tertiary recycling* refers to the reduction of polymers to low molecular weight materials, often monomers. This involves the breaking of chemical bonds, a process in which both enthalpy and entropy increase. Thus, from a thermodynamic point of view, this is not desirable. However, there are compensating advantages:

- a. Low molecular weight materials may be separated by conventional means such as distillation. Thus, mixed polymers which cannot be readily separated may be degraded to low molecular weight substances which can be.
- b. The low molecular weight products have appreciably lower viscosities so additives such as fillers and fibers may be separated by means such as filtration.
- c. Such low molecular weight substances may then be used for new chemical synthesis such as polymerization to make new polymer.
- d. Polymers prepared by such repolymerization are often not subject to the food additive restrictions imposed on those derived from primary and secondary recycling.
- e. The molecular nature of the resulting polymer, such as its molecular weight, branching, tacticity, etc. can be better controlled than is possible by mixing already made polymer.
- f. Non-renewable petroleum resources are conserved.

It follows that tertiary recycling renders polymers and polymer mixtures susceptible to recycling that would not be otherwise (15). A question is whether its cost is economically favorable over starting from virgin feedstock derived from petroleum. Even if the cost of tertiary recycling is higher, it may sometimes be justified in that it avoids litter in utilizing materials that might otherwise be carelessly discarded. For example, the use of "disposable cameras" has been criticized in that users tend to carelessly discard them. A procedure to collect them, e.g., by offering a rebate on the cost of a new camera, can lead to collecting significant amounts of potentially recyclable polymeric materials, often mostly PET. However, it is usually mixed with other materials from which separation is difficult. However, tertiary recycling is possible, serving to offset the negative image of this product.

There are regulations restricting the reuse for food applications of polymers such as PET derived from recycled beverage bottles. These restrictions are

relaxed when applied to the polymers derived from tertiary recycling.

For polymers such as polyolefins like polyethylene and polypropylene, degradation involves the breaking of C-C bonds, usually requiring pyrolysis. This requires more energy than for degrading polyesters and polyamides where linkages such as the ester linkage are susceptible to hydrolysis or alcoholysis. Thus, tertiary recycling of PET by alcoholysis can be attractive, particularly because the polymer formed by repolymerization can have high value added, especially if its molecular nature can be controlled so as to make it useful for products like textile fibers and bottles.

Another source that has been suggested (7) for feedstock for degradation is discarded carpets, mostly nylon. These usually contain dyes, fillers, backing material, etc., so secondary recycling is not feasible. Collection might be organized, for example, through the efforts of installers of new carpets. While the economics is still uncertain, it is a procedure that has been identified as having promise.

It has been proposed by some that it is possible to degrade polymers to produce combustible gases like methane and propane which may then be used for fuel. In such cases, of course, means must be provided to collect and separate such gases. From a conservation point of view, one wonders about the advantage of this as compared with obtaining the greater amount of fuel energy obtainable by directly burning the polymers. Of course, this needs to be done in an environmentally acceptable way so as not to produce toxic waste products.

The advantage of tertiary recycling in conserving resources may not be great. As previously indicated, only a very small fraction of petroleum is used to make polymers. The impact of bringing a fraction of this polymeric material back into the feedstock chain may not be significant. Furthermore, energy is consumed in the process using a fraction of this petroleum.

### Degradation

An alternative to primary, secondary, and tertiary recycling of polymers is to dispose of their waste through degradation. In this case, the polymer is converted to low molecular weight material, ultimately mostly carbon dioxide and water, by chemical or bacterial action. These processes are classified as *photodegradation* brought about by light, usually ultraviolet, *chemical degradation* caused by reaction with the surrounding media, or *biodegradation* resulting from bacterial action. As usually carried out, the energy and products of the degradation are not recovered, although in some cases, where methane is a product, this may be collected and used for fuel. Thermodynamically, this approach suffers as with tertiary recycling, that *both* enthalpy decreases and entropy increases. The case is more negative in that the products of the process are normally not utilized so that its justification is primarily that of disposal of a discarded material.

Polymers have the advantage that they are relatively stable materials and are long lasting, so that they may be used to fabricate containers, building and vehicle components, and textiles where long life is desired. Much effort has

been placed in stabilizing polymers so as to render them more resistant to degradation and to extend the life of such products. The formation of degradable polymers is an effort to do the opposite. It is evident that one cannot do both at once, unless there is a means for "triggering" the degradation of an otherwise stable polymer. Mixing degradable polymers with others often results in an increasing rate of property loss of the stable component. Such mixing is undesirable if one wishes to make a long lasting product from the recycled mixture but can be an advantage if one wishes to have the mixture degrade more rapidly. It should be realized, however, that when a degradable component is added to a stable one, physical properties of the product may be lost and it may disintegrate, but the stable component *will not disappear*. Its molecules remain and enter the environment. This may be esthetically appealing, but its environmental value is doubtful. An example is the procedure, now largely abandoned, of adding starch to polyethylene (16). The degradation of the starch causes the polyethylene to fall apart, but *the polymer still remains* in the form of small particles. Furthermore, adding enough starch to the polyethylene to be effective results in an appreciable loss of mechanical properties.

Polyolefin polymers having just C-C bonds are quite stable, although the tertiary carbon in polypropylene is more susceptible to oxidation. Thus, stabilizers are necessary when they are exposed to sunlight. Products made from polyethylene, such as six-pack rings and agricultural sheeting, often last longer than desired and can lead to environmental harm. For example, it has been found that young marine mammals can be strangled by poking their heads through the holes in six-pack rings (2). A means for accelerating the degradation of such materials at the end of their useful life is desirable. One way is to produce polyethylene through copolymerizing a mixture of ethylene and carbon monoxide. This results in a polymer containing a controlled number of -C=O groups in its main chain. These are chromophores in the ultraviolet, and the absorption of such radiation results in chain scission. The resulting small molecule fragments are then susceptible to further degradation through bacterial action.

By controlling the amount of carbon monoxide in the feedstock, the concentration of carbonyl groups, and hence, the time for degradation may be controlled. This illustrates the point that it is possible to make polymers *with controlled lifetimes*, which can be done economically since carbon monoxide is cheap. For this application, this is an environmentally desirable approach.

For some applications, like candy and snack food wrappings, users tend to be careless in disposal and litter is esthetically unpleasant. The mechanical property requirements are not significant, so a degradable plastic wrapper may have advantages. It should be realized, however, that the volume of plastic used for such purposes is small and will not have significant effects on landfill lifetime.

Thus, in principle, one can design a product with a lifetime appropriate for its use. However, in practice, because of the variety of uses of polymer products, the application of this approach has problems. One does not want the product to degrade before its time. It will not do to have the six-pack rings degrade

before the beer is consumed. Fortunately, glass shop windows filter out UV light and its content in indoor lighting is low enough so their degradation does not normally occur during storage in the shop or at home, and one usually does not leave beer sitting in the sun for long periods of time. However, such will not be the case for all products. One would not want shopping bags or oil jugs to fail while in use.

It is evident that not all products will be amenable to design for controlled lifetime. It is only those whose use cycle is predictable. For example, polyethylene sheets are used by farmers to cover fields to retard weed growth and water loss, where the desired crop grows through holes made in the sheeting. One wishes to have such sheeting last for a growing season, but normal polyethylene would not last for more than one. Also removing, storing, and replacing it would require much labor. Thus, it is desirable for such sheeting to photodegrade in a time somewhat longer than the growing season, but before the next season starts. Large quantities of such sheeting are used under fairly well controlled conditions and their controlled lifetime makes sense.

Some polymers, like PVC, noticeably photodegrade, as evidenced by their developing a yellow coloration, a consequence of the forming of conjugated sequences of double bonds arising from the loss of HCl. Stabilizers are added to PVC to retard this. Such photodegradation is not significant in the disposal of PVC, since the amount of molecular degradation accompanying even appreciable color change is small.

Polymers may also degrade when placed in a particular chemical environment. Ester bonds, for example, hydrolyze in acidic or basic environments. Enzymatic reactions can occur. One may take advantage of this in surgical applications for degradable sutures and surgical clamps. The degradation time can be controlled through changes in copolymer composition and can be matched to wound healing times. Drugs, such as contraceptives, can be included in a degradable polymer matrix so that their release rate is determined by the rate of polymer degradation. However, for some biological applications, such as for prostheses and artificial organs, one wants long lifetime and resistance to degradation. Other than for biological purposes, it is difficult to conceive of situations where chemical degradation plays a significant role in reducing polymer solid waste.

Some polymers will degrade when placed in contact with soil as a result of bacterial action. Some polymers like poly-ε-caprolactone and polylactic acid do so more readily than others, and studies are in progress for making useful products from such materials. They can be incorporated in copolymers and blends to accelerate their degradation. Often polymers derived from biological sources undergo such biodegradation (17,18). It has been said "What *nature* makes, *nature* destroys". Bacterial synthesized polyalkonates are being studied for such reasons. Another approach is to produce polymers through thermoplastic molding of starch (not to be confused with adding starch to conventional polymers) (19). At present, polymers made in this way are more expensive than equivalent conventionally made polymers.

Natural fibers such as cotton and wool biodegrade, albeit slowly. It has been proposed that synthetic fibers such as nylon and Dacron be abandoned for this

reason. However, there are doubts about the environmental desirability of this course of action, considering the vast agricultural area required for natural fiber production (an area the size of the state of Tennessee to replace one nylon plant), the use of fertilizers and fuel for tractors, and the greater cost and material and labor needed for maintaining articles made from natural fibers. In fact, means are available to facilitate the degradation of synthetic fibers (for example, by blending polylactic acid with nylon). However, such degradation is very slow and may not significantly affect the solid polymer waste accumulation problem. It is possible that a "happy medium" could be achieved whereby bioengineering might enable the non-agricultural production of synthetic fibers which mimic and even exceed the desirable properties of the natural ones. Today, spider silk remains as one of the most superior fibers!

It should be realized that one does not wish degradation to occur in conventional landfills. The current practice is to have sealers at the bottom of these to prevent seepage of material from the landfill which could contaminate water supplies. For this reason, it is desirable for material in landfills to be stable and not normally degrade. It is better to carry out biodegradation in a separate "composting" facility, perhaps in combination with degradation of food and agricultural wastes, the latter being an important contributor to the total volume of solid wastes (20). Poorly designed composting facilities may emit offensive odors. Attention has been given to proper design to avoid this. At present, the scarcity of adequate facilities limits the applicability of degradation. Also, it is necessary that there be a means for separating degradable polymers from those which are not, where the degradable ones are composted, and the remainder are recycled, incinerated, or landfilled.

Disposable diapers present a disposal problem, with their typically occupying of the order of 1% by volume of landfills. This has inspired proposed legislation to ban their use. The diapers are usually principally cellulose, a degradable natural polymer, but they are usually combined with a plastic backing, normally polyethylene, which is not. There are efforts to replace the polyethylene with a degradable polymer so that the entire diaper degrades. Again, there is the logistic problem, even more important with diapers, of keeping them separate and establishing suitable collection procedures.

## Incineration

While recycling, when possible, is the preferred route, and while degradation has its place, the majority of the polymeric material currently being landfilled still remains. One must face the issue of what to do with it. One route is to burn these with energy recovery. While thermodynamically, one increases entropy by doing so, the enthalpic value of the material is recovered. In this sense, it is just as desirable as burning the petroleum feedstock to begin with, the fate of over 90% of the petroleum now. There is the advantage that one has had the temporary use of the resource as polymer, and one has effectively "borrowed" the polymer for this purpose.

Incineration has had a bad name in the environmental community as a result of the production of toxic fumes and ash. This image primarily arises because of

the prevalence of *old fashioned incinerators* which were not designed to minimize pollution. By applying good chemical engineering principles to incinerator design, it is possible to achieve practically complete combustion so that the C, H, and O components of polymers are converted almost completely to CO<sub>2</sub> and H<sub>2</sub>O. (It is noted that degradation will ultimately lead to these same products, *without energy recovery*.) The production of low molecular weight organic species having toxic or carcinogenic properties is negligible. Other elements sometimes contained in polymers such as Cl and N can lead to products such as HCl, ClO<sub>2</sub>, and NO<sub>2</sub> which are undesired components of emitted gasses. These *can* be removed from the fumes by scrubbing, or one can minimize their presence in the polymer feedstock by rough sorting or by restricting the use of possibly offending polymers like PVC.

It should be realized that components of pure polymers *do not* form ash under conditions of proper combustion. Ash primarily consists of compounds, often oxides, of metals which are not normal components of polymers. These primarily arise from other materials mixed with the polymer, or from catalyst residues, stabilizers, or pigments. Notable efforts are being made by industry to minimize the content of the latter in polymers. A crude screening of incinerator feedstock, eliminating such contaminants as flashlight batteries, could decrease heavy metal oxide content in the ash. It is also possible to add substances like lime to the feedstock to form compounds with the ash which are stable and have low solubility.

If these metal-containing contaminants in this waste stream were not incinerated, they would then be included with material entering the landfill or composting facility and would eventually find their way into the environmental cycle in some uncontrolled way. If they were concentrated in the incinerator ash, one has the opportunity to dispose of the smaller volume in an environmentally acceptable manner.

Some contaminants could be desirable! For example, one means of disposing of used tires is to burn them as fuel in cement kilns. It has been demonstrated that this can be done in an environmentally acceptable manner, and that then iron, arising from the steel tire cord, is a desirable additive for the cement.

It should be emphasized that, in general, polymers are a good and clean fuel. Their energy value is high, and they burn as cleanly as most oils and more cleanly than coal. Burning them recovers most of the energy inherent in the petroleum used to make them.

While incineration *can be done cleanly*, it often is not (21). This is a consequence of the unwillingness of communities to allocate sufficient funds to construct "state-of-the-art" incinerators equipped with proper controls and scrubbers. These can be built, but their cost can be appreciable. However, in the long run, they can represent a course that is better for the economy and the environment than continuing with the ever-more-expensive landfilling.

### **The Bottom Line**

Most agree that the disposal of polymeric solid wastes is a problem which must

be faced by the polymer industry. Public pressure and legislation will force the solution if it is not done voluntarily. There is no single solution. A combination of methods suitable for the polymers and particular situations must be selected, respecting the irrevocable limitation of thermodynamics and economics (22-24). While recycling is the most environmentally appealing route, economics will limit the fraction of the polymer waste feedstock for which it is applicable. The decision will greatly depend upon crude oil price which often fluctuates in a difficultly predictable way, depending upon political situations ( ). However, the prognosis is that in the long run, as oil supplies become more scarce, prices will increase and recycling will become more favorable. With today's prices, PET can be recycled economically and polyethylene recycling is marginal. This is expected to change, and it may be wise to prepare for this development. Of course, such economics should take into account the cost of alternative disposal methods, and a "carrot and stick" approach may be necessary to encourage a greater fraction of recycling, but ultimately, *a limit will be reached*. Degradation has its place, but incineration with energy recovery using proper equipment and control is a necessary and desirable measure.

The NIMBY (not in my back yard) syndrome applies to landfills and composting facilities as well as incinerators. These are often not attractive facilities and are associated with undesired truck traffic delivering the refuse. With technological advances, smaller and more local facilities will become practical, which have the advantage of minimizing transportation costs and being subject to local control. For large institutions, "in-house" facilities may be feasible. They can be made more environmentally attractive and acceptable to communities. For example, in Japan, incinerators have been combined with heated swimming pools and athletic facilities. Composting facilities can be a source of compost to serve local gardeners. It has been said that *"all politics is local"*. Perhaps this same concept can be applied to the waste disposal problem.

In assembling this article, it became apparent that there is a lack of reliable data from unprejudiced sources to guide policy formulation. It was the recommendation of the committee formulating a recent report of the United States National Research Council (25) that:

"The committee recommends that an independent committee at the national level be appointed to accomplish the following:

- Analysis of the environment issues posed by materials, including polymers, and
- Scientific, engineering, and economic analyses of polymeric materials, production, use, recycling, and end-use disposal as a guide to environment policy making."

It appears likely that such a study will be undertaken.

### Acknowledgments

The author appreciates receiving the critical comments of several colleagues, particularly Mr. Jerome Schaul and Mr. Paul Stahlberg. He also appreciates the hospitality of Professor Takeji Hashimoto of Kyoto University, Japan for hosting him during the period that most of this manuscript was prepared.

### Literature Cited

1. Stein, R.S. *Proc. Nat. Acad. Sci.*, 1992, 89, pp. 835-38
2. *Troubled Waters*, A videotape produced by Electronic Field Production Services, Amherst, MA, 1993 (E. Urvater, *Producer*; R. S. Stein, *Coordinator of Project*)
3. *Plastics & The Solid Waste Issue*, Exxon Chemical Company, Baytown, TX, 1991
4. *Consequences of Abandoning Plastics in the Packaging Sector*, SRPM-Study, *Packaging Without Plastic*, distributed by The Association of the Plastic Producing Industry, Karlstr. 21, 6000 Frankfurt am Main, Germany, 1987,
5. Hocking,, M. B., *Science*, Feb. 1, 1991, p. 504
6. Rathje, W. J. , *The Atlantic Monthly*, December, 1989, p. 90
7. *How to Manage Plastic Waste; Technology and Market Opportunities*, A.L. Bisio and M. Xanthos, ed., Hanser Publishers, Munich, Vienna, New York, 1995
8. Stein, R.S., "Miscibility in Polymer Recycling", in *Emerging Technologies in Plastics Recycling*, ed. by G.D. Andrews and P.M. Subramanian, ACS Symposium Series , Washington, DC, 1992, No. 513, Chapt. 4, pp. 40 - 48
9. *Mixed Plastics Product Market Penetration Study*, by Delotta & Touche, July 27, 1990
10. Blatz, P. S. *Polymer Preprints*, 1991, 32, (No. 2), p.152
11. A.B. Lovins and L.H. Lovins, "Reinventing the Wheels", *Atlantic Monthly*, January, 1995
12. A. Lovins, "Supercars: Advanced Ultra light Hybrid Vehicles", *Wiley Encyclopedia of Energy Technology and the Environment*, Wiley, New York, in press
13. "Firm recycling polystyrene foam", (*Dade County, Florida*) *Sun-Sentinel*, Dec. 10, 1990
14. Koczek, M. J., "Developments in the Science and Technology of Composite Materials", and D. A. Weber, "Aspects of Recycling - Plastics Engineering Parts", *Fourth European Conference on Composite Materials*, Stuttgart, Germany, Sept. 25-28, 1990 [Proceedings obtainable from Elsevier Science Publishing, New York]
15. "From Soda Bottle to Soda Bottle", *Recycling News*, Hoechst Celanese Corp. ,Dec. 4, 1990
16. "'Degradable' Plastic: Support Breaking Down", *The New York Times*, Oct. 25. 1989,p. 1



17. Brandl, H., Gross, R. A, Lenz, R. W., and Fuller, R. C. 1988, 54, p 1977
18. "Totally Natural Plastic", *BioCycle*, 1989, 30, p. 58
19. "The Thermoplastic Processing of Starch", *Report of M.I.T. Starch Research Group*, Cambridge, MA, 1991
20. "The Packaging Industry's New Fancy - Composting Garbage", *The New York Times* Feb. 4, 1991, Sect. F, p. 4
21. "The Environmental Impact of Municipal Solid Waste Incineration", *Findings of the International Symposium on Solid Waste Incineration, Symposium: Washington, DC, Sept. 26-27, 1989* (Sponsored by The Coalition on Resource Recovery and the Environment. The U. S. Conference of Mayors)
22. "The Blueprint For Plastics Recycling", *Council for Solid Waste Solutions*, Washington, DC, Spring, 1991
23. Fox, E.A., (Procter & Gamble Co., Cincinnati, OH), "Recycling in the U.S., Progress and Position in Complete Waste Management", *Presentation at an International Conference in Davos, Switzerland, Apr. 3, 1991*
24. Lodge, G. C. and Rayport, J. T. "Recycling Plastics: A Holistic View", *Working Paper from Harvard Graduate School of Business Administration, Div. of Research*, Cambridge, MA, March, 1991
25. "Polymer Science and Engineering; The Shifting Research Frontiers", Committee on Polymer Science and Engineering, Board on Chemical Sciences and Technology, Commission on Physical Sciences, Mathematics, and Applications, National Research Council, *National Academy Press*, Washington, DC, 1994

RECEIVED September 22, 1995

## Chapter 4

# Automotive Recycling

R. A. Pett, A. Golovoy, and S. S. Labana

Ford Motor Company, P.O. Box 2053, MD 3198 SRL,  
Dearborn, MI 48121-2053

The technology of vehicle recycling today is capable of recovering and reusing about 75% of the weight of scrap vehicles. The 75% recycling rate is believed to be the highest recycling rate in durable goods. Moreover, with a technology that was developed in the '70s, vehicle recycling is a profitable undertaking and, consequently, a robust infra-structure for handling and recycling scrap cars exists today. The recovery of materials from scrap vehicles, however, is generally limited to metals, such as steel, iron, zinc, aluminum, and copper. Non-metallic materials are usually discarded to landfills. The technology of recycling plastics and other non-metallic materials, including fluids, from vehicles is at its infancy and its profitability in many cases is yet to be determined. Several trends are developing in the automotive industry which will have a positive effect on recycling. Examples are the recent applications of recycled plastics, elastomers and fluids, the marking of plastic parts, and the joint R&D recycling projects between the automotive companies, suppliers, and recyclers.

Recycling and proper disposal of materials are growing concerns throughout the industrial world. In the last decade in particular, a number of laws have been enacted to encourage the collection and recycling of food packaging and consumer goods materials. Of increasing concern has been the recycling and safe disposal of materials from durable goods. The automotive industry, because of its size, appears to be the focus of keen attention and may eventually become a target for environmental action.

Recycling of scrap vehicles is not new. In fact, in North America an elaborate infra-structure exists which successfully collects scrap vehicles, recovers useful components, and recycles ferrous and non-ferrous metals. These activities enable

0097-6156/95/0609-0047\$12.00/0  
© 1995 American Chemical Society

the recovery and recycling of about 75% of the weight of a vehicle. It is important to note that the vehicle recycling business is quite profitable in the U.S.A.

Today, the non-metallic materials are land filled. In the last 5 years, the automotive industry and its suppliers have initiated many efforts to address the recycling issues of automotive plastics, elastomers, and other non-metallic materials. This chapter reviews the existing infra-structure for vehicle recycling, recent technological and commercial developments in recycling thermoplastics and elastomers, and future trends.

### Infra-Structure of Scrap Vehicles Recycling

Broadly speaking, vehicle recycling consists of two sequential operations: vehicle dismantling and vehicle shredding. The industry for recycling scrap vehicles is very well developed in the U.S. and elsewhere. It consists of salvage dealers (wreckers and junkyards; about 15% in North America are members of the Automotive Recyclers Association - ARA), and shredder and secondary metal recovery operators (most are members of the Institute of Scrap Recycling Industries - ISRI). There are approximately 12,000 salvage dealers and 190 shredders in the U.S. salvaging and recycling about 10 million vehicles annually.

**Salvage Dealers.** Salvage dealers gather and store scrapped vehicles and are responsible for de-registration paperwork. They remove parts which have reasonable market value or are not accepted by the shredder operators. They supply many used replacement parts, in competition with the new replacement parts, to collision and repair shops. Some salvage dealers maintain warehouses which rival in sophistication OEM's parts distribution centers.

Components which have recycling value and are handled by the salvage dealer include engines, transmission, body panels, catalytic converters, batteries, radiators, and so on. In fact, any component which can be sold or reconstituted is salvaged. The salvage dealers also drain auto fluids, such as engine oil, engine coolant, brake fluids, and transmission fluids. Many salvage dealers now ship the drained fluids to reclamation companies or use the fluids as fuel. Collection of Freon (R-12) is required by law.

Examples of reclaimed/recycled components:

**Batteries.** Dead automotive batteries are collected at the point of sale of new batteries. A number of states have deposit laws or otherwise require the battery sales outlets to collect old batteries. Lead, acid, and plastic (from the case) are all recovered and recycled. Ford Motor Company is using large quantities of polypropylene recycled from battery casings in some of its cars.

**Catalytic Converters.** Precious metals can be recovered from discarded catalytic converters at a profit. Hence, the infrastructure for recovery and recycling

of precious metals from catalytic converters has developed rapidly. Converters are removed at the salvage yard and sold to precious metal processors.

Shredders do not accept tires, fuel tanks, and undeployed air bags. Fuel tanks are removed, and steel tanks are crushed and sold separately for metal recovery. Air bags are of significant concern to salvage dealers and the automotive industry. Procedures for the proper deployment of undamaged air bags have been developed by SAE and AAMA.

**Automobile Shredders.** All major automobile producing countries have more than adequate capacity to shred the supply of scrap automobiles. Shredders receive either whole or baled vehicle bodies from the salvage yards. Shredder capacity ranges from 200 to 1500 cars per day. Some shredders accept cars with engine blocks, and others will accept car bodies only with engine blocks removed. The car body is passed through a hammer mill and shredded into fist size fragments. The output is separated into magnetic fraction (ferrous metals) and non-magnetic fractions. The non-magnetic fraction is separated further, by density using water or air, into metallic fraction (zinc, copper, aluminum) and lighter non-metallic materials. More recently a separation process based on magnetic susceptibility of non-ferrous metals has come into use. The remaining lighter fraction is called automotive shredder residue (ASR) or fluff. Some shredders wash the lighter fraction to separate sand, soil, and ground glass from the rest of the light materials.

Shredders make their profit from the recovery of metals from scrap cars. Approximately 11 million tons of steel are recovered annually in the United States from scrap cars. Other metals which contribute significantly to shredder profits are aluminum, copper, zinc, and stainless steel. Not all shredders process non-magnetic metal fraction. These shredders sell this fraction to other processors who recover these metals.

A shredder generates 500 to 800 pounds of ASR (fluff) per car, composed of about 27% plastics (Table I) (1). The rest is ground up glass, sealers, sound deadeners,

**Table I: Auto Shredder Residue Average Composition**

Plastics	27%
Fluids	17%
Glass	16%
Textiles	12%
Rubber	7%
Other	21%

dirt, sand, fabric, adhesives, paint, fabric, rubber, and metal pieces attached to non-metallic materials. ASR has a heating value of 4800 to 6800 BTU's per pound, depending on the amount of glass, metal, water and dirt in it.

It is important to appreciate that what brought about the development of the vehicle recycling infra-structure is the profit opportunity. But the profit margin may be decreasing in the future. In the last 10 years, the number of landfill sites has been decreasing and the tipping fees escalating in some regions. A second possible reason for the decrease in profitability is the increasing use of lighter materials such as plastics and composites in newer vehicles. The overall increase in plastic will increase the amount of ASR per vehicle and the fraction of plastics in ASR is likely to increase in the future.

These changes may decrease the profit margins of the automotive recycling industry. One way to maintain profitability is to reduce the amount of ASR that goes to a landfill site. This applies to existing vehicles as well as future models. The major attempt will probably be to recycle plastics, rubber, and glass which are the major constituents of ASR. In addition to recycling, incineration and pyrolysis will probably play an important role.

To summarize the state-of-the-art in vehicle recycling: dismantlers and shredder operators recover and recycle parts and materials from scrap vehicles profitably. Thus, about 75% by weight of a typical vehicle is recycled today. Considering the complexity of auto design, a recycling rate of 75% is quite impressive. In fact, in the category of durable goods, vehicles have the highest rate of recycling.

### **ASR and Solid Waste in U.S.A.**

In 1992, the amount of municipal solid waste (MSW) generated in the United States was approximately 195 million tons. Out of the total MSW generated each year in the U.S., 80% is disposed of in landfills, 10% is incinerated, and 10% is recycled. To save shipping costs, most landfills are located close to population centers. A typical landfill site is designed with enough capacity to last 10-15 years. Many landfills are getting filled to capacity, and in recent years the rate of opening new landfill sites has been much less than the rate of closing landfills. For example, in 1979 there were 18,500 landfills in the U.S. In 1989, there were only 6,000, and the number is expected to decline to 4,000 by the year 1995. The situation is already severe in the Northeastern United States where tipping fees have reached \$120 per ton. For that reason, some shredders are now shipping shredder waste residue from the northeast to other parts of the country.

Plastics in the solid waste are of special interest to us since most do not, or are slow, to degrade. Because of this, plastics have been the target of increasing negative publicity and the manufacturers need to take appropriate action to deal with plastic waste. Most of the plastic waste which is disposed of in landfills is from packaging and non-durable consumer goods. It is estimated that this source of plastic waste is about six times that from automotive waste. The total plastic waste in 1992 was estimated at 15 million tons. Actually, this is a small fraction of the total solid waste, accounting for about 7.5% by weight. On a volume basis, however, the fraction of plastics, after compacting in landfills, is about 20%. In an uncompacted state, the volume fraction of plastic waste would be about one third.

The rate of growth of plastics, of the order of 5% per year, is higher than the growth rate of other materials. Plastics production in the USA during 1989 was of the order of 30 million tons; so there is considerable potential for an increase in plastics waste, which is estimated to reach 11% by weight, or 30% by volume, of the total solid waste in the year 2000.

As said earlier, only 10% of the solid waste is recycled. Specific examples of disposal and recycling data of principal materials in the United States are shown in Table II. You may note that the recycling of plastics and rubber is below 5%.

**Table II: Materials Recycling Comparison**

<u>Material</u>	<u>Recycling Rate, %</u>
Aluminum	30
Paper & Paper Board	40
Glass	7
Rubber & Leather	3
Iron & Steel	37
Plastics	1
<b>AUTOMOBILES</b>	<b>75</b>

Even in the case of aluminum and paper products, which are considered as the most recycled materials, the recycling is less than 30%. By comparison, the recovery and recycling of components and materials from scrapped automobiles, amounts to about 75%.

With this information in mind, let us look at the magnitude of automotive recycling. In a typical year, about nine million vehicles are shredded in the U.S. This operation generates 11.2 million tons of steel and 0.8 million tons of non-ferrous metals, most of which is recovered profitably. In addition, about 3.5 million tons of shredder residue is produced. At the present time, this residue is disposed of in landfills. Thus, the automotive shredder residue is of the order of 1.3% of the total municipal solid waste generated annually in the U.S.

With the technology available today, a sensible approach to deal with ASR seems to be energy recovery via incineration which would reduce ASR weight by 50% and its volume by about 80%. This approach was demonstrated at the SEMASS Project, a waste-to-energy facility located in Rochester, Massachusetts. Along with municipal solid waste (MSW), the facility routinely mixes 2.5% of ASR with incoming MSW. Rigorous monitoring of stack emissions and ash composition has indicated no apparent increase in environmental impact by adding ASR to MSW. In particular, no increase in dioxins has been observed.

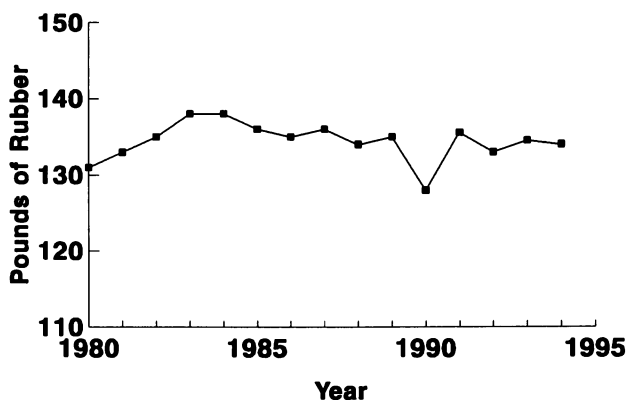
A similar incineration test, conducted by The European Association of Plastics Manufacturers in a municipal waste incinerator in Wurzburg, Germany, showed a decrease in furans and dioxins, when up to 15% of plastic waste was added to MSW. Even when extra PVC was deliberately added to the waste, the level of

dioxins produced during incineration was well below the German limit, which is the strictest in Europe.

In spite of these demonstrations, it is not likely that incineration of ASR will play a significant role in the USA in the foreseeable future due to negative cost benefits.

### Elastomers Recycling Technologies

**Automotive Use of Elastomers.** In a trend which has continued since the early 1980s, about 4¼ % of the weight of a typical U.S. car is rubber. Approximately 134 pounds of elastomers (2) are used on the typical North American automobile (Figure 1). Of this amount, about half is in the tires. Over six hundred other com-



**Figure 1: Pounds of Rubber in a Typical U.S. Car (2-5)**

ponents utilize the remaining material. Many different types of elastomers are used to meet the variety of thermal, chemical, and physical demands of these applications. The automotive environment provides extremes in temperatures, exposure to a variety of aggressive fluids, fatigue, abrasion, and exposure to chemicals in the environment. The wide variety of automotive operating conditions coupled with the multi-material nature of the systems provides a complex set of interactions.

The choice of an elastomer for use in a particular application is influenced by many factors (Table III) including the operating environment, component design, durability

**Table III: Technical Issues for Automotive Elastomers**

- heat resistance
- fluid resistance
- low temperature flexibility
- fracture behavior
- fatigue characteristics
- long term chemical stability
- dynamic properties and NVH
- permeability
- frictional characteristics
- recycling capabilities

targets, recyclability, use of recycled content in the component, manufacturability, quality, government regulations and economics (6).

In addition, the elastomers must last for a long time and be compatible with multi-material systems. Future elastomer components are being designed with the goal of lasting 10 years or 150,000 miles for both passenger car and light truck.

Most rubber compounds contain only 30-50% of base elastomers mixed with a variety of other materials (fillers, plasticizers, extenders, stabilizers, and curatives) in order to achieve the specific performance required. Because elastomer compounds are designed to maximize the performance, life and stability of components, these materials do not deteriorate rapidly and accordingly accumulate in disposal areas. However, the materials being disposed of may have value as the virgin elastomers range in price from less than \$2.00/lb to over \$55.00/lb.

**Recycling of Tires.** Elastomer usage is dominated by the automotive industry. Thus, the automobile is the main source of post-consumer elastomers and we cannot look to other sources for major volumes of post-consumer elastomer material. Further, because of the large quantity (Table IV) of scrap tires (over 2 billion, with 240 million generated per year) and the fact that they are often concentrated in disposal areas (7), tires will remain the major source of post-consumer ground rubber for the near term.

**Table IV: Projected U.S. Utilization of Scrap Tires (7)**

- annual consumption of 328 million scrap tires by 1997
- annual generation of scrap tires - about 240 million tires
- existing stockpile - over 2 billion tires

The Scrap Tire Management Council in their 1992 "Scrap Tire Use/Disposal Study" suggested scrap tires could be used as fuel in a variety of potential applications because the energy content is essentially that of coal (7). They also projected asphalt/paving applications, civil engineering applications, and product recovery via pyrolysis (Table V)(7).

**Table V: Alternative Scrap Tire Use or Disposal Methods (7)**

- supplemental fuel in cement kilns
- supplemental fuel in pulp and paper mills
- supplemental fuel in electricity generating facilities
- fuel in dedicated tire-to-energy facilities
- use in asphalt/paving applications
- product recovery via pyrolysis



K. B. Hoezen in summarizing the European situation and projecting the future noted that 23% of tires are currently retreaded, another 30% are recycled by various means, and the remaining 47% are disposed by landfilling (8). The potential for increasing the amount of retreading in Europe is considered very modest with only 25-30% of the tires being retreaded in the future (8). Total scrap generation is to be reduced by 10% (8). Recycling is to be increased to 60% (8). However, it should be noted that some parts of Europe currently classify fuel use as recycling. J. R. Dunn noted that 47% of scrapped tires in Japan are retreaded or reclaimed and 39% are used as fuel (9). By Japanese definitions this results in 86% being counted as reutilized (9).

**Putting Rubber Back to Use in the Vehicle.** A number of the issues for recycling automotive elastomers are shown in Table VI (6). Most elastomer compounds form permanent chemical bonds and cannot be easily remolded. Thermoset elastomers are either reclaimed through a severe chemical process which significantly alters the

**Table VI: Recycling Issues for Automotive Elastomers**

- complexity of elastomeric compounds
- reutilization of thermosets
- post consumer recyclate (PCR) as a compounding tool
- recycling infrastructure
- identification of PCR elastomers
- availability non-tire PCR
- communication with product engineers
- past perception of poor quality
- consistent quality
- effect on part longevity

elastomer properties or are ground into particles. Reclaimed rubber can be suitable for use in some rubber compounds. Ground cured elastomers have been used in modest amounts as a component of rubber compounds in the past. Most of this recycled content usage has been of the pre-consumer variety not post-consumer. Further, companies would often return the ground pre-consumer material into the same compound from which it originated. Post-consumer recycled material (PCR) needs to be recognized as a compounding tool (10). That is, the compounds should be developed initially using PCR and not simply adulterated with PCR after the fact. Even as we focus on the use of post-consumer recycled material in elastomeric components, we must be careful that we meet the needs of the automotive environment as well as the stresses imposed by interactions with other systems and components. Ford Motor Company will not compromise on quality or performance when elastomer compounds containing recycled content are utilized. Ford announced recently that it is testing a compound containing post-consumer recycled tire rubber in brake pedal pads on some of its vehicle lines. It is already using post-consumer recycled tire rubber in some parking brake pedal pads and Aerostar step plates. Other applications for materials containing recycled elastomer content are being vigorously explored.

Thermoplastic elastomers are often easily reprocessed. These materials account for about 15-20% of the non-tire automotive elastomer usage today and are continuing to make inroads into traditional thermoset elastomer markets (11). These materials may provide some aid to recycling in the future as well as a means of utilizing PCR.

**Challenges.** Product engineers are being introduced to the use of post-consumer recycled material, but a dialog with the rubber industry is necessary for them to be aware of the choices they have available. The Rubber Recycling Topical Group of the Rubber Division, American Chemical Society and the Vehicle Recycling Partnership, under USCAR are but two of the many forums which have developed to allow exchange of precompetitive information on elastomer recycling.

There are many challenges among the recycling technologies which need to be developed as shown in Table VII.

**Table VII: Development of New Recycling Technologies**

- devulcanization
- depolymerization
- multi-material coupling agents
- post-consumer material as compounding ingredient
- rapid, easy material definition
- low cost recovery and separation of rubber

New recycling technologies are needed to supplement those that we already have. Improvements in the technologies for devulcanization (breaking of crosslinks), depolymerization (breaking of backbone chains), and chemical modification are being explored as routes to high quality recycled material.

In the past, use of reclaimed rubber and ground rubber was not always held to stringent performance requirements (e.g. in some low cost after market tires). However, there have been innovative uses of ground rubber to prepare thermoplastic elastomers with modest but useful properties. Recent advances in the surface treatment of ground rubber have significantly improved the physical properties of the compounds in which they were included. Further, some companies are already selling high value recycled rubber which meets stringent quality and consistency standards.

The infrastructure to obtain steady, reliable sources of PCR of the various types of elastomers used in the vehicle is developing. The automobile companies are creating a demand for PCR in order to help stimulate this growth of the infrastructure as it makes economic sense in a free market place environment. The ingenuity of those who address the utilization of post-consumer recycled material is needed to provide rapid and effective means of identification of base elastomer types on parts coming from the vehicle. The availability of non-tire PCR needs to be increased so that we can address major areas such as the use of EPDM on the interior of the vehicle.

**The Future of Elastomer Recycling.** Only a year ago Ford reached the conclusion that it was prudent to encourage the use of pre-consumer recycled elastomer content in components because of the state of the technology. The purpose was to stimulate the necessary technological developments permitting the use of recycled rubber. Then, post-consumer recycled materials will be phased in as the technology and supply infrastructure permit. While this is still true in part, the rubber industry has shown us that it has much to offer that we have not yet fully utilized. However, substantial technological developments are needed for elastomer recycling to reach its full potential. Ford intends to aggressively utilize post-consumer recycled elastomers in every application where it makes sense on the basis of performance and economics.

### **Plastics Recycling Technologies**

So far most of the plastics recycling technologies have been developed for recycling non-durable consumer items, much of it in response to legislation at state and federal levels. Recycling of high density polyethylene (HDPE), polyethylene terephthalate (PET) and polystyrene has grown rapidly as a number of recycling facilities have been built. Success of this recycling business is derived from the sorting and collection programs of many municipalities providing a reliable supply of clean, segregated plastics.

A good example of the success of packaging focused recycling is the use of recycled PET by Ford Motor Company. Since 1988, Ford has used over 23 million lb of recycled PET from 2-liter bottles (ca. 50 million bottles/year). The recycled PET is used in the grill opening reinforcement and luggage racks of several car lines.

Contaminated and mixed plastics are extremely difficult to recycle. Technical efforts in the past have been focused on the development of separation processes and recovery of useful products from the individual plastic materials.

**Separation Techniques.** Many techniques to separate plastics from scrap automobiles and municipal waste have been investigated with varying degrees of success. To assist in the manual separation, plastic containers and automotive parts are marked with codes to identify the material used. Virtually all household plastic containers now carry these codes, but the practice is different for the automotive industry due to the number and complexity of the codes needed to mark automotive plastic parts. Manual sorting has not proved satisfactory for the household waste because of high cost and misreading of identification marks. For this reason high speed automatic separators based on mechanical techniques are being developed and a few of these are now in use. But most of these separators are designed to handle only a very limited number of plastic items, e.g. household bottles.

Other identification and sorting techniques based on density separation, bar code reading, computerized image analysis, infrared reflection, electrostatic charging, dissolution in solvents, selective melting, etc., are being investigated. When the number of mixed plastics is rather limited, some of these techniques show promising

results. But none of these techniques are considered feasible for separating automotive shredder residue into reasonably pure polymer fractions.

**Reprocessing of Thermoplastic Waste.** Clean thermoplastics can be easily reprocessed by using off-the-shelf equipment. Several hundred million pounds of polyethylene-terephthalate (PET) from pop bottles and high density polyethylene (HDPE) from milk jugs are reprocessed and recycled into useful products at a profit. With community support and consumer dedication, the separation of plastic articles, especially pop bottles and milk jugs, was achieved on a very large scale, laying the foundation for the recycling infra-structure we see today. But recycling of other waste plastic articles has not been as successful. Recycling of polystyrene foam, for example, is not as profitable as recycling of PET and HDPE and sometimes is unprofitable.

Most thermoplastic scrap (except some prompt scrap) is contaminated with paint, adhesives, and other materials, e.g., paper, glass, other plastics, and metals. The recycling of this type of plastic scrap, which includes most automotive thermoplastics, presents problems not encountered in the recycling of household bottles. Because different types of plastics are usually not compatible, the reprocessing of mixed thermoplastics scrap, for example from automotive sources and especially from shredder waste, generally, does not yield valuable products. More research and development work is needed to develop technologies for recovering, separating, and purifying scrap automotive thermoplastics and recycling them into valuable products.

To date, there are just a few successful cases of recycling automotive plastics. The recycling of PC/PBT bumpers from old Ford vehicles is one example. Scrap PC/PBT bumpers are collected at junkyards and body shops, the paint is removed, and the plastic material reconstituted by GE Plastics. The recycled bumper material is finding uses in several components of Ford cars. Another example is the recycling of PP from battery cases. Ford is using about 2.3 million pounds per year of the recycled PP for splash shields.

The recycling of more difficult components (e.g. vehicle interior, seats, carpeting, etc.) are being investigated by Ford, GM, Chrysler, and many collaborators. It is believed to be just a matter of time before many more automotive components will be recycled profitably.

A process has been developed jointly by ARCO Company and Ford Saline Plant to recycle instrumental panels made of styrene maleic anhydride (SMA) plastic covered with polyurethane foam and PVC skin. The separation process yields 99.8% pure SMA, which after addition of stabilizers is used in new instrument panels.

**Reprocessing of Thermosets.** Thermosets in general cannot be reprocessed like thermoplastics. An exception to this rule is polyurethane foam which is converted to carpet underlay and RIM scrap which can be pressed (under moist heat) into simple shapes to fabricate mud guards or sound deadener pads.

Both the SMC and RIM scrap can be ground and added to virgin materials. In the case of SMC, up to 15 percent of finely ground scrap can be mixed with virgin SMC and molded without any deleterious effects on the strength of the molded part. This process does not appear to be economical at this time. A new process, developed by Phoenix Fiberglass of Oakville, Canada, separates the glass fibers from the fillers and resin in SMC. The chopped glass fibers are used in bulk molding compounds (BMC). The remaining material is pulverized and sold as filler for SMC and BMC applications.

Pulverized RIM scrap can be mixed with RIM prepolymer up to 10% and the mixture reprocessed. Although the utility of this technology has been demonstrated at laboratory scale, some of the processing details and economics need to be established for commercial applications.

**Reprocessing of Mixed Plastics.** Mixed thermosets and thermoplastics, sometimes, can be processed into low strength products using specially designed extruders and molding machines. In such a process, thermoset material functions as a hard, non-melting filler and thermoplastic functions as a binder. Before the material is fed to the extruder, it must be shredded, chopped, pulverized, or densified and mixed with other ingredients (additional thermoplastic to provide enough binder, pigments, stabilizers and processing aids) to achieve consistent processing conditions and product quality. A number of commercial installations are processing mixed plastics to produce plastic lumber, fence posts, park benches, agricultural stakes, boat docks, walkways, etc. Recycling of mixed plastics has been slow to develop because the products generated are of low value and, in many cases, are not price competitive. Plastic lumber, for example, is at least twice as expensive as natural lumber.

### Trends in Vehicle Recycling

The main issues concerning vehicle recycling today are how to economically reclaim plastics, glass, and other non-metallic materials from scrap vehicles so as to minimize the environmental impact of ASR, and how to design future vehicles to enable total vehicle recycling. Much of the action today is focused on recycling automotive plastics. Some of the important trends are described below.

**Design For Disassembly.** Preliminary studies on components dismantling from vehicles, conducted by Ford Motor Company in collaboration with SPI and ARA, have demonstrated that for many components the dismantling time is too long to be economical. That is, the cost of labor to dismantle auto parts exceeds the value of the recovered plastic materials. In addition, in some automotive parts, different materials are put together in such a way that separation is not practical.

New design guidelines have been developed by Ford and distributed to engineers and suppliers in early 1994 to address the recycling roadblocks found in present and older models. These guidelines, which will be integrated into the product design and development process, will facilitate the recycling of future vehicles. The guidelines cover recommendations for materials selection, fasteners, adhesives, and

design for quick disassembly. In some cases, standardization of components might be advantageous to the industry. For example, in order to remove quickly engine coolant, or any other vehicle fluid for that matter, it may be easier for dismantlers if all vehicles were to have a common drain fitting with the same size and at about the same location.

**Trends in Automotive Plastic Materials.** Plastic materials serve many diverse functions in automotive applications. Today, there are many different types, and within each type different grades, of plastics. Generally, plastics usage in a typical vehicle is of the order of 10% by weight. Managing too many plastic materials can be overly complex and expensive. Do we really need the many different types and grades of plastics in vehicles? Probably not. In fact, Ford Motor Company recently reduced dramatically the number of different grades of certain plastics in the Company's vehicles. This action reduced cost but did not sacrifice performance.

An emerging trend in the automotive industry appears to be the minimization of the number of plastics to a small core group and wherever feasible using plastics which are compatible with each other.

While this trend was originally driven by cost considerations, today, it is also supported by recycling. Obviously, decreasing the variety of plastics will enable easier sorting and collection. But recycling adds some new demands to the selection of plastic materials. First, the materials should be recyclable with existing technologies. The availability of existing and proven technologies should be emphasized since many interest groups invariably tend to claim recyclability of their products whether or not recycling is occurring commercially. Second, the various plastic types used should be compatible when re-processed together. This is especially important when a component is made of two or more plastics and separation is not practical. Along this line it would also be desirable to have the fasteners easily accessible for quick removal or the adhesive to be compatible with the substrate materials.

These developments, obviously, generate some anxiety among suppliers of the automotive industry. How many and what are the materials of choice? There is no simple answer and, probably, may not be for quite a while. The trend suggested above involves many inter-related factors and the process of reducing the number of materials is complicated and inherently slow. It should be emphasized that quality, performance, function, and cost are paramount values in the automotive industry and whatever the materials of choice are going to be, they will have to have these values.

**Managing Substances of Concern.** Some vehicle components contain substances that can be toxic under certain circumstances (e.g. lead from the battery) and if not managed properly, can contaminate the ASR generated during vehicle shredding. In general, proper dismantling procedures prior to shredding would eliminate this problem, i.e. removal of battery, all vehicle fluids, air bags, etc. When properly

removed and separated, these materials (engine oil, gasoline, zinc, lead, etc.) can be recycled and sold profitably.

In other cases, some substances of concern may be compounded into the material formulation (e.g., Cd based pigments and lead stabilizers in plastics) or may be an integral part of a component (e.g. a chrome-plated bumper). The trend in the automotive industry, today, is to find non-toxic substitutes whenever possible and practical. Obviously, the automotive manufacturers must rely on the technical ingenuity of their suppliers to come up with acceptable substitutes. For example, beginning with the 1995 models, Ford Motor Company will only use Cd free pigments in plastic and paint formulations which were developed by its suppliers. Another good example is the substitution of CFC by HFC in air conditioning systems.

**Recycling Alliances and Partnerships.** The issues of recycling are equally important to auto manufacturers, parts suppliers, and raw materials manufacturers. It is therefore not surprising to see the development of joint projects and alliances among various organizations having common interest in advancing vehicle recycling. Some major alliances in U.S. are:

**Vehicle Recycling Partnership (VRP).** This is a consortium of Chrysler, Ford and General Motors which was established in November 1991. The objectives of the VRP include addressing all pre-competitive technology issues and concerns related to material recovery and recycling from scrap automobiles. Major emphasis is on the development of technologies useful to recycle materials and components from scrap vehicles, establishment of an understanding of the major technological and economic issues associated with various alternatives, and the development of criteria for materials selection and design guidelines which will facilitate recycling of future vehicles.

Recently, the VRP opened a vehicle recycling development center to study in detail the issues of dismantling and reclamation of parts and materials from scrap vehicles. Some of the goals of the center are to identify what are the hindrances to recycling, devise methodologies and tools to overcome these hindrances and facilitate higher rate of recycling, and develop generic design guidelines for future vehicles. Specific projects at the Vehicle Recycling Center include development of equipment and procedures for quick drainage and recovery of fluids, recycling of seats, carpets, and instrument panels. The VRP collaborates with the American Plastics Council (APC), Automotive Recyclers Association (ARA), and Institute of Scrap Recycling Industries (ISRI).

**American Plastics Council (APC).** A group of about 30 resin manufacturers formerly known as the Council for Solid Waste Solutions. APC is developing recycling technologies of plastics in general. A sub-group of APC is the Automotive Committee whose primary goal is to catalyze the recycling and recovery of automotive plastics. APC has established a multi-products recycling facility (MPRF) in Boston to study recycling technologies of various plastics.

As stated earlier, ARA and ISRI represent the existing infra-structure of recycling scrap vehicles. Today, these organizations collaborate with the VRP and APC in developing advanced technologies that will increase the recycling rate of scrap cars. In addition, agreement of joint projects with Argonne National Laboratory has been reached.

### Conclusions

Vehicle recycling activities have been going on successfully for more than 70 years. The existing infra-structure of dismantlers and shredders is capable of recovering 75% by weight of scrap cars. It is especially important to note that today this vehicle recycling is profitable.

In order to continue and improve the impressive track record of the existing auto recycling industry it is essential to have a free market-based system of vehicle recovery. The driving force for increasing recycling rate should be profit opportunity through development of new technology and products.

Many industries and companies are or will be affected by the new ways of doing business and, hence, cooperation is critical. Cooperation in a market-driven economic system will ensure continued improvement of automobile recycling.

### Literature Cited

1. Baumgartner & Associates, Inc., W. Z., *Shredder Residue: Environmental Information and Characterization Under RCRA*, Recycling Research Foundation, Washington, D.C., May, 1992.
2. 1994 *Ward's Automotive Yearbook*, p. 36, Fifty-Sixth Edition, Ward's Communication, Detroit, Michigan, 1994.
3. *Automotive Materials in the 90's: an overview and forecast of technology and applications*, Ward's Communications, Detroit, Michigan, 1989.
4. 1992 *Ward's Automotive Yearbook*, p. 36, Fifty-Fourth Edition, Ward's Communication, Detroit, Michigan, 1992.
5. 1993 *Ward's Automotive Yearbook*, p. 36, Fifty-Fifth Edition, Ward's Communication, Detroit, Michigan, 1993.
6. Pett, R. A.; Gullen, L. R., *Automotive Elastomers - The Challenge Continues*, Fall Technical Symposium, Detroit Rubber Group, Oct., 1992.
7. Kearney, A. T., *Scrap Tire Use/Disposal Study*, Scrap Tire Management Council, Oct., 1992.
8. Hoezen, K. B., *European Efforts in Rubber Recycling*, 144th Meeting of the Rubber Division, ACS, Orlando, Florida, Oct., 1993.
9. Dunn, J. R., *Recycling/Reuse of Elastomers - An Overview*, 144th Meeting of the Rubber Division, ACS, Orlando, Florida, Oct., 1993.
10. Smith, F. G., *Ground Rubber Use: Emerging New Market Trends*, 144th Meeting of the Rubber Division, ACS, Orlando, Florida, Oct., 1993.
11. Rader, C. P., *Thermoplastic Elastomers*, 142nd meeting of the Rubber Division, ACS, Nashville, Tennessee, Nov., 1992.

RECEIVED June 12, 1995



## Chapter 5

# Polymer Recycling: Economic Realities

Jeffrey R. Ellis

J. R. Ellis, Technical and Economic Services, Newton, PA 18940

Recycling is just one option for the disposing of polymeric wastes. Energy recovery by incineration, landfilling where there is sufficient space, use of degradable polymers where warranted, and the cracking of plastics into useful chemicals are all feasible alternatives. Source reduction and increased reuse of polymeric products will also impact the economic viability of plastics recycling. Research has shown that because of transportation and processing economics, polymer recycling will be of most value when it is part of an integrated waste management infrastructure encompassing all feasible options within a confined greater municipal area. Federal and state mandates for recycling only have the effect of imposing regressive levies on the costs of goods and services without contributing any useful solution to the nation's waste disposal problems.

Environmental activists have fought for and obtained legislative mandates, regulatory fiat and appealed to individual and business guilt to promote recycling as a solution to disposal problems not only for plastics, but also for other waste products such as paper and metals. Unfortunately, markets for collected waste have been much slower to develop than the ability to sort and amass. During the last business downturn, the price of recycled plastics, specifically polyethylene, was \$0.02 to 0.03 per pound higher than that of virgin resins (1). The recycling of other materials such as newsprint and even traditionally desirable aluminum cans has been hampered because these have been either a glut on the market or were no longer competitive with newly produced products. For many recyclable materials, collectors have paid handling fees to processing centers instead of being paid for what is collected. Within the

0097-6156/95/0609-0062\$12.00/0  
© 1995 American Chemical Society

last few years disincentives have generally outnumbered incentives for plastics recycling (Table I).

**Table I. Incentives and Disincentives for Plastics Recycling**

Incentives	Disincentives
1. Legislative mandates	1. Unfavorable economics
2. Regulatory fiat	2. Transport logistics
3. "Green" image	3. Lack of markets
4. Customer, community goodwill	4. Waning interest
	5. Regulatory restrictions
	6. Declining markets because of downgaging
	7. Competition from paper and virgin plastics
	8. Competing solutions to plastics waste problems

The public has generally been cooperative. People will separate plastics from other wastes although separation of one plastic from another even when these are embossed with easily identified symbols must generally be done separately. There is generally no payment made at the curbside. Studies commissioned by the American Plastics Council in its "Model Cities" program indicate that the incremental costs of collection of plastics at curbside is under \$0.05 per pound. However the other steps in the recycling process all add incremental costs. Sorting, baling, cleaning, flaking and/or repelletizing and the intermediate transportation steps bring the costs of recycling commingled plastics to a level of over \$1700. per ton. Those costs are at least ten times more expensive than that of recycling easily separable homogeneous plastic products (PET and HDPE bottles) or that of alternative disposal methods (see Table II).

**Table II. Economics of Waste Disposal Methods**

Method	Cost Estimate
Landfilling -	\$30 per ton
Incineration/Energy Recovery -	\$100 per ton
Recycling of PET and HDPE bottles -	\$100 - \$150 per ton
Cost of trucks/services for recyclables	\$30-\$50/ton
Separation and other processing costs	\$50-\$70/ton
Public education and marketing costs	\$20-\$30/ton
Recovered Value	\$10 /ton

Alternatives to landfilling are cost competitive only in the Northeast and in other areas where high tipping fees and transportation charges prevail.

SOURCE: Adapted from ref. 2.

### The State of Post Consumer Polymer Recycling

Recycling infrastructures have been put together for each of the commodity plastics (polyolefins, polyvinyl chloride, polystyrene, and thermoplastic polyesters) which make up the bulk of the waste stream. However, initial capacities have been underutilized and there have been major consolidations. What has most hindered the adoption of plastics recycling is the lack of nearby markets, associated with the unfavorable economics of transportation. Historically, sourcing clean consistent grades of recycled plastics has also been difficult although these problems are now largely overcome.

Success in recycling has generally been exhibited by small entrepreneurial companies which are involved with all phases of plastics recycling from collection to the manufacture of finished products such as plastic lumber and outdoor furniture. Many such companies have also failed. Despite both domestic and international incentives, it has been difficult for large companies to offer recycled plastics resins or blends thereof and to develop markets for these products. What incentives there are have not generally been from a profit motive per se, but more from trying to help customers promote an environmentally conscious or "green" image with the public. These customers are major consumers of plastic packaging materials. Among them are leading companies in the manufacture of household chemicals and lubricating products. Some food products and food service companies are beginning to demand a recycling infrastructure for all plastic packaging materials selected although these firms will not be likely to use recycled materials for the packaging of their own products. Automobile manufacturers and makers of business machines are also experimenting with using parts such as bumpers and electronics housings made from plastics with recycle content.

Resin suppliers, plastics processors and their customers must continue to respond to consumer, regulatory and legislative initiatives, usually on a local or statewide basis, which mandate implementation of solutions to solid waste disposal problems. Additional incentives are the desire to obtain public goodwill and endorsements of being "environmentally correct." Unfortunately, large plastic resin manufacturing companies and large users of plastics, the main targets for environmentalist and legislative pressures, usually can do very little except make public relations gestures, often at the expense of profitability, regarding direct implementation of solutions to the plastics waste problem. Partnerships of large companies with smaller ones operating locally have not been successful and most have been dissolved. Other firms have left the plastics recycling business or abandoned large segments thereof entirely.

As can be seen from Table II, landfilling is still the cheapest alternative. Landfills, especially in the Northeast U.S. continue to be closed, with no new ones opening, and the cost of landfill disposal is obeying the classic laws of economics. Incineration has been a difficult sell because of community "not in my backyard" (NIMBY) responses based largely

on fears of toxic ash, toxic or unpleasant fumes, or simply the amount of traffic generated - nor is it generally considered an environmentally appropriate solution. Waste-to-energy plants are more acceptable, but these also often face community opposition. Cooperation with a private utility, particularly one with existing high fuel costs is also necessary for construction of a commercially viable waste-to-energy facility.

Chemical modification and pyrolytic cracking of plastics has advanced to the point that useful chemicals are obtained. Indeed, chemical modification by methanolysis or glycolysis accounts for some of the infrastructure for the recycling of bottles made from amorphous thermoplastic polyester. Although not economical now, technology for the cracking of commingled plastics (much like that for the cracking of crude oil) into a mixture of useful chemicals has been demonstrated. Plastic scrap would then not have to be sorted, cleaned and reprocessed and transportation costs would be minimal. Existing refineries and land zoned for such purposes could be used.

Degradable plastics must be custom formulated and have been shown to have niche uses; for example, in agricultural mulch films and six-pack ring holders, but building in degradability is not a solution to the problem of what to do with over 90% of the billions of pounds of plastics waste being generated annually.

Some companies have solved their sourcing problems by developing their own infrastructure to collect, often from their customers, suitably clean and homogenous materials which can be made into useful products. For example, film grade polyethylene is recycled by collection of used shopping or merchant bags, dry cleaning bags, and other relatively clean products and made into trash bags, lawn and leaf bags, or even back into merchant bags. High density polyethylene (HDPE) bottles, originally used for milk and water, are made into oil or household chemical containers. Often the recycled material is sandwiched between layers of virgin material, which has better chemical and environmental stress crack performance, and also is probably more aesthetically pleasing to the ultimate consumer purchaser. However, it is unknown if these sandwich structures can be readily recycled because of progressive deterioration of the recycle layer.

The availability of competitive materials such as paper also imposes economic strictures on the costs that can be borne. Long term profitability of recycling ventures is also jeopardized by customers adopting source reduction techniques such as downgaging the wall thickness by using tougher materials, or by using less complex packaging constructions. The possibility of reuse is also being explored in North America. In Europe, reused soft drink bottles and molded automobile constructions are commonplace.

What has been the hardest obstacle to overcome for plastics recycling are transportation pricing structures based on weight and volume of materials. Trucks and rail cars are not economical methods of transporting low density materials such as molded or foamed plastics. The longer the distance hauled, the worse the

economics become. Unfavorable transportation economics inhibits the development of large scale markets and the participation of large companies and large organizations such as municipal governments. For this reason, the city of Philadelphia, PA has reduced its participation in plastics recycling programs. In contrast, Minneapolis, MN has a successful plastics recycling program. Administrators of the Minneapolis program think that the smaller size of the city, the more efficient use of labor, and most of all the commitment of an educated citizenry to recycling and waste reduction and separating the various plastics by type at the curbside or alleyway, have been the key elements of the program's success. Economic conditions, however, have made things difficult even for this program. Market development for recycled plastics has been stymied because of the low cost of virgin resins.

Another unknown which will be hard to plan for in advance is the commitment of governments to mandated recycling. Mandates or preferences for the purchase of products made from recycled materials as is currently proposed by the Environmental Protection Agency very often conflict with mandates to purchase the least expensive suitable product. Many potential end uses of recycled plastics are also overseen by regulatory agencies such as the Department of Transportation and the Food and Drug Administration. These agencies will require comprehensive testing of packaging materials and finished products made from recycled materials. Use of recycled materials in packaging has been allowed in certain cases, for example in egg cartons, and in pesticide containers. Industry standards setting organizations, for example, the Plastics Pipe Institute, will also require extensive testing before approval is given.

Interest in plastics recycling in the U.S.A. has generally declined over the last two years. The people of the State of Massachusetts, in 1992, rejected a far reaching law regarding plastics recycling. What is instructive is the experience of the Province of Ontario with its recycling law. The law was enacted with the support of nearly all groups of people affected by such legislation, and at least in the earlier stages, compliance (with fines being assessed for non-participation) has been high. In practice, the program works well in urban areas and is an economic liability in rural and sparsely populated areas. Tax programs are now proposed to help municipalities set up a recycling infrastructure and develop markets for the materials collected. A law passed by the State of California mandating recycle content in packaging, due to take effect in 1995, will be the first on a similar scale to be implemented in the U.S.

### Does Recycling of Post Consumer Use Plastics Make Sense

Plastics recycling has its successes. Thermoplastic polyesters from bottles are converted into fibrous products and to a small extent the basic chemical components of the resin. HDPE bottles are recycled into plastic lumber, film products for trash bags and other end uses even though the energy content is probably more valuable where the cost of energy is high (Table

III). These successes however represent almost 90% of the total amount of plastics recycled. Examples of smaller scale successes are the recycling of loose fill polystyrene packaging (for example in the San Francisco Bay area) and plastics used in automotive construction. Methanolysis and glycolysis of polyester are also feasible if feedstock costs are minimal (Table IV).

Table III. COMPARISON OF BENEFITS OBTAINED

Plastic	Waste to Energy Conversion	vs. Recycling
HDPE	\$312	\$120
PET	\$28-\$140	\$470

Based on \$0.14 per kilowatt/hour of energy.

SOURCE: Decision Resources (Waltham, MA), Personal Communication, 1991.

Table IV: Cost of Methanolysis of PET

	Cost per pound
Feedstock	\$0.30
Conversion & handling	\$0.20
Capital costs	\$0.15
Total costs	\$0.65

Total cost of DMT and EG from petroleum \$0.35

Cost of glycolysis is similar.

Source: Cornell, D., Eastman Chemical Co., Personal Communication, 1993-4.

According to spokespeople from DuPont and Hoechst-Celanese, current methanolysis programs being implemented are feasible because feedstock costs are minimal.

Materials recycling has been shown to be just as susceptible to the vagaries of the business cycle as are other industries. Planning must be long-term as well as immediate. Recycling operations in municipalities with unionized sanitation labor require special care. The combination of recession, lack of markets, unfavorable transportation economics, and the decline in grant and support money for implementation of recycling programs available from state funding sources have put them in a serious economic bind such that contracts are not being renewed, although to this point not summarily abrogated. To some extent this research money is being obtained through programs funded by private industry and the American Plastics Council. Money is particularly needed to finance education programs so that

residents know which materials are recyclable and thus will be separated from other waste prior to pick-up. Transportation routing programs designed to maximize efficiency must also be developed. If large municipalities are going to continue participating in curbside collection and sorting, contracts between partners, suppliers and customers must be drawn up to provide for contingencies in times of economic distress. Recycling programs in suburbs where money has been spent on education programs, and where carting is done by private haulers are generally considered much more manageable and successful.

With separation done at the curbside, and with separation of commingled plastics into uniform components prohibitively expensive, it is not likely that development of sorting technologies will be profitable. The City of San Diego has taken a major financial loss on its sorting plant which under current conditions has little to do. Current automated sorting technologies are based on differences in plastics density or on visual inspection of embossed number codes. The equivalent of bar code sensitization would be more desirable for reducing costs if a labeling system could be implemented.

Analysis of transportation economics leads inexorably to the conclusion that plastics recycling is best handled on a local or regional basis with region being defined as a greater municipal area. The American Chemical Society in its public outreach literature also endorses this view. It is municipalities which have the most problems with plastics and other wastes disposal. Municipalities also have the population and market applications densities required to set up economically feasible recycling infrastructures. It is at the municipal level at which solutions to solid waste problems must be implemented. Mandates from state legislatures, usually at least one level removed from such problems are often worse than useless. Such legislation usually does not provide any funding or even any mechanisms for solutions to be implemented. Entrepreneurship regarding development of products made from recycled plastics usually starts with small firms. Incubators, possibly in partnership with local universities, can be set up and financial incentives to help small businesses can be provided through standard assistance programs. Collectors of materials for recycling can be given licenses or franchises to collect at curbside or from accumulation centers. Municipal governments as one of the largest customers for finished goods in the region can even give preferences for products made from locally recycled materials. Funding for such programs may also be available from Federal sources.

What is the role of the plastics industry and plastics processors? Established plastics processors can certainly examine the possibility of making use of collected materials for recycling and, if economically feasible, use them to make products therefrom which can be readily sold. Occasionally, because processors service sensitive markets such as food packaging or medical products, separate facilities for the storage and processing of recycled resins may be necessary.

Large resin companies can also participate, but again mostly on a local basis. On a corporate wide basis, expertise can be made available on a consulting basis to municipalities and start-up firms on issues of plastics processing, the blending of recycled plastics with virgin resins, and information on how plastics performance will vary with how plastics are collected, cleaned, blended and repelletized. Some large companies committed to offering recycled resins are offering compounding expertise (such as with coloring agents or impact modifiers), or finished products such as insulation board, in an effort to develop profits from value-added products made from recycled resins. It is certainly hoped by all who have a stake in the success of recycling that the plastics industry, although it is under no legislative compulsion to do so, will develop markets for recycled materials. So far, market development for recycled products and the use of alternatives to landfilling have barely kept pace with the amount of trash generated. Between 1989 and 1991, the experience of the State of Pennsylvania is that recycling has not even been able to prevent a small increase in the total poundage of waste generated per person daily.

It is also going to be important to educate large national customers for plastic resins and finished products made therefrom that solutions to the plastic waste problem must be implemented locally. It may not even make sense or be harmful to have a national policy. For example, in desert environments or other regions of water scarcity, in the balance, it will be less environmentally damaging to incinerate or landfill waste rather than use precious water to clean it for recycling.

### Conclusions

The recycling of plastics, like other solutions to waste disposal problems, is subject to the laws of economics. Much as legislatures and regulatory agencies may try, these laws cannot be repealed. Plastics recycling programs must be market driven. Resin manufacturers, processors and end users must continue to battle against ill-conceived laws and regulations which would make plastics the equivalent of a controlled substance. The waste problems that the nation faces are primarily local in nature and are best solved at a local level. Local governments should consider all solutions, including recycling, to the materials waste problems. If necessary, municipalities must make unpopular decisions to site incinerators or waste-to-energy plants, or permit new cracking facilities or landfills if recycling or use of degradable plastics are either uneconomic or inadvisable to implement. Recycling should be encouraged, but not if the advantages gained are minimal and too costly to be supported by the existing economic infrastructure.

### Literature Cited

1. *Plastics News Resin Pricing Chart*, Crain Communications, Inc., Akron, OH, 1993.
2. Porter, J. W., *Recycling at the Crossroads*, Porter & Associates, Sterling, VA, 1993.

RECEIVED December 19, 1994



## Chapter 6

# Plastics Recycling: An Overview

David D. Cornell

Eastman Chemical Company, P.O. Box 1995, Kingsport, TN 37762

Like other businesses, plastics recycling is subject to similar pressures. Raw materials must be adequate in supply and price. Technology must convert raw materials to useful products. And the worth of products must return value to investors. Because plastics recycling requires capital investment, it must be profitable to be sustained. In the 1990's plastics recycling has thrived as public recycling of post-consumer plastics has created a plentiful, if chaotic, supply of raw material. Technologies have developed to process material as generic resins, mixed resins, regenerated small molecules, and as fuels. The business of plastics recycling, often suffering from capacity imbalances, has found uses for recycled plastics in the same products that use virgin resins.

### Overview

**The Business.** Plastics recycling is a business. No longer should the activity be seen as a sideline or an avocation. For some it has always been a serious business. As a business, certain characteristics exist and requirements must be met for plastics recycling to be successful. Raw material must be available. Technology and capital investment must be sufficient. Products must bring value-addition to be successfully marketed. And each member of the value chain must create sufficient economic value for the business of plastics recycling to continue. The typical measure of business success, return on invested capital, still applies even for an environmentally-relevant commercial activity. The chapters of this section discuss business and technical issues of plastics recycling.

To its many stakeholders plastics recycling means the recovery of any used plastic items that have been diverted from disposal. The diverted material could be pre-consumer or post-consumer in nature. The recycling of post-consumer plastics is a relatively new activity. Unlike the secondary materials market of producer scrap, which has grown for over 50 years, recycling of post-consumer plastics as the public recognizes recycling began in the late 1970's and reached critical mass only about 1990. Uncertainty hampered the growth of post-consumer plastics recycling. Both supply of raw material, collected post-consumer items, and development of

0097-6156/95/0609-0072\$12.00/0  
© 1995 American Chemical Society

markets have been chaotic. Even so, the recycle of used plastic bottles grew from 363 million pounds in 1990 to 891 million pounds in 1993, an annual growth rate of 35%(1). Government intervention in the United States at the state and local level spurred collection of used packaging by bottle-law deposits and mandated curbside collection of household recyclables. Markets for recycled plastics developed as extensions of traditional uses for wide-specification virgin materials and by government action, such as the option for recycled content in California in 1995 for non-food containers if a recycling rate were not met. The chaotic nature of the business, which was caused, in part, by mixed motivations and uneconomic constraints of the many stakeholders, has resulted in some plastic recyclers prospering and many quitting the business. From 1991 to 1993 113 plastics recycling businesses are estimated to have gone out of business and 248 new players entered the business arena (2).

**The Technologies.** The technology of plastics recycling can be directed at four modes of reuse of resources. Each has its economic role and none is justified as superior to the others except in value creation. Value creation here means the achieved economic and environmental benefits of recycling exceed the economic and environmental costs. As environmental benefits and costs are not commonly denominated into monetary units, value creation frequently reduces to just economic value. Recycling is a means to an end and not properly an end in itself. The purpose of the plastics recycling business is to create sustainable value within the economic context of the society in which it operates. For maximum sustainability that value should be achieved without subsidies or other artificial impositions. At the same time, recycling is a part of solid waste management which is conducted for its own set of reasons, such as maintenance of public health. As such, some aspects of recycling, such as initial collection, are societal responsibilities and should not be subject to the need for economic value creation.

The four modes of plastic recycling are as follows:

1. use as generic plastic,
2. use of mixed plastic,
3. regeneration of raw materials, and
4. use in energy recovery.

While a legitimate form of recycling, energy recovery is not here discussed in detail. Energy recovery is often called quaternary recycling. Such recycling recognizes the recoverable energy content of plastics that can be captured during combustion. Polyethylene has been characterized as "natural gas in solid form". This section discusses various aspects of generic plastics recycling, mixed plastic recycling, and regeneration of raw materials by thermal methods.

**The Technologies - Generic Resin Recycling.** Recycling to generic thermoplastic resin typifies the general perception of plastics recycling. Such recycling is also called secondary recycling. The processing begins with receipt of post-consumer items, like used bottles, and continues through cleaning, enhancement, and remelting to saleable pellets or fabrication of saleable items. The necessary steps of collection and sorting of plastic items from solid waste are not detailed in this section.

The first post-consumer recycle of generic polymer to gain notice was PET. PET, polyethylene terephthalate, is used to make carbonated beverage bottles.

Deposit laws passed in the late 1970's and early 1980's created a critical mass of potentially useful material. Entrepreneurial businesses developed to exploit the opportunities made possible by the supply of material. In 1993, 450 million pounds of post-consumer PET bottles, including 40% of all carbonated soft drink bottles, were recycled in the United States (3). By 1993 the supply from non-deposit systems surpassed the supply from deposit programs. The technology used to process used bottles to saleable generic polymer has been described by the Center for Plastics Recycling Research (4). Commercial processors use that basic scheme of bottle grinding, flake cleaning, and contamination separation or variations that include whole bottle washing. PET bottle recycling has been a successful business, particularly for well capitalized recyclers, such as Wellman Incorporated or Image Industries, who have forward-integrated into value-added uses. Problems have occurred, such as the shortage since 1990 of used bottles and contamination by incompatible materials. PVC and PET are mutually incompatible. By 1995 the quality and consistency of PET recycle permitted uses in higher value applications. Recycled PET is routinely used for carpeting and apparel fiber, thermoformed films for packaging, non-food bottles, and food bottles. PET recycling provides a model for and commentary on other plastics recycling. Initial uses of recycled PET were the lower valued applications for off-specification virgin polymer. With time, investment, and development recycled PET is now used in many higher valued applications once only satisfied by virgin polymer. So long as value creation exceeds cost, the business prospers.

Thermoplastics cannot be remelted indefinitely without adverse consequences to the polymer. Both condensation and addition polymers will sustain oxidative and thermal degradation upon repeated processing. Discoloration, changes in molecular weight distribution, and crosslinking may result from repeated remelting. As such, 100% closed loop recycling is not practical. Not only can repeated melting adversely affect polymer, but environmental exposure between melting can magnify the adverse effects (5). Thus, the application's life cycle exposure must be considered in any studies of the consequences of repeated processing on thermoplastics.

**The Technologies - Mixed Plastics Recycling.** Rather than isolate generic resins, some technologists have sought to mix incompatible plastics to form commingled plastic structures. Usually with large cross sections, plastic lumbers utilize a feed mixture that is particularly rich in polyethylenes. The resultant fabrications are typically made by the partial melting of the mixed resin feed during extrusion into a mold. One common process uses a slow, low pressure extrusion to fill light-duty molds. The fabrications often exhibit a mottled surface, which can be an advantage for use in marine decking. The fabrications also can contain voids and cracks and easily warp. The American standards organization, ASTM, has organized producers and users of plastic lumber to allow for consensus definitions, guidelines, and standards to facilitate the successful commercialization of plastic lumber. Since the earliest manufacture of commingled plastic lumber, technologists have recognized that the product lacked the flexural modulus of wood and could fail too easily in tensile, shear, and impact loading. Because of the slow production rate and alternate value of the plastic feedstock, plastic lumber has been priced at a premium to wood. On a lifecycle cost basis, however, for some applications plastic lumber can be economically favored over wood.

**The Technologies - Regeneration of Raw Materials.** Regeneration of raw materials is also called tertiary plastics recycling. Condensation polymers, such as PET and nylons, can be depolymerized via the reversible synthesis reactions to initial diacids and diols or diamines. Typical depolymerization reactions are alcoholysis and hydrolysis reactions. Methanolysis of PET recreates dimethyl terephthalate and ethylene glycol. Alcoholysis of PET with ethylene glycol, called glycolysis, results in the recreation of bis-hydroxyethyl terephthalate. Depolymerization of condensation polymers can be nearly stoichiometric in regeneration of initial raw materials. Both PET and nylons raw materials are commercially regenerated from waste or recycled plastic. The recovered raw materials are typically used to create new "virgin" polymer. Because recreation of small molecule raw materials creates species chemically identical to those derived from petrochemical sources, the new "virgin" polymer can be identical to traditional "virgin" polymer. Synthesis reactions for addition polymers, like polyolefins and polystyrene, are not generally reversible. For addition polymers regeneration of raw materials requires thermal depolymerization with recovery of a variable slate of small molecules at variable yields. The thermal processes to regenerate raw materials can also be used to create useful chemicals from condensation polymers, although not usually the original polymer precursors. This section includes chapters on thermal depolymerization of mixed addition and condensation polymers.

### Organization of the Section

The chapters of this section on plastics recycling are organized in three broad categories:

1. Mechanical recycling business for generic commodity resins
2. Mechanical processing technology topics
3. Thermal processing technology for re-creation of raw materials.

**Mechanical Recycling Business.** The first chapters on generic resin recycling address issues of unique and common experiences in recycling post-consumer packaging. Post-consumer plastics are, by experience, inhomogeneous. The recycling processor must accept highly variable feed materials and convert them to uniform generic resins.

Prioleau in his chapter points out a common problem to the plastics recycling business, overcapacity. Recyclers who cannot efficiently use all of their production capacity suffer economically. Atkins agrees with the need for more used plastic. In each of their chapters Prioleau for polypropylene, Thompson for polystyrene, and Burnett for PVC all comment on the importance of durable goods as sources of used plastics. Thompson and Burnett also cite the long standing practice of reprocessing pre-consumer scrap. Prioleau also points out two key problems of operating a plastics recycling business: achieving high productivity in bottle grinding and dealing with non-uniform, low bulk density flake. Product drying and pneumatic conveying are made more difficult by the variable nature of the chopped plastic. Atkins and Thompson discuss the use of recycled plastics back into food contact applications. Food contact reuse for used polyethylene food packaging is anticipated; used

polystyrene can for certain situations be reused in food contact applications. Thompson discusses the unique problems of dealing with low density polystyrene foam. Atkins sounds common themes on the need for responsible packaging design for recyclability and the need for householder cooperation in supplying bottles and avoiding adding inappropriate materials to the recycling stream.

**Mechanical Processing Technology.** The chapters on mechanical processing technology address four questions:

1. What is the nature of commingled, mixed plastic fabrications?
2. What can be done in melt processing to affect the properties of blends of incompatible recycled resins? The melt processing may be with or without compatibilization.
3. How can processing technology deal with networks of crosslinked polymers? Thermoset plastics are rarely recycled as polymers, but frequently as ground filler.
4. How can processing technology allow reuse of food packaging for food packaging again? Section V of this book will more fully develop this topic.

The performance properties of mixed plastic fabrications are highly dependent on the feedstocks used, the preparation of the feedstock, and the processing. The many performance negatives of the product are related to the lack of interfacial transfer of energy between incompatible phases or domains. Because the domains are very large, testing must be conducted on whole items and not typical test coupons. While incompatible resins, like PET and HDPE, are separated efficiently in generic polymer processing, interest is high in being able to combine the two most prevalent bottle resins, PET and HDPE. Simply mixed, PET and HDPE form a weak, low performance mixture. In their chapter Bhakkad and Jabarin explore the consequences of compatibilization and processing variables on PET/HDPE blends. Blends with 80% PET and varying amounts of HDPE and a maleic anhydride-grafted polyolefin show morphology changes due to melt temperature and extruder screw speed. The size of the discontinuous polyolefinic phase affects physical properties and depends on composition of the phase and screw speed. The beneficial effects of the compatibilizer are visually portrayed in adhesion to the PET phase. Improved impact resistance is noted with just the addition of the compatibilizing grafted polyolefin. The work suggests potential for extrusion blowmoldable blends based on the high melt viscosity of the ternary polymer blend.

When separation of generic resin items is not practical, the processing needs to convert mixed resins to useful material. Unlike plastic lumber which is usually uncompatibilized, compatibilized mixtures allow for stress transfer across domain boundaries which results in useful physical properties. Even though the most plentiful resin from post-consumer packaging will be a polyethylene, the mixture can contain virtually any thermoplastic plus organic and inorganic non-melting constituents. The business problem is to find compatibilizing systems that result in useful properties at low cost. Because polyethylene dominates the mixture, the compatibilized blend will at best have the relative value of polyethylene. Thus, expensive compatibilization will not be commercialized.

Thermoset resins do not lend themselves to easy recycle. Thermoset plastics have been ground and used as low-cost, low-performance fillers. Ideally, the polymeric network could be "unzipped" to recover monomeric species. While thermal degradation can create small molecules from the networks, those species are not the original monomers. A value-added process would recover monomers efficiently from crosslinked polymers. In their chapter Shiu et al discuss one route to decompose thermoset polyurethane. In a special case for which thermal or hydrolytic depolymerization is inappropriate, Shiu shows that the application of surfactants, solvent swelling, and ultrasonic irradiation can decompose a polyurethane matrix. Solvent swelling alone is inadequate to break the matrix. The addition of oxidants with the surfactants accelerates the polymer degradation under sonication. The degraded matrix material is then available to recover, purify, and reuse.

Reuse of recycled packaging resins back into food packaging represents a major technical and quality accomplishment. The widest use of recycled post-consumer plastic to food contact applications is for PET. In their chapter Bayer et al discuss the growing options to use recycled PET in food contact applications. PET can be cleaned readily for non-food contact applications by standard washing techniques. Additional cleaning techniques for flaked, used bottles can remove much contamination. Use of high temperature and vacuum, as is used to dry PET before melting or to solid-state polymerize PET to higher molecular weight, also removes contamination. Recycled PET can be used in food contact by relying on a barrier layer of virgin PET to prevent contaminants from reaching food at significant amounts. And tertiary recycling of PET through various depolymerization /repolymerization methods is used to allow recycled PET to safely be used for food-contact applications. Bayer discusses the "threshold of regulation" theory of assuring food safety for indirect food additives, such as packaging resins.

**Thermal Processing Technology.** The chapters on thermal processing to recover raw materials focus on primarily addition polymers in a mix of discarded plastics. The technologies available are discussed. Dealing with highly inhomogeneous materials is a specifically difficult problem. Feeding and slagging reactors are common operational problems.

Mackey in his chapter summarizes the forms of chemical and thermal depolymerizations. Thermal depolymerization can be conducted with or without the presence of oxygen or in the presence of hydrogen to produce primarily liquid or gaseous products. Mackey sets the stage for the chapters by Meszaros and Pearson on specific technologies. Mackey points out that a practical limit to mechanical recycling exists and is probably in the 10 to 15% range. Beyond that amount, plastics recycling will require gross treatment, like thermal decomposition. But, as a system to deal with solid waste, thermal depolymerization is less economical than other solid waste management options. Gasification, as discussed by Pearson, does potentially produce a higher valued synthesis gas product, but overall economics are still unattractive.

In his chapter Meszaros focuses on a parametric study of plastics thermolysis in an auger kiln to produce liquid naphtha, solid carbonaceous material, and non-condensable gaseous products. The test facility, located at Conrad Industries,

regularly pyrolyzes used auto tires. The study found the product species distribution depends on process temperature, feed rate, reaction residence time and feed type. PET was found to sublime to terephthalic acid which precipitated in the product lines. The study also showed that the process using post-consumer MSW plastics was uneconomical without a substantial subsidy. More work was suggested to better understand the effects of residence times. Meszaros suggests circumstances may exist for which generation of the product slate from used plastics could be economically acceptable.

Pearson et al in their chapter studied an approach to deal with highly heterogeneous polymeric feed with a spouted bed reactor. Their approach utilizes an ablative gasification in which high temperature steam is the fluidizing media. In the reducing atmosphere created, synthesis gas (hydrogen and carbon monoxide) are produced. The process was able to handle roughly shredded feed fed uniformly and in slugs. The process is expected to be cheaper than hazardous waste incineration, but still costly vs other solid waste management technologies. Pearson suggests further work is needed to continuously slag the inert solids from the reactor.

### Final Comment

Will plastics recycling ever essentially replace virgin polymer production? While some observers may consider the total replacement of virgin polymer production by recycling to be the desired final state, the thermodynamics dictate otherwise. Recycled polymers will either become exhausted or be expended as yields are less than 100%. Chapters in this section discuss property maintenance for generic plastics recycling and process yields for raw material recovery.

This overview suggests technology can recycle post-consumer plastics to value-added applications. The economics of post-consumer plastics recycling is dependent on the margin spread between the sales price of product and the cost of purchased raw materials. Characteristically, the margin for post-consumer plastics recycling has always been thin. In 1994 and 1995 the observer might think the plastics recycling business were great as selling prices of generic recycled polymer rose to high levels. The reality has been a troubled industry hamstrung by shortages of raw material and high raw material prices that squeeze margins. To address its economic problems the plastics recycling industry has always looked for vertical integration to secure less costly feedstocks and sell higher valued products. Another route to satisfactory economics has been size of capacity. Scale of operation is becoming ever more important as small producers, those selling less than 10,000,000 annual pounds of recycled plastic, will find themselves at distinct disadvantage. As the industry replaces the expensive labor component with capital, more automation and capital investment makes small operations non-competitive. But then the limitations of raw material supply become more critical. Thus, the investor must balance the business among supply of raw material, economic size for the chosen technology, the quality requirements of the sales product, and the economic value of the sales product.

Literature Cited

1. American Plastics Council, "Leaving a Lighter Footprint, Plastics Makes it Possible", Washington, DC, 1994
2. R.W. Beck and Associates, private communication
3. R.W. Beck and Associates, "1993 National Post-Consumer Plastics Recycling Rate Study", Orlando, Florida; June, 1994
4. Rankin, S., Plastic Beverage Bottle Reclamation Process, Center for Plastics Recycling Research, Rutgers University, New Brunswick, New Jersey
5. Boldizar A., "Simulated Recycling-Repeated Processing and Ageing of LDPE", Swedish National Testing and Research Institute, in R'95 Congress Proceedings, EMPA, Dubendorf, Switzerland, 1995

RECEIVED July 26, 1995



## Chapter 7

# Recycling of Polypropylene

Robert M. Prioleau

Exxon Chemical Company, 6011 Deerwood, Houston, TX 77057

In 1993 about 206 million pounds of post-consumer polypropylene were reclaimed, making this the third largest volume recycled plastic in the U.S. Over 90% of the polypropylene was reclaimed from lead-acid battery cases which are collected for recovery of the lead. However, other sources of discarded polypropylene include certain fabrics, containers, and components of automobiles and appliances. There are ten major reclaimers with over 320 million pounds per year of capacity. The technology for reclaiming polypropylene has developed by using equipment designed to grind, dry, extrude, and melt-filter other resins and adapting it to meet the unique requirements of polypropylene. The reclaimed resin is used in a variety of molding compounds and applications such as battery cases, automotive parts, cases, trays, and other rigid parts.

Polypropylene, which is the fourth largest volume plastic sold in the U.S., is also the third largest volume post-consumer recycled plastic. In 1993, the volume of polypropylene reclaimed in the U.S. was about 206 million pounds. Almost 93% of this came from the reclaiming of discarded lead-acid battery cases, and the balance was from reclaiming of post-consumer bottles, tubs and other rigid containers, film and various types of fabric.

The recovery of polypropylene from battery cases developed during the eighties when laws were enacted to ban the disposal of used lead-acid batteries in landfills or incinerators. As the infrastructure to collect batteries and recover the lead developed, reclaiming of the polypropylene battery case became economical. About 75% of the resin recovered is used in producing new battery cases, and new

0097-6156/95/0609-0080\$12.00/0  
© 1995 American Chemical Society

batteries typically contain about 50% recycled polypropylene. This is a large economically sustainable recycling business, which is expected to grow at a moderate pace.

Recycling of other polypropylene (PP) products has grown slowly due to the low prices for reclaimed PP, the challenges of collecting and sorting commercial quantities of PP containers, and the high costs of the reclaiming process itself. Polypropylene is only about 2% of the mix of blow-molded bottles and jugs, and about 11% of the entire group of rigid containers and closures. It is difficult to differentiate from HDPE containers in many cases, and frequently reclaimed PP is comingled with reclaimed HDPE where it can be present in concentrations up to 6-7% without significantly altering the properties of the HDPE.

Recycling of other PP products such as industrial fabrics, automotive parts, appliance parts, and other durables have been demonstrated but are not as well established as the reclaiming of battery cases. Some of these sources of post-consumer PP are discussed in the following section.

### **Markets for Polypropylene**

The challenge of collecting commercially significant volumes of post-consumer polypropylene (PP) products is illustrated in Table I which shows the approximate markets for PP in the U.S.A. in 1993. Polypropylene is used in a very wide variety of durable and non-durable products, only a few of which can be readily recovered, sorted, and collected after they've served their intended purpose.

Products formed by extrusion processing include fibers and filaments which go into textiles, films which are used in packaging, and sheet-stock which is further processed into thermoformed or stamped thin-wall products.

Polypropylene fibers and filaments are used extensively in producing carpeting as a woven backing fabric and as face yarn where it finds applications in commercial carpeting, wear-resistant residential carpets, automotive uses, and in outdoor uses. Recovery of plastics in used carpeting is complicated by the variety of resins, fibers, and adhesives used in producing carpets.

Polypropylene fiber is used in certain clothing and sports apparel primarily because of its tendency to promote transmission of moisture away from the body. It is frequently blended with other fibers in these uses.

Fabrics for agricultural use and construction are produced from woven filaments, split-film, and non-woven polypropylene. Geotextiles are used in preparing substrates for road stabilization or soil erosion control.

Non-woven polypropylene fabrics are widely used for medical drapes, gowns, and disposable products. Diapers generally have a PP inner-liner which draws moisture away from the skin. Polypropylene fabrics are used in a variety of industrial applications as bags for grains or dry products. Heavy duty fabric is also used to produce bulk-bags for transporting industrial materials. Polypropylene filaments are used to produce synthetic rope and cordage, and they have some uses as monofilament bristles.

Table I  
**U.S. Markets For Polypropylene (1993)**  
 millions of pounds

<b><i>Extrusion</i></b>		
<b>Fabrics &amp; Filaments</b>		
	Multifilament	860
	Non-Wovens	750
	Slit-Film	640
	Other	190
<b>Film</b>		
	Oriented	660
	Non-Oriented	140
<b>Sheet</b>		
	Thick Parts (10 Mil or more)	140
	Thin-Wall	120
<b>Other</b>		
		130
	<b>Sub-Total</b>	
		3630
<b><i>Injection Molding</i></b>		
<b>Rigid Packaging</b>		
	Closures	530
	Containers	270
	Other	60
<b>Consumer Products</b>		
	Housewares	350
	Medical	220
	Other	300
<b>Transportation</b>		
	Automotive	250
	Battery Cases	70
<b>Appliances</b>		
	Major	160
	Small	70
<b>Other</b>		
		200
	<b>Sub-Total</b>	
		2480
<b><i>Blow Molding</i></b>		
<b>Consumer</b>		
		90
<b>Medical</b>		
		60
	<b>Sub-Total</b>	
		150
<b><i>Compounding &amp; Resellers</i></b>		
		2040
	<b>Total</b>	
		8300

Extrusion of polypropylene into film can be sub-divided into oriented (OPP) and cast film. The OPP film has grown rapidly as a high-strength clear packaging film which is often coated or laminated with other resins to improve its barrier properties. Cast film is used for packaging clothing, consumer goods, and food produce.

Polypropylene sheet can be transformed into large parts such as automotive panels or liners by thermoforming. Thin sheeting can be formed into food containers, disposable trays, and other types of packaging. In general, PP has good moisture barrier and attractive clarity when oriented. Because it is frequently combined with other resins in laminated structures recovery of pure polypropylene can be very difficult.

Injection molded PP parts include caps and closures for many bottles and rigid containers. Polypropylene is used for some blow-molded bottles where its properties are important (eg. in hot-fill applications) and it is an economical resin for thin-wall molded cups and tubs. It is widely used in injection molded housewares, cases, luggage, and other durable goods.

In major appliances, PP is found in washing machines and dish washers where its resistance to hot water and detergents is important. Recovery of components (eg. agitators, pumps, etc.) is being evaluated. Applications in smaller appliances such as coffee-makers, blenders, mixers, etc. also take advantage of the temperature resistance, imperviousness to water and chemicals, and good mechanical properties of PP. However, recovery of PP components from small appliances and housewares is not practical.

Automotive applications include interior trim, fender liners, ducts, housings, and some under-hood uses. The development of PP dashboard assemblies and bumper components could result in improved prospects for recovery during disassembly of a scrapped car.

As mentioned previously, the PP copolymer used to produce battery cases is being successfully reclaimed in conjunction with the collection and recovery of lead from discarded batteries. About 190 million pounds of PP was reclaimed from this source in 1993, much of which is reused again as a blend with virgin copolymer to make new battery casings.

### **Polypropylene Reclaiming Capacity**

Polypropylene reclaiming first became significant in the early eighties when recovery of lead-acid batteries was mandated. Discarded batteries were drained and after being disassembled the lead was collected for secondary recovery. The battery cases which were mostly copolymer polypropylene were chopped into "chips" and sent to reclaimers where they would be further ground, washed, dried, and extruded into pellets. All heavier materials (eg. other polymers, adhesives, metal residue, etc.) were removed in sink-float tanks, and the extrusion step frequently included continuous melt filtration to remove any wood, paper, or other

non-polymer contaminants. Reclaimed PP is generally pigmented black, and may contain some added stabilizer to minimize breakdown of high the molecular weight components.

About 75% of the PP reclaimed from battery cases is used to mold new cases, in many cases by blending with virgin PP resin. Loss of physical properties is negligible since the total battery population has about 40% original equipment which are generally made from 100% virgin polymer.

As Table 2 shows, the largest PP reclaimer in the U.S. is KW Plastics Recycling Division which has two plants with a combined capacity of about 200 Mlbs per year of reclaimed PP resin. They have also added facilities to reclaim PP fabric such as bale wrap, but this capacity is believed to be dedicated to reclaiming HDPE film at the present.

The second largest PP reclaimer is Exide Corporation which operates a battery recovery plant at Reading, PA. producing 35 Mlbs per year of PP. Other battery reclaimers in the top ten include: Richardson Battery Parts in Indianapolis, IN with 12 Mlbs per year capacity, Resource Plastics (a division of Gopher Smelting) in Eagan, MI with 10 Mlbs per year, and Tulip Corporation with about 8 Mlbs per year of capacity. There are other smaller battery recyclers who also either sell the PP chip or reprocess it into PP pellets.

Aside from reclaiming battery cases, PP is also recovered from discarded cotton bale wrap or other PP fabric used in the textile business. Washington Penn Plastic operates a plant in Summerville, SC which produces about 17 Mlbs per year of homopolymer PP which is recovered principally from sources such as woven PP bale wrap, non-woven PP wrap, and other types of PP industrial fabrics. This plant can also handle PP film and filament plant scrap as feed stocks.

Other similar plants include Tech Polymer in Naples, FL. with 12 Mlbs per year of capacity, Cycletex in Dalton, GA. with 12 Mlbs per year capacity, and Kelley (a division of Thermofil) in Tunnel Hill, GA with about 10 Mlbs per year of capacity. These plants are all designed to handle waste woven and non-woven fabrics as a feedstock, and can produce high-quality extrusion grade PP resin.

Reclaiming of PP bottles and rigid containers has not developed as a large output since the concentration of PP in mixed recovered bottles is very low, and reclaimed HDPE can accommodate up to 6% wt. PP with very little effect on the properties of the reclaimed HDPE. However, the Polymer Resource Group (which is jointly owned by Himont and ITC) operates a 5 Mlbs per year facility in Elkton, MD to produce reclaimed PP from rigid bottles.

The overall capacity for reclaiming PP in the U.S. in '94 is believed to be somewhat ver 350 Mlbs per year. Production of reclaimed PP in '94 is expected to be about 50 Mlbs indicating a 71% utilization of capacity. However, there are some indications that not all this capacity is demonstrated, and effective capacity at year-end 1994 may be closer to 280 Mlbs, which would mean an operating rate of about 90%.

Table II  
 U.S. Polypropylene Reclaiming Capacity as of Year-End 1994

Reclaimer	Primary Feedstock	Location	Capacity Mlbs/yr.
K W Plastics Recycling Division	Batteries	Troy, AL	160
		Bakersfield, CA	40
Exide Corporation	Batteries	Reading, PA	35
Washington Penn Plastic	Fabric	Summerville, SC	17
Tech Polymer	Fabric	Naples, FL	12
Richardson Battery Parts (Div. of Witco)	Batteries	Indianapolis, IN	12
Cycletex	Fabrics	Dalton, GA	12
Kelley & Associates (Div. of Thermofil)	Fabrics	Tunnel Hill, GA	10
Resource Plastics (Div. of Gopher Smelting)	Batteries	Eagan, MN	10
Tulip Corporation	Batteries	NY State	8
Polymer Resource Group	Containers	Elkton, MD	5
	<b>Subtotal</b>		321
Others			29
	<b>Total</b>		350

## Trends In Technology For Recycling

Reclaiming of PP uses many plastics processing steps such as grinding, washing, drying, extrusion and melt filtration which have been well developed over the years. However, the diversity of the feeds and the special requirements for reclaiming post-consumer plastics has challenged engineers and equipment suppliers to provide technology and machines to meet the needs of commercial recycling.

**Size Reduction.** Whether feeding battery cases, rigid containers, woven fabrics, or film the first step in reclaiming is size reduction. Recovered battery cases are frequently converted to chips of resin at the recovery site, and then shipped in this form to a reclaiming plant. Bottles or rigid containers are generally baled for shipment, and must go through a bale-breaker to provide loose containers for feed to a granulator. Recovered woven fabric or film is generally shipped as a bale, and must pass through a chopper or shredder to reduce it to a suitable size for feed to a granulator.

Granulators for rigid cases or containers are typically rotary grinders with a large cavity to draw material into the cutting chamber and chop it quickly into small granules which can pass through a screen with holes of about 1/2 inch diameter. Grinders for woven or non-woven fabrics and films, on the other hand, may have a semi-closed design with more blades and staggered placement to provide a less aggressive cutting action. Close tolerances are essential for good shearing of film or fabric. There are incentives to run at reduced speed to avoid excessive heat build-up and reduce noise. Cooling is provided by drawing ambient air through the cutting chamber by a blower on the discharge line. There have been many improvements in knife blade metallurgy and knife mounting techniques to extend the blade life and minimize the time required to change blades. Extruded PP filament and/or fabric is difficult to grind, and machines in this service must have ample power and adequate cooling. Knife blade changes may be required every three-five days depending on the type of feed, any mineral fillers, and non-plastic impurities in the feed.

Careful consideration should be given to protection of personnel and equipment in this size reduction process. The feed conveyors should be equipped with emergency shut-offs, and all moving parts should be adequately shielded. Grinders should be designed for acceptable noise levels, or acoustic insulation may be required. Generally a metal detector is installed on the feed conveyor to the grinder to indicate the presence of any tramp metal before it reaches the cutting chamber.

In some cases, a combination of a shredder and a smaller grinder provides better throughput and performance than a single larger machine.

**Drying.** Unless the ground PP is exceptionally clean and free of paper, adhesives, labels, tags, and other contaminants it is generally necessary to wash and rinse the reclaimed PP. During washing of the ground PP the water is removed between stages. This can be done with a shaker table which leaves about 20-30% moisture. However, after the last stage of washing the polymer must be dried to 0.5%

moisture or less for feed to an extruder. Special dryers have been developed to accomplish this by a combination of spin-drying and hot-air. In these dryers wet polymer slurry is introduced at the bottom of the cylindrical dryer where it contacts a rotor with paddles. The resin is thrown against a perforated screen which permits much of the water to pass through, and at the same time the polymer is moved up the dryer. Hot air is introduced at the top of the dryer and flows counter current to the polymer. Such a combination spin-dryer and hot-air dryer can dry flaked PP from rigid products (eg. battery cases, bottles, etc.) to about 0.3 - 0.6% moisture ready for feed to an extruder. However, if the PP is a finely shredded fluff from grinding fabric or film the moisture content is likely to still be 4-8% after the spin dryer, and a final drying step is needed in a moving-bed dryer supplied with a cross-flow of hot air to finish drying the polymer to 0.5% or less moisture. Careful control of the hot-air and polymer temperature is needed to avoid sticking or fusing of the polymer to the dryer bed.

**Extrusion.** Conventional single screw extruders can handle flaked PP from battery cases or rigid containers quite readily. The feed hoppers can be provided with bridge-breakers, and the extruder normally has a vent section to take off any residual moisture or volatiles.

However, feeding ground PP from fabric or film poses a challenge because of the extremely low bulk density of the dried fluff. In addition to providing the feed hopper with augers or bridge-breakers, the extruder can be fitted with a reciprocating ram stuffer to force the fluff into the feed throat. Development of a machine with a larger diameter screw in the feed section has also been used to solve the problem of feeding at an adequate rate to match the screw output capability.

The extruder typically has a vented barrel to allow for removal of any residual moisture or volatiles. The polymer vent should be shielded to protect an operator in the vicinity from any sudden release of hot gas or polymer. The combination of feeding, venting, and achieving a discharge pressure adequate for melt-filtration often results in an screw design of 30-35 L/D ratio.

An alternative to enhanced feed capability is to provide a pre-densifier which converts the fluff to free-flowing granules which are then in turn fed to the extruder in a conventional manner.

**Melt-Filtration.** Although filtration of molten polymer through screen-packs is well established, handling reclaimed plastics introduced major challenges because of the greater contamination. As a result there has been a rapid development of continuous screen changes with automatic back-flushing to provide smoother continuous operation and reduce the cost of screens. With these systems a screen pack can be used for a hundred cycles or more before needing replacement.

Continuous melt-filtration with backflushing is accomplished by designs which use slide blocks or rotating wheels to house the screen-packs. In the case of the rotating wheel filter, there are about ten cavities with large screens and the entire wheel is indexed slowly to constantly present fresh screen to the melt. A slip-stream of filtered polymer is used to back-flush a small area of the screen that has just been rotated out of the melt flow. These machines make it possible to use 250



mesh screen (55 micron) or even as fine as 325 mesh screens to achieve a high degree of filtration on the reclaimed PP. The filters operate at pressures up to 5000 psig and rely on very carefully machined surfaces and precise assembly to maintain a good polymer seal. Proper precautions should be taken to protect operators from contact with hot polymer or the metal surfaces of the melt-filtration unit.

### **Properties and Uses For Reclaimed Polypropylene**

The quality of reclaimed PP can be controlled by careful selection of feedstocks and close attention to operations. Identification of various types of PP (eg. homopolymer, copolymer, etc.) and eliminating the presence of any other polymers in the feedstock is essential to produce uniform materials and avoid contamination by other polymers. It is also desirable to separate the PP into consistent melt-flow-ranges (MFR) to provide grades of reclaimed resins which are suitable for various fabricating techniques (eg. extrusion, injection-molding, etc.).

The physical properties of the resin are not altered significantly in reclaiming but there may be some increase in MFR of the melt. In some cases it may be advisable to add an anti-oxidant or processing stabilizer to minimize changes in melt flow characteristics.

Feedstocks are often segregated by color to produce reclaimed resin that is non-pigmented, light-color, or black. In the case of black grades, some carbon-black masterbatch is generally added to improve the appearance.

Most reclaiming facilities employ pellet blenders to improve lot-to-lot product uniformity. This also facilitates obtaining representative samples for quality control analysis before shipping. The product is normally tested for MFR, moisture content, and pellet size or count. Composition and density can be characterized by the type of feedstock used to produce the reclaimed resin. Special tests can be used to determine the cleanliness of the resin by running a sample through a laboratory extruder and noting the rate at which pressure builds up ahead of a fine-mesh screen.

In addition to reusing reclaimed PP copolymer in battery cases, reclaimed PP is used in a variety of injection molding applications. It can be incorporated into blends or filled molding compounds, and is widely used as a general purpose molding resin for automotive parts, liners, components, industrial containers, commercial trays, and consumer housewares or cases. Reclaimed PP which has been gone through a fine mesh screen should be suitable for extrusion into filaments or industrial film.

RECEIVED March 13, 1995

## Chapter 8

# Polystyrene Recycling: An Overview of the Industry in North America

David A. Thomson

Canadian Polystyrene Recycling Association, 7595 Tranmere Drive,  
Mississauga, Ontario L5S 1L4, Canada

Polystyrene (PS) is a versatile thermoplastic material used in a wide range of durable and single use applications. Post consumer PS is being commercially recycled throughout the United States and Canada, largely through the efforts of corporations involved in the synthesis, conversion and distribution of PS products. Markets for recycled polystyrene that can provide a basis for a sustainable industry are being developed.

Polystyrene, a product that has been closely associated with a litany of environment issues ranging from overburdening of solid waste disposal facilities to global ozone depletion can, and is, being recycled throughout the United States and Canada.

Recycled polystyrene materials are now commercially utilized in the electronics, horticultural, houseware, and construction industries.

In recent developments, post consumer recyclate has been approved for use in the manufacture of food packaging materials.

### Synthesis

Polystyrene is an amorphous thermoplastic produced by either the batch suspension, or mass-continuous polymerization of styrene monomer.

In the batch suspension process, styrene monomer is dispersed in water in a stirred reactor. Free radical initiators are used to control the polymerization parameters. A colourless polystyrene bead, similar in appearance to table salt, is generated from the reaction.

The batch suspension process is commercially used to produce expandable polystyrene (EPS) moulding beads through the addition of 5% - 8% (weight) of a hydrocarbon blowing agent, such as one of the isomeric pentanes, to the monomers prior to suspension in water. Dense EPS beads prepared in this manner are shipped to other locations, where they are expanded and formed into the desired product. Direct foam moulding of intricate shapes can be readily achieved near to the point of use, minimizing the cost of transport of the low density foam.

0097-6156/95/0609-0089\$12.00/0  
© 1995 American Chemical Society

EPS possesses good insulating value, light weight, low water pick-up, high rigidity, and excellent cushioning properties. These properties, combined with the relatively low costs associated with the production of EPS products, have resulted in the large scale commercial use of expandable polystyrene. The mass-continuous (or solution) process, made after technological advances in the 1950's made control of the exothermic heat of reaction and the handling of the highly viscous materials possible, has developed as the process of choice for all grades other than EPS.

Styrene monomer, solvent and occasionally an initiator, are passed through a series of heat exchangers until the desired degree of polymerization is achieved. Residual monomers and solvents are stripped from the polystyrene and recirculated to the front end of the reactor. Careful manipulation of residence time, reactor temperature, solvent content, and initiators produce polystyrene of high purity and low residual monomer content over a broad range of molecular weights and molecular weight distributions.

The homopolymer general purpose polystyrene (GPPS), produced from this process exhibits excellent clarity and is widely used in applications where transparency is required. GPPS extruded sheet can be foamed with the introduction of a suitable blowing agent during the extrusion process or formed into tough, clear sheets by biaxial orientation of the sheet in an operation downstream of the extruder.

Impact resistant polystyrene (HIPS) can be produced in the mass-continuous process by the addition of an elastomer, usually polybutadiene rubber, during the polymerization reaction. Alternatively, specialty impact grades can be produced by post reactor compounding of styrene butadiene block copolymers into a base resin.

HIPS derived by the former, more prevalent method, are translucent to opaque while the latter technique, which is considerably more costly is capable of yielding tough resins with good clarity.

Mass-continuous polymers are converted to finished goods in well known plastics processing operations such as injection moulding (solid and structural foam), solid extrusion, foam extrusion and blow moulding.

Typical products of these various fabrication techniques are shown in Table 1.

### Additives and Copolymers

GPPS and HIPS have attained significant commercial success as a result of their versatility, ease of fabrication, thermal stability, low specific gravity, and low cost. Additional benefits can be achieved through the use of additives to modify performance or enhance processing. The range of additives includes flame retardants, lubricants, antioxidants, ultraviolet light stabilizers, nucleating agents, and colorants. The use of additives and copolymers, while extremely desirable in the initial fabrication process, can create substantial challenges for subsequent recycling operations.

The range of properties of styrene homopolymer can be greatly broadened by copolymerization. Common commercial copolymers include Styrene-Acrylonitrile (SAN), Acrylonitrile-Butadiene-Styrene (ABS), Poly(styrene-Co-Methyl Methacrylate) (SMMA), and Poly(styrene-Co-Maleic Anhydride) (SMA).

<sup>1</sup>GPPS is often referred to as crystal polystyrene (XTAL), although this term refers only to the clarity of the resin, and not its other properties.

**Table 1**  
**Typical Single Use Application**

<b>Fabrication Technique</b>	<b>Single Use Products</b>	<b>GPPS</b>	<b>HIPS</b>	<b>EPS</b>
<b>Injection Moulding (Solid)</b>	Beverage Containers Cutlery Garment Hangers Dairy Containers Packaging (personal care products, medical supplies etc)	X    X	X X X X X	
<b>Extruded Sheet (Solid)</b>	Cup Lids Salad Boxes Dairy Containers Plates Baked Goods Containers Vending Cups Closures Trays: - Retail Display - Medical Disposable - Horticultural	X   X   X X X	X  X X X X X	
<b>Extruded Sheet (Foam)</b>	Meat (Poultry Trays) Produce Trays Clam Shells Hinged Lid Containers Egg Cartons Cafeteria Trays Foam Cups	X X X X X X X		
<b>Blow Moulding</b>	Bottles (Vitamin, etc)	X		
<b>Foam Moulding</b>	Cups and Containers Loose Fill Packaging Cushion Packaging			X X X

### Commercial Use

Polystyrene is the fourth largest volume commodity thermoplastic, ranking behind polyethylene, polypropylene, and PVC. The demand and nameplate production capability for PS and EPS in Canada and the United States are illustrated in Table 2 [1].

**Table 2**  
**Polystyrene Capacity**

Country	1993 Demand Metric Tonnes x 1000	1993 Capacity Metric Tonnes x 1000
United States	2,330	2,910
Canada	170	182
Total	2,500	3,092

NOTE: Some data from ref. 1.

Polystyrene, in its various forms, is employed, almost equally in the production of both durable and disposable (single use) goods. Table 3 shows the consumption of polystyrene for each of the common fabrication processes [2].

**Table 3**  
**Polystyrene Consumption Patterns**

Durable	Consumption Metric Tonnes x 1000	% of Total Consumption
Injection Moulding (Solid)	615	25.6
Extrusion (Solid)	202	8.4
Extrusion (Foam)	99	4.1
EPS	128	5.5
Total Durable	1,044	43.5
Disposable	Consumption Metric Tonnes x 1000	% of Total Consumption
Injection Moulding (Solid)	294	12.3
Extrusion (Solid)	557	23.2
Extrusion (Foam)	297	12.4
EPS	206	8.6
Total Disposable	1,354	56.5

NOTE: Some data from ref. 1.

### Recycling Polystyrene

Scrap polystyrene can be readily refabricated through direct introduction as regrind flakes back to the original moulding or extrusion process, or into alternate application after an extrusion and pelletizing step. The pelletizing process is particularly beneficial in cases where the ground flake material may contain contaminants, or consists of different grades

or colours. This practice has been common for many years as a method to recover defective parts, sprues, runners, sheet extrusion trim scrap, and web trim from vacuum forming operations. These pre-consumer scrap sources are generally of high quality, contain minimal contamination, and are available in quantities that support economic transportation and processing.

An industry aimed at the recycling of post consumer, or post use, polystyrene began to emerge in the late 1980's in response to demands for an alternative to landfilling or incinerating of single use polystyrene packages. Despite accounting for only some 12% of total polystyrene consumption, much of the early effort has focused on management of the foam single use packaging wastes.

Various alternatives to traditional disposal methods have been proposed and researched.

### **Mechanical Recycling**

Polystyrene materials sorted or segregated from the solid waste stream can be subjected to a process that may include some or all of the following elements; densification (foam), granulation, washing, drying, extrusion, and pelletizing. The resulting product is a pellet that possesses properties similar to the virgin resin and may be converted to finished goods in the same processes used in the initial fabrication operations.

In certain applications, post-use polystyrene may be left as a component of a mixed plastic stream where it may be useful in improving properties of "lumber" manufactured from commingled plastic.

Applications have been developed for the inclusion of granulated polystyrene foam directly into lightweight concrete mixtures or as a soil amendment to retain moisture and prevent compaction.

Fabricators of moulded EPS cushion packaging and insulation board have successfully incorporated granulated post consumer EPS directly into the production of new foam products.

### **Energy From Waste (EFW)**

Incineration plants that convert the stored energy in solid waste into electrical energy are available throughout many industrialized nations. Polystyrene constitutes a significant source of energy at 46,000KJ/Kg. For comparison, the calorific value of heating oil is 44,000 KJ/Kg <sup>[3]</sup>.

In areas that EFW facilities are permitted, it represents a viable alternative when polystyrene volumes do not support economic mechanical recycling operations, or that energy required to collect, sort, and transport the product exceed the energy demands of virgin production.

### **Thermal and Chemical Recycling**

Methods of thermally or chemically decomposing polystyrene and other plastics have been employed in commercial or pilot plant operations. The American Plastics Council (APC) in conjunction with Conrad Industries Inc., of Centralia, Washington currently operate a pilot plant in what is perhaps the most well known example of advanced thermal recycling in North America.

Polystyrene industry initiatives such as The National Polystyrene Recycling Company (NPRC), The Canadian Polystyrene Recycling Association (CPRA), and The Association of Foam Packaging Recyclers (AFPR) have focused on mechanical recycling activities and the challenges faced in developing a viable industry based on post consumer recycled (PCR) materials.

### Recycling Challenges

Some of polystyrene's most valuable properties create some of the most challenging impediments to economical recycling of post consumer materials.

Single service food packaging and cushion packaging are light weight. Beneficially, little plastic material is used in the manufacture of these products. Detrimentally, the quantity of material available at any given location is relatively small. Forty five kilograms per week of polystyrene packaging is produced by an average fast food restaurant or by a school cafeteria program.

Light weight and low volumes require that materials be consolidated for transport, or that imaginative systems be employed to reduce the impact of transportation economics on the recycling industry. In one such initiative, the NPRC is able to make polystyrene available to all school cafeterias across the contiguous states through a venture with United Parcel Service.

The consistency has resulted in FDS non-objection status for use of PCR at up to 50% in certain foam trays and containers [4]. Students remove residual substances from the polystyrene foam service tray widely utilized in school lunch programs, and stack the trays back into the original shipping box. A pre-printed label is applied and the boxes of used trays are collected by UPS for delivery to one of the three NPRC facilities in Bridgeport, N.J., Lincolnshire II, or Corona, California. This system provides a feed source of uniform, high heat, general purpose polystyrene.

The AFPR operates an extensive network across the United States. Over 100 EPS moulders provide backhaul of used packaging to their customers. Individual consumers may have access to drop off locations in some communities.

The Canadian Polystyrene Recycling Association has developed a network of private waste management and recycling companies that provide collection of single service food service packaging across a broad base of industrial, commercial, and institutional generators. CPRA encourages the collection of solid polystyrene materials together with foam products to increase capture rates and to improve the weight to volume ratio. Specialized drying equipment in the CPRA Recycling plant in Mississauga Ontario is capable of separating foam from solid prior to extrusion.

Large volume generators of EPS cushion package, or Material Recovery Facilities (MRF) handling this product, frequently utilize baling devices to raise the bulk density of cushion packaging above its loose value of 15Kg/m<sup>3</sup>. Typical downstroke balers will increase the bulk density to roughly 30 Kg/m<sup>3</sup>, although horizontal unit balers are available to produce bales of densities in the area of 250-400 Kg/m<sup>3</sup>. High density baling makes cleaning of the product in subsequent operations difficult. It is, therefore, imperative that all contaminants be excluded before baling. Baling at a point close to the source greatly improves transportation economics.

Polystyrene is versatile, which enhances its appeal as the material of choice in a host of disposable and durable applications. The diversity of products, from foam cups to refrigerator liners, make recognition difficult for the uninitiated. Much of the recyclable

polystyrene is not recovered simply because it does not resemble the foam cup or cushion packaging generally associated with the polymers. Data from Ontario, Canada curbside collection program show a recovery of foam that is highly disproportionate to resin consumption patterns (Table 4).

**Table 4**  
**Distribution of PS Products in Curbside Collections**

	% of PS Disposables	Recovered Ontario Curbside Collections		
		Mississauga	Halton	Quinte
Solid Extrusion & Injection	62.8%	1.1%	5.9%	27.4%
Extruded Foam	21.9%	84.5%	37.0%	38.1%
EPS	15.3%	14.4%	57.1%	34.5%

Polystyrene often competes with other polymers for a share of the same market. "Look-alike" products enter the waste stream and must be removed from the polystyrene if a quality product is to be produced. Polyvinyl Chloride (PVC), and Polyethylene Terephthalate (PET) are frequently confused with injection moulded GPPS or sheet extruded polystyrene single service food packaging and drink cups. Polypropylene and polystyrene are both extensively utilized in the production of disposable cutlery.

The properties of polystyrene can be enhanced with additives. Additives that perform admirably in their original intended use frequently pose problems for recyclers. Primary among these are the flame retardant additives, typically a halogenated organic compound with or without an antimony trioxide synergist. Flame retardant EPS reacts rapidly under normal extrusion conditions, resulting in severe chain scission and evolution of halogen gases. If moisture is present, acid compounds will be generated and equipment corrosion problems can arise. Recycled flame retardant EPS will exhibit molecular weight loss to values in the order of 140,000 or less, at which point the properties of the material are seriously compromised.

The presence of rubber from HIPS in a resin intended for an extruded foam process can inhibit the proper expansion of the foam sheet. Lubricants, such as metallic stearates commonly added to moulding resins can accelerate the decomposition of flame retardants, residual nucleating agents, or particulate contaminants that act as nucleators, can cause loss of control over foam cell structure.

The recycler must take care to segregate polymer grades and match applications to feed stock properties in order to produce quality products for secondary applications.

### **Durables and Semi Durables**

Durable goods manufactured from polystyrene may have a useful life ranging from several months to many years. These applications include housewares, toys, appliances, construction materials, and a gamut of other products, that eventually become part of a solid waste stream. Efforts have recently been directed at recovering and recycling polystyrene from these sources. Eastman Kodak Company's Fun Saver Camera [5] return



program, and Pitney Bowes, Laidlaw Waste System, Purolator courier partnership aimed at office machines and components, are successful examples of the reuse and recovery of polystyrene from durables.

Durable goods recyclers frequently encounter challenges with metallic components, and the presence of non-compatible polymers. Manual disassembly operations are frequently used to segregate polystyrene from the unwanted materials. Some applications, however, lend themselves to automation. CPRA and The Nova Group of Bocca Raton, Florida collect and recycle garment hangers from the retail industry. Both operations have developed technologies to separate the non-compatible polymers and metal hooks and clips common in these products.

## Outlook

Polystyrene recycling is good business, and there are growing indications that a sustainable industry is emerging.

Although polystyrene packaging is still viewed as environmentally unfriendly by a significant majority, a public opinion survey commissioned by CPRA showed that 80% of the population said their opinion would improve if they were better educated about the recyclability of polystyrene, and nearly half stated that their opinion would change "a lot". It is important to note that almost 20% indicated that they would "go our of their way" to visit a fast food restaurant that recycles its polystyrene [6]. In the relatively short time that post use polystyrene has been commercially recycled, substantial results have been observed.

The Polystyrene Packaging Council (PSPC) reports that in the United States the recycling rate for post use EPS in 1993 reached 10,570 tonnes, or 10.9% of the total EPS cushion packaging market, making it the third most recycled plastic product, behind soda bottles and milk jugs. The total post use polystyrene recycled in the same period exceeded 19,000 tonnes [7].

Consumer awareness of polystyrene recycling has risen dramatically as demonstrated in the results of CPRA's polling. In 1990, only 18% of consumers surveyed believed it was possible to recycle polystyrene products, a number that had risen to 46% in the March 1994 poll [8].

Fuelled by growing public awareness, strong markets, generated in part by minimum PCR content regulations, and a solid industry commitment, the outlook for polystyrene recycling is encouraging, although the industry must convert increasing consumer awareness into increased consumer action, to generate the volumes required for sustainable development of facilities and markets.

## References

- [1] *Modern Plastics*, 71(1) (1994) pp73-81
- [2] *Modern Plastics*, 71(1) (1994) pp73-81
- [3] *The World of Plastics*; Society of the Plastics Industry of Canada; pg71
- [4] *Modern Plastics Int.*, 23(12) pg10
- [5] Eastman Kodak Company, *SPE Recycling Conference, 14-16 June, 1993*
- [6] Angus Reid, Canadian Polystyrene Recycling Association, internal unpublished poll
- [7] *Recycling Polystyrene - Polystyrene Packaging Council, 5(1) (1994) pg2*
- [8] Angus Reid, Canadian Polystyrene Recycling Association, internal unpublished poll

RECEIVED July 7, 1995

## Chapter 9

# Progress in Poly(vinyl chloride) Recycling

Robert H. Burnett

Vinyl Institute, 65 Madison Avenue, Morristown, NJ 07960

This paper discusses the progress that has been made to integrate vinyl plastics into the solid waste management infrastructure. It includes an update on those systems designed to separate vinyl from other post-consumer plastic packaging and describes where they currently are in commercial use. It references some of the efforts underway to develop auxiliary technologies, which could result in even purer plastic recycle. It describes the vinyl industry's work to encourage the commercialization of new products made from recycled vinyl and describes those products already being produced. Levels of activity among companies recycling vinyl and producing recycled content products are discussed. Details of prototype recycling programs for non-packaging applications are provided and an update of key regulatory developments related to vinyl recycling in the U.S. and Europe is presented. Trends in use of vinyl packaging for various applications -- film, sheet and bottles -- are included.

The subject of PVC recycling may be an unfamiliar one to many people, but there is plenty to say about it. Indeed, many individuals believe that PVC -- or, preferably vinyl, cannot be recycled, or is not being recycled. That is certainly not the case, and the purpose of this paper is to provide evidence to the contrary, as well as give an indication of where vinyl recycling is headed in the future.

### Profile of the Vinyl Market

Vinyl is one of the most established plastic materials on the market today. The first applications for vinyl were commercialized over 75 years ago, and the first widespread use occurred over 50 years ago, when vinyl was substituted for rubber wire insulation on World War II battle ships. Today, vinyl is the world's second largest selling plastic material, exceeded in volume only by low density polyethylene.

0097-6156/95/0609-0097\$12.00/0  
© 1995 American Chemical Society

Last year, over 10 billion pounds were produced in the United States, and over 30 billion pounds worldwide.

By far, the largest market for vinyl is the construction industry, which accounts for about 60 percent of all vinyl resin sales, while the largest use for the other major plastics tends to be packaging. This distinction certainly sets it apart from the other resins, and has, as a result, earned it a reputation as the "infrastructure plastic." In construction, vinyl's broad range of formulating possibilities allows it to be used in everything from large diameter water distribution pipe to flexible baseboard moldings. In addition to packaging, other major markets for vinyl include electrical and electronic uses, transportation (primarily, automotive applications), furniture and furnishings, and consumer goods.

Within the packaging market, major uses for vinyl include rigid, blow-molded bottles, which currently consume just under 200 million pounds of resin a year in the U.S. These bottles largely are found in what is called the "custom market," which essentially consists of any type of plastic bottle other than soda bottles or milk jugs. Vinyl is used to package a variety of products, ranging from cooking oil to shampoo. In Europe, a very large market is in bottled water. In the U.S., vinyl is particularly popular with smaller, regional brands, because the economics in these cases favor vinyl over the competitive polymer, polyethylene terephthalate, or PET.

The other major use for vinyl packaging is in film applications. This includes rigid film, used in pharmaceutical packaging, as well as many other types of so-called "blister packaging" and flexible film, including wrap for both fruits and vegetables, as well as meat. Other uses for flexible film range from pallet wrap to tamper-evident seals for over-the-counter drugs. Together, rigid and flexible film applications also consume about 200 million pounds of vinyl resin per year.

### Vinyl in the Waste Stream

Given the relatively small amount of vinyl that goes into the packaging market, it's also not surprising to find out that it's a relatively inconsequential part of the total packaging found in the municipal waste stream. This has tended to present both advantages and disadvantages from the perspective of overall waste management. In the case of either landfilling or incineration, it's an advantage, because the relatively small volume of vinyl involved does not present significant obstacles to the process.

Like other plastics, vinyl is extremely stable in landfills, does not break down or leach chemicals into groundwater. In fact, vinyl is often used to make landfill liners because of its excellent resistance to the chemicals that are sometimes found in these facilities.

In incinerators, vinyl does generate hydrogen chloride, which must be neutralized as part of the process, but it is not unique in this regard. Moreover, recent research has found that this can be done at relatively little cost -- about one percent of overall incineration costs. As to dioxin formation in incinerators, which is one of the issues currently being studied by the EPA as part of its dioxin reassessment, the most authoritative work in this area -- the work conducted by the New York Energy Research and Development Authority in 1987 -- indicates that the presence or absence of vinyl has no impact on the generation of dioxins. It is, instead,

controlled by incinerator operating conditions, especially, temperature. These results have recently been confirmed by the Association of Plastics Manufacturers in Europe.

But what about the third common waste management technique, recycling? Here, industry has faced its greatest waste management challenges, for two reasons. First, vinyl is a relatively small amount of the process, which means that the economics of collecting and processing it are different than they are for the two commonly recycled materials, PET soda bottles and HDPE milk jugs. Second, visually, PET and vinyl are similar. Since both materials are commonly used in the custom bottle market, this complicates the plastics sorting process. However, the vinyl industry has done a significant amount of work to address these challenges, and has some very positive advances to report as a result.

### Vinyl Recycling Advances

As is the case for all other materials retrieved from the waste stream, vinyl recycling involves four basic steps: collecting the material, separating different materials from each other, processing the resulting streams into a useable form -- in the case of vinyl, a dried flake, -- and converting the reclaimed, reprocessed material into a second generation product.

Large-scale plastics recycling really took off in the mid-80s, fueled by growing concerns over the perceived decline in landfill space, as well as the rejuvenated environmental movement. In fact, it was the infamous "Long Island garbage barge," that really sharpened the focus on plastics recycling.

The first plastics recycling ventures were extremely labor-intensive, and far from economic. In the earliest days, the approach was simply to visually separate out the milk jugs and soda bottles, and scrap everything else. As a result, recyclers were landfilling a lot of potentially valuable material.

The vinyl industry knew, for instance, from a study conducted by the University of Toledo in 1989, that there were over a hundred potential uses for recycled vinyl. More important, the demand for the material was estimated to be over twice as large as the potential supply, indicating that pricing would also be good.

The addition of the SPI resin identification code was the first step in opening up the recycling market for the other plastics, like vinyl. Those codes enabled consumers to sort their plastics for curbside pickup or drop them off at central locations according to the individual resin. In other cases, it greatly enhanced the separation process within recycling plants.

But most of that separation work was still being done by hand, making it a high-cost process. And, even under the best of circumstances, it was subject to either consumer or worker error -- meaning that bales of "custom" PET bottles frequently contained one or more stray vinyl bottles. Those who know anything about the melt temperatures of these two polymers will quickly appreciate the problems this presented: recycled PET polymer with charred bits of vinyl.

It was for these reasons that the vinyl industry took the lead in sponsoring the development of automated separation technology -- one of which is the technology developed by National Recovery Technologies, of Nashville, Tennessee. Essentially, this technology, and similar systems developed by other companies, relies on the

chlorine content of the vinyl bottle to separate it from PET. The Vinyl Institute provided significant funding to commercialize the NRT system, and also provided funding to another company, Magnetic Separation Systems, also of Nashville.

Industry also provided funding for pilot program testing and demonstration sites, where refinements for the NRT and MSS systems were identified and integrated. Tests run on these systems indicate that both can achieve nearly 100 percent purity in their PET/vinyl streams under proper operating conditions. Not only has this technology helped build a market for vinyl recycling, but it has proven to be a tremendous boon to custom PET recycling as well.

Today, both companies market a variety of equipment that is designed to serve processing facilities of various sizes, and have systems in place throughout the United States and in Europe. In the future, other companies are expected to enter this market, which should help bring further price competition into play, making the equipment more affordable for more processors, and thus increasing the volume of vinyl reclaimed from the waste stream. It is also likely to spur development of auxiliary technologies, which should result in an even purer stream of recycled material. Both of these factors are likely to encourage even broader use of recycled vinyl in various end-uses.

### **Further Recycling Support**

At the same time that the vinyl industry has been working to overcome the obstacles associated with the separation process, it has also established a number of other efforts to support the recycling industry in general, and the development of end-market uses in particular.

One of these is the Vinyl Environmental Resource Center, or VERCE, as it is commonly known, which was established in 1991. Operated by the Vinyl Institute, VERCE is a national information clearinghouse that serves as a networking resource for the recycling industry. Through VERCE, the VI operates a toll-free "hot-line," accessible throughout the U.S. and Canada, maintains a computerized database of environmental and recycling contacts, conducts media and environmental monitoring work, and maintains a centralized file of industry research related to environmental topics. A large amount of the work VERCE does involves networking within the recycling industry -- matching people with material to sell with those who need it, and otherwise facilitating the process of vinyl recycling.

VERCE also publishes two directories: The *"Directory of Companies Involved in the Recycling of Vinyl (PVC) Plastics"* and the *"Directory of Companies Manufacturing Products from Recycled Vinyl."*

Finally, VERCE also administers something called the "Tool Pool" program, a nationwide effort designed to encourage the commercialization of new products made out of recycled vinyl. The program uses a request-for-proposal process to identify and provide limited tooling support to qualifying companies in exchange for modest royalties on the finished product. Commercial product is already on the market as a result of this program.

VERCE has been a highly successful undertaking. Even though the Center is over three years old, use of the hotline remains very high, and now averages over 150

calls per month -- most of them from recyclers. As an additional indication of success, *The Directory of Recycled Products*, which listed 43 companies in the first edition, lists 57 in the second. More impressive, the *Directory of Companies Involved in Vinyl Recycling*, has grown from 47 listings in the first edition, to 170 companies in the third edition published in May 1994.

### Trends in Vinyl Recycling

Research conducted for the American Plastics Council tells us that currently, about 6 million pounds of post-consumer vinyl packaging is being recycled in the United States. Another 6 million pounds of post-consumer vinyl is being recycled from non-packaging applications. Clearly, this amount pales in comparison to the levels being reported for PET and HDPE, but it *is* 12 million pounds of material that otherwise would have been landfilled.

The gap between vinyl and PET and HDPE is expected to remain somewhat constant as long as recycling continues to focus primarily on packaging. First, because current activity is largely driven by states with deposit laws for beverage bottles, which has provided a tremendous boost to PET soda bottle recycling. Second, because until automated sorting becomes more widely used, economics for plastics recycling tend to favor the "ones" and "twos."

If one looks beyond the packaging market however, there is enormous potential for vinyl recycling -- especially in the construction market, which generates tremendous amounts of scrap each year from new product installation as well as replacement work. In fact, there has been a sharp increase in environmental awareness in the building industry in just the last eighteen months or so, with builders and suppliers alike now touting the "greenness" of their projects and products.

The Europeans are far ahead of the U.S. in the area of so-called "durables" recycling, which is not surprising given the fact that there has been much more interest in Europe to date among architects and specifiers about "building green." The vinyl industry in Europe, represented by the European Council of Vinyl Manufacturers, has responded to this interest by establishing several prototype recycling programs for construction and demolition scrap. These include a successful program in France to use post-consumer reclaim in pipe, and another program in Germany to recover vinyl flooring. Given the relative shortage of landfill space in Europe, the high "green" consciousness there, and the somewhat simpler logistics that the compressed geography offers, there should be more of these programs in the future.

### Encouraging Further Growth

The U.S. vinyl industry has just begun to look at what it might do to encourage these types of efforts here. Preliminary thinking on this indicates that the highest likelihood for success probably will involve working with large-volume materials users or scrap generators who can collect sizeable amounts of scrap in a contained geographic area.

But it also, conceivably, could involve wholesalers, or even the major do-it-yourself retailers. In fact, the Vinyl Siding Institute recently launched a pilot program for

recycling scrap vinyl siding in North Carolina, which it hopes can be duplicated throughout the country. That program, which involves six collection sites in a 200-hundred mile radius, generated 50,000 pounds of scrap in its first three weeks of operation.

The construction market is really just the tip of the iceberg as far as non-packaging recycling is concerned. The automotive market, for instance, now routinely refers to "designing for disassembly," and there is similar growing interest in recycling among appliance manufacturers, in the wire and cable business, and among computer makers, who are beginning to talk about the "green machine" -- the new environmentally friendly personal computer. Is there a future for vinyl recycling in these applications? Absolutely. Will it take time to establish an infrastructure that can make these ambitious goals a reality? Even more absolutely. But it can be done, given the right technology, the right programs, and most important, the right economics.

### **The Hidden Recycling Market**

This paper would be incomplete if it did not address one more aspect of the vinyl recycling story: the millions of pounds of "pre-consumer" scrap generated every year by American industry -- everything from trim scrap to off-grade resin. Many recycling purists tend to dismiss pre-consumer material as something that shouldn't really be counted in the recycling mix. But those who embrace the true spirit of recycling -- landfill avoidance and maximum use of materials and resources -- realize how significant pre-consumer recycling is to the country's long-term objectives of reducing dependence on landfills for waste management. It's difficult to say how much pre-consumer vinyl is recycled each year, but it is clear that large quantities of this material are finding their way into the marketplace each year, in a surprising range of products that have a great deal of utility to all of us.

What *are* some of the end uses for recycled vinyl -- both pre-consumer and post-consumer? Not surprisingly, given the fact that most applications for virgin vinyl are outside the packaging market, most uses for recycled vinyl also, currently, are in other types of applications. Some of it's going into durables applications, such as pipe with a recycled vinyl core sandwiched between two layers of virgin vinyl, or into other uses in the construction market, such as non-structural lumber or the substrate for vinyl siding. Still more is being used to make a variety of industrial and consumer products such as floor tiles and mats, garden hoses, notebook covers, pond liners and traffic cones.

There are also a number of companies that are producing bottles with significant levels of post-consumer vinyl, some that produce rigid sheet for blister packaging containing post-consumer vinyl, and several that produce clamshells, trays and other custom packaging. It is particularly heartening to see this type of activity on the increase because of the growing interest at the state level in imposing regulations that require certain amounts of post-consumer content in various types of packaging in order to encourage recycling.

### Predictions for the Future

As it becomes clearer and clearer that post-consumer vinyl can and is being recycled, industry expects to see a decline in the move away from it as a packaging material. In the U.S., the amount of vinyl used in bottles has declined, but appears to be leveling off at roughly 200 million pounds a year. Some of this decrease may be due to the trend toward source reduction -- or "downsizing" of the package itself. In film and sheet packaging, however, the use of vinyl is actually growing. This is very significant, because the packaging market has always been at the forefront of change vis à vis environmental policy development, and decisions on material use made there tend to influence material selection in other markets.

It's also clear that society is becoming more and more committed to the concept of resource conservation and environmental preservation. Obviously, recycling is one of the most efficient ways to achieve those goals. Products that can be easily processed for recycling, and have ready use in second-generation applications, will thrive under these conditions. The work industry has done to make vinyl recyclable, and the work it's still doing to encourage the use of recycled-content end products, means that there will continue to be a place for vinyl in the new world market.

The technical feasibility of vinyl recycling has been clearly demonstrated. Now, the challenge for polymer producers and recyclers alike is to work together to refine the technologies, develop the systems and support the municipal efforts that will expand vinyl recycling to the level that will make the process work on a day-to-day, city-by-city basis.

RECEIVED March 16, 1995



## Chapter 10

# A Resin Producer's Perspective and Experiences in Polyethylene Recycling

W. Keith Atkins

Solid Waste Management, Union Carbide Corporation, 39 Old Ridgebury Road, Danbury, CT 06817-0001

Recent trends in environmental marketing coupled with the need to comply with recycle-content packaging laws enacted in a number of states, have significantly increased the demand for high quality recycled polyethylene sourced from post-consumer feedstocks. Union Carbide's experiences in entering the mechanical recycling business are discussed with specific examples given that define quality requirements and future industry trends, including the need for color-sorted products that are consistent in quality and reproducible.

Embarking on a new business venture has always been a prospect akin to a roller coaster ride. It's exciting, to be sure, but sometimes you leave the pit of your stomach at the top of the coaster loop while your car descends to the depths. Yet, ironically, when the roller coaster arrives at its terminal, you usually want to ride again. Union Carbide embarked on its own recycling business odyssey in 1991 with the opening of its Plastics Recycling Plant in Piscataway, New Jersey. This venture came with its own unique set of challenges. Plastics recycling is an industry still in its infancy - - there is no history to guide us, and rapid change is the only constant. When you contrast this situation with the well-established 50-year-old virgin polyethylene industry, you can readily understand why plastics recycling is a whole new world.

Union Carbide's recycling raw materials, which come from community collection programs within a 250-mile radius of the plant, make their own journey from the curbside, to municipal recycling facilities (MRF's) where they are separated from other materials and baled, and finally, to our plant for processing. We actively seek out only those suppliers who can meet our contamination level requirement of less

0097-6156/95/0609-0104\$12.00/0  
© 1995 American Chemical Society

than 2%, because high quality recycle feedstock is required to produce high quality recycled resin. Carbide's primary objective is to provide our customers with post-consumer resins (PCR) whose quality and performance levels approach that of virgin resins.

In Carbide's plant, sorting had been the first stage of a three-part operation that included sorting/grinding, washing/drying and extruding. In the early days, there was a lot of hand labor involved. On our 90-foot sortation line, which was one of the largest in the industry, the recyclables would move past sorters as they separated bottles by color and resin type into unpigmented PE bottles, pigmented detergent bottles, clear and green-tinted soda bottles and the like. After sorting, the bottles were delivered to one of four large grinders which whirled at high speed to cut up the bottles into confetti-like pieces, ready for washing and drying.

Today, our new PRISMA™ resin color-sorting system allows unsorted bottles to be delivered by MRF's, then automatically color-sorted at the plant. The ground flakes are then conveyed to the washer/dryer system. In the first of three wash/rinse phases, the plastic flakes are loaded into a wash tank where they are agitated much like clothes in a washing machine. The chips are then transported into rinsing units where dirt, labels and glue are separated from the clean flakes. These chips are dried in large spin dry units and air-conveyed to extruders for pelletizing.

The compounding and extrusion stages come next. Inside a 20-foot long extruder, a variety of additives and stabilizers are added to create the post-consumer resin which Carbide markets as CURBSIDE BLEND® PCR®. The resin is then packaged according to our customers' preferences in sizes from 1000-lb. boxes to 180,000-lb. rail hopper cars. Delivery is then made in truckloads by common carrier, or via a hopper car fleet dedicated exclusively to the recycling business.

**Automation.** Because of the higher price of virgin PET and the fact that PET reclaimers are forward-integrated (i.e., consume their own product), PET recycling has attained profitability. Unlike PET, PE has yet to be a profitable business. A number of things have to happen first before that goal is reached. Companies throughout the recycling industry are actively looking for ways to decrease costs. One item that should help to reduce cost is manufacturing automation. Experience has shown that plant capacity must be at least 40 million pounds per year in order to enjoy economies of scale. To get to that point automation is needed that will allow us to get more volume out of existing investments, or allow people to build larger plants. So people went back to the laboratories and came up with automated sorting,

debalancing and other equipment that would save time, process faster and let processors enjoy those economies of scale.

Production rates in plastics recycling are now beginning to parallel what happened in the virgin resin business. Virgin polyethylene reactors in the 1960's produced 2500 pounds/hour; today, these typically run at about 90,000 pounds/hour. The trend in plastics recycling is also toward larger sorting lines. Whereas 2000 pound/hour lines were considered optimum in the beginning (ca. 1990), we now see 6000-8000+ pound/hour lines.

**Color Measurement.** The way we measure resin color today is a far cry from the recycling industry's fledging years. In those days, the human eye was the only means of determining resin color quality. Samples were graded A, B or C - - it was as simple as that, based entirely on personal judgment calls. This system just will not do for today's needs. Customers have very specific resin color needs, so a subjective approach had to give way to a purely objective one. The industry recognized that a way had to be found to clearly communicate resin color values that were backed by analytical data. So, the right tool had to be found and it turned out to be a hand-held colorimeter. Carbide, and a growing number of reclaimers, use the HunterLab MiniScan.

The Hunter unit makes color measurements along three axes in a 3-dimensional color body matrix. One coordinate goes from red to yellow, another from blue to green. The third coordinate goes from pure white to pure black. The colorimeter makes measurements along the three axes and calculates a CIE number which we use as a measure of the whiteness of the natural PCR resin.

During the recycling process, high dirt levels in the raw materials can give recycled resin an unattractive appearance. The colorimeter has been invaluable in determining dirt levels and helping us to control them. The lower this level is, the whiter the PCR - - and this is of prime importance to our customers. In addition, after grinding the flakes can be checked with the colorimeter for the whiteness level before they go on to the washing stage, to assist in determining process conditions in this stage.

Now, color measurement is being used to characterize color-sorted materials, so that we can make process adjustments to ensure that the resulting PCR is acceptable to our customers. For example, before we got into machine-based color measurement, the red-orange-yellow PCR known in the industry as ROY, would wander in terms of box-to-box color consistency, varying from red to orange to tan or yellow. Since we've been using the colorimeter technology along with our new color

-sorting system, we can consistently produce PCR to our customers' increasingly demanding requirements.

The codifying and standardizing of color measurement is not only helping to ensure better communication about the color quality of a recycled resin, it also is lending more credibility and professionalism to the whole recycling industry.

**Detergent.** The above-described colorimeter also determines the amount of detergent that is required for the cleaning process. In the case of natural resins, color measurements of the flake are taken after cleaning. If the MiniScan indicates that these "PASS" our whiteness requirement, then the flakes are conveyed to the extrusion stage, but if they "FAIL" our requirement, they're sent back for further cleaning.

Union Carbide realized early on that detergent cleaning of the flakes was a critical step in the reclamation process. We approached Oakite, a leading compounder and marketer of industrial cleaning chemicals, to get some help, and subsequently formed a joint development program with them. For our part, we gave Oakite our color requirements and samples that represented the material "dirtiness" issues we faced. Also, we provided Oakite with information on specific cleaning problems, such as residual glue and paper removal, etc. Oakite's scientists would work on these issues, then we would perform joint plant runs to determine if improvements had been made.

**Color Matching.** Plastic Packaging (e.g., bottle, tub, overwrap, etc.) manufacturers are always concerned about the color quality of the items they produce, including item-to-item consistency, and fundamental color characteristics. These concerns are driven by the specifications imposed by customers of packaging manufacturers.

The use of HDPE PCR as a component resin in the manufacture of packaging presents new challenges to those responsible for color quality. In the case of natural HDPE PCRs, these resins contain inherent color bodies, that vary in both type and intensity. For this and other reasons bottle manufacturers often use multilayer blowing molding equipment to produce PCR-containing products. The exterior, or "skin," layer of the bottle is composed of a pigmented virgin resin that masks the color variability of an interior layer, containing the PCR. Even with this technique, there is often a trade-off between pigment loading (and therefore cost) in the "skin" layer and achieving acceptable bottle aesthetics.

To illustrate with an example, Helene Curtis' Salon Selectives shampoo bottles are manufactured by Silgan, using three-layer blow

molding equipment. The center layer contains natural HDPE PCR provided by Carbide. During the development of these bottles Carbide made a step-change improvement in the "whiteness" of its natural HDPE PCR. In spite of the pigments used in the exterior layer of the bottle, the change in the "whiteness" of the PCR changed the apparent color of the bottle. As a result, Silgan and its color concentrate supplier, Allied Color, had to go back to the laboratory to formulate a modified concentrate to offset the change resulting from the PCR improvement.

Concerning a related subject, the color characteristics of PCR derived from random mixtures of recovered, post-consumer, pigmented HDPE bottles have been the primary impediment to developing high value-added markets, e.g., packaging uses, for these resins. Typically, the PCR resin recovered from these types of bottles is a "muddy" green or gray color. These unaesthetic and variable color characteristics are difficult to hide, except in the darkest, e.g., black, and most opaque coloring schemes. Because of these characteristics the demand for post-consumer pigmented bottles has, historically, been weak, resulting in a lower value for this raw material source. Communities have been more reluctant, therefore, to collect this type of container. To illustrate this point, in 1993 the recycling rate of pigmented bottles was about 9%, compared to a rate of 25% for unpigmented milk, water, juice, etc., bottles.

At Carbide, we believe that the best approach to achieving a higher value for pigmented bottles is to produce recovered resins that have uniform and more marketable colors. The processing approach we have taken to achieve this higher value is a sophisticated color-sorting system which allows Carbide to market a line of products trade-named PRISMA™. It is our hope that the availability of this approach will stimulate communities to add pigmented HDPE bottles to existing recyclables collection programs.

**PRISMA™ PCR Copolymer Resins.** Union Carbide installed a unique color sorting system at its Piscataway plant in late 1993. This system represents a significant departure from the way plastics had been sorted previously. With this system, unsorted bottles can be delivered by municipal recovery facilities, then in-process material is color sorted at the plant using automated machines. It is a high-speed system that provides our customers with unparalleled batch-to-batch color consistency. Any color that can be obtained from the feedstock mixture, can be reproduced for a consistent batch-to-batch color quality, within very narrow tolerances. So, customers simply select the desired resin color, which is programmed into the system, and the same shade is produced within a narrow band each time a PCR batch is run.

PRISMA® resins produced by the system are true "value-added" products. Batches of PCR with a targeted color are typically produced in 40K pound lots. Our customers prefer this lot size not only because of the excellent color uniformity, but also because of the uniform processability and continuous superior performance over long production campaigns. Our customers normally adjust extrusion hardware once per blend with PRISMA PCR's vs. the continuous adjustments they have experienced with competitor's color-sorted PCR®, resulting from box-to-box color variation. Minimum adjustments to customer hardware results in reduced staffing requirements and higher profits.

Based on the mix of post-consumer pigmented bottles currently available the types and yields of color-sorted PRISMA resins produced by the system are as follows: orange-based resin, 35-40%; blue-green-based resin, ca. 30%; white resin, 30-40%; and residual (predominantly black), 5%. While expanding the number of available colors is technically feasible, it is our view that the slate of products listed above is the best compromise between the investment cost in color-sorting hardware, and the value of the resulting products.

More broadly, creating a viable market for post-consumer pigmented bottles is essential. The demand for post-consumer HDPE packaging is likely to exceed the supply of PCR available from recovered unpigmented milk, water, juice, etc., bottles. As a result, increased collection of post-consumer pigmented HDPE bottles is needed. The availability of the PRISMA resin color-sorting system is, in our view, instrumental in providing sufficient value to both material recovery facility operators and packaging manufacturers to support increased collection of post-consumer pigmented HDPE bottles.

**FDA Letter of "No Objection".** Because FDA clearance is crucial to the use of post-consumer resins in food, drug and cosmetic applications, Union Carbide has embarked on comprehensive testing of its post-consumer products and resin operations to prepare a clearance application. Our current goal is to secure an FDA letter of "No Objection" for our process technology to reclaim polyethylene from natural, post-consumer bottles. The tests we're conducting are those recommended by the joint Society of the Plastics Industry, Inc., and National Food Processors Association Plastics Recycling Task Force protocol. The point of these tests is to determine if a recovery process is able to reduce contaminants in PCR to FDA "de-minimus" criteria - - that's the minimum allowable human exposure without hazard. If these conditions are met reproducibly, the FDA could consider Union Carbide-produced natural PCR to be within its clearance guidelines.

FDA clearance of recycled resins would provide many benefits. First, it would set the stage for us to enter the food, drug and cosmetics packaging markets. Second, a letter of "No Objection" will enable our customers to comply with the legion of plastics recycling-related initiatives throughout the country in such bellwether states as Oregon, California and Florida. Third and last, consumers and the environment will be beneficiaries. A significant amount of post-consumer plastics will be diverted from landfills, back into the marketplace. Consumers will also be able to feel a lot better about choosing plastic packaging, because it will comply with state-mandated recycled resin content. This will allow consumers to accept plastic packaging for the reasons they did in the first place: freshness-preserving, tamper-resistant, lightweight packaging, with unique health and safety benefits, that can be recycled again and again.

**Feedstock Quality.** Union Carbide's suppliers are still plagued by the quality of feedstocks, especially in the pigmented bottle area. Householders can do a lot to help remedy this problem. For example, they could remove caps, particularly those on "pump" bottles. These caps have metal springs and ball valves - - and they all wind up in the bottom of our float-sink tank. Time and again we've had to shut down operations due to dirt, sludge and springs in the bottom of the tank.

Packagers must do their part to make recycling viable because the efficiency of each stage along the PCR manufacturing route can be severely compromised by packaging and labeling choices. Consider multi-layer packaging. The inner layer may be of a very different color, but the sorter sees only the outside layer. The blended final product is a muddy-toned PCR. Even worse is the case in which a bottle made from several different materials is identified only by the SPI code for the principal resin. While a barrier layer is there for product protection, the materials in all the layers ought to be melt compatible.

Packaging choices can also foul the metal detector process that the materials go through before grinding. Aluminum foil seals come in two types: the pull-away seal and the destruct type. The pull-away is easy to handle, leaves no foil on the bottle, and is ideal for recycling. The destruct type has to be broken open and leaves foil on the ring which gets detected as metal contamination by the detector. If the detector stops the line each time foil appears, the efficiency suffers. On the other hand, if the detector is tuned too low, it will be unreliable for detecting actual metal in thick-layer bottles. This metal will get into the grinders and necessitate repairs.

Labels are the worst problem in the wash and dry stage. Certainly printing inks containing toxic materials, such as lead, shouldn't be

used. As inks dissolve, they could put lead into the wash water and in contact with the plastics. Metallized labels look good, but they too introduce metal into the process. Glue becomes a culprit when labels are sealed over the entire surface, such as those on some PET bottles, rather than just at the seam. Minimizing the amount of glue used as well as using water-soluble glues should be important recycling goals. Because some packagers are concerned that labels will come off with condensation, we need a glue that will be solubilized when in contact with hot detergent water, but will not loosen on the store shelf or store cooler.

Hot melt glues are real troublemakers. The types that soften only at very high temperatures use up energy and require more detergent to remove, as well as consuming very hot water that can be a safety hazard. Obviously preferred are those that melt with warm wash water and little or no detergent.

During the rinse cycle, polyethylene floats and is skimmed off while PET sinks to the bottom of the unit. This is where some PVC cap liners will cause problems. With the same specific gravity as PET, the PVC will sink to the bottom with the PET and mix with it in the final product. When PET is refabricated, the molding temperature is so high that the PVC burns, showing up as a charred spot.

When metal foil is heat-sealed onto plastic, the only place where foil can be removed is on the extruder melt filter. This greatly increases the amount and frequency of screen changes, creating high cost. It is to the advantage of processors, fabricators and their customers to work through packaging design questions themselves rather than have packaging design legislated.

**Applications.** Our CURBSIDE BLEND® PCR shows up in an increasing variety of end-products. A quick look at our customer list discloses such uses as trash containers, oil bottles and drainage pans, bleach, shampoo and kitty litter bottles, book binders and dividers, money bags, consumer products containers, as well as various film and Household/Industrial/Chemical bottle applications.

**Future Industry Trends.** As I look into my crystal ball, I see definite trends, some of which appear inevitable. I believe we're going to see:

- \* Larger production line capacities and larger overall plant capacities.
- \* Improved grinding because this is a high-cost maintenance operation.
- \* Grinding shifted to the MRF's, which will eliminate the need to bale materials.
- \* Increased emphasis on the recycling of durables, such as auto parts and computer housings. We have already seen the beginning of this



trend. For example, automotive companies are now making the effort to design recycle-friendly auto parts as well as technology that will allow easy disassembly of auto parts.

\* Automatic sorting technology for packaging. This could involve fixed position sensing and separation systems that would handle packaging.

\* Identification and sorting of durables. This ID system may be a portable one with a sensing head connected by a fiber optic system to allow correct identification of plastic type during disassembly of computer housings and other durables.

An expansion of the present sorting commodity resins such as HDPE and PET to sorting some of the engineering plastics (such as nylon and polycarbonate) which have a higher intrinsic value.

Plastics recycling is still in its infancy. Its future depends to a great extent on efforts to educate the public about plastics recycling, on cooperation between processors, fabricators and their customers, on the increasing use of pigmented bottles and on a more cost-effective manufacturing process.

RECEIVED March 13, 1995

## Chapter 11

# Morphology and Properties of Poly(ethylene terephthalate)–High-Density Polyethylene Blends

### Effects of Processing Variables

S. A. Jabarin and V. V. Bhakkad<sup>1</sup>

Polymer Institute, University of Toledo, Toledo, OH 43606–3390

Ternary blends of poly(ethylene terephthalate) (PET) high density polyethylene (HDPE) and compatibilizing agent (CA) have been studied with respect to blend composition and processing variables. Resultant changes in rheological, morphological, mechanical, thermal and spectroscopic characteristics have been investigated. Processing conditions such as temperature of melt blending and screw speed have been found to exert major influences on the phase morphologies of the blends. Changes in particle size and size distributions of the minor phase, have been elucidated with the technique of scanning electron microscopy. Mechanical properties of the blends have been correlated with the particle size distribution of the dispersed phase. It has also been shown that processing variables influence the extent of compatibilization and its effects on the crystallization behaviors of the major phases. The degree of chemical interaction among the phases has been monitored with infrared spectroscopy, to reveal low energy hydrogen bonding between the PET and the compatibilizer.

A compatibilized Poly(ethylene terephthalate)(PET)/High Density Polyethylene (HDPE) blend can be expected to have numerous commercial applications in recycling the two plastics. Since clean, useable recycled PET and HDPE are commercially available today, it is desirable to exploit the inherent chemical resistance of PET and the processing characteristics of HDPE. PET and HDPE are mutually immiscible and form a two-phase alloy when processed as binary blends. Miscibility is not, however, a necessary condition for the development of useful blends. In many applications, two-phase or multi-phase blends are required in order to achieve optimum balances among the characteristics of the individual components.

Although ample literature is available regarding blends of PET or HDPE, only a few investigations have dealt with blends composed of both PET and HDPE. Traugott, et al (1) studied the behavior and properties of PET/HDPE blends upon addition of a styrene-butadiene triblock copolymer. Rheological parameters during processing, have been shown by Wu (2) and various other workers, to determine the

<sup>1</sup>Current address: RheTech, 1500 East North Territorial Road, Whitmore Lake, MI 48189

morphology and hence the mechanical performance of blend materials. In the work pursued by Jabarin, et al (3), the authors have attempted to modify and study the blow-molding and extrusion characteristics of PET by blending it with blow-molding grade HDPE and 5% compatibilizer. Results indicated that processability, mechanical and optical properties of the blends were improved by the presence of the compatibilizer. Results of orientation studies on PET/HDPE blends, performed by Jabarin and Sambaru (4) showed evidence of a significant amount of compatibilization between the two components in blends containing 85% (weight basis) PET, 10% HDPE and 5% compatibilizer.

The current study investigates the morphology and properties of PET/HDPE blends containing 80% (wt./wt.) PET. Ratios of HDPE to Admer compatibilizer have been varied, as have processing parameters utilized during twin screw extrusion. Resultant changes in morphologies and properties of the ternary blend systems have been evaluated and related to variations in composition and processing conditions. Rheological, morphological, mechanical, thermal and spectroscopic techniques have been used to characterize the various blends.

## Experimental

**Materials.** Resins used for this study include Goodyear Cleartuf 8006 (0.8 I.V.) PET, Allied Signal Paxon type AA 60-003 extrusion blow molding grade HDPE, and Mitsui Admer AT 469C (now SF 700A) maleic-anhydride grafted polyolefin resin compatibilizing agent.

**Blend Preparation.** All materials were dried before being blended or processed. PET resin was dried, to moisture levels of less than 0.005%, in a Conair dehumidifying air dryer at 150°C for 10-12 hours. HDPE and Admer were dried overnight under vacuum at 75°C.

A Werner & Pfleiderer (ZSK-30) self-wiping co-rotating twin screw extruder was used for all melt blending operations. Previously dried resins were hand mixed for approximately 5 minutes and fed into the feed-port of the twin screw extruder placed at the front end of the barrel. Zone 1 of the barrel was set at 240°C, zones 2 through 4 were set at 285°C, and zone 5 was set at 265°C. The temperature of zone 5 was reduced in order to increase extrudate melt strength. Extrudate from the twin strand die was immediately quenched to ~15°C in a water trough and pelletized using a Conair (Jetro Division) Model 304 pelletizer. The speed of the pelletizer was adjusted to maintain a continuous strand from the die to the pelletizer and obtain pellets at a constant output rate of 12-13 kg/hr. The above described extrusion conditions were used to prepare ternary blends with the following weight percent compositions:

PET 80/HDPE 15/Admer 5  
 PET 80/HDPE 10/Admer 10  
 PET 80/HDPE 5/Admer 15

With other processing conditions held constant (unless specified) each of the above ternary blends was extruded at twin screw speeds of 100, 200, 300 and 350 rpm.

In order to provide property comparisons based on compositional variations, additional non-blended and binary blend samples were prepared at processing conditions equivalent to those used during production of 300 rpm ternary blends. Binary blends were prepared with the following weight percent compositions:

PET 80/HDPE 20	PET 97/Admer 3	HDPE 5/Admer 15
	PET 94/Admer 6	HDPE 90/Admer 10
	PET 89/Admer 11	HDPE 85/Admer 15
	PET 84/Admer 16	

**Sheet Preparation.** Each pelletized blend material was vacuum dried at 110°C for 12 hours in a Forma Scientifica Model 3237 vacuum oven, before it was processed through a lab scale Brabender single screw extruder to yield narrow sheets, 41 to 55 mm wide and 0.48 and 0.64 mm thick. A general purpose screw (diameter = 19 mm) was used at a speed of 50 rpm with temperatures of 240°C in zone 1 and 260°C in zones 2, 3 and the die. The sheet extrudate was quenched to room temperature using a winder consisting of water cooled rolls operated at 10 rpm to maintain a constant minimum draw ratio.

**Rheological Properties.** The pelletized blend material was vacuum dried at 110°C for 12 hours in a Forma Scientifica Model 3237 vacuum oven. Melt viscosities of the dried blends were measured at 270°C using a constant-shear rate, Instron model 3211, capillary rheometer. The capillary diameter was 0.1016 cm and its length was 2.0889 cm. The force on the load cell was measured at five different plunger speeds, which were 0.076, 0.76, 2.54, 7.62 and 25.4 cm/min. The viscosity at each of these shear rates was calculated employing a Rabinowitch correction to account for the deviation of polymeric melts from Newtonian behavior.

**Morphological Analysis.** An Hitachi S-2700 Scanning Electron Microscope (SEM) was used to observe surface characteristics and particle sizes of samples freeze fractured in liquid nitrogen. Fractured samples were sputter coated with 8 nm of gold-palladium alloy before analyses. Representative areas of the observed surfaces were photographed at 1000 X magnifications. Approximate particle size distributions were then calculated for each blend sample, from these micrographs, as described in the following paragraph.

Each micrograph (4.5" x 3.5") was divided into five equal areas (0.9" x 3.5") and from each of these areas, a total of ten particles that represented the particle sizes in that area were chosen. Their sizes were measured with a scale. A total of 50 particles per micrograph (i.e. per blend sample) were therefore measured and plotted. It should be noted that since the micrographs were of 1000 X magnification and the scale used for manual measurement had an accuracy of 1 mm, the smallest accurately measurable particle has a diameter of 1 mm on the scale = 1 micron ( $10^{-3}$  mm). Although a small number of particles per sample (50) were actually measured, the procedure ensured that the measured particle size distributions represented the qualitative particle size distributions. For ellipsoidal particles, the minor (a) and major (b) axes lengths were measured and the diameter (d) of a circular particle of equivalent area was calculated using equation 1 and recorded as the particle size.

$$\text{Area of an ellipse} = \frac{\pi ab}{4} \quad \text{Area of a circle} = \frac{\pi d^2}{4}$$

equating the two areas, gives,

$$d = \sqrt{(ab)} \quad (1)$$

**Mechanical Properties.** Tensile mechanical properties were evaluated at both high and low strain rates. Tensile impact properties were evaluated according to ASTM 1822. In this case a swinging pendulum type Custom-Scientific Tensile Specimen-in-base Impact tester was used to determine the high strain rate, tensile impact, properties of the blend samples. Low strain rate tensile properties were determined with a table model Instron 1101 Tensile tester, according to ASTM 1708. Microtensile samples were stretched at a crosshead speed of 25.4 mm/min. (1"/min).

**Thermal Analysis.** A Perkin-Elmer differential scanning calorimeter (DSC-2) was used to monitor thermal properties under dynamic conditions. Single screw extruded sheets of the blends were vacuum dried at 110°C for 12 hours in a Forma Scientifica Model 3237 vacuum oven before analyses. The oven temperature was turned off after 12 hours and the samples were allowed to cool to room temperature under vacuum, to avoid moisture absorption during cooling. All analyses were performed under a nitrogen purge to prevent oxidative degradation. The heating and cooling rates for all scans were maintained at 10°C/min. Samples were heated to 300°C and held at that temperature for 5 min. to remove effects of previous thermal histories. The dynamic crystallization behavior was studied by cooling this melt from 300°C to room temperature at a rate of 10°C/min. A reheat cycle was also performed. Area and other calculations are based on the standard Perkin-Elmer TADS 3600 software.

**Spectroscopic Analysis.** Extruded sheets of blend materials were evaluated in terms of hydrogen bonding, with the aid of Fourier transform infrared (FT-IR) spectroscopy. The Perkin-Elmer 1600 series FT-IR was equipped with an attenuated total reflection (ATR) accessory which permitted the measurement of thick and/or opaque samples. Samples were also analyzed in the transmission mode. Sixty-four scans were performed on each sample. Instrument resolution was 4 cm<sup>-1</sup>. Spectra were found to be influenced by the presence of moisture, therefore, all samples were vacuum dried at 110°C for 12 hours before analyses.

## Results and Discussion

**Rheological Properties.** All materials were processed through the twin screw extruder, using equivalent temperature profiles, which varied from 240°C in the feed zone, to 285°C in the central region and 265°C in the end zone. In order to represent the average extrusion temperature experienced by these materials, an intermediate measurement temperature of 270°C was chosen for rheological characterization of all blends and pure materials. The Rabinowitch corrected viscosity versus shear rate behaviors of PET, HDPE and Admer used in this study and measured at 270°C, are shown in Fig. 1. These results indicate that at low shear rates, HDPE is the most viscous of the three materials and PET is considerably less viscous than the other two materials. The shear sensitivity, defined as the ratio of the viscosity at 1 sec<sup>-1</sup> to that at 1000 sec<sup>-1</sup>, is shown in Table I, for various materials and blends. Note that the HDPE is highly shear sensitive, indicating that it is an extrusion blow molding grade material. The shear sensitivity of PET is relatively low and that of Admer is intermediate to that of PET and HDPE. Upon blending PET, HDPE and Admer in three different ratios as shown in Table I, it is seen that the shear sensitivity of the blends is almost twice that of pure PET. This suggests that ternary PET blends should be more suitable for extrusion-blow molding than pure PET.

Table I. Shear Sensitivities of Unblended Polymers and Ternary Blend Compositions Processed at 285°C and Twin Screw Speeds of 300 rpm

Material/Blend	Shear Sensitivity
PET	2.2
HDPE	33.9
Admer	8.5
PET 80/HDPE 15/Admer 5	4.2
PET 80/HDPE 10/Admer 10	4.0
PET 80/HDPE 5/Admer 15	3.9

The observed viscosity versus shear rate behaviors (measured at 270°C) for pure PET and the three blend compositions are shown in Figure 2. The viscosity of the blends is seen to decrease as the HDPE component (the most viscous of the three pure polymers) in the blends decreases, consistent with earlier results (3).

Additional melt viscosity versus shear rate measurements were performed on ternary blend resins, prepared at twin-screw processing speeds of 100, 200, 300 and 350 rpm. Viscosities, measured at each shear rate, were found to be relatively consistent for each blend composition, regardless of extrusion speed. Results indicate that melt viscosities of these ternary blends are dependent upon blend composition, but independent of the twin screw speed of processing. This behavior can be attributed to the relatively homogeneous distribution of the dispersed phase which was attained, even at the slowest screw speed of 100 rpm.

**Morphological Observations.** An Hitachi S-2700 scanning electron microscope (SEM) was used to examine morphological characteristics of the various blend compositions, produced at twin-screw extrusion speeds from 100 through 350 rpm. In preparation for SEM evaluations, most dried, pelletized, samples were subjected to capillary rheometry at very low shear rates ( $\sim 90 \text{ sec}^{-1}$ ), to produce strands of each material. Low shear rates were utilized in order to avoid imparting additional mixing or phase distortion, and to allow comparisons of the phase distributions among the samples. One set of samples, processed at various twin screw speeds, was analyzed in the form of extruded sheets rather than rheology strands. As a result of this processing history, these samples exhibit elongated rather than spherical particles, embedded in the PET matrix. Rheologically prepared strands or extruded sheets were freeze fractured, coated and photographed to give the following morphological results.

Photomicrographs of three different rheologically prepared blend compositions are shown in Fig. 3 (a, b, and c). These blends were processed at equivalent twin-screw extrusion conditions, with speeds of 300 rpm. The micrographs show that at these compositions, the HDPE and Admer are dispersed in the form of discrete microspheres embedded in the PET matrix.

Binary blends of PET 80/HDPE 20 and PET 84/Admer 16 contain relatively similar concentrations of PET. Equivalent processing conditions, with 300 rpm screw speeds, were used during extrusion of both blends. Particle size distributions of the HDPE and Admer phases in the PET matrix of each rheologically prepared blend, are shown respectively in photomicrographs a and b of Fig. 4. The measured particle size distributions of HDPE and Admer in each blend are plotted in Fig. 5. These figures clearly show that the average particle size of the Admer component is much lower than that observed for the HDPE component. Since the processing twin screw speed was held constant, this difference can be attributed to the difference between the properties and behavior of the HDPE and Admer phases. It is also apparent that the distribution of particle sizes for the HDPE phase is wider than that of the Admer phase.

Particle size distributions exhibited by ternary blends, processed at equivalent conditions are shown in the micrographs of Fig. 3 and plotted in Fig. 6. Consistent with the binary blend results, the particle size distribution data for ternary blends, processed at twin screw speed of 300 rpm, also show reductions in average sizes of the dispersed phase particles, with increasing Admer and decreasing HDPE content.

Wu (2) has shown that the particle size of a dispersed elastic phase in a viscoelastic matrix is a function of the shear rate,  $G$ . Since the viscosities of polymeric materials are observed to be functions of both strain rate and temperature, it is difficult to determine an average value of the applied strain rate during twin screw blend extrusion. Nevertheless, it can be assumed that for a given composition and constant processing parameters, (except the screw speed) the applied shear rate

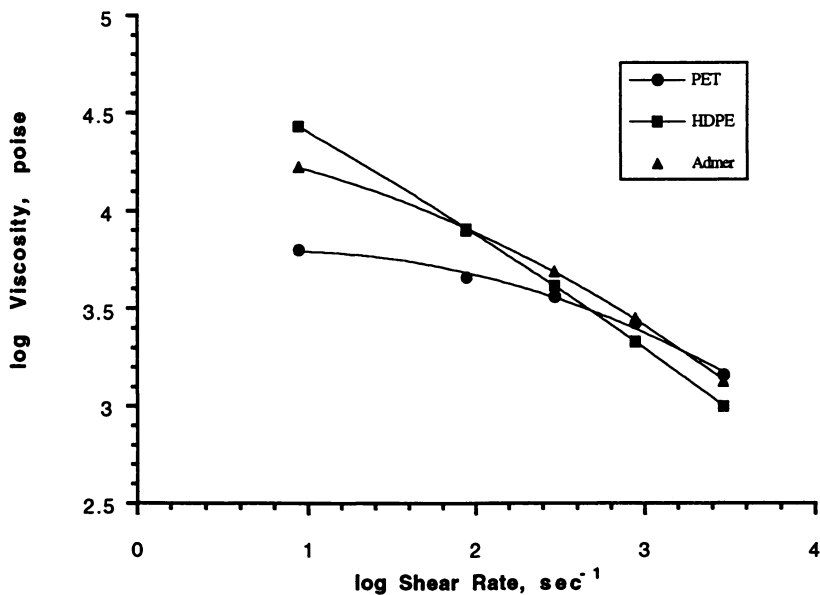


Figure 1. Comparisons of 270°C viscosity versus shear rate behaviors of unblended PET, HDPE and Admer.

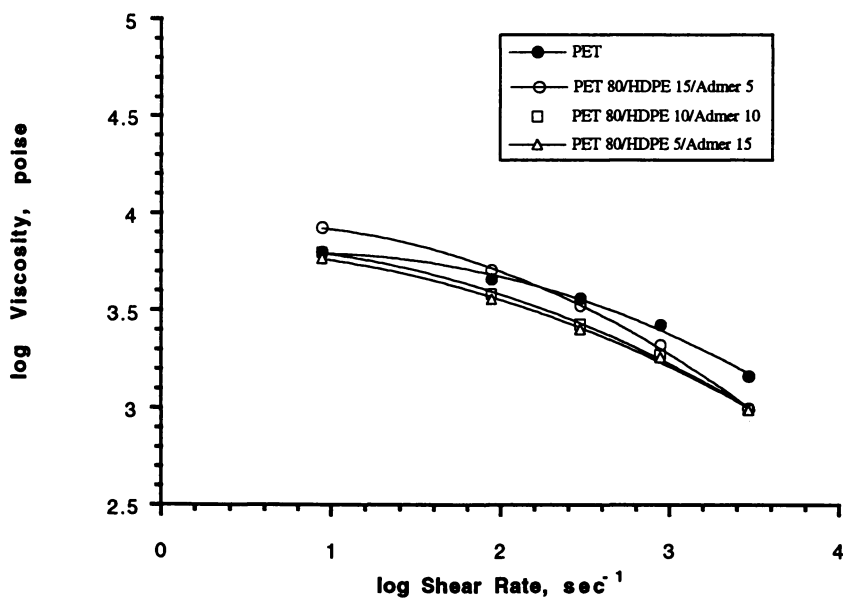
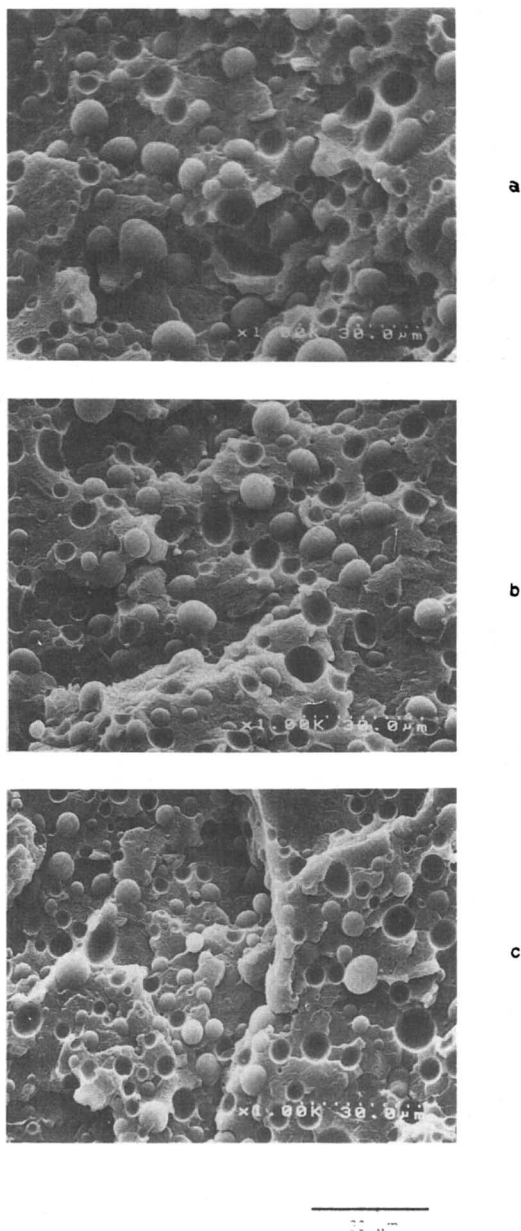
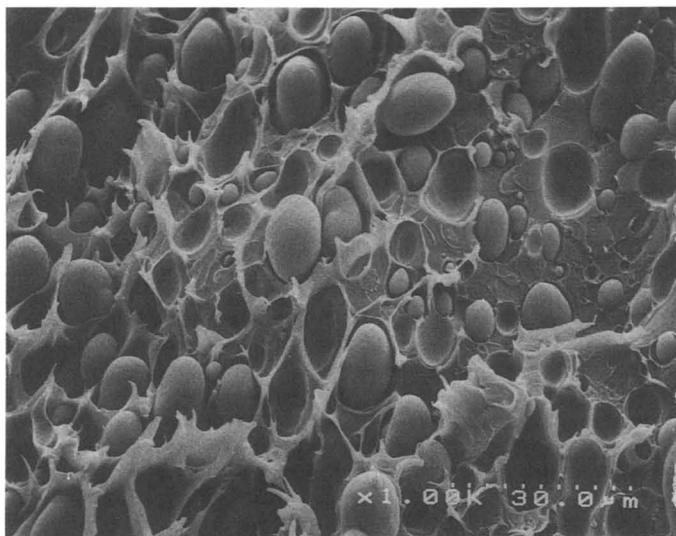


Figure 2. Comparisons of 270°C viscosity versus shear rate behaviors of unblended PET and three ternary blend compositions.

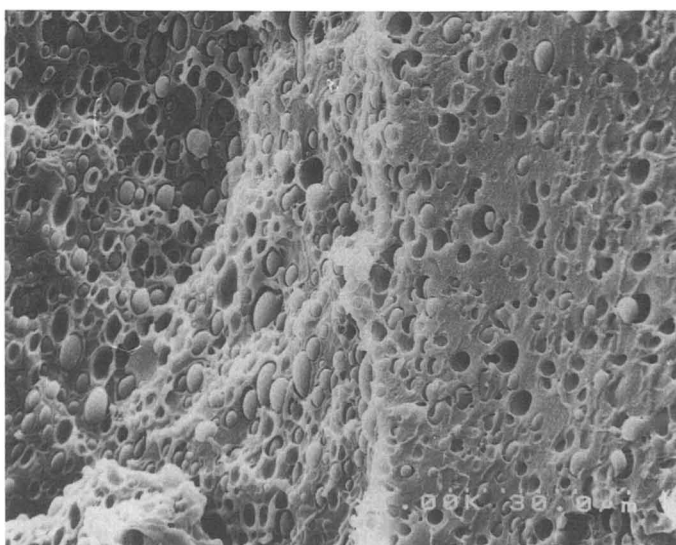


**Figure 3.** Scanning electron micrographs of ternary blends of various compositions, processed at 285°C and at a twin screw speed of 300 rpm. (a) PET80/HDPE 15/Admer 5, (b) PET 80/HDPE 10/Admer 10 and (c) PET 80/HDPE 5 /Admer 15.





a



b

---

30 μm

**Figure 4.** Scanning electron micrographs of (a) PET 80/HDPE 20 and (b) PET 84/Admer 16 binary blends processed at 285°C and at a twin screw speed of 300 rpm.

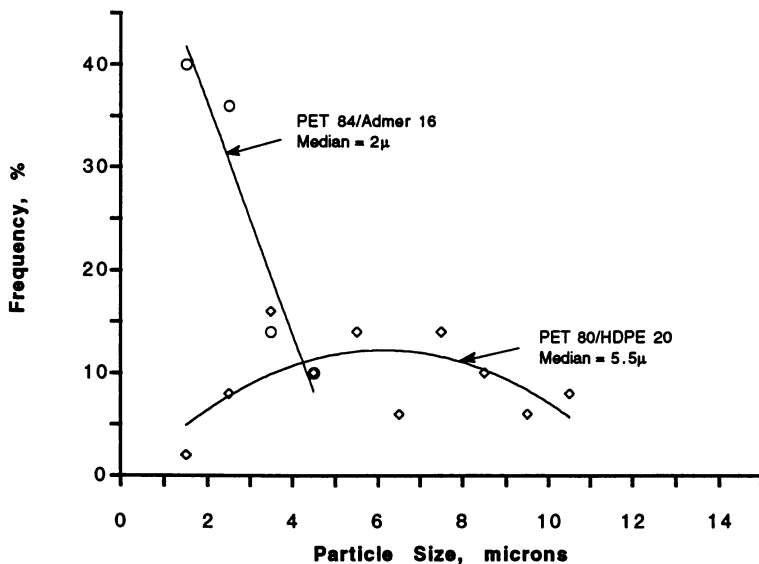


Figure 5. Particle size distribution curves of PET 80/HDPE 20 and PET 84/Admer 16 binary blends, processed at twin screw speeds of 300 rpm. (second order polynomial curve fit).

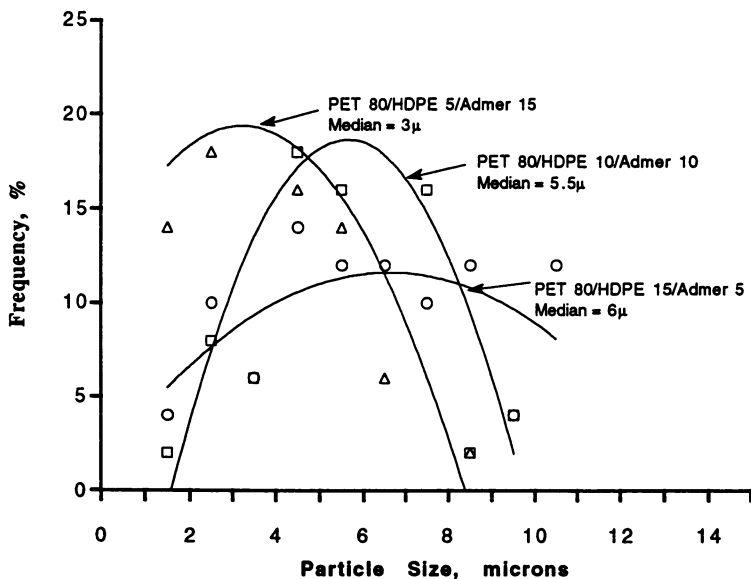


Figure 6. Particle size distribution curves for ternary blends of various compositions, processed at 285°C and a twin screw speed of 300 rpm. (second order polynomial curve fit).

August 10, 2012 | http://pubs.acs.org  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch011

increases with increasing screw speeds. Results achieved in this study have substantiated such a prediction for each of the three ternary blend compositions. An example of this relationship is given in Fig. 7. Blend composition is maintained at PET 80/HDPE 10/Admer 10 and processing conditions are constant except for screw speed. These samples were analyzed in the form of extruded sheets rather than rheology strands. As a result of their extrusion histories, particles have been elongated and are elliptical rather than spherical as seen in previous rheologically prepared samples. Average particle sizes, however, can be seen to decrease, as screw speed is increased, from 100 rpm (a), to 200 rpm (b), and finally to 300 rpm (c). Although not directly comparable to spherical particle size data, particle size distribution curves of Fig. 8, clearly indicate a decrease in average dispersed phase particle size with increasing speed of twin screw processing.

**Mechanical Properties.** Traugott, et al (1983) tried to compatibilize PET and HDPE using Kraton G 1652, produced by the Shell Chemical Company and Epcar 847, sold by the B. F. Goodrich Company. Their results showed that addition of 20% by weight of compatibilizer to mixtures of PET and HDPE improved the ductility of the blends over that of binary uncompatibilized HDPE/PET blends. In spite of this, they were unable to detect any strong adhesion between the PET and HDPE phases. Although the chemical structure of the compatibilizer used in the current study is quite different from that used by Traugott, et al (1983), similar improvements in blend ductility have been observed.

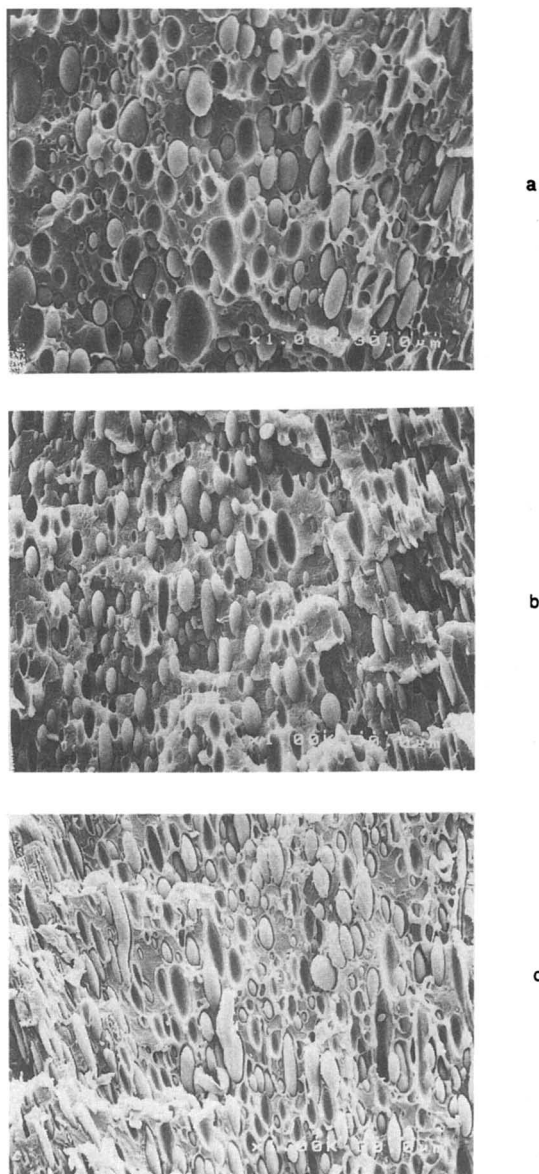
At room temperature, amorphous PET (with a  $T_g$  of  $\sim 80^\circ\text{C}$ ) is a glassy polymer, known to exhibit brittle impact failure. Dispersion of a material, such as Admer and Admer/HDPE blends, within a PET matrix, could act to introduce a toughening effect to the resultant blend. In this case the dispersed phase could act to absorb energy during impact testing as well as initiate and terminate crazes in the manner of rubber particles.

The improved impact resistance of the glassy PET matrix with the addition of Admer compatibilizer, is apparent in Fig. 9. This figure shows the relationship of tensile impact energy to HDPE and Admer concentrations, for ternary blends prepared at twin screw speeds of 300 rpm.

Examples of stress-strain curves obtained for pure PET, PET 80/HDPE 20, and PET 84/Admer 16 during Instron testing are shown in Fig. 10. It is apparent that the addition of Admer compatibilizer to PET imparts increased strain-to-break behavior, while addition of non-compatibilized HDPE gives decreased elongation of the resultant blend.

Compositional effects on mechanical properties of ternary blends (prepared at 300 rpm) are summarized in Figures 11 and 12. These figures respectively show strain to break and break stress plotted as functions of HDPE and Admer concentrations. As can be seen (Fig. 11) strain to break of the blend containing 15% Admer is almost three times that of the binary (non-compatibilized) blend. This is similar to behavior obtained during tensile impact analyses (Fig. 9) and indicates increased impact resistance with increased Admer blend concentration. Break stress (Fig. 12) is seen to increase as Admer content is increased up to 10%, implying an increasing strain-hardening effect. At 15% Admer content, however, the ductility introduced in the matrix due to Admer content overrides the strain-hardening of the PET chains, showing a decrease in the break stress. In terms of compositional effects, the addition of Admer to PET/HDPE blends has been seen to result in overall improvements in the mechanical properties of the ternary blends.

As twin screw processing speed is increased, shear rates increase and dispersed phase particle sizes decrease. Since mechanical properties are dependent upon dispersed phase particle sizes, blend mechanical properties are expected to be dependent upon extruder screw speeds. Figure 13 shows the strain to break as a function of twin screw speed for each of the ternary blend compositions. The blend



**Figure 7.** Scanning electron micrographs of PET 80/HDPE 10/Admer 10 blends processed at 285°C and varying twin screw speeds: (a) twin screw speed of 100 rpm, (b) twin screw speed of 200 rpm and (c) twin screw speed of 300 rpm.

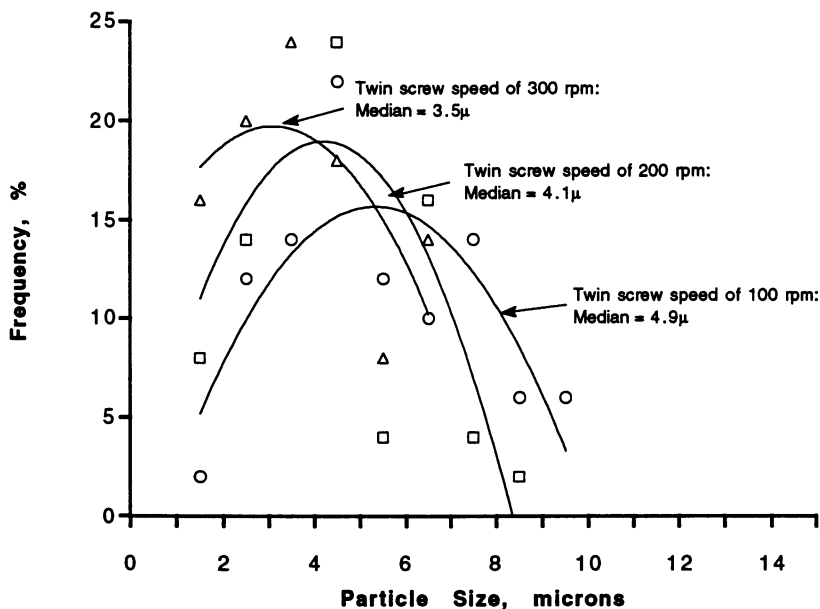


Figure 8. Particle size distribution curve for PET 80/HDPE 10/Admer 10 blend processed at 285°C and various twin screw speeds. (second order polynomial curve fit).

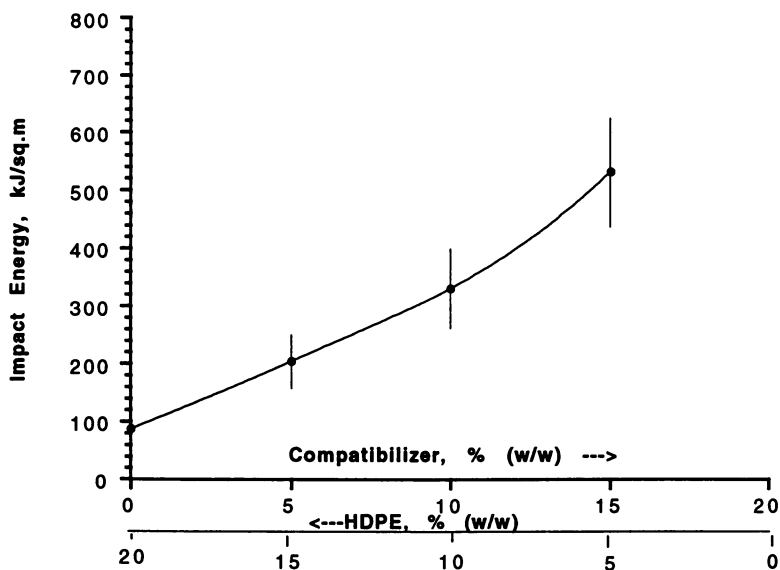


Figure 9. Impact energy as a function of composition, for blends processed at 285°C and twin screw speed of 300 rpm.

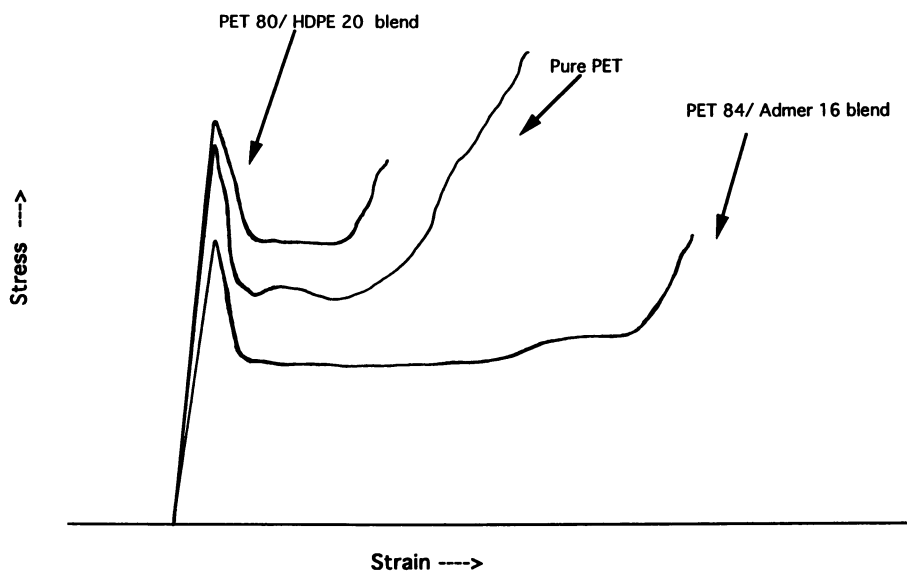


Figure 10. Typical stress-strain relationship for specimen of Pure PET, PET 80/HDPE 20 and PET 84/Admer 16 blends.

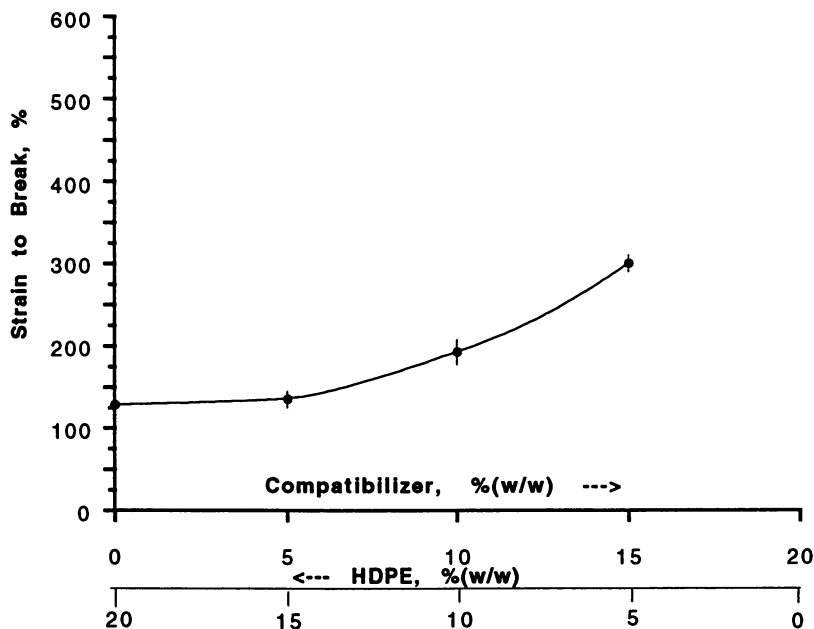


Figure 11. Strain to break as a function of composition, for blends processed at 285°C and twin screw speed of 300 rpm.

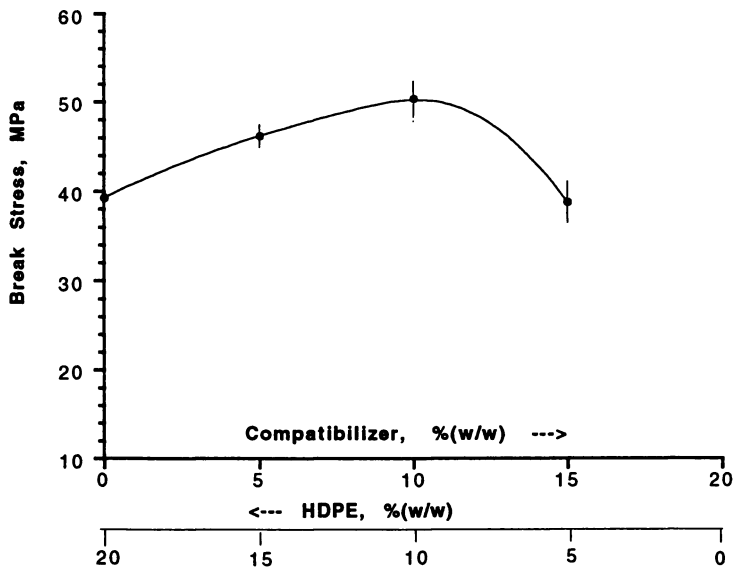


Figure 12. Break stress as a function of composition, for blends processed at 285°C and twin screw speed of 300 rpm.

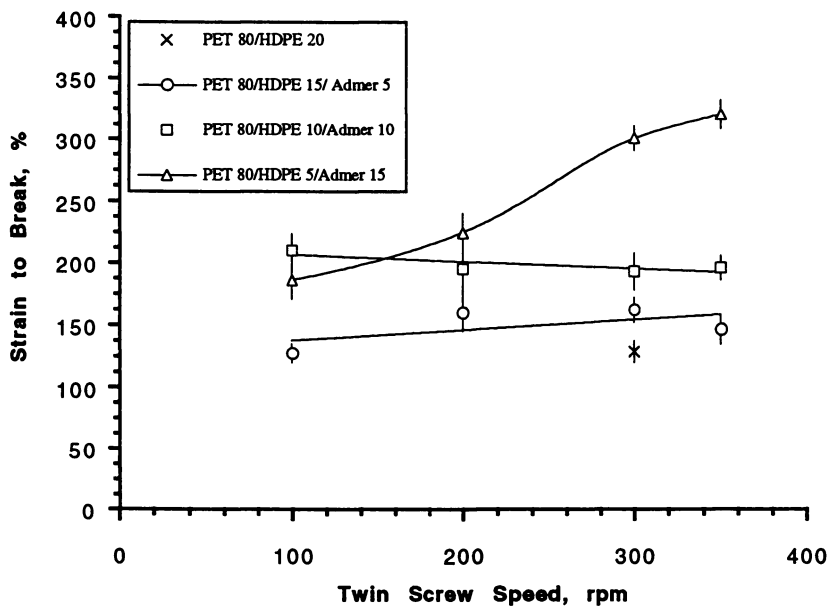


Figure 13. Strain to break as a function of twin screw processing speed (rpm), for ternary blends of various compositions, processed at 285°C.

containing 15% Admer is seen to exhibit considerably higher elongation before breaking, as a result of being processed at faster screw speeds. Blends containing 5 and 10% Admer showed no significant improvements in strain to break, even at higher screw speeds. This behavior suggests that the improvement in mechanical performance may be due primarily to the Admer content. The Admer phase adheres well to the PET matrix and shares the applied stress, leading to improved impact resistance of the PET matrix. The HDPE phase however, does not adhere sufficiently to the PET matrix and therefore does not share the applied stress adequately, causing a decrease in impact resistance of the PET matrix. It therefore seems that addition of sufficient amounts of Admer reduces the detrimental effects of HDPE chains on the blend impact properties.

**Thermal Properties.** As each of the blend components is heated and cooled during calorimetry, characteristic thermal transitions are recorded. When more than one component is present in a specific sample, overlap of these transitions may occur. If blends containing amorphous PET are heated in a DSC, the PET crystallization exotherm could overlap and interfere with measurements of HDPE and Admer melting endotherms. Fortunately, crystallization exotherms recorded for PET and HDPE, while they are being cooled from the melt, do not overlap. Examples of these separate, distinguishable, exotherms are shown in Fig. 14. The broad peak at about 175°C corresponds to PET crystallization and the relatively sharp peak at about 115°C corresponds to HDPE crystallization. From these scans, it is also apparent that a HDPE exotherm would occur over the same temperature range as that of Admer, and therefore mask the smaller Admer transition, if both components were present in a blend. Since the enthalpic contributions of Admer are small compared to those of HDPE, at the levels present in this study (up to 15% Admer), they have been neglected in these discussions.

In order to elucidate the nature of interactions among the ternary blend components, various binary blends were thermally analyzed. All blends were processed under equivalent conditions, with compositional comparisons made among those extruded at screw speeds of 300 rpm.

Thermal crystallization results obtained for cooled binary blends of HDPE and PET are shown in Table II. Heats of crystallization (henceforth called  $\Delta H_{C,PET}$  and  $\Delta H_{C,HDPE}$ ) and peak crystallization temperatures (henceforth called  $T_{C,PET}$  and  $T_{C,HDPE}$ ) are given respectively for the PET and HDPE components of the PET 80/HDPE 20 binary blend in comparison to equivalent transitions of unblended materials. Upon being blended with 20% HDPE, the  $\Delta H_{C,PET}$  decreases from that of pure PET by approximately 25% (from 36 to 28 kJ/kg) and the  $T_{C,PET}$  decreases by almost 15°C. Both of these changes indicate a decrease in the crystallization rate of PET, as a result of being blended with HDPE. The  $\Delta H_{C,HDPE}$  decreases by approximately 12% and the  $T_{C,HDPE}$  decreases by 2°C, upon being blended with 80% PET. These changes indicate that PET and HDPE mutually hamper each others' crystallization processes.

Table II. Peak Crystallization Temperatures and Heats of Crystallization (normalized to 100% pure polymer) for PET and HDPE, Unblended and as Binary Blend Components

	PET COMPONENT		HDPE COMPONENT	
	Unblended	PET 80/ HDPE 20	Unblended	PET 80/ HDPE 20
$\Delta H_C$ (kJ/kg)	36	28	209	183
$T_C$ (°C)	183	168	119	117



Crystallization behaviors of binary blends containing PET and Admer were also evaluated. Admer is a maleic-anhydride grafted polyolefin resin, with relatively low enthalpic values. Changes in crystallization were, therefore, recorded in terms of the influence of Admer upon PET behavior. Figure 15 shows that the presence of Admer, in amounts ranging from 3 to 16% by weight, does not significantly affect PET crystallization temperatures, however, in Fig. 16 the  $\Delta H_{C,PET}$  of all the binary blends is observed to be about 10% higher than that of unblended PET.

Results obtained for binary blends of PET/HDPE versus PET/Admer are quite different. In the case of HDPE blends, PET crystallization appears to be inhibited, while in the case of Admer blends, it may be somewhat enhanced. Bataille, et al (5) suggested that the positive deviation from the linear additivity rule, observed in the elastic modulus of the PET 80/PP 20 alloys, resulted from enhanced crystallinity developed by PET in the presence of polyolefins (PP). This difference in crystallization behavior was attributed to the presence of tertiary carbon atoms in the polypropylene chain, which were thought of to act as side chains and provide the necessary nucleation sites. Since these tertiary carbons are absent in the HDPE backbone, PET crystallization is not enhanced in the case of PET/HDPE binary blends. Blends containing PET/Admer, however, were found to crystallize to a slightly greater extent than unblended PET, perhaps in accordance with Bataille's work.

Crystallization values were also measured for binary blends prepared from HDPE and Admer. These results are shown on Table III. The  $T_{C,HDPE}$  and the enthalpy of crystallization of the HDPE component are observed to remain nearly constant, as the percent Admer is increased from 5 to 15%. These observations indicate that rates and amounts of HDPE crystallization are relatively unchanged by the addition of Admer compatibilizer.

Table III. Peak Crystallization Temperatures and Heats of Crystallization (normalized to 100% Pure Polymer) for the HDPE Component of Binary HDPE/Admer Blends

HDPE/Admer	$\Delta H_{C,HDPE}$ (kJ/kg of HDPE)	$T_{C,HDPE}$ , °C
95/5	187	119
90/10	198	119
85/15	198	119

Thermal properties of ternary blends have been analyzed as functions of composition and twin screw processing speed. Composition variations were found to cause similar trends in blend property changes at all processing speeds. Results obtained for blends processed at 300 rpm were therefore chosen to represent these trends.

The constant factor in the composition of all the ternary blends chosen was the 80% PET content. The remaining 20% was divided between HDPE and Admer in ratios of 3/1, 1/1 and 0.33/1. Normalized PET heats of crystallization ( $\Delta H_{C,PET}$ ) are shown in Fig. 17, plotted as functions of both HDPE and Admer blend concentrations, since these concentrations are mutually dependent. It can be seen that  $\Delta H_{C,PET}$  increase with increasing Admer and decreasing HDPE concentrations. In a

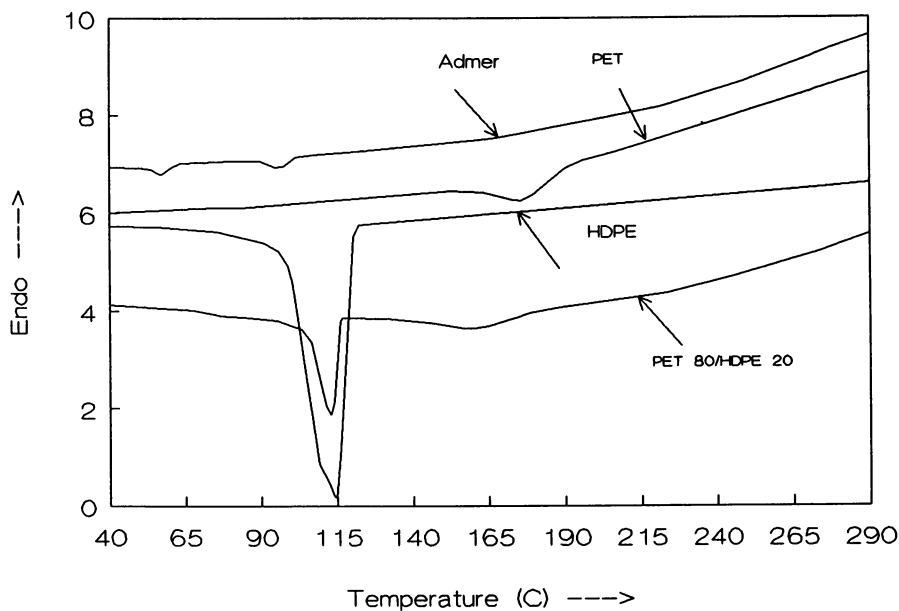


Figure 14. Typical DSC cooling scans.

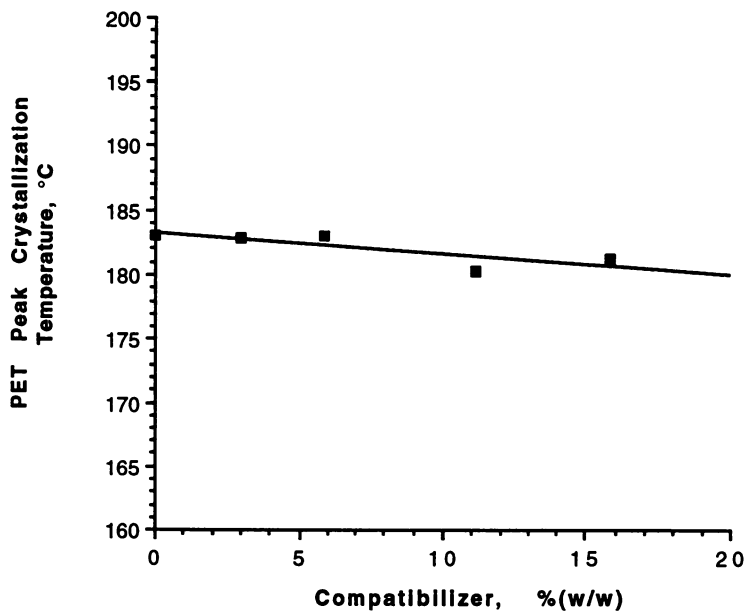


Figure 15. Peak crystallization temperatures of the PET component in PET/Admer binary blends, as a function of weight percent compatibilizer.

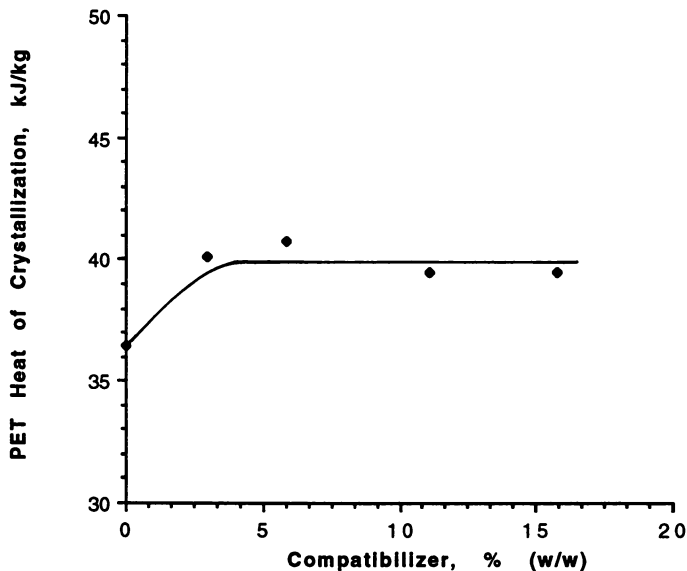


Figure 16. Heats of crystallization of the PET component (normalized to 100% PET), in PET/Admer binary blends, as a function of weight percent compatibilizer.

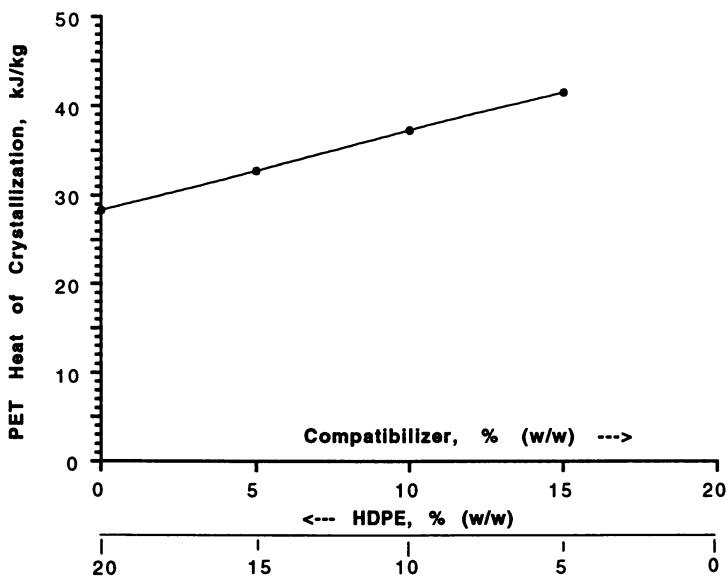


Figure 17. Heats of crystallization of the PET component (normalized to 100% PET) in ternary blends processed at twin screw speed of 300 rpm, as a function of weight percent compatibilizer.

similar manner, the  $T_{c,PET}$  has been shown to increase from 168°C, for a binary blend containing 20% HDPE and 80% PET, to 182°C for a ternary PET blend containing 15% Admer and only 5% HDPE. These results indicate that as with binary blend compositions, increased concentrations of HDPE inhibit crystallization of the blended PET component, while the addition of Admer may slightly increase PET crystallization. The observed effects on PET crystallization rates in the ternary blends could, therefore, be attributed to a balance between the opposing effects of HDPE and Admer concentrations.

Changes in the crystallization behavior of HDPE have also been observed in the ternary blends. As the amount of compatibilizer increases from 0 to 15%, the  $T_{c,HDPE}$  is observed to decrease from 117°C to 113°C for blends processed at 300 rpm. Table IV compares the ratio of PET to HDPE in a blend composition with the observed  $T_{c,HDPE}$ . Taking into consideration that the HDPE/Admer binary blend studies showed no effect on  $T_{c,HDPE}$ , while PET/HDPE binary blend studies did indicate an effect on  $T_{c,HDPE}$ , it can be seen in Table IV that as the PET/HDPE ratio increases, the crystallization of HDPE is delayed.

Table IV. Effect of the PET/HDPE Ratio on the Peak Crystallization Temperature of Blended HDPE

PET/HDPE/Admer	PET: HDPE Ratio	$T_{c,HDPE}$ , °C
80/20/0	4:1	119
80/15/5	5.3:1	117
80/10/10	8:1	116
80/5/15	16:1	113

In addition to composition, crystallization of the HDPE component of ternary blends, has been found to be dependent upon the operating speed of the twin screw during extrusion. Blends previously extruded at faster speeds, exhibit decreased heats of crystallization while being cooled from the melt. Results obtained for three ternary blend compositions are shown in Fig. 18 as functions of processing speed. A higher speed of twin screw processing is thought to impart larger shear rates onto the polymer melt, thereby increasing the extent of mixing between the blend components. The extent of mixing is directly proportional to the interfacial area between the components of a mixture, therefore, by increasing the extent of mixing between the PET and HDPE components, the interfacial area between the two components has been increased. At higher twin screw speeds, more surface area of the PET matrix has an interface with the HDPE dispersed particles, resulting in increased interactions between the PET and HDPE chains. The relative nature of the interfacial areas between the matrix and dispersed phases in the range of particle sizes of 1-30  $\mu$  (size range relevant to the observed morphology in this study) is shown in Figure 19. These calculations are based on the assumption that the dispersed phase particles are all exactly identical, spherical in shape and of equal radius, and are dispersed in a PET matrix with no voids in the structure.

The PET component of ternary blends was also found to be sensitive to twin screw extruder speed. As shown in Fig. 20, the  $\Delta H_{c,PET}$  of all three ternary blends increased slightly as a result of increased twin screw speed. A similar observation was made for the  $T_{c,PET}$ . This behavior is a compromise between the opposing

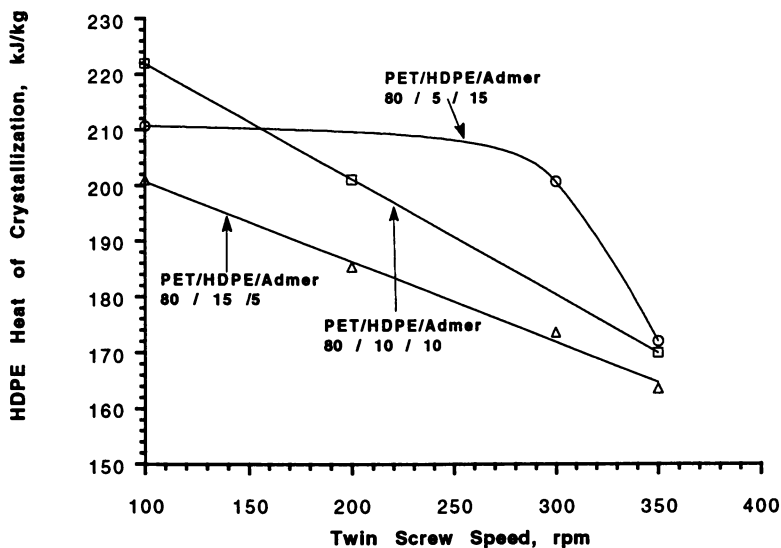


Figure 18. Heats of crystallization of the HDPE component (normalized to 100% HDPE) in ternary blends, as a function of the twin screw speed.

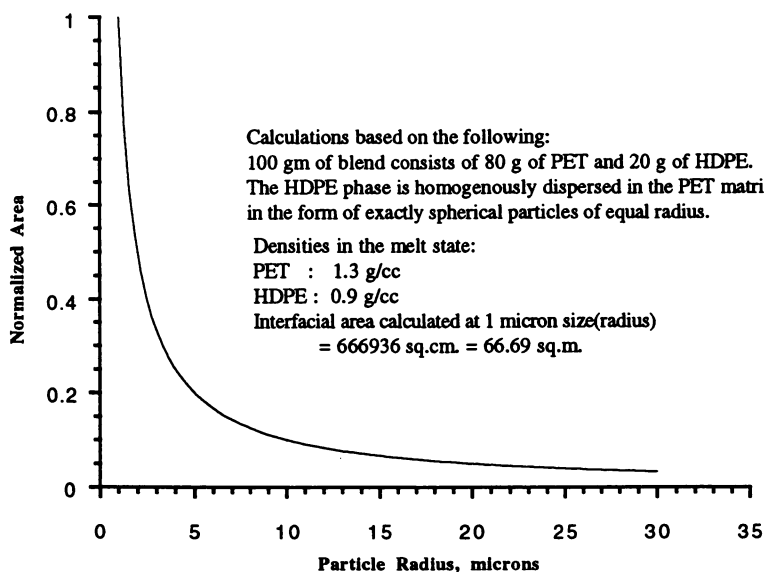


Figure 19. Calculated interfacial area between PET and HDPE phases in a PET 80/HDPE 20 binary blend, normalized to the interfacial area calculated for a dispersed phase particle size of one micron.

effects of HDPE and Admer chains on PET crystallization rates. If HDPE alone were dispersed in the PET matrix, a decrease in crystallization rates would be expected with increasing twin screw speeds. This effect could be explained with an argument similar to that offered previously for decreases in HDPE crystallization rates. A higher twin screw speed imparts higher amounts of shear onto the molten material in the extruder barrel, giving rise to a smaller size (average) dispersed particles. With the total volume of the dispersed phase remaining constant, this decrease in size must be accompanied by an equivalent increase in the number of dispersed phase particles. Larger numbers of dispersed phase particles indicate larger interfacial areas between the matrix and the dispersed phases. The observed PET crystallization appears to be a combination of a decrease in PET crystallization due to HDPE and an increase due to Admer interactions.

**Spectroscopic Analysis.** In work done earlier on PET/HDPE/Admer ternary blends by Jabarin, et al (1992), the authors have speculated about the existence of a specific interaction between the anhydride group of the Admer and terminal hydroxyl group of the PET chain. Such interactions could include formation of hydrogen bonds. Additional hydrogen bonding could also occur between carbonyl groups of the PET and hydroxyl end groups of hydralyzed maleic anhydride (maleic acid). The current study has utilized infrared spectroscopy to monitor hydrogen bonding in various PET blends, prepared at twin screw speeds of 300 rpm.

Infrared analysis of blends is made complex by the dependence of the vibrational spectra on many parameters such as: sample composition, thermal history, crystallinity, thickness, moisture content, method of preparation, extent of mixing and temperature of the test. Spectra of polymer blends have been observed by Hsu (6) to change with time. In the present study, considerable effort has been made to hold constant all blend parameters, except composition. Samples were vacuum dried for 12 hours at 105°C and equilibrated at room temperature (23°C) before analyses. This study is based on the extensive FTIR analysis work done by Coleman, et al (7-10) in the field of hydrogen-bonding in polymer blends. The various blends studied by Coleman exhibited hydrogen-bonding interaction between the carbonyl group of one of the components and the hydroxyl group of the other component. Current blends have therefore been examined in the manner utilized by Coleman, et al.

Hydroxyl stretching frequencies are generally observed between 3100 and 3600  $\text{cm}^{-1}$ . Transmission spectra of unblended PET materials exhibit hydrogen-bonded hydroxyl group bands centered at 3553.6  $\text{cm}^{-1}$ . This peak is seen to shift to 3551.0  $\text{cm}^{-1}$  in ternary blends containing 15% Admer indicating a slight increase in levels of hydrogen bonding. Table V gives peak wave numbers measured for each blend composition.

Table V. Peak Infra-red Wavenumbers ( $\text{cm}^{-1}$ ) Observed for Hydrogen-Bonded Hydroxyls and Carbonyls of PET and Various Ternary Blend Compositions

Composition	Transmission-FTIR Peak Wave Numbers of Hydrogen-bonded Hydroxyls, $\text{cm}^{-1}$	ATR-FTIR Peak Wave Numbers of Hydrogen-bonded Carbonyls, $\text{cm}^{-1}$
PET	3553.6	1713.5
PET 80/HDPE 15/Admer 5	3553.5	1713.5
PET 80/HDPE 10/Admer 10	3552.0	1712.3
PET 80/HDPE 5/Admer 15	3551.0	1710.0

Additional infrared analyses have been based on changes in carbonyl stretching frequencies which occur between 1650 and 1800  $\text{cm}^{-1}$ . Krimm (11), Patterson, et al (12), and Ward (13) have attributed the 1725  $\text{cm}^{-1}$  band in the PET spectra to carbonyl stretching. These ATR analyses of unblended PET have, however, revealed a broad band centered around 1714  $\text{cm}^{-1}$ . This band is attributable to a reasonably wide distribution of inter-PET hydrogen bond distance and geometries, linked with the carbonyl groups of the unblended PET chain. Similar observations have been made by Coleman, et al (10) for blends of Poly(vinyl alcohol) and Poly(vinyl phenol) (PVPh).

As Admer blend concentrations are increased from 5 to 15% the carbonyl bands are shifted from 1713.5 to 1710.0  $\text{cm}^{-1}$ , indicating increased hydrogen bonding with the carbonyl of the PET chain. These shifts are listed in Table V. Cangelosi et al (14) have shown that hydrogen bonding can alter the force constants of both the proton donor group and the proton acceptor group. Hydrogen-bonded stretching absorptions are thus moved to longer wavelengths (lower frequencies), usually accompanied by increased intensity and band widening. The amount of shift is a measure of the strength of the hydrogen bond, as explained by Keskkula (15). The band widening results from the fact that hydrogen bonds are usually associated in aggregates of various shapes and sizes, producing a variety of different types of hydrogen bonds of various strengths.

Shifts to higher frequencies, such as those noted for blends with higher Admer concentrations have been observed by Coleman et al (10) during studies of Polycaprolactone (PCL)-PVPh blends. These authors attributed the shift to a weaker hydrogen bonding interaction between the carbonyl of the PVPh and the hydroxyl of the PCL, compared to the stronger intra-molecular hydrogen bonding in pure PVPh. In the same manner, the observed band shift in the present blend system may be attributed to combinations of the relatively weaker hydrogen bonding interactions between the carbonyl of the Admer and the terminal hydroxyl of the PET chain, hydrogen-bonding among the PET chains, and hydrogen bonding of Admer hydroxyl groups (possibly formed as a result of maleic anhydride hydrolysis) with PET carbonyls.

**Correlations and Conclusions.** Ternary blend properties have been found to be dependent upon both composition and processing conditions. Sizes of the dispersed phase particles distributed in the PET matrix, have been observed to strongly influence blend mechanical behavior. Wu (2) has shown that the particle size of a dispersed elastic phase in a viscoelastic matrix is a function of the shear rate,  $G$ , the viscosity ratio,  $p$ , and the specific polar interaction between the two components. The author has also shown that for a viscosity ratio,  $p > 1$  ( $p$  = viscosity of dispersed phase/viscosity of PET matrix), the average dispersed phase particle size,  $a_n$ , can be approximated by (2):

$$a_n \approx \Gamma (p)^{0.84} / \eta_m G \quad (2)$$

where  $\Gamma$  is the interfacial tension between the two polymeric components and  $\eta_m$  is the viscosity of the matrix phase (PET in our case). In the equation above, note that the particle size increases with increasing viscosity ratio, ( $p$ ) and decreases with increasing shear rate, ( $G$ );

$$\begin{aligned} \text{i.e., } a_n &\propto (p)^{0.84} \\ \text{and } a_n &\propto (1/G) \end{aligned}$$

The shear rates exerted on the polymer in the extruder and the viscosity of the polymer, both vary along the length of the extruder as well as in the radial direction of the screw cross-section. Moreover, the viscosity of a polymeric melt is a function of both the temperature and the shear rate. This interdependence between the viscosity, shear rates, the temperature and the complex strain field in the extruder makes it difficult to estimate a single value of viscosity or shear rate for calculation purposes. No mathematical calculation has therefore been undertaken; instead a qualitative analysis of the dispersion process is presented.

Since the composition of the ternary blend essentially determines the viscosity ratio ( $p$  = viscosity of dispersed phase/viscosity of PET matrix), preliminary calculations of the viscosity ratios as functions of shear rates have assumed linear additivity of the viscosities of the HDPE and Admer components. The viscosities of the pure components have been measured at 270°C with an Instron Capillary Rheometer. The assumption is made that 270°C is the average temperature experienced by the material during twin screw extrusion. The details are shown in Fig. 21, where viscosity ratios ( $p$ ) are plotted as functions of shear rates, for various dispersed phase compositions, namely, pure HDPE, HDPE/Admer blends in 3/1, 1/1 and 0.33/1 ratios and for pure Admer. Note that for each of the compositions, the viscosity ratio decreases with increasing shear rates. Also note that for shear rates less than 100 sec<sup>-1</sup>, the viscosity ratio decreases with decreasing HDPE content or increasing Admer content in the blend.

Figure 5 gives a plot of the measured particle size distribution of the PET 80/HDPE 20 and PET 84/Admer 16 binary blends. The plot clearly shows that the average particle size of the Admer component is much lower than that observed for the HDPE component. Since all other parameters were held constant, this difference can be attributed to the difference in viscosity ratios and the specific polar interaction of the two components with PET. It is also apparent that the particle size distribution of the HDPE phase is wider than that of the Admer phase. Thermal analysis was used to deduce that the phase adhesion between PET and Admer phases was much stronger than adhesion between PET and HDPE. Both these observations help to clarify the difference in stress-strain behavior of the binary blends observed in Fig.10. The Admer phase adheres to the PET matrix and shares the applied stress leading to increased mechanical performance. The HDPE phase however, does not adhere sufficiently to the PET phase and hence does not share the applied stress. This leads to an increase in stress concentration in the PET matrix, ultimately lowering the strain to break. It should be noted that the improvement in strain to break, due to addition of Admer, is not solely a function of the adhesion between the two phases. As shown in Fig. 19, with decreasing particle size of the dispersed phase, more and more interfacial area is available for sharing the applied stress. This leads to improvement in mechanical performance.

The effective shear rate range for twin screw speeds of 100-300 rpm has been empirically calculated to be less than 100 sec<sup>-1</sup>. Figure 21 shows that at shear rates less than or equal to 100 sec<sup>-1</sup>, HDPE is more viscous than Admer and has a higher viscosity ratio,  $p$ . In the ternary blends, as the Admer content in the dispersed phase increases from 25 to 75%, the calculated viscosity ratio of the dispersed phase decreases. For a constant shear rate, this calculation would predict a reduction of the average particle size with increasing Admer content. This prediction is confirmed in Fig. 3. It can be seen in Fig. 6 that the mean particle size decreases with increasing Admer content, as expected. This observation is consistent with results presented in Figs. 9 and 11, which show improved mechanical performance with increasing Admer content. Work done by Wu (2) has shown that an elastic phase is most readily dispersed in a viscoelastic matrix at a viscosity ratio,  $p = 1$ . From Fig. 21, it



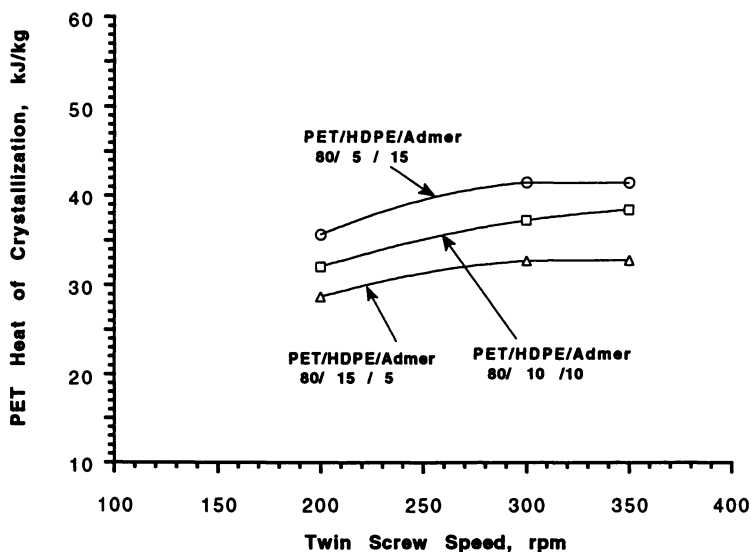


Figure 20. Heats of crystallization of the PET component (normalized to 100% PET) in ternary blends as a function of the speed of twin screw processing.

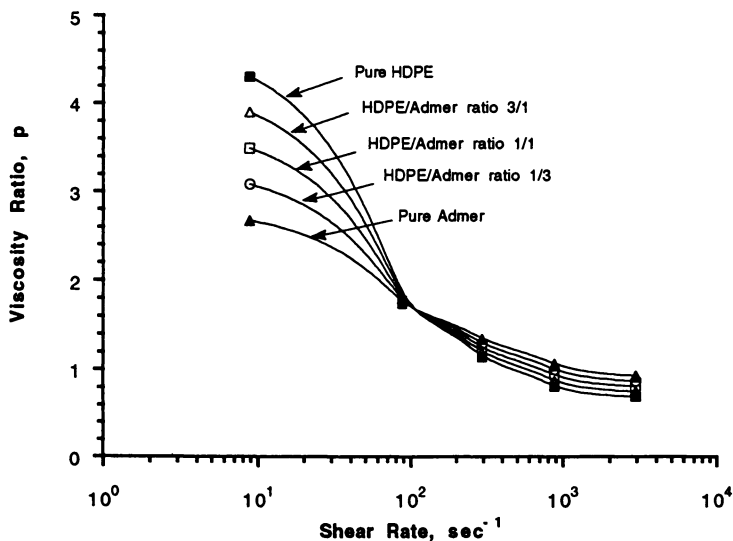


Figure 21. Viscosity ratio versus shear rate calculated for the three different blend compositions. Viscosity ratio:  $p = (\text{Viscosity of: HDPE, Admer or HDPE/Admer blend}) / (\text{Viscosity of PET})$ .

can be seen that for effective shear rates of less than  $100 \text{ sec}^{-1}$ , the viscosity ratios, ( $\eta$ ), for all compositions of the dispersed phase are greater than one and are therefore far from the minimum possible particle size.

Specific conclusions, based on morphological and property characteristics of ternary blends are described below, in relationship to variations in composition and processing conditions.

- Rheological properties of ternary blends are seen to be composition dependent; however, no change is detected in the rheological behavior of blends processed at different twin screw speeds. Measurements made in a capillary rheometer at  $270^\circ\text{C}$  show that the PET resin is less shear sensitive than HDPE or Admer resins. All ternary blends exhibit shear sensitivities, approximately twice as high as that of PET and melt viscosities that are slightly higher than that of PET. Both these property changes indicate that the rheology of the ternary blends is more suitable for extrusion blow molding than that of pure PET.
- Scanning Electron Microscopy shows that the HDPE and Admer phases have been dispersed in the PET matrix in the form of discrete droplets. The particle size distribution is a function of the composition of the dispersed phase (HDPE and Admer) as well as the processing twin screw speed. With increasing Admer content, the average sizes of the dispersed phase particles decrease. The average sizes of the dispersed phase particles in the PET 80/HDPE 10/Admer 10 blends also decrease with increasing twin screw speed, indicating increasing interfacial area between the components.
- As Admer concentrations are increased, significant improvements in ternary blend impact resistance are observed. For binary blends, the HDPE dispersed in the PET matrix does not seem to adhere adequately to the PET matrix, causing a decrease in the impact resistance of the blend. Unlike HDPE, the Admer phase adheres to the PET matrix quite well and participates in stress sharing upon application of stress. This adhesion between the Admer chains and the PET matrix causes a toughening effect in PET, leading to a decrease in modulus, accompanied by a drastic improvement in impact resistance.
- The mechanical properties of an incompatible blend are determined by the dispersed phase particle sizes and their distribution. The sizes of the dispersed phase particles are controlled in part by the shear rates exerted on the polymeric melt during the melt-blending operation. The impact resistance of the ternary blends is seen to increase with increasing speed of twin screw processing.
- Thermal results show that PET and HDPE chains hamper each others' crystallization processes. The effect is more pronounced for PET than HDPE. It is speculated that the decrease in crystallinity of the components is localized in the interfacial areas between the phases. Surface tension studies on polymeric materials, conducted by Wu (16), have shown that semicrystalline polymers tend to be covered with an amorphous surface layer because of the lower surface tension of the amorphous phase. This suggests that the observed decrease in crystallinity of both the components is probably localized around the interfacial area between the two components. Ternary blend characteristics are determined by blend composition and twin screw speed. The PET component in ternary blends with higher amounts of Admer and lower amounts of HDPE, exhibits crystallization rates higher than those of PET/HDPE binary blends or ternary

blends containing greater amounts of HDPE. Higher speeds of twin screw extrusion are seen to increase the interfacial areas between the phases, thereby causing a decrease in crystallization rates of the HDPE component.

- Infrared analysis of the ternary blends indicates the presence of some weak low-energy hydrogen bonding interactions between the carbonyl of the Admer and the terminal hydroxyl group of the PET chain. This hydrogen bonding interaction is seen to be weaker than the intermolecular hydrogen bonding among the PET chains. Additional hydrogen bonding also appears to have occurred between carbonyl groups of the PET and hydroxyl groups formed in the Admer, perhaps as a result of hydrolysis of the anhydride groups.

### Literature Cited

1. Traugott, T.R.; Barlow, J.W; and Paul, D.R. *J. of Appl. Polym. Sci.*, **1983**, Vol.28, pp. 2947-2959.
2. Wu, S. *Polym. Sci. & Eng.*, Mid-March **1987**, Vol. 27, No. 5, pp. 335.
3. Jabarin, S.; Lofgren, E.; and Shah, S. In *Emerging Technologies in Plastics Recycling*, "High-Density Polyethylene-Poly(ethylene terephthalate) Blends - Compatibilization and Physical Properties", Editors: Gerald D. Andrews and Pallatheri M. Subramanian, American Chemical Society Symposium Series No. 513, **1992**, Chapter 17.
4. Jabarin, S. and Sambaru P., *Polym. Eng. Sci.*, Mid-July **1993**, Vol. 33, No. 13, pp. 827.
5. Bataille, P.; Boisse, S.; and Schriber, H. P. *Polym. Eng. & Sci.*, **1987**, Vol. 27, pp. 622.
6. *Comprehensive Polymer Science*; Hsu, S. L.; Pergamon Press, NY **1989**, Vol. 1, Chap. 20, pp. 429.
7. Coleman, M. *Macromolecules*, **1986**, Vol. 19, pp. 2149-2157.
8. Coleman, M. and Moskala, E.J., *Polymer*, March **1983**, Vol. 24, pp. 251.
9. Coleman, M.; Serman, C. J.; and Painter, P. C. *Macromolecules*, **1987**, Vol. 20, pp. 226-232.
10. Moskala, E. J.; Coleman, M.; Painter, P. C. and Howe, S. E. *Macromolecules*, **1984**, Vol. 17, pp. 1671-1678.
11. Krimm, S. *Fortschr. Hochpolym. - Forsch.*; **1960**, Bd. 2, S, 51, pp. 172.
12. Patterson, D. and Ward, I. M. *Trans. Faraday Soc.*, **1957**, Vol. 3, pp. 291.
13. Ward, I. M. *Trans. Faraday Soc.* **1958**, Vol. 7, pp. 1406.
14. Cangelosi, F. and Shaw, M. T. In *Polymer Compatibility and Incompatibility Principles and Practices*, Editor, K. Solc, MMI Press Sym. Series; Harwood Academic Publishers, New York, NY, **1982**, Vol. 2, pp. 107.
15. Keskkula, H. In *Polymer Compatibility and Incompatibility Principles and Practices*, Editor, K. Solc, MMI Press Symposium Series, Harwood Academic Publishers, New York, NY, **1982**, Vol. 2, pp. 323.
16. Wu, S. In *Polymer Blends*, Editors: Paul, D. R. & Newman, S., Academic Press, Inc. New York, NY, **1978**, Vol. 1, pp. 243.

RECEIVED March 1, 1995

## Chapter 12

# A Recovery Process for Spent Polyurethane-Based Propellants

### Feasibility Studies

Frank J. Y. Shiu<sup>1</sup>, Iris C. Y. Yang<sup>1</sup>, T. F. Yen<sup>1</sup>, and Donald D. Tzeng<sup>2</sup>

<sup>1</sup>Environmental and Civil Engineering Department, University of Southern California, Los Angeles, CA 90089–2531

<sup>2</sup>United Technologies Chemical Systems, San Jose, CA 95161–9028

The valuable inorganic components—energetics and fuel—of solid propellants are successfully separated and recovered by using swelling and ultrasound. In this study, the inert polyurethane-based propellant is first comminuted in various solvents as swelling media, and an appropriate solvent is then selected. Subsequently an ultrasound induced cavitation reaction for interfacial treatment is performed with the use of a mild oxidant. Through the process, the polymer binders are partially degraded and the propellant network is destroyed, enabling inorganic and metallic constituents to be released and separated.

To meet military need, solid composite propellants have been extensively developed and manufactured in the past. Following the end of the cold war, these large quantities of propellants from the demilitarization of missiles brought about the urgency of safe propellant disposal. While noted for their high energy release and explosion, the spent propellants become hazardous wastes and need to be disposed with caution. In compliance to the Resources Conservation and Recovery Act (RCRA) and EPA regulations, the conventional and primary disposal method of spent propellant—open-pit burning—is no longer legal. These stringent environmental regulations and uprising pollution concerns have prompted the study of the recovery process for spent propellants.

To recover the useful inorganic components from the spent propellant, the most common methods of breaking the polyurethane backbone macro-structure under vigorous conditions, such as thermal and hydrolytic cleavage, are not applicable. Currently, several techniques are actively being pursued by different groups. These include: aqueous maceration and extraction of propellant by Thiokol, cryogenic washout by General Atomic, and ammonia extraction at supercritical or near-supercritical conditions by Hercules. In addition to these, alternative methods leading to a mild recovery process are being sought.

0097–6156/95/0609–0139\$12.00/0  
© 1995 American Chemical Society

### Approach for The Feasibility Studies

At the outset of the research, we considered our approaches to be a matrix modification. Previously we have successfully separated naturally-occurring composite systems, such as oil shale or coal, into meaningful fractions (1-2). The fragmentation of crosslinked systems, such as asphalt, through solvent swelling has been achieved in several studies (3-5). As shown by Young's modulus and other mechanical properties, the physical integrity of the composites has been drastically changed due to embrittlement, so that the composite integrity is destroyed.

For a number of years, ultrasound irradiation has been utilized as a method of tar sand separation to aid the recovery of bitumens in our research (6-7). The ultrasound method has been used for heavy oil upgrading to crack the high molecular weight asphaltene into low molecular weight oil (8-9), as well as for the dechlorination of trihalocarbons in water (10). The results are very promising and may lead to some novel petroleum recovery techniques (11).

Therefore, the approach which included solvent swelling and ultrasonic degradation is included in this study. Later, a feasible process to recover the useful components from the spent propellant is also outlined. Quantitative as well as qualitative determinations were performed in order to follow the changes in polyurethane after the treatment processes. These measurements included a) mass balance analysis by dry weight measurements of each separated fraction, and confirmation of the targeted substance by chemical analysis; and b) molecular structure determination by UV/visible spectroscopy for qualitative detection of the degraded products.

### Propellant Composition

Polyurethane-based propellants have become more important since the mid-1950's due to the need for higher ballistic performance and the precise mechanical requirements of large rocket motors. The composition of the solid propellants is a 3-dimensional cross-linked matrix with oxidizer, metallic fuel, and other solid components uniformly dispersed throughout. Regardless of types, all polyurethane propellants contain binders that can be cured through the reactions of polyols with isocyanates, with or without a plasticizer. These substances belong to the formal class of polyurethane (PU) elastomers, especially those that recently contain hydroxyl-terminated polybutadiene (HTPB) (12-14). The HTPB-based polyurethane elastomers are superior to the common polyester- and polyether-based elastomers because they possess properties of lower water permeability, better stability in a moist atmosphere, higher electrical insulation, and lower glass-transition temperature ( $T_g$ ) (15-17).

The solid components of the propellants range between 70 to 90%, and their higher limit depends on the processability. The energetic component is the most important and accounts for the largest percentage in the composition. The preferred energetic compounds used in current solid propellants are nitrate or perchlorates, such as AP (ammonia perchlorate), RDX (trinitrohexahydrotriazine),

and HMX(tetranitrotetraazacyclooctane). Aluminum powder is the most frequently used fuel to boost specific impulse and may be found in quantities up to 25%. These materials are trapped in the cross-linked network without chemical bonds. The inert portions of coloring matter, and other plasticizers such as dioctyl adipate (DOA), are also added in some instances (18).

Due to their highly explosive nature, inert samples were initially used instead of the original propellant in this research. In the inert propellant the energetic, AP or HMX, is excluded and replaced with a combination of salts having a similar density, the composition of which is given below:

**TABLE I.** Inert Propellant Composition

Ingredient	Percentage (W/W)
Sodium chloride	35.1
Aluminum, MD-10	31.3
Ammonium sulfate	18.7
R-45 (HTPB)	
Isophorone diisocyanate (IPDI)	14.4
HX-752 (aromatic difunctional aziridine)	0.3
Protec 2705	0.1
Blue Dye	0.1
	<u>100.0</u>

The HTPB/IPDI based polyurethane matrix forms the main structure of the propellant, and aziridine is a bonding agent which brings inorganic salts into the organic environment. In the formulation, the organic, inorganic, and ammonium powder are 14.9%, 53.8%, and 31.3% respectively. To eliminate the interference of the fillings in the inert propellant during the investigation, a one-shot polyurethane elastomer was synthesized with 3% plasticizer and a HTPB to IPDI ratio equal to 9:1, and used for the experiments.

### Solvent Swelling

The chemical linkages for a linear chain of homopolymers are rather easy to break and form into a uniform polymer solution just by stirring, and bond breakage can often be detected by viscosity reduction. For the three-dimensional cross-linked network, however, this type of bond breakage is often ineffective. The introduction of an organic solvent to a cross-linked system can cause the network to expand.

In many chemical comminutions, this expansion can exceed the internal force holding the network or crystallite system together, thus causing the dissolution process. The dilation of a brittle solid can be expressed by

$$S = \frac{2}{9} \left( \frac{1 + \nu}{1 - \nu} \right) G \left( \frac{\Delta V}{V} \right)$$

where  $S$  is strain energy per unit volume,  $\nu$  is the Poisson's ratio,  $G$  is shear modulus, and  $V$  is volume. The fracture of a brittle solid can be expressed as

$$F = \frac{\sigma^2}{2E}$$

where  $F$  is fracture energy per unit volume,  $\sigma$  is tensile stress, and  $E$  is bulk modulus. Comminution will occur when  $S \geq F$ . The swollen network can be broken in order to cause the linkage or the bonds to rupture.

Based on statistical mechanical principles, the internal energy of the substrate should be matched by the internal energy of the invading solvent. Interpreting this in another way, the selection of the solvent must be based on the concept of Hildebrand solubility parameters (19). In many cases of matrix modification methods, we have experienced a total dissolution by the solvent introduced.

The swelling measurement plays a critical role in the study of polymers because it can reveal the polymer structure, density, and other significant information (20). In order to find the suitable solvent for the polyurethane, swelling experiments were conducted with several kinds of solvent. A good solvent can extend the polymer bonding and loosen up the entire structure, which will make the polymer network easier to destroy. The swelling experiment was performed to select proper solvents for the sonication process. The samples were cut into 4x4x4 mm cubes and submerged in various solvents for one week. For the most effective solvents, detailed measurements were further conducted by recording the change in size daily.

Swelling of a network will always exert strain on the whole system. Doubtlessly the binder-filler interaction will be decreased until the filler particles can be rejected. Our experiments will show the evidence of filler separation, which is the major objective of this study.

We noticed in our initial experimental work that the compatibility of solubility parameters of the polymer network and those of the solvents should be matched. For solvent systems, this match cannot be made with dispersion effects alone; the best match is with the total cohesion parameter, i.e.,

$$\delta_d^2 + \delta_p^2 + \delta_h^2 = \delta_t^2$$

where

$\delta_d$  - dispersion cohesion parameter

$\delta_p$  - polar cohesion parameter

$\delta_h$  - hydrogen cohesion parameter

$\delta_t$  - total cohesion parameter

Accordingly, the swelling results with various solvents and their solubility parameters are summarized in Table II. Toluene, THF, and chloroform showed the best swelling effect on the polyurethane; therefore, daily based swelling experiments were conducted with these three solvents for one month. The results from the swelling experiments are shown in Figure 1. Overall, chloroform, THF, and toluene would swell the sample to about ten times the volume in six days. After five days, the volume did not change notably.

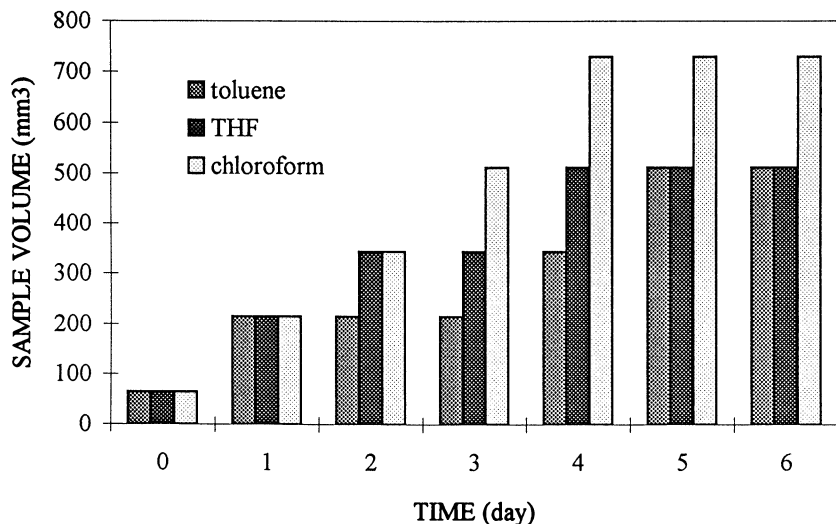


FIGURE 1. Swelling Effect of Various Solvents  
(with 4x4x4 mm cube of inert propellant)

However, a swollen sample which had been submerged in chloroform for more than one month yielded a volume about twenty times the original. This illustrates that creep swelling existing after six days will finally make an important difference in the long run.

Through the swelling experiments, solvents possessing solubility parameters around  $18.7\text{MPa}^{1/2}$  are most effective for HTPB and IPDI based polyurethane. This is quite consistent with the estimation in the CRC handbook (21-22).

A similar study of the swelling of polyurethanes was carried out by Apukhtina et al (23). They concluded that polyurethanes swell to a greater extent in proton-accepting solvents with solubility parameters, such as dioxane and benzene, because the presence of proton-accepting groups favors the formation of a complex due to H-bonding with the urethane groups of the polymer. Dioxane had been tested but did not show any swelling effect on the inert propellant sample, which indicated that the PU from different compositions (polyols and isocyanates) would behave differently even though they all contain urethane functional groups. Actually, the solubility parameter is associated with three types of intermolecular cohesive energy. Besides H-bonding, dispersion interactions and polar interactions are also important. To obtain the precise information for solubility parameters of polyurethane-based propellants, all three types of interactions should be discussed. In other words, certain types of polymer have specific solubilities for H-bonding and dispersion and polar interactions, and only the solvent which matches all three values can completely dissolve this polymer.



**TABLE II** The Results of PU Swelling with Various Solvents and Their Solubility Parameters

Solvent	Hildebrand and Hansen parameters $\delta/\text{MPa}^{1/2}$				Result
	$\delta_d$	$\delta_p$	$\delta_h$	$\delta_t$	
Heptane	15.3	0.0	0.0	15.3	-
Octane	15.4	0.0	0.0	15.4	-
Cyclohexane	16.5	3.1	0.0	16.8	-
Toluene	16.4	8.0	1.6	18.3	++
THF	13.3	11.0	6.7	18.5	++
Benzene	16.1	8.6	4.1	18.7	++
Chloroform	11.0	13.7	6.3	18.7	++
Acetone	13.0	9.8	11.0	19.7	-
Ethyl acetate	13.4	8.6	13.5	20.8	-
Pyridine	17.6	10.1	6.3	21.7	+
Dioxane	14.8	11.3	13.9	23.2	-
Methanol	11.6	13.0	24.0	29.7	-

After the swelling, the samples became very fragile and the entire structure loosened. By forcing the fragile sample through a screen or membrane with hydraulic or mechanical pressure, the size of the swollen sample could be significantly reduced (<1 mm). At this stage most of the targeted energetic components trapped inside could be released, but the aluminum powder (fuel) was found to be still tightly combined with the polymer. The solvent extraction (organic) and water extraction (inorganic) accounted for around 8% and 47% of the sample weight. 45% remained as residue. Therefore, after most of the fillings had been released, the propellant binder was more likely to be degraded into smaller oligomers. The ultrasound process was conducted immediately following the swelling process.

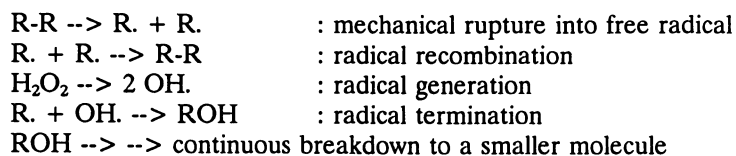
### Ultrasound Irradiation

Ultrasonic energy may activate various mechanisms to promote the degradation or separation of a propellant matrix. It is generally believed that three phenomena occur under the effects of ultrasonic irradiation. First, a rapid movement of fluid caused by a variation of sonic pressure causes solvent compression and rarefaction. Second, the formation and collapse of microbubbles is responsible for most of the significant chemical effects observed. A theoretical consideration, in an aqueous system, is that the instantaneous pressure at the center of a collapsing bubble is about 75,000 psig (5,100 atm). Through a similar estimation, its temperature can reach a value as high as 20,000°C. Third, there is microstreaming in which a large amount of vibrational energy is confined in small volumes with little heating (24).

Several theories (25-26) have been established for the mechanism of ultrasound degradation, but none of them is comprehensive enough to explain the real effects. In the early stage of development, it had been suggested that chain breakage is caused by friction force raising between the fast moving solvent

molecules caused by ultrasound and slower polymer molecules. This leads to the conclusion of physical bond cleavage for the polymer degradation through the analysis of molecular weight distribution by gel penetration chromatography (GPC). The other major and more important mechanism is the free radical reaction. Cleavage of a covalent bond can occur in two ways: homolytically, resulting in one electron from the bond going to each fragment to produce a radical species; or heterolytically, with both electrons going to one fragment, leading to the formation of an ion pair. Both of these possibilities have been observed. Evidence for the presence of radicals was obtained by carrying out the sonication in the presence of unsaturated, polymerizable monomers after trapping the radicals using  $\alpha,\alpha'$ -diphenyl picryl hydrazyl (DPPH). In this experiment, both GPC and the viscometer were not able to be used due to the inconsistency of the polymer solution. The uniform polymer solution was not able to be achieved because of the incomplete dissolution of the 3-dimensional network. Only the change in the solubility can be measured through the dry weight measurement, and the soluble fraction of the polymer can be further analyzed.

By the free radical reactions in this cavitation environment (instantaneously high pressure and high temperature), the high molecular weight polymer can be degraded into low molecular weight oligomers. The mechanism of polyurethane degradation under ultrasonication may be suggested as:



The ultrasonication process was conducted with a model VC-50 ultrasonic probe (Sonics & Materials) operating at 20 kHz in a 50 mL beaker containing 20 mL chloroform with 0.2 gram inert propellant which has been fully swollen and pulverized. Both the propellant and PU gum stock were used for analysis.

The prepared solutions were subject to different durations of sonication (0, 10, 20, 30, 40 and 50 minutes), and the soluble portions of PU in each treated solution were measured by filtering out the insoluble portions and being allowed to dry up overnight in the vacuum oven. Figure 2 shows that the dissolved portion of the polyurethane and inert propellant samples in chloroform was increasing with the durations of sonication.

The processed propellant solutions were further analyzed with a UV/visible spectrophotometer. The UV spectra (Figure 3) shows that the characteristic peak of polyurethane groups (at about 243 nm) increased with the duration of sonication. This indicated that the integrity of the polyurethane network had been destroyed and the degraded fragments became soluble in the chloroform.

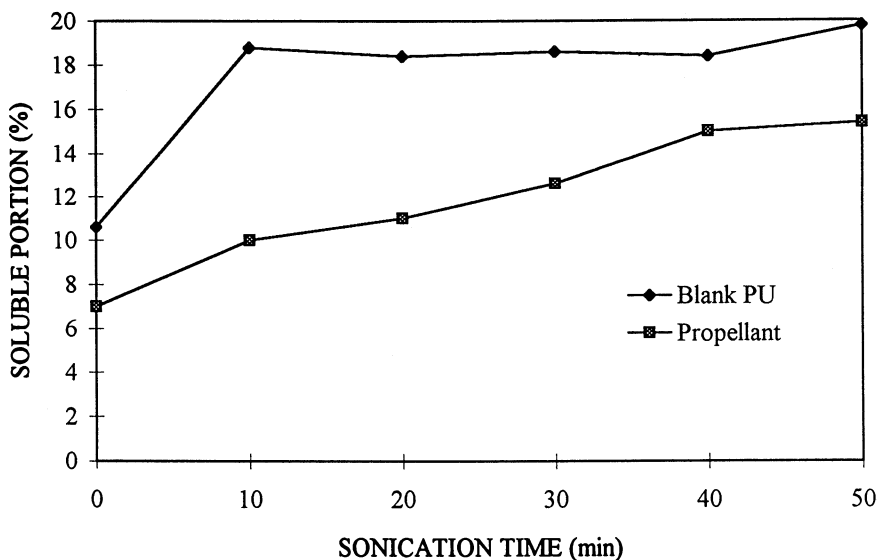


FIGURE 2. Sonication Effect on Solubility  
(0.2 g sample in 20 mL chloroform)

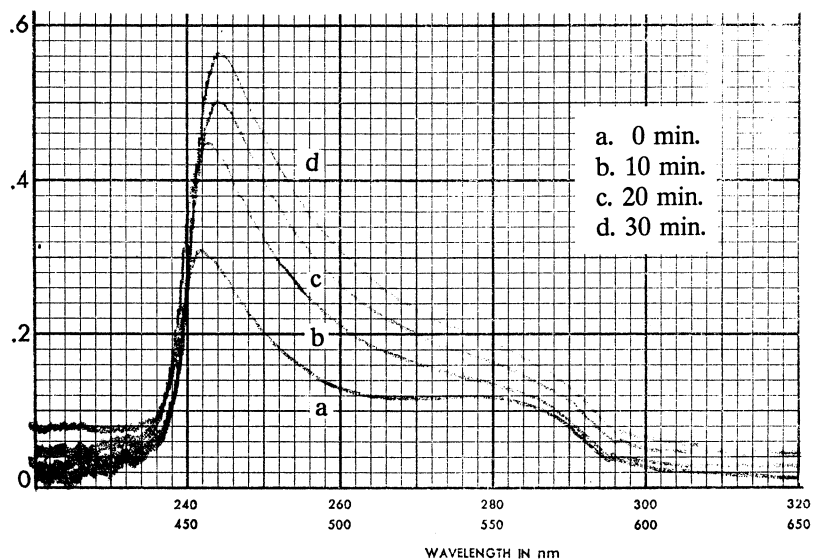


FIGURE 3. UV Spectra of Propellant Solution  
after different duration of sonication  
(0.2 g propellant in 20 mL chloroform)

The residue after solvent and water extraction was analyzed with chemical methods. It shows as expected that aluminum is the dominant content, with up to 85% of its total quantity recoverable. To obtain aluminum with high purity, a simple treatment can be further applied to the residue.

### Enhancement

The surfactants are amphiphathic molecules that contain both distinct hydrophobic and hydrophilic regions. A polymer will form either Hartley micelles or reversed micelles from its interaction with the surfactants. During the rearrangement of the molecules in these micelles, functional groups are likely to orient toward the liquid phase, which will maintain the tendency of particle size reduction and greatly increase the free radical reaction rate. Therefore, various surfactants were also used in the process to enhance the degradation effectiveness.

First, three different types of surfactants, cationic (dowex-2), anionic (1-octanesulfonic acid) and nonionic (1-nonanol), were selected for studying the enhancement. In a 20 mL inert propellant solution, 0.1% (V/V) of each surfactant was added respectively, and subsequently was subject to a 20-minute sonication. After conducting various surfactants, the nonionic surfactants could enhance the solubility of the polyurethane most with sonication.

The relationship between the amount of nonionic surfactant and its effectiveness then was studied. The results (Figure 4) indicate that the addition of a surfactant can increase the solubility of PU during the sonication process.

Subsequently, an analysis of the oxidant effectiveness was performed with ultrasonication. The addition of oxidants causes polyurethane to undergo oxidative degradation in an oxidation environment. The commonly used oxidants, such as hydrogen peroxide and benzol peroxide, were added to accelerate the aging and bond-breaking process. To each 20 mL inert propellant solution was added a different amount of oxidant (benzoyl peroxide), and then the solutions were sonicated for 20 minutes. The insoluble portion of the sample in each solution was determined after process. The results, in Figure 5, show that the solubility of PU also increased with the amount of oxidants added.

### Optimized Process for Recovery

An optimized process was conducted with selected solvents and the adding of selected surfactants and oxidants based on previous experimental results. A two-stage extraction was used. The sample was first extracted by a 20-min sonication in the presence of an efficient organic solvent to degrade and extract the organic portion, and the extracted solution then was separated from the sample residue for analysis. The second sonication was carried out with 20 mL water added to dissolve and separate the inorganic portions from the metal. The sample weight measurement was performed with the solvent medium, water medium, and residue obtained from the interfacial ultrasound process to compare with the composition of the inert propellant.

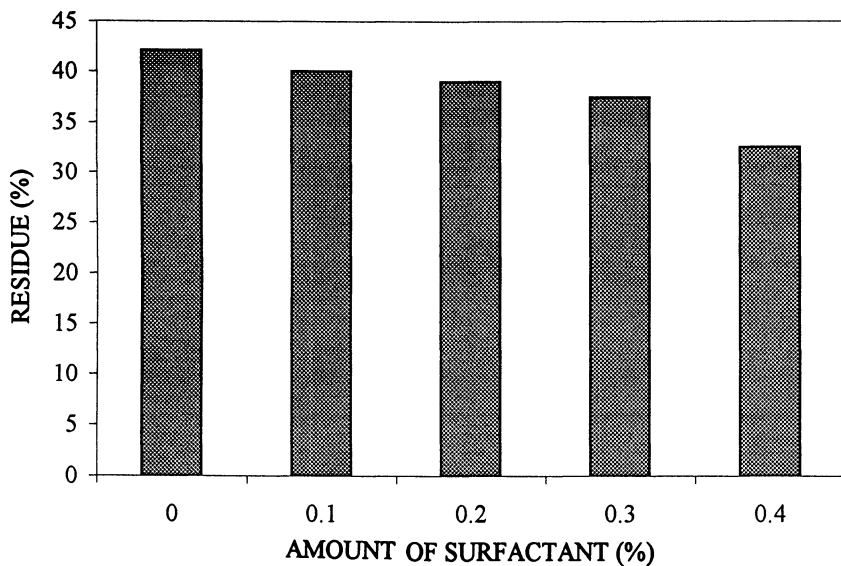


FIGURE 4. Surfactant Effect on Solubility  
(0.1 gram inert propellant in 20 mL chloroform  
with different amount 1-nonanol sonicated 20 minutes)

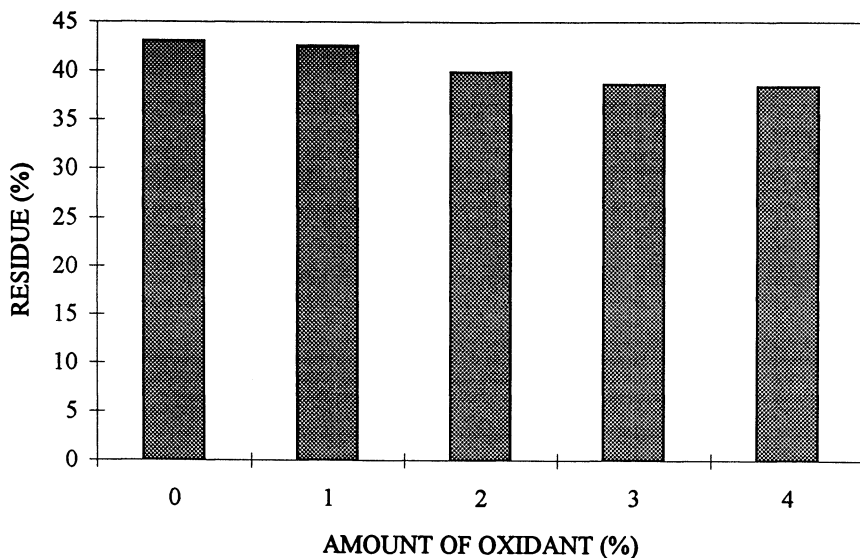


FIGURE 5. Oxidant Effect on Solubility  
(0.1 gram inert propellant in 20 mL chloroform  
with different amount benzoyl peroxide sonicated for 20 min.)

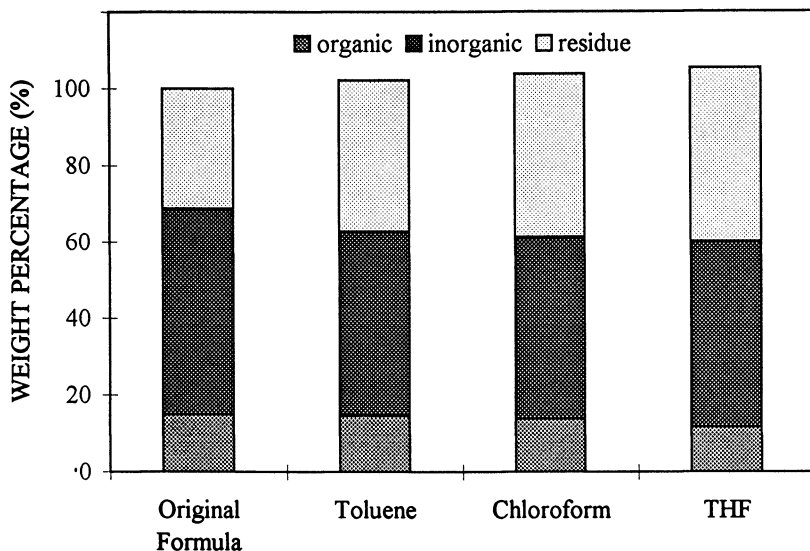


FIGURE 6. Separation Results by Optimal Process (0.2 g inert propellant in 20 ml effective solvent with 2% benzoyl peroxide and 0.5% 1-nonanol after 20 min. sonication)

An optimized recovery process with ultrasonication was developed based on the results from previous experiments. Figure 6 indicated that the separations of three portions (organic, inorganic, and residue) are quite satisfactory after 20-minute sonication in all three effective solvents with the addition of 2% benzoyl peroxide and 0.5% 1-nonanol (nonionic surfactant), especially for the chloroform run.

Most of the energetic components were recovered after the swelling and subsequent physical breakdown of the propellant, and only aluminum powder was still tightly combined with polyurethane fragments. With the aid of ultrasound and oxidants, these two portions could be separated, since the polyurethane was susceptible to oxidative degradation. As far as the degradation due to ultrasound is concerned, there was no drastic change (Figure 2). This, however, can be interpreted as being due to a low power configuration (50W). In the future for large scale process, more powerful equipment (600W) can be used.

## Conclusion

The polyurethane-based propellant recovery with solvent swelling and ultrasonication is proven to be feasible. The results from swelling tests indicated that chloroform, THF, and toluene can expand the IPDI/R-45M based polyurethane effectively. The polyurethane network is more easily broken down after being fully swollen. The separation as well as recovery of the inorganic components such as ammonia sulfate, sodium chloride, and aluminum powder

from the polyurethane binders was quite successful in the study through ultrasound irradiation with the aids of surfactant and oxidant. The addition of surfactants can enhance the degradation efficiency, especially with nonionic surfactants. This suggests that the active portion or inorganics for propellants can be recovered.

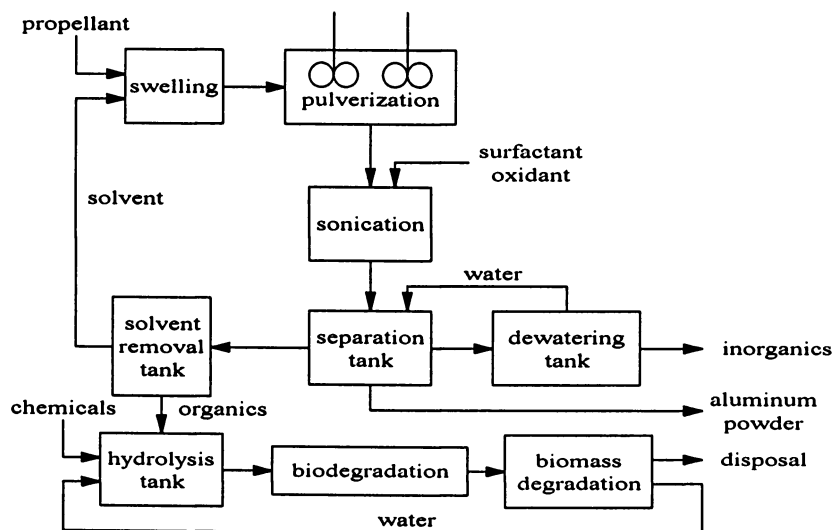


Figure 7. The Flow Chart of Recovery Process

Our results indicate that the 3-dimensional cross-link network structure is degraded into lower molecular weight oligomers through these approaches. The result from this study indicates that a chemical comminution with the appropriate room temperature ultrasound field can recover the bulk (-90%) of the spent propellant. Valuable components of all energetics (inorganics) can be separated from the polyurethane binder. With proper procedures developed, the energetics can be recovered. The remaining recovery waste streams which contain partially degraded polyurethanes can be recorded or can be treated by a microbiological method (see Fig. 7).

### Acknowledgements

We would like to acknowledge the financial support provided by the United Technology Chemical System, San Jose, CA.

### References

1. Sadeghi, M. A., Shama, M. M. and Yen, T. F. 1982. *Proc. 17th Inter. Energy Conv Eng. Conf.*, vol. 17(2):899-904.

2. Yen, T. F.; Lee, W. C. 1979. *Inter. Energy Conv. Eng. Conf.*, 14:832-861.
3. Chan, M.; Yen, T. F. 1981. *Fuel*, 60:1174-1176.
4. Yen, T. F.; Chan, M. 1985. U.S. Pat. 4,522,265 June 11.
5. Lee, A. S.; Sadeghi, M. A.; Yen, T. F. 1988. *Energy and Fuel*, 2:88-93.
6. Sadeghi, K. M.; Sadeghi, M. A.; Yen, T. F. 1990. *Energy and Fuel*, 4:604-608.
7. Sadeghi, K. M.; Sadeghi, M. A.; Kao, J. F.; Jang, L. K.; Lin, J. R.; Yen, T. F. 1992. *Chem. Eng. Comm.*, 117:191-203.
8. Lin, J. R.; Yen, T. F. 1993. *Energy and Fuel*, 7:111-118.
9. Sadeghi, K. M.; Lin, J. R.; Yen, T. F. 1994. *Energy Resources*, 16:461-471.
10. Chen, J. R.; Xu, X. W.; Yen, T. F. 1990. *Env. Tech.*, 11:829-836
11. Sadeghi, K. M.; Sadeghi, M. A.; Kao, J. F.; Jang, L. K.; Yen, T. F. 1990. U.S. Pat. 4,891,131, Jan. 2.
13. Sorenson, W. R.; Campell, T. W. 1962. *Preparative Methods of Polymer Chemistry*, Interscience, NY, NY.
13. Woods, G. 1990. *The ICI Polyurethanes Book*, 2nd ed., ICI Polyurethanes and John Wiley & Sons, Netherlands.
14. Fu, B.; MacKnight W. J.; Schneider, N. S. 1985. *Rubber Chemistry and Technology*, 59:896-911.
15. Cohen, D.; Seigmann, A. 1987. *Polymer Eng. and Sci.*, 27:286-293.
16. Siegmann, A.; Cohen, D. 1987. *Polymer Eng. and Sci.*, 27:1187-94.
17. Vimalasiri, P. A. D. T. R.; Burford, P.; Haken, J. K. 1982. *Rubber Chemistry and Technology*, 60:554-577.
18. Stu, B. 1994. *C&EN* January 18-22.
19. Weinberg, V.; Yen, T. F. 1981. *Fuel*, 59:287-289.
20. Mark, J. E.; Sung, P. H. 1982. *Rubber Chemistry and Technology*, 55:1464-1468.
21. Barton, A. F. M. 1990. *CRC Handbook of Polymer - Liquid Interaction Parameters and Solubility Parameters*, CRC Press, NY, NY.
22. Cheremisinoff, N. P. 1989. *Handbook of Polymer Science and Technology*, NY, NY, Vol.1.
23. Apukhtina N. P.; Erenburg Ye. G.; Rappopor, L. Ya. 1966. *Vysokomol. Soyed*, 8:1057-1062.
24. Lin, J.R. 1992. *Asphalt Waste Minimization*, Ph.D. Theses, Univ. of South. Cal., LA, CA.
25. Mason, T. J. 1990. *Chemistry with Ultrasound*, Elsevier Applied Science, Lodon.
26. Price, J. G. 1990. *Advances in Sonochemistry*, JAI press Ltd., New York, New York, Vol.1.

RECEIVED March 16, 1995



## Chapter 13

# Consideration of Poly(ethylene terephthalate) Recycling for Food Use

F. L. Bayer, D. V. Myers, and M. J. Gage

Coca-Cola Company, 1 Coca-Cola Plaza NW, Atlanta, GA 30313

The United States used approximately 1.6 billion pounds of PET plastic packaging resins in 1993, with approximately 480 million pounds being recycled. Regulatory and environmental pressures and the need for environmentally sound programs have dictated the need for responsible approaches to recycling. There exist multiple approaches to recycling of PET. This creates complex relationships between establishing suitable recycling technologies and achieving regulatory requirements for food-grade applications. This paper focuses on the interrelationships of the various approaches to generate safe, recycled, food-grade PET and existing or proposed regulatory requirements in the U.S. and Western Europe.

U.S. resin sales in 1993 were 68 billion pounds, with PET accounting for approximately 3 billion pounds (1). Half of that volume - 1.6 billion pounds, went into some form of plastic packaging (2). These numbers dictate a need for responsible waste management through recycling. This need will only increase in the future.

Where do we stand today with respect to plastics recycling? Let's focus on plastic packaging, and more specifically, on PET. The 1993 recycling rate of plastic packaging overall was 6.9%, with PET at 28%. If we focus closer on just plastic bottles, then the overall rate is 19.2% with PET at 30%. If we further restrict our view to PET soft-drink bottles, we had a recycling rate of 41% for 1993 (2). Clearly, since the 1960's, public awareness of environmental issues such as solid waste has been increasing.

Although plastics constitute a small proportion of the solid waste stream, (about 8 %) (3), plastic food containers, particularly PET soft-drink bottles, have a disproportionately high environmental profile. Consequently, a rash of environmental legislation over the last decade has appeared in the United States,

0097-6156/95/0609-0152\$12.00/0  
© 1995 American Chemical Society

enacted both by individual States and the Federal Government. Notably, this type of legislation is not restricted to the U.S. Internationally, some member countries of the European Union also have introduced mandatory recycling of plastics. Suffice it to say, the concept is catching on worldwide. Any international consumer packaging company is acutely aware of this trend.

As a major user of plastic containers for food use, and as a leader in the beverage industry, The Coca-Cola Company has been involved in PET recycling from the start. In fact, we were the first company to introduce food containers using recycled plastic. Based on a cooperative effort with Hoechst Celanese, in January 1991 they received the first "no-objection" letter from the U.S. FDA (4), allowing the use of recycled PET for food-contact applications. Shortly thereafter, in April, The Coca-Cola Company commercially introduced PET soft-drink bottles containing recycled material. Since 1991, the FDA has issued nine "no-objection" letters on the use of recycled plastic for food containers, particularly PET.

Since this ACS Symposium is technical, it is most pertinent to focus on the regulatory and technological issues of recycling PET into food containers. From a regulatory standpoint, PET is the first plastics test case that regulators have had to deal with on this issue. It should be mentioned that most regulations worldwide covering the use of plastic packaging in food-contact applications were well in place, and did not anticipate the usage of recycled plastic for food applications. From a technical standpoint, these topics offer a fertile field of discussion because the chemical nature of PET permits a broad array of recycling options (5,6). Therefore, from both a regulatory and technical standpoint, we are in a rapid learning curve on this issue.

This paper is structured into three major areas:

1. Review of approaches to PET recycling;
2. Considerations for use of recycled PET -- technical and regulatory, and
3. An update on the worldwide status of recycled PET being used in the market for food packaging.

### **Approaches to PET Recycling**

A brief review or reminder of how plastic recycling can be classified is in order. In May 1992 (7), the U.S. FDA prepared a most useful set of guidelines to help those interested in assuring the consumer safety of their recycling processes. In this document, plastic recycling was divided into three classes.

Primary recycling is the recycling of plastics which are plant scrap, and have never had consumer exposure. Secondary recycling involves the physical cleaning of post-consumer plastic by physical processes such as washing, vacuum, and heat treatment. Tertiary recycling involves the chemical treatment, usually depolymerization, of the plastic, and later reconstitution to the polymer. Obviously, all plastics can undergo primary and secondary recycling, but only plastics having somewhat labile bonds, such as polyesters, can be recycled through tertiary recycling.

Let's review the recycling options for PET resin. As with any plastic,

PET can undergo secondary recycling by being physically cleaned. However, being a polyester, PET can also undergo tertiary recycling chemically through depolymerization followed by repolymerization. This attribute of PET enables the monomers and/or the oligomers to be purified and then reassembled, rather than removing any impurities that may be present directly from the polymeric material itself.

### PET Manufacturing

Before discussing the PET recycling approaches, we should briefly review the manufacturing process for the resin. PET is made by the poly-condensation of ethylene glycol and terephthalic acid or the corresponding methyl ester to result in a linear polymer of alternating ethylene and terephthalate moieties. The free-acid approach involves ester formation between the hydroxyl groups of ethylene glycol and the terephthalate carboxyl groups; whereas in the ester approach, ester interchange occurs between the methanol and the ethylene glycol. In either case, the fundamental monomer of PET, bis-hydroxyethyl terephthalate (BHET), is formed. In a series of condensation steps at high temperatures, polyethylene terephthalate is formed. The molten PET at 280-290° C is extruded, and usually cut into small pellets. The number of repeating units per polymer chain, or degree of polymerization (DP), is critical in terms of the functional use of the resin; and for applications such as soft-drink bottles, where the rate of permeation of CO<sub>2</sub> is to be as low as possible, one requires a high DP, or molecular weight, of PET to permit the fabrication of oriented bottles.

To increase the DP to as high a value as possible, the process of solid-stating is used. Solid-stating involves the heating under vacuum of the resin, and this process promotes further linear poly-condensation of the polymer to increase the molecular weight, and hence, improve the properties of PET.

### PET Recycling Options

Secondary and tertiary processes of PET recycling are illustrated in Figure 1. Starting with the physical, or secondary, approaches, cleaning with detergents and/or caustic is used routinely by PET and other plastic recyclers, for the cleaning of flake. Generally, this type of cleaning will sanitize the resin, and render it suitable for use in non-food applications. However, the cleaning process might not always be adequate to allow the material to be used directly for some food contact applications -- a "deeper" cleaning process may be required.

Physical cleaning processes having a greater penetration of the resin than that of simple washing offer promise for use in recycling for food applications. There is a patent on the use of super-critical fluid extraction, or SFE, using CO<sub>2</sub> (8). Perhaps other suitable non-toxic super-critical extractants could be used to clean PET. Another option involving physical cleaning is the use of solvents having high penetrating power for PET resin. In this connection, a patent also has been issued which uses propylene glycol to clean PET (9.)

The last physical approach that could be effective is the use of high

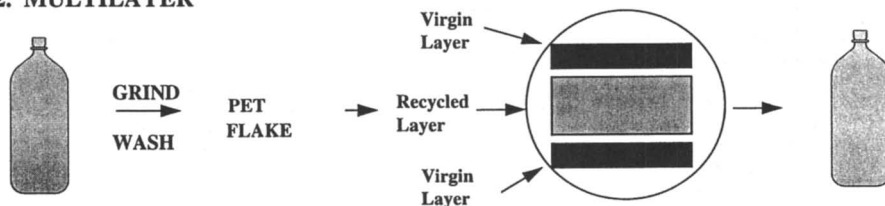
**1. DEPOLYMERIZATION****2. MULTILAYER****3. MONOLAYER**

Figure 1. PET recycling options.

temperature and vacuum to clean the resin. These conditions of high temperature and high vacuum remove any volatile impurities, and often are used as purification steps in tertiary recycling processes.

**Secondary Recycling.** An ingenious way to use secondary recycled PET is to place the post-consumer recycled resin between two layers of virgin resin, thus making a "post-consumer multilayer PET sandwich," if you will; or by having the recycled layer on the exterior if only two layers are used. Commercially these are termed multilayer approaches (10,11). Migration into the product of any impurities that might be present, even after cleaning of the recycled resin, is considered to be negligible based on data submitted to various regulatory agencies. Not only is the rate and extent of impurity migration very slow, the virgin-resin barrier that exists between the product and the recycled resin assures consumer safety and product quality (12). Extensive testing and the commercial use of the multilayer approach in soft-drink packaging applications have confirmed the feasibility of this approach.

**Tertiary Recycling.** Tertiary recycling, which involves chemical approaches, offers a "very deep" cleaning in the recycling process because the intrinsic structure of the polyethylene terephthalate is destroyed by depolymerization, eliminating all potential of any impurities binding to the polymer chains. Physical methods are then used to separate (purify) the monomers and/or oligomers from any impurities. The chemical approaches can result in total depolymerization to the monomers, or in partial depolymerization to the oligomers.

Commercially, PET resin producers conducting recycling receive a ground flake meeting certain specifications for quality (resulting from physically cleaning post-consumer bottles). This material is then depolymerized, purified, and repolymerized into recycled resin/bottles.

The agents of depolymerization routinely used to lyse the ester bonds are water (hydrolysis), methanol (methanolysis), and ethylene glycol or diethylene glycol (glycolysis). Basic catalysts are often used to promote hydrolysis or ester interchange.

Methanolysis results in the stoichiometric formation of dimethyl terephthalate (DMT) and ethylene glycol (EG). The process may be viewed as passing through two steps. The first involves dissolution of the PET flake with partial glycolysis followed by methanolysis, yielding DMT and EG. The resulting DMT is purified by crystallization and distillation, to afford a high-purity, recycled monomer.

Hydrolysis relies on the use of high pressure and temperature to depolymerize the PET into the monomers of terephthalic acid (TPA) and ethylene glycol. Commercially, hydrolysis is not being used as an approach to producing food-grade recycled PET, predominantly due to costs associated with purification of the recycled TPA. When glycolysis is conducted, the true monomer of the polyester condensation, bis-hydroxy-ethylterephthalate (BHET), along with the oligomers ( $n \approx 2 - 10$ ), are formed. After depolymerization, the monomers and/or oligomers are recovered, purified via vacuum distillation, and repolymerized in the presence of ethylene glycol to reform PET.

The ethylene glycol produced from all three processes (methanolysis, glycolysis and hydrolysis) can also be separated from the reacted mass by distillation, and, if desired, can be rectified to the stage whereby it can be reutilized in the repolymerization step to PET. Because the physical nature of the terephthalate monomers that are formed in the three different chemical depolymerizations differ, the purification steps for the monomers also vary.

### Technical and Regulatory Considerations of Recycling

One of the most stringent, or “worst case” packaging application is that of a clear (colorless) beverage container. A clear container with recycled PET capable of being used for carbonated soft drinks represents a good example of the most demanding packaging application for three reasons:

1. The food-contact surface is exposed to a liquid food, and if any migration of materials from the resin would occur, it would most likely be under these circumstances.
2. The recycled resin must be of high quality; otherwise it is incapable of being used to form bottles having good CO<sub>2</sub> retention, and meeting all of the other important physical characteristics that are necessary for containers of carbonated soft drinks.
3. Package quality is very evident because the bottle is clear (colorless). Any discoloration (yellowing) of the recycled PET resin would be evident at point-of-sale, or certainly after the contents of the bottle have been partially consumed. This may have a negative effect on the consumer’s perception of product quality. Concerns about product and package quality are equally as important to the user of recycled plastics/PET in his food packaging as are concerns for consumer safety.

**U.S. FDA Regulatory Guidelines.** The basic guiding principles in regulating any packaging (including recycled plastic) are: (1) the package shall not endanger the consumer through product adulteration by migration of material from the package, and (2) the package will not detract from the organoleptic properties (taste, smell) of the food. These basic tenets are encoded in all worldwide packaging regulations.

As stated earlier, most plastic food packaging regulations were in place before the concept of using recycled plastic in food packaging emerged as a result of environmental pressures. The U.S. FDA was first to formally consider this issue and prepared guidelines in 1992 (7) which assist interested parties in testing the safety of their recycling process. Additionally, the recycled plastics would have to comply with all existing regulations promulgated for virgin plastics.

The fundamental concept underlying these guidelines is the principle of *de minimis*, a Latin phrase roughly meaning “below a level of concern,” also referred to as a “Threshold of Regulation” (13). How is this concept put into practice? One contaminates 100% of the PET feedstock in the form of either bottles or flake for a period of 2 weeks at 40° C with periodic agitation. Contaminants are then drained from the flake with subsequent processing. This may involve cleaning as in a commercial preprocessor (flaking operation), followed by depolymerization and

analysis. In the case of tertiary recycling (chemical depolymerization), you can spike the reactor directly with a level of 0.1% of contaminant per weight of flake as an alternative procedure.

What type of “contaminants” are used? FDA has established criteria for using contaminants representing the various physical/chemical categories. These would include the categories of polar volatiles, polar non-volatiles, non-polar non-volatiles, non-polar volatiles and metallics/organometallics. The end results dictate that the material (purified monomer, resin, preforms, or bottles) containing recycled content would meet the *de minimis* concept. This corresponds to the residual concentration of a contaminant that corresponds to an acceptable upper limit of dietary exposure of 1 ppb. (One-half ppb is the proposed new limit).

The maximum residual levels have been established for various plastics based on certain assumptions and calculations involving the density of the material; its thickness; mass-to-surface ratio; the amount of food contact per square inch; the amount of food consumed in this type of container (consumption factor) and the food-type distribution factor. The calculation which is shown in Reference 7 results in a maximum residue level of 430 ppb (215 ppb based on the newly proposed threshold of regulation) for a contaminant in PET corresponding to a total dietary exposure level of 1 ppb.

These guidelines are more than adequate to provide for consumer safety. There are four key assumptions that overestimate the risk to the consumer:

1. The assumption that 100% of the material subjected to the regime is contaminated; industry believes that post-consumer PET bottle contamination with toxicants may be as low as 1 in 10,000.
2. The assumption that neat or user-strength solutions are used for contamination; the consumer doesn't always have access to these levels of concentration.
3. The consumption factors used assume that 100% of the food application will use recycled resin.
4. The assumption that the food container will have 100% recycled content.

The *de minimis* concept is a rational approach for establishing risk assessment, and, more importantly, gives industry a tangible basis for evaluating various recycling processes. Unfortunately, *de minimis* is not universally accepted throughout the world. In Europe, where there is considerable need for recycling due to an abundance of environmental pressure, they take a totally different approach.

### **PET Recycling Status Worldwide**

**European Regulatory Criteria.** Most of Europe is governed by the European Union, although national laws exist for all member countries. Historically, about 30 years ago, European regulators began establishing positive lists of substances for manufacturing plastics intended for food packaging, providing specific migration levels for residues of the substance or the maximum amount of the residue in the plastic article. Unfortunately, this led to a broad diversity of regulations covering packaging materials. The European Commission (Union) has worked hard in harmonizing packaging legislation within Europe - or shall we say - bringing “chaos

into order.” The European Union, like the U.S., has no regulation governing the use of recycled PET, and has not established guidelines for recycle food-grade applications. Thus, the current governing regulations have a problem in dealing with certain processes for the recycling of PET for food-contact applications. To understand this dilemma, we must understand the basis of the establishment of guidelines for the manufacture of food-grade PET. The European Union has established a Directive (90/128/EEC) (14) which mandates a “Positive A List” of approved monomers with specific migration limits (SML’s) and Global Migration Limits (QML’s).

The specific migration limits (SML’s) establish a residual limit for that monomer on the A list that migrates into the foodstuff or a simulating liquid. The level is generally equal to the Acceptable Daily Intake (ADI) or the Tolerable Daily Intake (TDI) of the substance times 60. The maximum quantity of residual substance (QM) represents the residual level of the substance in the finished product. QM is generally expressed as 10 mg/dm<sup>2</sup> of packaging or 60 mg/kg of foodstuff.

How does Directive 90/128/EEC affect recycling? First, there are no specific food law regulations covering the use of recycled plastics in the European Union, with the exception of Spain and Italy, which have prohibitive provisions. In principle, tertiary recycling processes resulting in purified monomer complying with the provisions of Directive 90/128/EEC should be authorized. In fact, the Commission and several member states have issued their equivalent of a “no-objection” letter for recycling via methanolysis. Unfortunately, the problem is that the European Union’s “Positive A List” approach has difficulty with processes other than tertiary recycling that yield monomer. For example, there is no provision for a barrier layer approach such as multilayer. Presently, the Commission is deliberating over this very issue. Additionally, processes which would have the ability to extract/remove any and all contaminants directly from the flake are excluded. In other words, “Super Cleaned Flake” cannot be regulated because it is not a monomer and, therefore, is obviously excluded from the “Positive A List.”

### Conclusion

Where do we go from here? Industry and regulatory agencies must continue to work cooperatively to find the appropriate answers to establish workable criteria for regulators, industry, legislators and the consumer. As an example, a recent meeting of U.S. and EU regulators was held in Europe under the auspices of ILSI (the International Life Sciences Institute) to discuss how the “*de minimis*/threshold of regulation” concept can harmonize the approach of risk assessment as it applies to packaging safety. This meeting is an important step toward harmonization of worldwide regulations pertaining to the use of recycled materials in food packaging. The results of this meeting have been reported as positive, and progress is expected to be made in this critical area.

The concepts embodied in the 1992 FDA Guidelines have gained some acceptance in assessing the risk of using recycled packaging for food outside the United States. Several processes for recycling PET for food packaging applications



have been approved by regulatory bodies outside the U.S. In the UK, MAFF (Ministry of Agriculture, Fisheries and Food) approved a methanolysis process in 1992, and shortly thereafter, the same process was approved by the European Union. In 1992, Japan also approved the use of methanolysis for the recycling of PET for soft-drink bottles. In 1993, Australia approved the use of multilayer recycling, followed by New Zealand in 1994.

The need and opportunities for recycling of plastics for food packaging have been recognized by industry, and they are working diligently to find meaningful and cost-effective solutions for this issue.

### Literature Cited

1. *Modern Plastics* January 1994, 73-84.
2. Beck, R.W. 1993 *National Post-Consumer Plastics Recycling Rate Study*.
3. *Characterization of Municipal Solid Waste in the United States - 1992 Update*. Report 530-R-92-019, U.S. Environmental Protection Agency, Washington, DC, July 1992.
4. Rulis, A. Food Additive Master File No. 428, No Objection Letter to R. Simmons, January 9, 1991.
5. Menges, G. *International Polymer Sci. & Tech.* 1993, 20 (8), T10-T15.
6. Leaversuch, R.D. *Modern Plastics* 1991, 68 (7), 40-43.
7. *Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations*. U.S. FDA, Center for Food Safety and Applied Nutrition (HFS-245), Washington, DC, April 1992.
8. U.S. Patent No. 4,764,323, August 16, 1988. Al Ghatta, Cobarr S.p.A., Anagni, Italy.
9. Patent No. 4,680,060, July 14, 1987. Gupta, A.S., Camp, J.T. The Coca-Cola Company, Atlanta, GA.
10. Coleman, E.C. Food Additive Master File No. 518, No Objection Letter to R.A. Simmons, April 14, 1993.
11. Coleman, E.C. Food Additive Master File No. 518, No Objection Letter to R.A. Simmons, May 5, 1994.
12. Begley, T.H., Hollifield, H.C. *Food Technology*, November 1993, 109-112.
13. Machuga, E.J., Pauli, G.H., Rulis, A.M. *Food Control* 3 (4), 1992, 180-182.
14. European Community Council Directive No. 90/128/EEC, Council Directive of 23 February 1990 Relating to Plastics Materials and Articles Intended to Come into Use with Foodstuffs. CEC, 1990, *Official Journal of the European Communities*, L75/19.

RECEIVED March 8, 1995

## Chapter 14

# A Review of Advanced Recycling Technology

George Mackey

Granville Research Laboratories, Dow Chemical Company, P.O. Box 515,  
Granville, OH 43023-0515

This paper is intended as a review of the various processes put forth to convert mixed and unwashed waste plastic to a product with some economic value. Conventional mechanical or melt recycling of plastics works well when the processes can acquire large quantities of reasonably clean, single polymer articles such as PET soda bottles or natural HDPE milk bottles. The remaining rigid or flexible plastics in the waste streams are often heavily contaminated, multilayered, heavily pigmented, and difficult to sort into single polymer streams.

This portion of the waste plastic stream, nicknamed the third bale, is best recycled using a thermal process to convert the mix to a liquid product which is suitable as a refinery feedstock. The three major process subgroups used are 1) pyrolysis, 2) gasification, and 3) hydrogenation. Pyrolysis converts the material to a liquid in the absence of oxygen while gasification converts the plastic to a mix of carbon monoxide and hydrogen in a limited oxygen atmosphere. Hydrogenation is a variant in the gasification process whereby hydrogen is added during the polymer cracking phase.

An overview of the advantages and disadvantages of each process is described in this paper.

The recovery of monomers or oil from waste plastic by a depolymerization process is called tertiary recycling. Reprocessing scrap as part of a product production is defined as primary recycling, while melt recycling is considered secondary recycling, and burning with energy recovery is considered quaternary recycling.<sup>1</sup>

0097-6156/95/0609-0161\$12.00/0  
© 1995 American Chemical Society

### Chemical vs Thermal

There are two types of tertiary recycling, chemical and thermal as shown in Figure 1. Depolymerization of the plastic by chemical means is called solvolysis, and the process produces a monomer or oligomers. Condensation polymers such as polyethylene terephthalate (PET), polyurethane (PUR), polycarbonate (PC), and polyamide (nylon) contain specific functional groups which allow reversal of the original polymerization reaction. These depolymerization reactions are known as methanolysis, glycolysis, hydrolysis, aminolysis, acidolysis, etc. and each process requires a single pure polymer stream for good results. These processes are widely used at the manufacturing point of these polymers in order to recycle plant scrap, off-grade material or post-consumer waste.<sup>2</sup>

The decomposition of polymers by heat is called thermolysis. If the process is done in the absence of air, it is called pyrolysis or if done with a controlled amount of oxygen, it is called gasification. Pyrolysis will produce a liquid fraction which is a synthetic crude oil and should be suitable as a refinery feedstock. The non-condensable fraction created during pyrolysis is normally used to provide process heat and any excess is flared. Gasification of plastic takes place at a higher temperature than pyrolysis and with controlled oxygen addition. The result is a syngas that is composed primarily of carbon monoxide and hydrogen. As a mixture, the syngas is valued only as a fuel. But if the gases are separated, the carbon monoxide and the hydrogen are valued as chemical intermediates, which can have 2 to 3 times the fuel value of the mixture.

A third form of thermolysis is hydrogenation, which is a modification of the oldest catalytic process for refining petroleum. Here the plastic is both depolymerized by heat and exposed to an excess of hydrogen at a pressure of over 100 atmospheres. The cracking and hydrogenation are complementary, with the cracking reaction being endothermic and the hydrogenation reaction being exothermic. The surplus of heat normally encountered is handled by using cold hydrogen as a quench for this reaction. Hydrotreating can remove many heteroatoms. The resultant product is usually a liquid fuel like gasoline or diesel fuel.

Thermolysis is a much more versatile and forgiving technology for tertiary recycling than solvolysis. It can handle mixed polymer waste streams along with some level of non-plastic contaminants. Solvolysis will require a relatively pure polymer stream and has little tolerance for contaminants; therefore the raw material preparation costs are larger. Thermolytic processes can be used for mixed polymers streams from municipal solid waste, auto shredder residue, medical waste, and mixtures of rubber and plastic. Some pre-treatment for sizing or certain contaminant removal may be needed, but it will be much less than that required for solvolysis.

### Markets

Each year the United States produces about 60 billion pounds of plastic of which about 75% are addition polymers and 25% are condensation polymers. The distribution of addition polymers produced in the US and appear in the waste stream are as shown on Table I. The breakdown of condensation polymers is

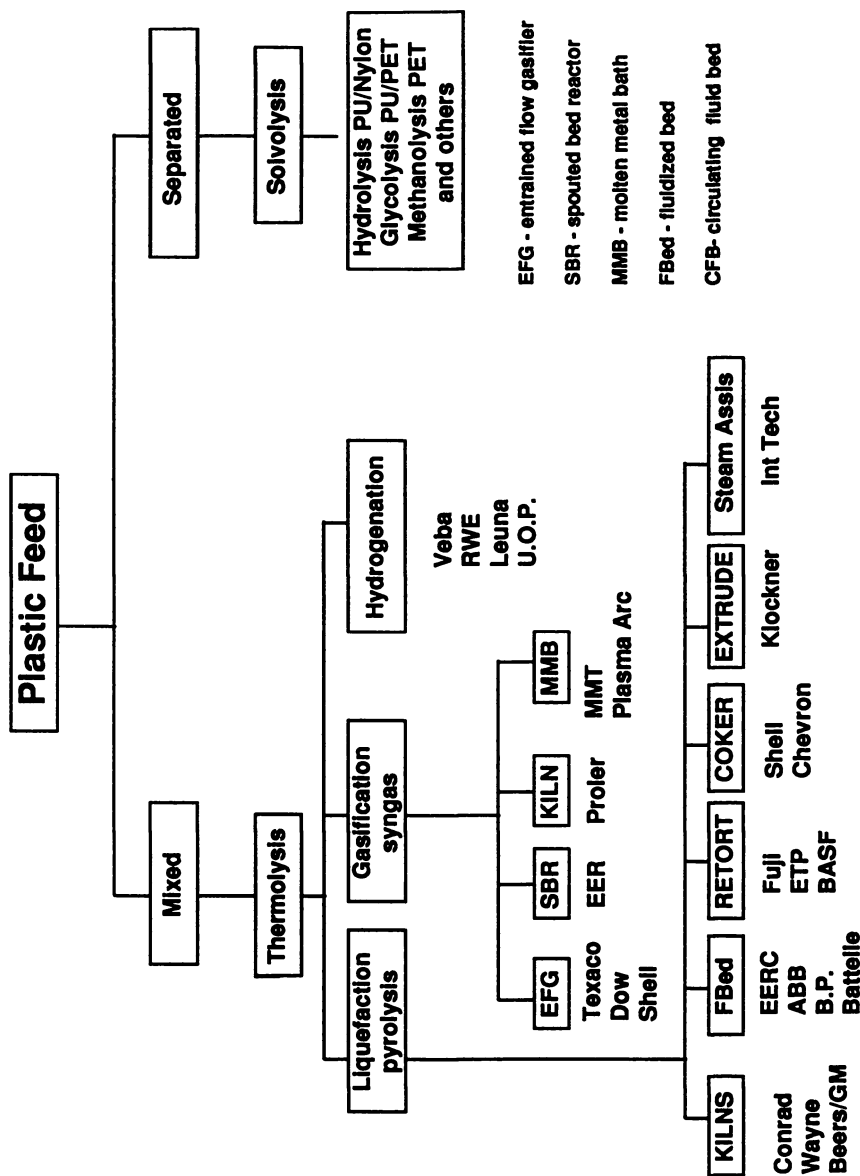


Figure 1. Tertiary Recycling

August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch014

shown on Table II. Only about 9% of condensation polymers (5% polyurethane and 4% polyethylene terephthalate) are suitable for existing solvolysis processes. Therefore, if one wanted to make the largest impact on the solid waste stream with some form of tertiary recycling, it would be with thermolysis. This decision is reinforced by examining the available raw material streams.

Raw Material Streams for Plastic Recycling <sup>3</sup>	
Municipal Solid Waste	20.0 (70% Olefin)
Carpet/Textile	2.5 (75% mixed)
Automotive	2.0 (mixed)
Wire and Cable	0.5 (60% Olefin)

Based on a DOE sponsored study at the Polymer Processing Institute at Stevens Institute of Technology, Hoboken, NJ.

These statistics would support a decision to focus on thermolysis as the process most likely to address the largest part of the problem.

Another reason for focusing on thermolysis becomes apparent when we look at the proposed legislative mandates for recycled plastics. Material recycling seems to have viable markets for certain recycled plastics at recycling rates of 10% to 15%.<sup>4</sup> If the industry is forced to go to higher rates we must deal with a more contaminated material. These contaminated mixed polymer streams become very costly to separate, and there are few markets for the resin produced. Many initiatives propose national recycling rates for plastic packaging of 25% to 40%. The tolerance of thermolysis to polymer mixtures and contaminants makes it a good candidate process to meet the higher percentage rates. However, there is still some argument that converting plastic back to crude oil should not be credited toward meeting the recycling rates. If the crude oil produced is used as a fuel, the argument is that tertiary recycling becomes a form of incineration and should be classed as energy recovery.

### Processes

If we survey the processes most commonly discussed for thermolysis of waste plastic, they would include those shown on Figure 2. For the most part, these processes have been well developed by utilizing other raw materials, and only recently have they been addressing waste plastic. The following is an attempt to make some generalizations about the applicability of these processes to the thermolysis of waste plastic.

### Kilns & Retorts

As a group, they all primarily produce a liquid product whose yield is dependent on the time/temperature process conditions shown on Table III. The noncondensable fraction produced is normally used for process heating and any excess is wasted. Because the product produced is normally intended for a refinery customer, any heteroatoms present can be a problem. Halogens are

**TABLE I**  
**ADDITION POLYMERS FOR**  
**PYROLYTIC PROCESS**

RESIN	% OF U.S. SALES
LDPE	20.0
HDPE	15.1
PVC	15.0
PP	13.4
PS	10.0
ABS	1.8
Acrylics	<u>1.1</u>
	76.4

**TABLE II**  
**CONDENSATION POLYMERS FOR**  
**SOLVOLYSIS PROCESS**

RESIN	% U.S. SALES
PUR	5.0
PET	4.0
Phenolics*	4.0
U/F M/F*	2.5
Epoxies*	<u>&lt;1.0</u>
	15.5

\*Future

### KILNS / RETORTS

USA	Conrad, Wayne, GM
Europe	Veba, BASF
Canada	Vacuum Pyrolysis
Japan	Fuji Tech

### HYDROGENATION

Canada	CanMet
Europe	Veba, RWE

### FLUIDIZED BEDS

USA	EERC, Battelle
Europe	BP

### GASIFIERS

USA	Texaco,
	EER, MMT
Europe	Veba, Shell

### DEGRADATIVE EXTRUSION

Europe	Klockner ER-WE-PA
--------	-------------------

Figure 2. Global Survey Advanced Recycling Technology

particularly a problem due to concerns over corrosion and catalyst poisoning in a refinery.<sup>5</sup>

These kiln and retort type processes normally require a lower capital investment, but they still suffer from poor economics. This is largely due to the fact that the processing costs are nominally 10¢/lb, but the value of product manufactured is that of crude oil or 6¢/lb or 7¢/lb at 1994 oil prices.

### **Fluidized Bed**

Fluidized beds as a class of equipment allow somewhat better temperature control and heteroatom capture in the bed, but they suffer from reliability and durability concerns shown on Table IV. Waste streams are notoriously non-uniform and the possibility of eutectic mixtures of salts forming in the bed and plugging the flow is a large concern. The product produced by a fluidized bed may rank a little higher in value than a liquid product from a kiln but will not more than offset the inherent processing costs.<sup>6</sup>

### **Degradative Extrusion**

This process has been studied largely in Europe but it has never been commercialized; see Table V. The potential of damaging contaminants in the raw material waste stream will require an extra cost pre-processing step. Also the high capital costs for mechanical extrusion seem to put the economics in jeopardy. The best application for this type of process may be in the dehydrohalogenation of PVC as a preprocessing step.<sup>7</sup>

### **Hydrogenation**

The hydrogenation or hydrocracking process was developed in Germany by I.G. Farben Industries around 1927, for converting lignite to gasoline; Table VI. In a refinery, hydrocracking is usually combined with catalytic cracking on an aromatic cycle oil and coker distillate feedstock. These feeds are very heat resistant but under high pressures and in a hydrogen atmosphere they become easy to crack. These feeds are somewhat similar to that which results from liquefying waste plastic. The problem of heteroatom content in waste plastic is handled quite nicely with hydrogenation. The sulfur, chlorine, nitrogen, etc. have hydrogen added to their cracked bonds, and the acids formed are neutralized to an easily disposed salt. Any other solid inerts are an easy disposal problem.

In Europe the companies which have indicated an interest in using their existing hydrogenation facilities to process a certain amount of waste plastic are all German, those being Veba Oel, RWE, and Luena. Each of these companies already has plants in operation but each needed to add a feed preparation step which will liquefy the plastic and eliminate heteroatom problems.

### **Gasifiers**

Gasifiers as a group enjoy the greatest list of advantages as a process group. They are of reasonable capital to build and have high throughput rates; Table VII. They have good heteroatom capture, and they produce a product which has a high value (e.g. Co and H<sub>2</sub>). The solids stream they produce is usually vitrified and can be treated as a nonhazardous waste. The greatest hurdle for gasifiers is

**TABLE III  
ADVANCED RECYCLING METHOD****KILNS / RETORTS**

- Liquid yields depend on feed, temperature, time
- Heteroatom capture is a problem such as for PVC
- Carbon build-up on walls of reactor
- Low capital but lower rate
- Feeding can be a problem (air lock)
- Solids and liquid disposal potential problem
- Processing costs = 10-15 cents/lb
- Value of Product Manufactured equals crude oil prices

**TABLE IV  
ADVANCED RECYCLING METHOD****FLUIDIZED BEDS**

- Liquid yields are excellent
- Good temperature control
- Heteroatom capture with bed material
- Solids removal from bed a problem
- Eutectic mixtures can slag the bed
- Process durability needs proof
- Higher capital but higher rate
- Product may have higher value than kiln production
- Process costs 13-16 cents/lb

**TABLE V  
ADVANCED RECYCLING METHOD****DEGRADATIVE EXTRUSION**

- Studied but never commercialized
- Doubts about reliability
- Partial heteroatom capture
- Rates are low, therefore costs high
- Best as feed for coker



**TABLE VI  
ADVANCED RECYCLING METHOD**

### **HYDROGENATION**

- Liquid phase hydrogenation
- Bergius - Pier technology
- 150 - 250 bar pressures
- Extremely high capital
- High value product
- Good heteroatom handling
- Viable in refinery setting

**TABLE VII  
ADVANCED RECYCLING METHOD**

### **GASIFIERS**

- Liquefaction of feed for Entrained Flow Gasifier (EFG) types
- Excellent heteroatom capture
- Solids waste as vitrified slag
- Gas emissions subject to clean-up
- EFGs have 50 years of process experience
- Molten Metal Technologies and Spouted Bed Reactors are new to scene
- Syngas valued as fuel
- CO and H<sub>2</sub> may have 2.5 times fuel value of 20 cents/therm

the requirement to convert the waste plastic to a liquid feed. This extra processing step adds some cost but can pay some dividends in that it allows for halogen removal and some insoluble extractions.<sup>8</sup>

### **Summary**

As we look at the entire economic picture of advanced recycling, Table VIII, we note that the collection and sortation costs of the recycling process quickly overwhelm the profit potential. If we exclude the acquisition cost, only the gasification route comes close to a break-even situation.

In summary the advanced recycling methods examined to date will not

<b>TABLE VIII</b>	
<b>ECONOMIC OVERVIEW</b>	

Collection of recyclables	\$140 / ton	
Sortation of recyclables	\$200 / ton	
	Pyrolysis	Gasification
Feed prep	\$160 / ton	\$160 / ton
Processing cost	<u>\$220 / ton</u>	<u>\$180 / ton</u>
Total cost	\$720 / ton	\$680 / ton
VPM	\$120 / ton	\$300 / ton
Loss	(\$600 / ton)	(\$380 / ton)

provide the conditions to attract free market capital unless subsidies are provided. When they are provided, the approach could be a viable alternate to waste to energy incineration but it will not compete with low cost landfilling.

1. *Tertiary Plastic Recycling*; A Report Prepared by the Canadian Plastics Institute for the Environment and Plastics Institute of Canada, EPIC, Sept. 1993.
2. Tertiary Plastics Recycling Second Report A Report Prepared by the Canadian Plastics Institute for Environment and Plastics Institute of Canada EPIC, Feb. 1994.
3. "Plastic Recycle Opportunities from Polymer Discard Streams", *Plastic Recycling Research Needs*, A DOE Sponsored Study at the Polymer Processing Institute at Stevens Institute of Technology, Hoboken NJ. A draft copy for peer review 1993.
4. "Feedstock Recycling-Vision or Illusion" A Presentation by Dr. J. Brandrup, Hoechst Aktiengesellschaft, presented at P-3 and European Recycling Technology Exchange Chemical/ Tertiary Recycling, Hilton Head Island, SC, Oct. 12, 1992.
5. "Feedstock Recycling of Old Plastic Packaging by the BASF Process". Presentation by Dr. Herbert Wanjek, BASF AG. at the *Third APME/APC Technology Exchange on Advanced Recycling*, Stevenson, WA, May 23, 1994.
6. "BP Polymer Cracking Project" A presentation by DC. Wilson, BP Chemicals UK at *APME/PWMI-APC Exchange on Energy Recovery and Feedstock Recycling*, Brussels/ Genval July 6, 1993.
7. "Preparation Steps for Feedstock Recycling with Special Emphasis to Degradative Extrusion" by Georg Mengesa presentation at APC/APME technology exchange May 23, 1994 *ibid*.
8. "Texaco Process for the Gasification of Waste Plastics", a presentation by J. Winter, Texaco APC/APME exchange *ibid*.

RECEIVED June 6, 1995

## Chapter 15

# Advances in Plastics Recycling

## Thermal Depolymerization of Thermoplastic Mixtures

Mark W. Meszaros<sup>1</sup>

Amoco Chemical Company, 200 East Randolph Drive,  
Chicago, IL 60601-7125

Technologies which convert plastic wastes back to their starting materials are a promising development in plastics recycling. These starting materials can then be reassembled back into new polymers or used as petrochemical feedstocks. An initial challenge for these new recycling technologies is to develop cost effective and versatile process units which can handle the variety of mixed plastic resins and additives typically found in post-consumer waste streams. The Conrad Unit has successfully met this challenge and demonstrated this technology during extensive parametric studies evaluating various resin streams and operating conditions.

A new approach to recycling post-use plastics is underway in the United States and elsewhere that may offer a means of significantly increasing the overall quantity of plastics that can be recycled.(2-5) Called "advanced recycling technologies," these new approaches may provide advantages that overcome problems associated with some conventional plastic recycling efforts: namely, costly sorting of the different types of plastics; concerns about quality of end products; and finding reliable markets for products made from the recycled material.

Advanced recycling recovers the chemical or feedstock components of plastics. These versatile and marketable end-products are the building blocks from which new plastics and a variety of other products can be manufactured. This is achieved by converting plastics back to raw materials, either directly to monomers or to the petrochemical feedstocks that are used to make monomers and many other petrochemical products. Advanced recycling processes can accept almost all types of plastics and do not require them to be washed or sorted by color or type. Advanced recycling also eliminates some of the grinding, shredding and extruding processes used in conventional plastics recycling. Lastly, the chemical and feedstock products from an advanced recycling process are virtually indistinguishable from products made from virgin materials and will have wide market applicability.

Several advanced recycling processes are under development in Europe, Japan, Canada and the United States and will supplement existing conventional recycling processes.(2-7) Integration of these new recycling options with the existing plastics

<sup>1</sup>Current address: Flinn Scientific, Inc., P.O. Box 219, Batavia, IL 60510

recycling infrastructure will provide a long-term solution for plastics by increasing the amount and types of plastics recycled.

**Conrad Recycling Project.** The Conrad recycling process converts mixtures of plastics into a liquid petrochemical product that is similar to a high quality "sweet" crude oil or a partially refined crude oil fraction such as naphtha or gas oil. The Conrad process, like all advanced recycling processes currently under development, is not economical without tipping fees or subsidies. It is, however, a reliable and robust recycling unit capable of recycling mixed plastic waste streams into easily marketable products at a lower overall cost than conventional recycling processes.

Advanced recycling processes are inherently uneconomic because the principle product, a naphtha-gas oil stream, has a value of only six to eight cents per pound at current crude oil prices of eighteen dollars a barrel. With this revenue stream, it is difficult to cover manufacturing and capital costs unless economies of scale are reached with large, refinery-scale facilities. Unfortunately, the cost for collection, transportation, and logistics to acquire and prepare the feedstock is substantial. Nevertheless, advanced recycling processes may provide the most economical route to handle large volumes of mixed plastics. Germany, which has federal mandates to recycle 60 percent of all plastic packaging, has recently announced projects to recycle over a billion pounds per year of plastics using advanced recycling processes.<sup>(6,7)</sup> The German projects are all large-scale processes integrated with an existing refinery or petrochemical facility. Because of the structure of the petrochemical industry in the United States, smaller process units that convert plastics into easily transportable liquids may be more attractive.

The Conrad process meets this requirement, and the American Plastics Council (APC) is working with Conrad Industries, Inc., (Chehalis, Washington, 206-748-4924) to demonstrate the viability of smaller advanced recycling process for recycling plastics back into liquid petrochemical feedstocks. The project is part of APC's overall program to increase the recycling rate for plastics and to develop or improve recycling technologies. The Conrad process was chosen because of its simplicity, versatility and safety features. More important, its size and low cost allows for a rapid progression from pilot to commercial scale process units.

The objective of the partnership between Conrad and APC is to determine the technical and economic feasibility of recycling plastics back to liquid petrochemical feedstocks. To meet this objective, a series of parametric studies has been conducted to examine how various types of plastics perform under different operating conditions. Studies on various chlorine capture processes are also being conducted. Data acquired from these studies have been used to define process conditions for commercial-scale demonstrations, identify potential design improvements for future units, and develop preliminary process economics.

**Conrad Recycling Process.** The Conrad recycling process is an auger kiln reactor that applies heat to plastics and/or tires in the absence of oxygen to produce liquid petroleum, solid carbonaceous material and noncondensable gases.<sup>(8)</sup> The unit was originally designed to recycle tires, but with minor modifications is well suited for plastics. Developmental studies on plastics and tires are ongoing at the Chehalis facility where two Conrad process units are operational. Parametric studies on plastics have been performed primarily on a 200 lb/hr pilot unit but a 2000 lb/hr commercial scale unit is also available. Both units are fully automated and process data is downloaded to a computer on a continuous basis.

The feed system for the pilot unit is designed for granulated or pelletized plastics, consisting of a simple rotary air lock followed by an auger feeder. Feed systems to handle whole plastic bottles, films, and other plastic components are under investigation and will be incorporated in future Conrad recycling units. The horizontal auger kiln, or retort, is of a proprietary design and is well-suited for the

depolymerization of plastics to volatile products. The gases exit at the top of the discharge end of the retort and pass through a venturi scrubber, bubble cap condenser, and water cooled condenser. Gases that are not condensed are used within the system to generate heat for the process. Solid products, such as carbonaceous or inorganic materials exit at the bottom of the discharge end of the retort to the solids collection drum.

The operating conditions for the auger kiln are adjusted to maximize liquid product yields while still providing enough gas to sustain fuel requirements for the heating of the retort. High temperatures produce high yields of light hydrocarbons ( $C_1 - C_5$ ) but unless a facility is located in close proximity to a market for light gases, the product gases will be difficult to market. At current operating conditions, liquid products represents about 70 to 80% of the final output of this system. The carbon produced is of such a small yield (1-3%) and low quality due to contamination from inorganic impurities that it will have limited markets. The liquid product is shipped to refineries and plastics production facilities for conversion into feedstocks for products such as synthetic fibers, new plastics and other petroleum-based derivatives.

## Results & Discussion

Thermal degradation of plastics to liquid hydrocarbons is a simple concept, similar to many refinery cracking processes. Waste plastics, however, are not crude oil and pose some intriguing challenges, including logistics, economics, and the ability to produce a marketable product. Favorable economics are difficult to achieve because the volume of plastics will never approach the scale of most petrochemical operations since only 3-4% of crude oil is converted into plastics. In addition, preprocessing the plastics, e.g. excessive sorting, washing and size reduction, is expensive. The economics of an advanced recycling process will improve if the process can handle and remove the impurities typically found in post-use plastics such as surface contamination (e.g. food, detergents, water, paper), additives and fillers incorporated in plastics, and nonhydrocarbon elements such as chlorine and nitrogen.

On the positive side, plastics are aliphatic-rich materials that easily convert into a product stream, rich in petrochemical building blocks or a high octane refinery feedstock. BP Chemicals have demonstrated that the liquid resulting from the thermal cracking of mixed plastics is an excellent feedstock for steam crackers or cat crackers.<sup>(9)</sup> In the steam cracker, the plastics generated feed produced higher yields of ethylene (34% vs. 28%), propylene (17% vs. 15%) and butylene (12% vs. 7%) compared to the traditional naphtha feed. In the cat cracker, plastics generated feed gave over 86% yield of a naphtha grade product versus 62% yield from vacuum oil.

The challenge, therefore, is to develop a simple and robust process unit that can accommodate a variable feedstream and produce a consistent product, free of nonhydrocarbon impurities. The Conrad project has demonstrated that an auger kiln reactor can meet this challenge and may offer some economic and operational advantages over other processes because of the lack of feed preparation required, variable residence time in the reactor, and the simplicity and robustness of the unit.

Feed preparation is simplified in the Conrad process because minimal size reduction, washing, and removal of non-plastic contaminants is required. Plastics are introduced into the retort without oxygen through a rotary air lock if the plastics are granulated, or by using a ram feeder (e.g. V-ram, reciprocating, or conical auger) if the plastic products are still in their original form. Inorganic contaminants do not disrupt the process and ultimately exit the unit with any unreacted materials or carbonaceous products. The plastics do not have to be fluidized or molten to enter the process resulting in reduced preprocessing requirements.

The Conrad process allows for a variable residence time in the reactor producing a more uniform product distribution. The plastics initially melt upon entering the hot retort and the auger keeps the molten mass moving. The molten plastics continue to

be heated until carbon-carbon bond cleavage (depolymerization) begins and continue until volatile products are produced. The gaseous products are swept out of the reactor and nonvolatile fragments continue to be heated until becoming volatile. Plastics that are easily depolymerized (e.g. polystyrene or polypropylene) are quickly cracked and removed from the reaction vessel before undergoing further cracking, thus keeping molecular weight as high as possible. Plastics that require more energy to cleave their carbon-carbon backbone (e.g. polyethylene) are either catalyzed by reactive species (radical or carbonium ions), generated by the easily cracked polymers, or remain in the retort until sufficient energy is applied to affect depolymerization.

Parametric studies sponsored by the APC on a fluidized bed unit at the Energy and Environmental Research Center (EERC) at the University of North Dakota showed a synergistic effect from the thermal cracking of plastic mixtures.<sup>(10)</sup> A 50:50 mixture of polypropylene and polyethylene cracked at a lower temperature than polyethylene does alone and produced a more narrow distribution of products than either polypropylene or polyethylene would separately. Polypropylene normally cracks at a lower temperature than polyethylene, and the consensus is that the reactive species from this depolymerization catalyzes the cracking of polyethylene which in turn hinders further cracking of the polypropylene fragments to lighter products by chain termination steps. The result is that both polymers depolymerize at polypropylene cracking temperature and more attractive products are produced.

The Conrad unit has also proven to be both a robust and efficient unit. During the parametric study, the system continuously ran for five day periods. It takes between 8 to 12 hours for the unit to warm-up and line-out, but after start-up minor changes in feed rate, auger rotation, and oven temperatures are easily accomplished. Additional work on a versatile feed system is required but once the plastics entered the reaction vessel, the auger kiln easily handled them.

**Parametric Study.** An eighteen-month parametric study has been underway to assess the Conrad recycling process.<sup>(11)</sup> The objectives of this study were to identify process bottlenecks, develop operating parameters, and begin to assess product value and markets. A base feed mixture of 60:20:20 high-density polyethylene, polypropylene and polystyrene (HDPE:PP:PS) was chosen as representative of the major constituents found in the post-consumer plastic stream and was used during the start-up and initial phases of the study. Off-spec resin pellets were used as feed material throughout the first phases of the study to eliminate feed composition variation. It also simplifies the preparation of mixtures and feeding the unit. The last phase of the program focused on using post-consumer plastics to gain an understanding of the effect that contamination and variable feed stream have on the process.

**Base Feed.** Overall, liquid product yields and composition from the 60:20:20 HDPE:PP:PS base feed exceeded expectations. However, a delicate balance does exist between temperature (Table I), feed rate, residence time and product yields. Lower temperatures produce a high quality naphtha grade stream and high yields of paraffin waxes (which result from incomplete depolymerization of the plastics, especially polyethylene). Reducing the feed rate and slowing the auger rotation results in a reduction of wax formation and increased yields of liquid products. Better insulation and more efficient heating of the discharge end of the retort also reduces the yield of waxes in the solids collection drum. Because of these challenges, reported liquid yields from the early phases of the parametric study are the combined liquid product yields and paraffin wax products yield found in the solids collection drum.

**Table I. Product yields from Base Mixture at Various Reaction Temperatures**

Oven Temperature (°F) <sup>a</sup>	Liquid Yield (wt%) <sup>b</sup>	Gas Yield (wt%)	Solid Yield (wt%)
1450	28	64	8
1300	48	51	1
1200	73	27	-
1100	79	21	-

<sup>a</sup> Retort temperatures are about 200°F cooler than oven.

<sup>b</sup> Combination of liquids and paraffin waxes from solids collection drum.

Part of the difficulty in determining the optimum combination of temperature, feed rate and auger speed is inherent in the design of the pilot unit. The Conrad pilot unit is a single pass retort with a relatively short kiln length (~6 ft. heated zone). Commercial scale Conrad units consist of two larger retorts in series that substantially increases residence time. Nevertheless, valuable engineering and design data has been collected from the pilot unit that will undoubtedly improve the efficiency of the Conrad recycling process.

Gas chromatographic analyses of the liquid and gas products from the first phase of the parametric study are shown in Table II. The liquid products from the first phases of the parametric study were combined and 6,000 gallons of product oil were shipped to the Lyondell-Citco Refinery in Houston Texas, and used as a feed in its coker unit. The coker unit was chosen because it minimizes risks to the refinery and the light end gases from the coker go directly to several monomer production facilities, including Mobil's steam cracker. Analysis of the oil shipped to Lyondell is shown in Tables III and IV.

**Table II. GC Analysis of Products from Depolymerization of Base Mixture<sup>a</sup>**

Oven Temp. (°F)	1300	1200	1100
Auger Temp (°F) <sup>b</sup>	1095	980	895
<b>Partial Oil Analysis (wt%)</b>			
Benzene	7.0	2.3	1.1
Toluene	20.0	11.0	9.1
Ethylbenzene	9.0	5.7	4.8
Styrene	20.0	17.0	14.7
C <sub>10</sub>	10.0	9.4	6.8
C <sub>11-C<sub>15</sub></sub>	14.5	16.6	13.1
C <sub>16-C<sub>20</sub></sub>	8.6	9.9	14.5
C <sub>21-C<sub>25</sub></sub>	3.0	3.5	6.4
C <sub>26-C<sub>30</sub></sub>	1.7	1.7	4.5
C <sub>31-C<sub>40</sub></sub>	1.1	1.5	4.2
<b>Partial Gas Analysis (vol.%)</b>			
H <sub>2</sub>	4.0	2.6	2.2
Methane	18.0	13.6	10.5
Ethylene	19.4	18.1	13.8
Propylene	21.4	21.8	21.0
Isobutylene	5.0	6.1	6.8

<sup>a</sup> Paraffin waxes found in the liquid product tanks are included in this analysis.

Waxes from the solids handling drum are not part of this analysis.

<sup>b</sup> Auger temperature was measured via thermocouple inserted inside the auger shaft at the midpoint of the retort.

**Table III. Simulated and Actual Distillation of Conrad Product Oil**

Weight %	Simulated Distillation Temperature (°F)	Actual Distillation Temperature (°F)
10	191	146
20	244	188
30	288	294
40	304	334
50	339	395
60	403	472
70	474	564
80	563	654
87.5 <sup>a</sup>	636	669
90	684	—
99	899	—

<sup>a</sup> The oil began to crack at 669°F and the distillation was suspended.

**Table IV. Analysis of Product Oil Shipped to Lyondell-Citco**

Specific Gravity	0.8860
RVP, psi	4.1
Pour Point, °F	20
Viscosity @ 75 °F, cst	3.5
Viscosity @ 122 °F, cst	1.5

**LDPE, PS, and PET-rich feeds.** To increase the understanding of process capabilities and product yields, studies were performed using the base feed spiked with either LDPE, PET, or additional PS. Again, only off-spec resin pellets were used to simplify the studies and reduce the variables.

An LDPE-rich feed mixture containing 20:48:16:16 LDPE:HDPE:PP:PS behaved similarly to the base mixture and resulted in similar product yields and composition (Table V). Slightly higher yields of C<sub>12</sub>-C<sub>15</sub> aliphatics were observed and higher molecular weight aliphatics decreased. No operating difficulties were observed.

A PS-rich feed mixture containing 48:16:36 HDPE:PP:PS also behaved similarly to the base mixture and resulted in similar product yields and composition. In the liquid product, styrene yields almost doubled and slightly lower yields of higher molecular weight (>C<sub>12</sub>) aliphatics were observed, as would be expected. Ethylbenzene yields did not significantly increase with the increased polystyrene level suggesting that ethylbenzene may not result exclusively from polystyrene depolymerization but rather from the cyclization and dehydrogenation of various aliphatic compounds at elevated temperatures.

A PET-rich feed mixture containing 20:48:16:16 PET:HDPE:PP:PS did not behave like the base mixture. It was difficult to run the mixture at the lower temperatures (1100-1200°F), due to extensive production of solids. Upon analysis, the solids were identified as >95% terephthalic acid. The remaining 5% of the solids were found to be mono and bis-hydroxyethyl esters. The solids were easily filtered, but due to the design of the pilot unit a substantial portion of the solids remained in the cooling tower, product tanks, and piping. Terephthalic acid yields were estimated at around 15 mol% at 1200°F. At higher temperatures, the PET and/or terephthalate moieties decarboxylated to produce CO<sub>2</sub> and aromatic products. There must be enough water encapsulated in the PET and other resins to supply the water for hydrolysis and at the lower temperatures, the terephthalic acid sublimates out of the retort before it undergoes decarboxylation.



**Table V. GC Analysis of Products From Depolymerization of Base Mixture and LDPE, PS, PET<sup>a</sup>**

Feed	Base + LDPE			Base + PS			Base + PET		
Temp. (°F)									
Oven	1300	1200	1100	1300	1200	1100	1450	1300	1200
Auger <sup>b</sup>	1100	1010	925	1100	1000	910	1180	980	870
<b>Yields (wt%)</b>									
Liquids	41	45	50	36	45	50	32	55	59
Solids <sup>c</sup>	3	8	32	3	8	28	1	7	21
Gas	56	47	18	60	47	22	67	38	20
<b>Aliphatics</b>	30.5	43.1	50.8	23.5	30.9	46.5	16.7	46.3	8.5
<C25 Saturated	6.2	7.7	10.8	5.5	5.5	7.5	3.8	6.8	10.9
<C25 Unsaturated									
1 Unsaturation	13.9	23.9	27.5	9.7	16.8	25.8	5.9	25.7	32.9
2 Unsaturation	6.8	7.7	6.1	6.1	4.7	7.1	4.5	8.1	8.7
C25+ Aliphatics	1.7	1.7	5.4	0.8	2.7	4.9	1.7	3.4	5.0
<b>Aliphatics by Carbon #</b>									
<C10	20.1	27.5	21.2	14.4	16.6	23.2	5.0	28.2	21.3
C11-C15	4.6	8.5	12.6	4.1	7.7	9.4	3.0	9.2	17.6
C16-C20	2.8	3.8	7.2	3.1	2.3	5.9	5.0	2.9	9.9
C21-C25	1.4	1.6	4.1	1.1	1.5	2.9	2.0	2.5	4.7
C26-C30	0.6	0.7	1.8	0.4	0.9	1.9	0.7	1.7	2.2
C31-C35	0.4	0.4	1.2	0.2	0.7	1.2	0.4	0.7	1.2
C36-C40	0.2	0.2	0.8	0.0	0.5	0.7	0.2	0.3	0.6
C40+	0.2	0.2	0.8	0.0	0.4	0.8	0.1	0.2	0.4
<b>Aromatics</b>	63.5	49.3	39.8	71.5	62.4	42.4	76.1	40.4	29.2
Benzene	7.0	3.2	1.0	6.3	1.9	1.4	19.6	3.0	1.4
Toluene	15.7	10.8	8.0	16.2	10.5	7.3	16.5	7.2	3.8
Ethylbenzene	7.6	5.5	4.6	8.6	7.9	5.5	3.14	3.7	2.6
Xylenes	2.1	1.3	0.5	2.2	1.1	0.7	2.0	1.4	1.1
Styrene	16.7	16.6	14.6	20.6	27.1	17.0	12.0	8.9	8.2
C3-Benzenes	6.8	5.4	4.9	7.4	7.4	4.7	5.7	3.8	3.9
C4+Benzenes	2.8	3.4	4.2	3.0	3.7	3.9	4.1	5.8	4.5
Naphthalenes	4.7	3.2	2.0	7.0	2.8	2.1	13.1	6.8	3.7
Unidentified Compounds	6.8	7.5	9.4	5.0	6.7	11.1	7.3	13.3	12.3

<sup>a</sup> GC analysis are of samples taken directly from the retort effluent prior to the condenser. Temperatures and yields are then averaged over a 4-8 hour period.

<sup>b</sup> Auger temperature was measured via thermocouple inserted inside the auger shaft at the midpoint of the retort.

<sup>c</sup> Solids yield are a combination of carbonaceous and paraffin wax products found in the solids collection drum. Most of the solids were xylene soluble and should be considered part of the "liquid yield".

The PET-rich feed mixture also cooled the retort more than other feeds. Typically, the oven temperature is set at between 1200 and 1300°F and the temperature inside the auger is measured at the midpoint of the retort and at the feed entrance. At an oven temperature of 1300°F the auger mid-point temperature is around 1100°F and the auger feed entrance temperature around 930-940°F for base, PS-rich base, or LDPE-rich base mixtures. The PET-rich base mixture had an auger mid-point temperature of 986°F and an auger feed-entrance temperature of 675°F. At an oven temperature of 1200°F, auger mid-point and auger feed-entrance temperatures of 880°F and 500°F were observed for the PET-rich mixture compared to typical temperatures of 1000-1020°F and 800-825°F for other base mixtures. More endothermic reactions must be taking place in the first part of the retort when PET is present than with polyolefins. Melting the PET, hydrolysis of the PET, and subliming the terephthalic acid may explain this observation.

**Polypropylene Feed.** Polypropylene (100%) was depolymerized at a retort temperature of 950°F to give high yields of aliphatic (48%) and aromatic (40%) products (see Table VI, PP). Single unsaturated, low molecular weight (<C<sub>15</sub>) aliphatics were a major component of the products but ethylbenzene (19.1%) was the

**Table VI. GC Analysis of Various Depolymerization Runs**

	PP <sup>a</sup>	PS <sup>b</sup>	PVC <sup>c</sup>	PVC/PET <sup>d</sup>	PCR-1 <sup>e</sup>	PCR-2 <sup>f</sup>
<b>Aliphatics</b>	47.9	7.7	41.3	42.3	44.4	22.7
<C <sub>25</sub> Saturated	4.3	2.5	6.7	6.7	9.6	6.0
<C <sub>25</sub> Unsaturated						
1 Unsaturation	25.0	2.9	23.5	23.1	23.3	10.5
2 Unsaturation	10.3	1.8	5.3	6.7	5.9	4.2
C <sub>25+</sub> Aliphatics	6.9	0.5	4.7	4.4	4.0	1.2
<b>Aliphatics by Carbon #</b>						
<C <sub>10</sub>	22.1	0.7	18.2	19.8	19.4	12.0
C <sub>11</sub> -C <sub>15</sub>	10.1	1.4	10.9	9.2	13.7	5.2
C <sub>16</sub> -C <sub>20</sub>	4.8	3.8	5.1	6.1	4.9	2.9
C <sub>21</sub> -C <sub>25</sub>	3.5	1.4	2.3	2.8	2.2	1.4
C <sub>26</sub> -C <sub>30</sub>	2.4	0.3	1.6	1.8	1.3	0.4
C <sub>31</sub> -C <sub>35</sub>	1.5	0.1	1.0	1.0	0.8	0.2
C <sub>36</sub> -C <sub>40</sub>	1.3	0.0	0.8	0.6	0.7	2.0
C <sub>40+</sub>	1.4	0.0	0.9	0.3	0.7	0.2
<b>Aromatics</b>	40.4	91.0	49.2	54.9	49.9	73.1
<b>Benzene Derivatives</b>						
Benzene	2.0	0.7	2.0	4.9	2.9	7.6
Toluene	1.3	10.0	7.9	8.4	7.1	22.0
C <sub>2</sub> -Benz.	22.5	67.6	28.1	26.9	25.0	27.4
C <sub>3</sub> -Benz.	2.8	7.7	5.4	5.9	6.4	6.9
C <sub>4</sub> -Benz.	6.6	0.9	1.4	3.9	4.3	3.9
Naphthalenes	2.4	0.5	1.5	2.7	2.1	3.2
Phenathacenes	2.7	3.6	1.4	1.8	2.1	2.1
<b>Unidentified Compounds</b>	11.8	1.3	9.5	2.8	5.8	4.2

<sup>a</sup> 100% polypropylene

<sup>b</sup> 100% polystyrene

<sup>c</sup> 3% PVC in a 60:20:20 HDPE:PP:PS base mixture

<sup>d</sup> 1% PVC, 5% PET in a 60:20:20 HDPE:PP:PS base mixture

<sup>e</sup> Post-consumer plastic containers; retort temp was 977°F

<sup>f</sup> Post-consumer plastic containers; retort temp was 1058°F

Table VII. GC Analysis of Gas Products<sup>a</sup>

	PP	PS	PVC	PVC/PET	PCR-1	PCR-2
Hydrogen	5.3	10.5	5.2	5.3	7.1	8.3
Carbon Monoxide	1.1	39.5	1.1	0.7	2.0	2.8
Carbon Dioxide	0.2	16.1	0.0	0.0	0.3	0.7
Methane	11.9	9.4	11.9	14.9	13.0	16.1
Ethylene	14.7	9.6	15.4	17.6	15.1	15.7
Ethane	9.3	1.2	4.0	8.7	8.8	8.5
Propylene	19.9	2.9	21.7	20.6	19.0	17.9
Propane	3.2	0.0	4.9	2.5	2.9	2.2
C <sub>4</sub>	21.4	2.9	24.2	20.3	20.5	16.8
C <sub>5</sub>	4.1	0.9	4.8	1.7	2.1	1.5
C <sub>5</sub> +	8.7	7.0	6.9	7.8	9.3	9.5

<sup>a</sup> Volume %, normalized after subtracting N<sub>2</sub> and O<sub>2</sub>. Samples are same as Table VI.

major individual product. High levels of propylene (23%), isobutylene (21.4%) and C<sub>5</sub> gases (13%) were found in the gas products. Ethylbenzene yield was determined by GC analysis and the possibility that another compound other than ethylbenzene also elutes at the exact time as ethylbenzene cannot be ruled out at this time, but is unlikely. GCMS analysis of products from previous base mixture runs using similar conditions as the routine GC analyses clearly identifies a C<sub>9</sub>H<sub>18</sub> isomer, ethylbenzene and *m*- and *p*-xylene all eluting in close proximity. All three of these peaks are clearly seen in the GC's from the PP run. In addition, a spiking experiment with ethylbenzene and *m*- and *p*-xylene confirmed that ethylbenzene and not a xylene elutes at the same position as the peak identified as ethylbenzene. A second, slower GC temperature program also gave similar results. The mechanism for converting branched aliphatics to ethylbenzene is unclear but ethylbenzene is a major product in almost all cracking runs with polyolefins.

**Polystyrene feed.** Post-consumer and post-industrial polystyrene have been used as a feed and produced very high liquid yields that are rich in styrene. Over two days 8,173 pounds of post-industrial polystyrene were fed to the Conrad pilot unit resulting in 7,495 pounds of liquid product for a 91.7% overall liquid yield. Only 70 pounds of solids were collected and the noncondensable gases yield was estimated to be 280 pounds. GC analysis of the liquid and gas products from this run are shown in Tables VI and VII as PS.

The auger temperature throughout the PS run was between 900 and 1025°F depending on the feed rate and oven temperature and led to slight variation in the yields of individual components (see Table VIII). Styrene, consistently the major product, accounted for about 60% of the liquids for a total yield from incoming polystyrene of 55%. Toluene, propylbenzene, and styrene dimer yields are all temperature dependent. At higher temperatures (>1000°F), toluene yield increased and propylbenzene and the styrene dimer yields decreased; the opposite occurred at lower temperatures. Benzene yields were consistently low suggesting that conditions were not severe enough to cause significant cleavage of the benzylic carbon-carbon bond.

Post-consumer food service polystyrene was evaluated and gave slightly lower liquid yields, but similar styrene yields, presumably due to the higher levels of contamination. The product mixture is being evaluated to determine its value as a feed for styrene production.

**Table VIII. GC Analysis of Products from Polystyrene Depolymerization<sup>a</sup>**

Feedrate (lb/hr)	150	150	150	150	150	150	195	195	250	250
Temp. (°F)										
Auger <sup>b</sup>	995	1025	995	1022	1002	999	915	898	837	981
Feed <sup>c</sup>	824	840	806	806	802	794	750	738	710	812
<b>Partial Oil Analysis (wt%)</b>										
Benzene	0.4	0.8	0.5	0.6	0.4	0.7	0.3	0.3	0.2	0.6
Toluene	9.1	12.4	10.0	11.5	9.8	10.0	6.6	5.7	5.7	8.9
Ethylbenzene	7.2	9.0	6.7	7.3	6.7	6.7	5.7	6.2	7.2	5.7
Styrene	62.3	59.3	59.3	60.5	61.1	60.9	62.1	59.1	56.9	64.9
C <sub>3</sub> -Benzene	6.2	5.5	5.5	5.7	6.3	6.6	7.3	8.0	10.4	5.8
Styrene dimer	5.0	2.9	4.6	4.0	4.9	4.9	8.4	10.4	10.5	5.4

<sup>a</sup> Samples collected for GC analyses every four hours.

<sup>b</sup> Auger temperature was measured via thermocouple inserted inside the auger shaft at the midpoint of the retort.

<sup>c</sup> Auger feed temperature was measured via thermocouple inserted inside the auger shaft at the point where the feed drops into the retort.

**Chlorine Capture Studies.** The second phase of the parametric study focused on halogen capture. Any post-consumer plastic stream will contain some halogens in the form of polyvinylchloride, polyvinylidenechloride, brominated flame retardants, halogenated additives, food waste, or salt. Therefore, two issues must be addressed. First, the gas stream resulting from the depolymerization of plastics must be scrubbed to remove any halogenated gases (HCl, HBr, Cl<sub>2</sub>, Br<sub>2</sub>, etc.) to satisfy emission controls. Second, halogens in the liquid product must be minimized to increase its value and marketability.

Parallel APC studies at the Energy and Environmental Research Center (EERC)(9) and Energy and Environmental Research Corporation (EER, Irvine, CA; personal communication with G. Kryder, EER and G. Mackey, Dow Chemical, 1994) showed that feeds containing as little as 3% PVC produced up to 10,000 ppm of chlorine in the liquid products. Most of the organochloride formation is thought to occur during the condensation step, not during depolymerization. Also, the aliphatic carbon-chlorine bond is fairly weak and is probably facile at reaction temperatures. Therefore, if the chlorine can be captured prior to condensation, the organochloride level in the liquid product should be minimized.

The first chlorine capture process studied attempted to capture the chlorine from the hot effluent gas prior to the condensers. Hot calcium oxide fixed beds placed between the retort and the condensers were evaluated. Initial tests on a bench scale auger kiln showed that a plastics mixture containing 3% PVC produced liquid products with <25 ppm chlorine. However, difficulties arise when PET is present because the terephthalic acid and CO<sub>2</sub> produced during PET depolymerization react with the calcium oxide and lead to premature plugging of the calcium oxide beds.

A second approach attempted to capture the chlorine while it was still in the retort. Calcium oxide or hydroxide (hydrated lime) was added directly into the retort along with the plastic feed. This approach was effective even when PET was present in the feed. Several months of the parametric study were devoted to optimizing this approach and the results are shown in Table IX. Total chloride concentrations in the retort effluent, heavy oil product and light oil product were measured by Dohrmann microcoulometer.

Mostly through trial and error, a calcium hydroxide loading of 10 wt% was found to give good results over a wide range of feed compositions. If only PVC is present, a lower loading is effective but PET can consume large quantities of calcium

hydroxide. Total chlorine levels of the liquid products were consistently less than 50 ppm and frequently less than 20 ppm.

The samples that contained higher levels of chlorine were also washed with water to remove any calcium chloride blowover and soluble HCl and reanalyzed. Chlorine levels were reduced as shown in Table IX, run 1b. In a commercial unit, a centrifuge or cyclone may be installed in front of the condensers to reduce blowover. Identification of the organochloride compounds in the product oil is not possible due to their low level. Distribution of chlorine in the product oil was analyzed as shown in Table X. Most organochlorides are in the 180-350°F boiling range.

**Table IX. Summary of Chlorine Capture Runs**

Run #	PVC (%)	PET <sup>a</sup> (%)	Feedrate lb/hr		Temp (°F)	Cl (ppm)
			Feed	Ca(OH) <sub>2</sub>		
25	3.0	0.0	80	-0-	1215	2500-3500
34	0.5	0.0	134	10	925	4-19
35	1.0	5.0	120	12	950	4-12
36	1.0	10.0	120	12	975	6-13
41a	3.0	0.0	120	9	900	90-140 <sup>b</sup>
41b	3.0	0.0	20	9	900	120 <sup>c</sup>
41b'	3.0	0.0	120	9	900	80 <sup>d</sup>
41c	3.0	0.0	120	12	900	60-70

<sup>a</sup> Percent PVC/PET in base mixture.

<sup>b</sup> Average from run.

<sup>c</sup> Individual sample from run, analyzed unwashed.

<sup>d</sup> Same sample as 41b, but washed to remove inorganic chlorides

**Table X. Distribution of Organochlorides in Product from 3% PVC in Base Feed distribution**

Fraction (°F)	ppm Cl	Wt% of Oil	Cl
100-180	1328	6.95	17.1
180-350	1041	38.90	75.1
350-650	98	24.85	4.5
650+	64	27.85	3.3

The effect of lime stoppage on the generation of organochlorides was studied and found not to be as severe as expected. To evaluate the effect, a 3% PVC in base mixture (60:20:20 HDPE:PP:PS) and 6 molar excess of hydrated lime were added to the retort at an auger temperature of 980°F. Samples of the retort effluent were collected directly from the retort prior to the condenser section of the pilot unit. The total chlorine level in the retort effluent was around 200 ppm before lime stoppage. The initial chlorine level was higher due to low calcium loadings and the retort effluent samples were not washed prior to analysis so some inorganic chloride blowover was probably occurring. Ten minutes after the lime stopped being added to the retort, the total chlorine level was still at the 200 ppm level, and at 20 and 35 minutes the chlorine level was still only 500 and 650 ppm, respectively. After 40 minutes, the chlorine level started to rise significantly and was over 1500 ppm. Apparently, the lime is actively capturing chlorides throughout its journey through the retort and not just in the first few feet of the retort.

**Post-consumer plastics.** Several post-consumer plastic streams have been evaluated as feedstock for the Conrad process. The first stream used as a feed was from a

curbside collection program. The plastics were analyzed and found to be 8-10% PET, 0.5-2.0% PVC, 75-80% HDPE, 8-10% PS, and 5-7% PP. Plastics were fed into the system at a rate of 100 pounds per hour and hydrated lime added at a rate of 10 pounds per hour. Oven temperature was set at 1250°F and the auger temperature was between 1050-1100°F. Overall liquid yields were about 40% but the organochlorides in the product oil were consistently below 25 ppm.

Two GC analyses from the post-use plastics are shown in Tables VI and VII (see PCR-1 and PCR-2). The auger temperature for PCR-1 was 977°F and the liquid products were evenly split between aliphatic and aromatic compounds. At an auger temperature of 1058°F, the component mix dramatically changes to aromatic compounds with toluene and benzene more dominant products.

**Economics.** The economics for the Conrad recycling unit are still unclear. Economic driving forces such as labor rates, scale of economy, transportation costs and feedstock costs all dramatically impact the overall economics. Small scale (<20 million lbs/yr), stand alone units may require tipping fees around 5 cents/pound to break even. Integrating a Conrad recycling unit with a conventional recycling facility, however, may allow existing recyclers to lower overall costs while increasing revenues. Existing recyclers may be able to accept a lower quality bale of plastics, extract those resins that have good market value via conventional mechanical recycling and recycle the remainder through a Conrad unit. Feedstock, landfilling, and transportation costs may be reduced and revenues increased from the sale of products from the Conrad process.

### Experimental Section

Samples of oil that were representative of the immediate process conditions were obtained by removal of the hot pyrolyzate vapor from the exit of the retort. Samples were drawn by means of a Manostat Varistaltic Jr. peristaltic pump operating at 1000 mL min<sup>-1</sup>. The pyrolyzate was condensed at 5°C and collected in a removable 2-L distillation flask.

Total halides in the oil were quantified using a Dohrmann DX-20 B microcoulometer. Several (3-5) determinations were made for each sample using a furnace temperature of 950°C and an analysis time of 5 min.

Routine gas chromatography analyses of the oil were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 15 m x 0.53 mm i.d. HP-1 capillary column (0.88 μm film thickness) and a flame ionization detector. The temperature program consisted of a 10°C min<sup>-1</sup> ramp from 35°C to 350°C with a 10-min hold at 350°C. Samples were prepared by dilution into CS<sub>2</sub> and introduced with a Hewlett-Packard 7673 automatic sampler. Chromatograms were recorded on a Hewlett-Packard 3396 Series II integrator, which quantified the chromatographic peaks by integrated area percent. Identification of the chromatographic peaks was accomplished by duplicate GC/MS analysis using a Varian 3700 gas chromatograph with a 60 m x 0.25 mm i.d. DB-1 capillary column (0.25 μm film thickness) interfaced to a VG 70E-HF dual sector (EB geometry) mass spectrometer operating in EI mode at a source temperature of 200°C. The GC temperature program was identical to that described above.

Gas samples were collected at the exit from the heating cyclone and at 1-3 psi above ambient pressure in a continuously flushed, 2.5-L stainless steel bomb. Routine GC analyses of the gas product were performed on a second Hewlett-Packard 5890 Series II gas chromatograph, that was specially configured for simultaneous, automated analyses of fixed gases and light hydrocarbons. Chromatograms were recorded on a Hewlett-Packard 3396 Series II integrator, that quantified the chromatographic peaks by comparison with peak areas for a standard calibration gas mixture, and converted the responses to gas volume percents. The GC was equipped

with 0.25 mL sample loops, two thermal conductivity detectors and four valves interfaced with the following five 1/8 in stainless steel packed columns: (1) 2 ft 20% Sebaconitrile on 80/100 Chromosorb PAW, (2) 30 ft 20% Sebaconitrile on 80/100 Chromosorb PAW, (3) 6 ft Porapak Q 80/100, (4) 10 ft Molecular Sieve 13X 45/60, (5) 4 ft Molecular Sieve 13X 45/60.

Liquid yields are determined by measuring the weight of liquid product pumped from the pilot unit to the storage tanks over a period of time versus feed consumption. Gas yields are calculated /determined from gas meters, corrected for N<sub>2</sub> the specific gravity of the gases as determined from the GC.

## Conclusion

The Conrad advanced recycling project has led to a better understanding of the viability of advanced recycling and, in particular, the Conrad process. High quality liquid products are produced during the process, but technical and economic hurdles still remain. Additional studies on the Conrad bench, pilot, and commercial scale units will further advance industry's knowledge of the process and its potential usefulness. Both advanced and conventional plastics recycling are viewed by the plastics industry as important elements of an integrated solid waste management system that will introduce new products to commerce, conserve resources, and reduce landfill bound wastes.

## Acknowledgments

This project was supported by the American Plastics Council and directed by the Advanced Recycling Technical Committee. D. Warner, D. Leong and G. Sarver from Mobil Chemical Company were instrumental in managing the parametric study and providing valuable engineering expertise. J. Randall (Exxon), T. Balsano (Amoco), G. Mackey and C. Smith (Dow), and J. Sosa (Fina) were also part of the Conrad technical team and contributed to the success of the program. K. Strode was the on-site analytical chemist and efficiently managed all data collection and analytical results. D. G. Demianiw was the on-site process engineer and his insight and expertise were invaluable. Lastly, the engineers at Kleenair Products and the staff and operators at Conrad Industries were responsible for the design and operation of the pilot unit and their efforts are greatly appreciated.

## References:

1. Liedner, J., "Plastics Waste, Recovery of Economic Value", Marcel Dekker, Inc., New York,
2. Menges, G.; Fischer, R.; Lackner, V. *Intern. Polymer Processing VII* **1992**, *4*, 291.
3. Leaversuch, R.D. *Modern Plastics* **1991**, *July*, 40.
4. Ehrig, R.J. "Development and Commercialization of Tertiary Plastics Recycling", Decision Resources Inc., Burlington, Massachusetts, July, 1992, Spectrum report 26-1.
5. Randall, J. C.; Meszaros, M. W.; Adams, A. A.; Lohr, J. E. *Modern Plastics Encyclopedia* **1992**, *mid-December*, 54.
6. Mapleston, P. *Modern Plastics* **1993**, *November*, 58
7. *European Chemical News*, **1994**, *April 25*, 37.
8. Oeck, R.C. U.S. Patent. 4,412,889, 1982
9. *European Chemical News*, **1993**, *Feb 15*, 27.
10. "Thermal Recycling of Plastics, Final Report to the American Plastics Council," Energy & Environmental Research Center, Grand Forks, ND, March, 1994.
11. Powell, J. *Resource Recycling* **1993**, *May*, 52.

RECEIVED March 24, 1995

## Chapter 16

# Spouted Bed Reactor for the Advanced Thermal Recycling of Mixed Plastic Waste

S. J. Pearson, G. D. Kryder, R. R. Koppang, and W. R. Seeker

Energy and Environmental Research Corporation, 18 Mason,  
Irvine, CA 92718

This paper summarizes the pilot-scale (24 tons/day) development and testing of a novel waste gasification system designed for advanced (thermochemical) recycling of wastes that contain mixed plastic polymers. Energy and Environmental Research Corporation (EER), with coordinated funding from the US-EPA, the Gas Research Institute, and the Southern California Gas Company has developed a pilot scale technology based upon the "spouted bed" fluidization regime. The EER Spouted Bed Reactor is a novel method for ablative gasification, in which heterogeneous solids are gasified and aggressively comminuted into fine particulate. The objective of the subject technology development is the thermochemical conversion of high heat content wastes into environmentally safe recoverable products. The design of the pilot scale facility will be described and the results of preliminary testing on automobile shredder residue will be discussed in this paper.

Annual municipal and industrial waste generation in the U.S. is approximately 237 million tons of which nearly 80% is currently disposed in landfills. Plastics account for 4% to 11% by weight of the entire municipal waste stream.(1) Automobile shredder residue (ASR) is the one of the largest waste streams in the US, and it contains  $\approx$  30% synthetic polymers. A recent market assessment completed by EER suggests that the quantity of ASR available in the US may be adequate to support over 100, 100 tons/day spouted bed reactors for the production of syn-gas.(2) Like other mixed wastes, ASR is sometimes contaminated with toxic organics and heavy metals which may put additional restrictions and requirements on landfill disposal of this waste.

An alternative to landfill disposal for municipal and industrial waste has been first generation thermal destruction technologies which rely upon incineration (oxidation) to destroy the organic compounds in the waste. Many municipal and industrial wastes are contaminated with halogens, such as chlorinated species, and toxic heavy metals, such as lead and cadmium. Incineration of chlorine containing wastes can result in the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF).(3, 4) Thus, environmental pollution and public health are major concerns associated with waste incineration technologies, particularly where high energy wastes are concerned. The relatively large gas volumes and high acid gas emissions (i.e., HCl & NO<sub>x</sub>) resulting from combustion with air make incineration costly in terms of back end clean-

0097-6156/95/0609-0183\$12.00/0  
© 1995 American Chemical Society



up. Using incineration methods allows only the recovery of heat, which is a low value resource. It is much more desirable to reclaim the chemical value in the waste in some high value form other than heat energy.

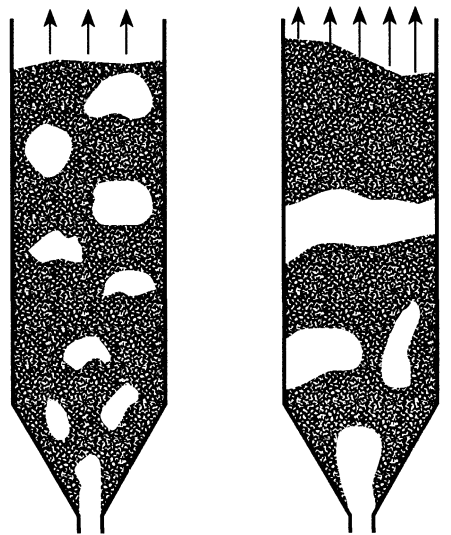
Thus, a pyrolysis or gasification process capable of processing a wide range of wastes and recovering the energy content as high value added non-contaminated products (off-setting costs or generating net revenue) would be of significant national importance. World wide, numerous pyrolysis and gasification strategies have been researched and developed during the past five decades. Commercial success has been limited to gasification of traditional feedstocks, primarily coal, and not applied to wastes because of processing difficulties. However, escalating disposal costs and more stringent air and water regulations require new approaches to the problem.

The primary objective of the subject Spouted Bed Reactor (SBR) technology for advanced thermal recycling is substantial recovery of product value at costs significantly below incineration and with regulatory compliance of all ash and effluent streams. "Advanced Recycling" is the term coined by the American Plastics Council to describe thermochemical recovery methods, though specifically excluding incineration processes. Advanced Recycling concepts are favored by the general public and are well received by the regulatory and permitting agencies.

### Technology Overview

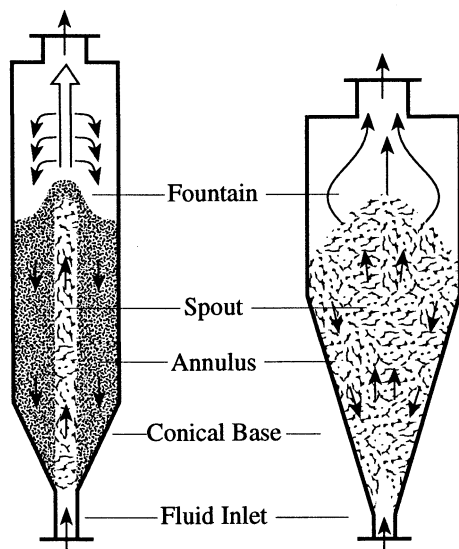
Energy and Environmental Research Corporation (EER), with coordinated funding from the US-EPA, the Gas Research Institute, and the Southern California Gas Company has developed a pilot scale Advanced (thermochemical) Recycling technology based upon the "spouted bed" fluidization regime. The EER Spouted Bed Reactor is a novel method for ablative gasification, in which heterogeneous solids are aggressively comminuted into fine particulate within the bed via high shear velocities in the jet and abrasion. The solids circulation properties of a traditional bubbling fluidized bed, a conventional spouted bed, and a jet-spouted bed are shown in Figure 1. Typical fixed, slugging, and bubbling beds have unidirectional, nearly flat gas velocity profile flows through the bed. Spouted beds have core zones with extremely high shear forces and reverse bed flow on the periphery (i.e., internal bed recirculation). These features facilitate the processing of difficult wastes.<sup>(5)</sup> The unique attributes of the "spouting regimes" provides heat transfer rates comparable to traditional fluid beds, while providing robust circulation of highly heterogeneous solids, concurrent with very aggressive comminution (size reduction through abrasion.) Synergistic benefits are obtained by using a multi-stage approach. The SBR primary spouted bed is used as the solids processing zone, resulting in the conversion of heterogeneous solids and sludges into a gaseous stream laden with fine particulate. The free board column provides residence time for solid separation and further thermochemical processing. The hot cyclone then uniformly elevates the temperature of the particulate laden gas stream, extracting the mineral solids, further cracking the organic gases at high temperature and, optionally, vitrifying the solids. For some waste feeds the addition of slagging capability in the secondary cyclone may be desirable allowing the waste mineral content to be converted into vitrified aggregate having salable properties. The product gas stream is then purified for subsequent use.

Operation under reducing (gasification) conditions with steam and partial oxidation significantly diminishes system capital costs by decreasing equipment volumes to 1/4th the size of comparable incineration with combustion air (oxidation) systems. The reducing atmosphere, with excess steam present at high temperature, has been proven to be a good method for converting organic compounds into environmentally benign low molecular weight gases with recoverable value. The reducing atmosphere precludes conditions which result in formation of toxic products of incomplete combustion (PIC), such as dioxins, and avoids the formation of  $\text{NO}_x$ . The focus of the development activities are on a novel method for partial oxidation of solid wastes into a syn-gas



(a) Bubbling Bed

(a) Slugging Bed



(c) Conventional Spouted Bed

(d) Jet-Spouted Bed

Figure 1. Various fluidization regimes.

product from which high value products can then be derived, such as clean syn-fuel, hydrogen, methanol.

Estimated break even processing costs with no tipping fee are \$50/ton to \$100/ton for 250 to 24 tons per day SBR facilities, respectively, with capital investments less than 1/2 the cost of incineration systems.<sup>(2)</sup> Improved cost effectiveness is one technology benefit, though improved environmental performance and enhanced public acceptance because of the recycling ability are both considered highly significant advantages of the technology.

### Waste Applicability

The SBR advanced recycling technology is particularly suited to wastes with significant heat content (2,000 to over 14,000 Btu per pound) which are contaminated with toxic organic compounds and heavy metals. Hazardous soils contaminated with coal tar residues, chemical wastes, and petroleum refinery wastes are also appropriate for processing in the SBR advanced recycling system. Municipal Solid Wastes (MSW), mixed (radioactive) waste, munitions and rocket propellants, are also candidate feed materials. Energetic materials can be either recycled or incinerated, depending on the project parameters. In either case, primary gasification in the SBR system is highly advantageous (very high energy explosives are first uniformly diluted with inert materials prior to thermal processing).

The PVC bound chlorine content in ASR has been reported to average 3%. Gasification of wastes with high chlorine content, such as ASR, using high temperature steam is a preferred method of thermochemical recycling relative to incineration. The impact of waste chlorine content on PCDD/PCDF emissions during waste incineration is the subject of much debate in the literature with some studies showing a strong correlation (3, 4, 6, 7) and others showing no correlation.<sup>(8-10)</sup> Although results of these studies are mixed, it is clear that a chlorine donor is necessary for the formation of dioxins and furans. The reducing atmosphere in the SBR favors hydrogenation reactions whereby chlorine and sulfur are extracted from macromolecules and converted efficiently to HCl and H<sub>2</sub>S. These acids then react rapidly with in-situ sorbents to form salts such as calcium chloride.

Nitrogen containing polymers in mixed plastics feedstocks can form toxic intermediate compounds under some operating conditions. ASR contains urethane materials which are composed of isocyanates, molded plastics made from urea-formaldehyde resins, polyamides, such as Nylon carpeting, and polyacrymids. All of these polymers contain nitrogen which could form toxic cyanide compounds such as cyanogen chloride and hydrocyanic acid gases during incineration or pyrolytic thermal destruction. Since ASR contains metals, complex cyanides, such as nickel and iron species, are also possible. Hydrogen is produced under high water vapor, reducing conditions by the water shift reaction. Both hydrolysis and hydrogenation reactions are thus promoted by the presence of superheated steam under reducing conditions. Hydrolysis is applicable to the treatment of polyesters, polycarbonates, and polyamides. Hydrogenation reactions also split the polymer chain at reactive sites (unsaturated carbon-carbon bonds) to reduce molecular weight.

### Detailed SBR Technology Description

The initial development and testing has focused on thermochemical recycling of low-end mixed plastic wastes, exemplified by ASR, which has been used in the initial test runs. EER's Spouted Bed Reactor technology has been constructed at the Process Development Unit (PDU) scale of 24 tons per day. The existing PDU (Figure 2) incorporates a waste feeder, the SBR reactor, a hot cyclone, heat recovery section, and a baghouse.

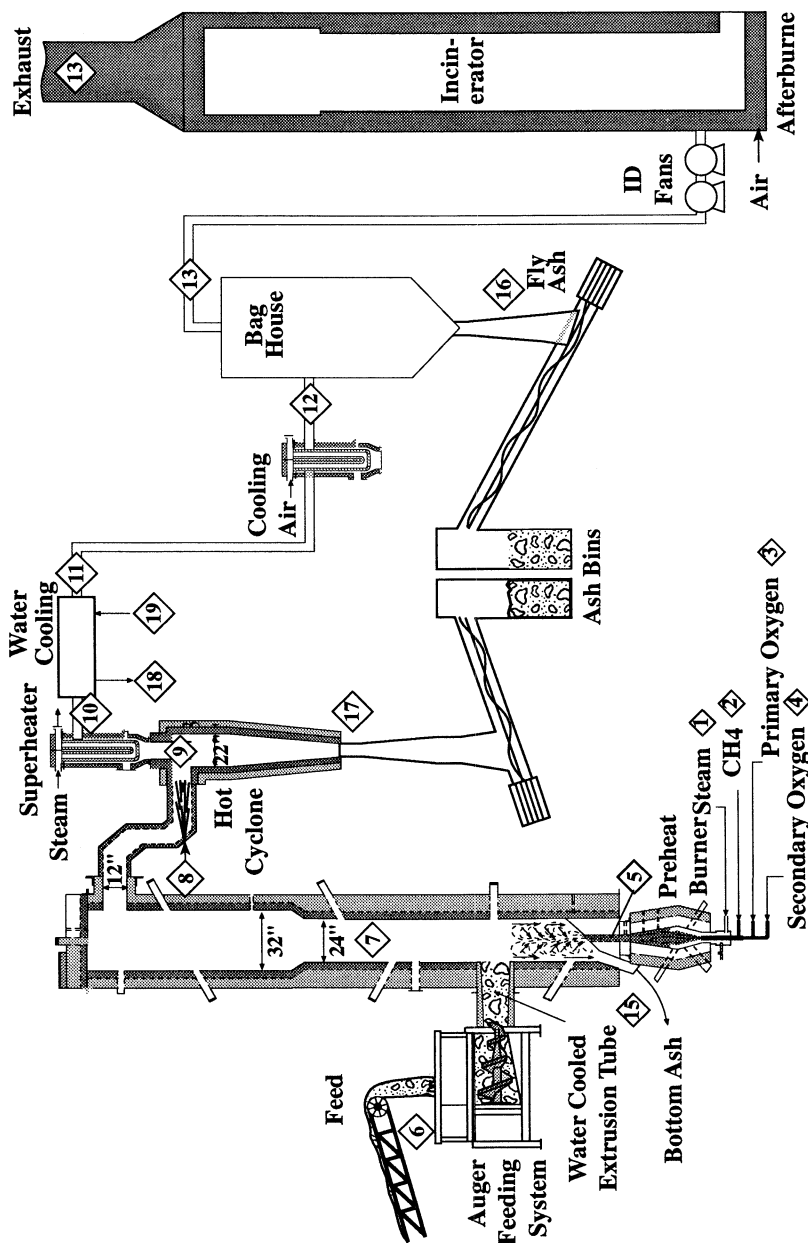


Figure 2. 24 TPD currently configured SBR process development pilot plant.

August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch016

**Extrusion Feeding.** Lightly prepared waste is fed to a high-thrust, extrusion feeder which forces heterogeneous waste materials into the primary reactor.

**SBR Reactor.** In the spouted bed thermochemical reaction zone solids are comminuted and gasified at temperature (1,000-1,600°F). Large solids remain in the bed until they are reduced in size through attrition, pyrolysis, and gasification reactions. The high velocity inlet spout at the exit of the preheat burner causes aggressive size reduction of heterogeneous feedstocks through ablative gasification reactions. Particle size is rate limiting for heat and mass transfer reactions, including pyrolysis and carbon gasification. Therefore, rapid solid size reduction significantly increases reaction rates. Oxygen and steam are added selectively to control the composition and temperature profile within the reactor. In the presence of excess steam at high temperature, toxic organic compounds are reduced to H<sub>2</sub>, CO, CO<sub>2</sub>, HCl, metals and metal oxides, and water.

**Hot Cyclone.** Steam and gaseous products elutriate fine particles out of the reactor and into the hot cyclone where the temperature may be water quenched below the ash softening temperature or increased by the addition of oxygen. The ash may be slagged in the cyclonic slagging system under reducing conditions, and recovered as a medium density granular solid in a water quench tank.

**Heat Recovery.** For full-scale applications, the gas stream would be cooled via a waste heat boiler to raise the process steam. In the pilot plant, a free standing boiler is used to generate process steam for injection into the preheat burner. Waste heat recovered after the hot cyclone provides steam super-heat to 600°F. However, most process heat is rejected to atmosphere via an air cooling heat exchanger prior to the 450°F baghouse. Steam used for the spouting fluid is highly superheated by a small in-line oxygen-methane burner. Superheated steam provides some heat for endothermic pyrolysis reactions, along with exothermic heat resulting from partial oxidation of wastes which react with sub-stoichiometric levels of oxygen injected into the spouted bed primary.

**Optional Fines Recycle.** The fine particulate is optionally removed in a traditional or hot ceramic baghouse. The fine particulate recovered in the baghouse may be recycled to the SBR. Thus, all the solids may be recovered as a vitrified product with salable properties, within EPA leachability limits for heavy metals and trace organics. When the hot cyclone is operated at slagging temperature, the baghouse ash may be recycled back to the primary spouted bed along with any trace contaminants for incorporation with the slag. Subsequent purification of the H<sub>2</sub>/CO/CO<sub>2</sub> gas stream can be accomplished using conventional or emerging particulate, acid scrubbing, or gas separation technologies.

## Test Results

Preliminary tests were conducted to characterize the waste feed system required, the spouted bed dynamics, and to characterize the end product syn-gas. To date, the operation of the SBR with ASR has been limited to several short duration trial runs. Relatively trouble-free feeding of "raw" unsegregated ASR has been accomplished at a feed rate of 1,400 lb/hr. Typical ASR feed is characterized in Table I. The ASR feed was previously wet shredded through a hammer mill having 6" x 6" grates using traditional auto shredder industrial methods and allowed to air dry. The bulk of the ferrous metals had been extracted magnetically and nonferrous metal had been hand picked from a conveyor belt. However, the feed still contained a high tramp metal and wire content which characteristically makes ASR difficult to handle. The ASR was

Table I. Auto Shredder Residue Analysis - 12 Shredder Fluff Samples (11)

Parameter	Mean	Low	High
% H <sub>2</sub> O (moisture)	9.71	2.2	33.8
% Ash	43.97	25.1	71.3
% Ash (dry basis)	49.28	25.7	72.9
% Volatiles (fabric, foam, plastics)	43.37	23.9	66.0
% Fixed carbon	2.94	-5.2	11.7
Btu/lb (higher heating value)	5,400	2,900	9,260
Btu/lb (dry basis)	5,906	3,020	9,480
% Sulfur	0.36	0.23	0.51
% Chlorine	3.79	0.73	16.88
% Metals > 12 mesh*	61%		
% Metals <12 mesh**	13%		

\* Primary components Cu, Zn

\*\* Primary components Pb, Fe, Al

manually fed to the reactor via a 24" belt type feed conveyor. The belt conveyor delivered the ASR feed to the open top auger feeder.

The auger feeder was precalibrated with ASR in order to relate the screw rpm to the waste feed rate (pounds per hour). The auger feeder was installed on tracks with rollers at four corners such that it can be retracted from the SBR for performing calibration procedures. The feed rate was determined by filling 55 gallon drums weighed on an industrial scale. Feeding 1,400 lb/hr required stoking the feeder fairly continuously to keep pace with the auger. No problems were experienced during the feeding operations. This was a significant accomplishment considering the difficult characteristics of the ASR feed material. The auger extruder dropped the material from the extruder in chunks rather than continuously. The inventory and the thermal mass of the bed were sufficient to avoid bed temperature fluctuations with somewhat uneven feeding. However, when large quantities of feed were extruded into the bed, the gas evolution rate increased substantially, particularly when the feed contains PVC plastics which gasify at a very high rate. The reactor pressure was maintained at approximately -4" water vacuum, however, feed surges the reactor tended to fluctuate the reactor pressure towards atmospheric pressure.

The spouting action of the bed at pilot scale has been demonstrated to be very stable when operated with superheated steam as the spouting fluid. Six pilot runs without ASR lasting from 36 to 48 hours have been carried out to evaluate spouting stability with a variety of bed materials. Bed materials tested have included 2-5 mm silica sand, approximately 1/4" pea gravel, 1/4" alumina balls, and 2 mm steel shot. All these materials demonstrated stable spouting action with steam mass flow rates between 1,300 and 1,600 #/hr.

The temperature of the superheated spouting steam was operated between 1,000°F and 1,800°F. An auxiliary boiler supplied the 250°F saturated steam which was then heated to 600°F via a heat exchanger which absorbs heat from the process gases (>1,300°F) leaving the hot cyclone. The steam was further superheated by an in-line oxygen/methane burner, and then expanded through a 3" spouting orifice. The ratio of the reactor diameter (24") to spouting orifice (3") diameter was 8. The bed depth was varied from 1 to 3 ft. The bed materials began to radiate significantly at about 1300°F. The vigorous spouting action could be viewed very clearly looking through a sight port located on the top of the reactor. The appearance of the spout (looking down from the top) may be analogous to looking into the mouth of a violently erupting volcano. Some small particles impinge on the sight glass located approximately 20 feet above the

spouting orifice, though most of the bed materials drop from about five feet above the expanded bed. The top eight feet of the reactor is increased to 32" ID as a disentrainment section. Process gases exit the primary reactor through a 12" ID duct located on the side at the top of the reactor.

Bed temperatures have typically been near or above ash softening temperature resulting in some bottom ash slagging. Slag formation can interfere with ash removal and inhibit bed fluidization. However, the spouting regime of fluidization was relatively tolerant of heterogeneous materials in the bed. The pilot plant was operated inadvertently in this mode with a low melting phase. Unlike the traditional fluid beds, the spouting action continues to turn over the bed materials. However, unless the fused materials are removed periodically, large agglomeration of solidified bed materials result which then tend to obstruct the spout and eventually slump the bed. The pilot plant has been operated in this failure mode without any catastrophic results. The reactor was cooled and the agglomerated clinkers were removed and the bed restarted.

Gas samples were obtained at the top of the primary spouted bed prior to addition of tertiary oxygen in the hot cyclone. Therefore, the gas samples are very rich in hydrocarbon and have a high Btu content (Table II). The reactions which assure destruction of toxic organic compounds are accomplished in the hot cyclone where the equilibrium temperature is raised above 1,500°F with the addition of oxygen.

The beneficial reducing action of steam, through the water shift reaction with CO is carried out above 1500°F where free radical molar concentrations increase to about 10<sup>-4</sup>. The destruction of toxic organic compounds using high temperature steam under reducing conditions has been well demonstrated by others.<sup>(12, 13)</sup> The initial pilot plant work has focused upon the mechanical issues relative to the spouted bed reactor. Subsequent work will confirm the ability to obtain high destruction efficiency of principle organic hazardous constituents (POHCs) by passing the process gases and particulate through the high temperature zone for reduction of organics to H<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O.

Table II. Product Gas Analyses

Compound	Preliminary Results*	Optimal Conditions
Hydrogen (%)	12.6	30-40
Oxygen (%)	2.4	< 1
Nitrogen (%)	6.4	< 2
Methane (%)	10.5	0 - 10
Carbon Monoxide (%)	20.9	15 - 30
Carbon Dioxide (%)	30.6	> 30
Hydrocarbons (ppm)		
C <sub>1</sub>	123000	< 100,000
C <sub>2</sub>	41300	< 20,000
C <sub>3</sub>	8040	< 200
C <sub>4</sub>	545	< 200
C <sub>5</sub>	611	< 200
C <sub>6</sub>	353	< 200
Heating Value (Btu(LHV)/scf)	410	> 400
HCl (ppm)		< 50
H <sub>2</sub> S (ppm)		< 20

\* Data collected at EER's PDU March, 1993.

The ASR ash contains a significant fraction of iron oxide which is an active gasification catalyst. The comminution of the solids in the spouted bed are hypothesized to provide high surface area, fine particulate which may contribute to catalytic activity. Iron is also effective as a sorbent for chloride. The hot cyclone catch showed metals leachability below regulatory limits. However, the volatile metals were condensed on the baghouse ash. This ash passed leachability tests for all metals but lead and cadmium.

From the testing program, accomplishments to date include the design, construction, shakedown, and preliminary operation of a pilot scale SBR facility capable of processing 1,000-2,000 lb/hr of waste. Data obtained during limited test runs has demonstrated the conversion of ASR to hydrocarbon rich process gas (320-430 Btu/scf), with negligible tar formation, and with 1-2% carbon remaining in the ash constituents.

### Potential Products of Advanced Waste Recycling

Thermochemical recycling of plastic wastes can generate a variety of end products, including hot syn-fuels, pyrolysis liquids, olefins, or syn-gas. The SBR technology can be operated at low, medium, or high temperature in order to generate these end products. EER has reviewed the possible commercialization paths using ASR feed stock and has tentatively selected a conservative approach. Initial commercial projects will focus on co-firing a partially cleaned syn-gas product in an existing combustion system, such as a utility boiler or prime mover. More sophisticated recycling scenarios such as hydrogen recovery or syn-gas utilization for hydrogen synthesis will follow. Thus, the near term objective is to develop the technology for production of a syn-gas containing primarily H<sub>2</sub> and CO. This product gas can be readily purified to specifications even when ASR feedstocks are contaminated with hazardous constituents. The following products might ultimately be produced from Advanced Waste Recycling methods:

Solid Aggregate -	Ash and mineral matter are converted to a glass-ceramic aggregate.
Process Gas -	Medium BTU gas is beneficially co-fired in boilers, furnaces, and prime movers.
Synthesis Gas -	Syn-gas composed of H <sub>2</sub> and CO, used for hydrocarbon synthesis.
Hydrogen -	Purified gaseous or liquid hydrogen for transportation or merchant use.
Hydrocarbons -	Crude pyrolysis oil for chemical feedstocks, benzene, toluene, & xylene.
Olefins -	Ethylene, propylene, butylene, used for synthesis of plastics and higher chemicals.
Oxygenates -	Methanol, ethers, methyl formate, or oxygenated fuel additives.
Other Products -	Clean burning Diesel, wax, or non aromatic containing gasoline.

### Summary of SBR Technology Features

The Advanced Waste Recycling market opportunities are technology and economically driven. To address these market need, the technology incorporates the following novel features:

- The ability to gasify lightly processed, commingled heterogenous wastes without excessive size reduction or pretreatment.



- Rapid ablative gasification and comminution of solids while operating below bed slagging temperatures.
- Vitrification of the waste mineral content, generating an environmentally inert product with salable properties (for example, <math>3/8''</math> glass ceramic aggregate useful in asphalt formulations).
- High temperature steam gasification under reducing conditions eliminating toxic compounds while generating low molecular weight syn-gas products.
- In-bed additives for acid gas and slagging control.

As a point of reference, a 250 tons/day rotary kiln hazardous waste incinerator could cost about \$15 million, installed, with processing fees on order of \$1000/ton. The proposed SBR technology would cost about 1/3 (\$5 million) and at a tipping fee of \$100/ton. The above features are highly attractive for economical waste recycling. Specific technical and development issues to optimize and integrate these features and the methods for resolving the outstanding technical issues will be addressed in a new co-funded program.

### Literature Cited

1. Franklin, *Characterization of Municipal Solid Waste in the United States: 1992 Update*, EPA/530-R-92-019, July, 1992.
2. Energy and Environmental Research Corporation, *Market Assessment -- Gasifier Waste Processing with Natural Gas as an Auxiliary Fuel*, report to GRI, October, 1994.
3. Theisen, J. et al., *Determination of PCDFs and PCDD in Fire Accidents and Laboratory Combustion Test Involving PVC-Containing Materials*, *Chemosphere*, Vol 19, pp 423-428, 1989.
4. Christmann, W. et al., *Combustion in Polyvinyl Chloride - An Important Source for the Formation of PCDD/PCDF*, *Chemosphere*, Vol. 19, pp 387-392, 1989.
5. Mathur, K. B.; Epstein, N., *Spouted Beds*, Academic Press, NY, 1974, pp 6-13.
6. Marklund, S. et al., *Determination of PCDDs and PCDFs in Incineration Samples and Pyrolytic Products*, Editors, Rappe, C.; Choudhary, G.; Keith, L. H., In *Chlorinated Dioxins and Dibenzofurans in Perspective*, Lewis Publishers, Chelsea, MI, 1986.
7. Liberti, A.; Brocco, *Formation of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in Urban Incineration Emissions*, In *Chlorinated Dioxins and Related Compounds: Impact on the Environment*, Noyes Publications, Park Ridge, NJ, 1982.
8. Johnke, B.; Stelzner, *Results of the German Dioxin Measurement Programme at MSW Incinerators*, *Waste Management and Research*, No. 10, pp 345-355, 1992.
9. Nielsen, P., *Significance of Operating Conditions and Chlorine sources on Dioxin Formation - Experience of the Danish Incinerator Study*, Presented at International Conference on Municipal Waste Combustion, Hollywood, FL, April 11, 1989.
10. Visalli, J., *A Comparison of Some Results from the Combustion - Emissions Test Programs at the Pittsfield, Price Edward Island and Peedskill Municipal Solid Waste Incinerator*, *Jour. of the Air Pollution Control Assoc.*, Vol. 37, No. 12, 1987.

11. Hubble, W. S., I. G. Most, M. R. Wolman, *Investigation of Energy Value of Automobile Shredder Residue*, DOE/ID/12551-1, August, 1987.
12. EPA Proceedings, Fifth Forum on Innovative Waste Treatment Technologies, Chicago, IL, May 3-5, 1994, *The Eco-Logic Process*, p 11.
13. Maznar, J.; Corella, J.; Delgado, J.; Lohoz, J., Improved Steam Gasification of Lignocellulosic Residues in a Fluidized Bed, *Ind. Engr. Chem. Res.*, Vol. 32, pp 1-10, 1993.

RECEIVED March 13, 1995

## Chapter 17

# Recycling of Rubber

Charles P. Rader

Advanced Elastomer Systems, L.P., 388 South Main Street,  
Akron, OH 44311-1058

The recycle of rubber lags far behind that of thermoplastics. This lag results primarily from a great preponderance of rubber articles being fabricated from thermoset materials. As a result, the most facile means of disposing of many used rubber articles, including pneumatic tires, is through incineration to generate energy. This situation will continue until new technology is generated for the fabrication of recyclable rubber articles. Promising technology toward this end is now being offered by thermoplastic elastomers -- materials with properties of rubber but which can be processed as a conventional thermoplastic.

The recycle of rubber lags significantly behind that of thermoplastics. Ironically, used rubber articles have been recycled since 1853 (1). The motivation for this recycling, however, was primarily the generation of a useful rubber compounding material -- reclaim -- with little, if any, interest in reducing the amount of waste discarded to landfills. Since World War II, the trend to higher quality in fabricated rubber articles (especially radial tires) has generated a progressive decrease in the use of rubber reclaim, with the percentage of recycle in 1990 being approximately one-sixth that in 1941 (2).

The slow pace of the recycle of rubber arises from the immense dominance of thermoset over thermoplastic rubber. Prior to the 1960's, all commercial rubber was thermoset. Today, in the mid-1990's, all pneumatic tires -- which consume approximately 51 percent (3) of the rubber used in the world -- are fabricated from thermoset rubber. The remaining 49 percent (the non-tire segment of the industry) is presently about 88 percent from thermoset rubber and 12 percent thermoplastic elastomers (TPEs). Thus, approximately 94 percent of the rubber consumed in the world is still thermoset.

0097-6156/95/0609-0196\$12.00/0  
© 1995 American Chemical Society

In the non-tire segment, TPEs are making major inroads in replacing thermoset rubber (4). However, their prospects for replacing thermosets in pneumatic tires are quite poor (5). It is highly unlikely that any of the TPEs now commercially available will be able to penetrate significantly the tire segment of the rubber industry. Such a penetration will have to await the development of markedly novel polymer systems for use as TPEs.

### **Dominance of the Motor Vehicle**

By far the most important market for rubber articles and their recycle is provided by the motor vehicle -- in the vehicle itself and also in the roadways over which it travels. Pett, Golovoy and Labana, in a previous chapter of this volume, have summarized the impact of the automotive industry on rubber and plastics recycling. These authors provide an inside view of current recycling practice in the U.S. automotive industry and the necessary infrastructure for this recycling in both today's and tomorrow's marketplace. Approximately 75 percent of the materials in today's on-the-road motor vehicle are now recycled, with the polymeric materials --- plastics, rubber, textiles, etc. --- being greatly eclipsed by the massive quantity of metals recovered. Much stress is placed on the needed logistics and technology for recovering value from the materials in a discarded motor vehicle. Pett, Golovoy and Labana give a most interesting view of the effect of materials recovery and recycling on the design and materials to be used in tomorrow's automobile. An ongoing and perplexing problem in automotive recycle is the recovery of value from the 130-140 pounds of rubber in a modern U.S. car. The proper reuse of this automotive rubber is a major challenge for today's technologists and entrepreneurs.

Serumgard and Eastman in their chapter give an update of the massive problem of scrap tire recycle, asserting much reason why today's stockpile of approximately 3 billion scrap tires should largely disappear by the turn of the century. This disappearance will result primarily from incineration to recover the approximately 300,000 BTUs of energy in the average scrap tire, and not from recycle. The recycle of the rubber from a pneumatic tire is just not practical when one considers it as a highly engineered composite of several different compounds reinforced with both textile fiber and steel wire.

Just as the motor vehicle provides direction to the rubber recycling effort, so does the road pavement on which the vehicle travels. In his chapter, Smith describes in detail the utilization of the 140 pounds of scrap rubber from a 2400 pound automobile, as a toughening additive in highway asphalt. Fostered by heavy support from the U.S. Department of Transportation, this use of recycled rubber is growing rapidly and will so continue for the rest of the decade.

It is safe to conclude that whatever future course the recycle of rubber takes, it will be deeply impacted by the automotive and highway construction industries.

### Logistics and Technology

The required technology for recycling rubber articles (of which the great majority are thermoset) is much more formidable than that for thermoplastics. On the other hand, the logistics are quite comparable. In a motor vehicle, household appliance or other assembled device, disassembly is required to obtain component rubber and plastic parts for recycle. A rapidly growing trend (6) is the design of these devices for quick, economical disassembly. The rubber, plastic and metal parts from this disassembly must then be separated, cleaned and segregated on the basis of their chemical composition and mutual compatibility.

The recycle of thermoplastics (and TPEs) simply requires melting and refabrication by molding or extrusion. This recycle involves only reversible physical change (7). The recycle of a thermoset rubber requires an irreversible chemical change, that of devulcanization to remove the chemical crosslinks between the polymer chains. This gives rise to a massive technological barrier to the recycle of the massive amount of fabricated rubber which is thermoset.

The most difficult thermoset rubber articles to recycle are those reinforced with a steel wire, textile fiber or both. In this category are pneumatic tires, drive belts, hose and a variety of fabric-reinforced articles. In the past, these articles could be treated chemically to generate reclaim for subsequent use as a compounding agent. The demise of the reclaim industry has rendered impractical all attempts to recycle reinforced rubber articles. Thus, the most practical use of these articles is as a high energy fuel in heat generation, as detailed by Serumgard and Eastman. This end use is still vastly superior to disposal in a landfill.

Thermoset rubber articles loaded with carbon black are only slightly easier to recycle than articles reinforced with metal wire or textile fibers. In this case, it is easier to reduce the size of the rubber pieces by cutting, grinding, etc. The chips, pellets or particles thus obtained are still pieces of vulcanized rubber to be used as such (e.g. in asphalt) or treated chemically to cleave the chemical crosslinks. In the case of most vulcanizates, chemical treatment will involve the cleavage of relatively weak C-S and S-S chemical bonds. Warner's chapter in this section provides a complete, up-to-date summary of the chemistry of cleaving these crosslinks to effect devulcanization of thermoset rubber, which can be done by either chemical reagents, electromagnetic radiation or ultrasonics. These methods are primarily of interest in the analysis of rubber vulcanizates, with some ancillary importance in the commercial recycle of thermoset rubber.

The most promising technology for recycling rubber parts is through the use of TPEs (8). Payne's chapter in this section points out in detail the recycling advantages of TPEs over conventional thermoset rubbers. Since a TPE is a material with the properties of a rubber and the processability of a thermoplastic, a rubber article fabricated from a TPE can be recycled in essentially the same manner as a conventional thermoplastic. Thus, the recycle of a TPE part involves, 1) collection of parts from the disassembled device, 2) separation of these parts into a mutually compatible group, 3) cleaning of these parts to remove all foreign matter, 4) grinding them into processable pellets, and 5) refabricating the pellets into a useful

rubber article. This recyclability of TPE parts has recently been demonstrated (9) with rack and pinion steering gear boots from motor vehicles in service for more than five years.

Multiple recycle of the same TPE material should be both possible and practical, since the physical properties are essentially unchanged after repeated recycles (10). This multiple recycle of TPEs thus opens up a vista of recycling opportunities.

The recycle of automotive rubber parts from TPEs is so similar to that of plastic parts that the Society of Automotive Engineers (SAE) has classified (11) commercial TPE materials generically to enable their segregation into mutually compatible categories for recycle purposes. In this classification scheme, the TPEs are categorized in the same manner as that used for rigid thermoplastics such as polypropylene (PP) and polystyrene.

### Uses for Rubber Recyclate

In today's economy and surroundings, the key reason for recycling rubber articles is to prevent their discard to the environment. For this effort to make good business sense, it is imperative that suitable utility be obtained from the used rubber parts. In many cases -- pneumatic tires, hose, belting -- the best use is often incineration, to produce energy which can have a multitude of uses.

A quite promising application of used rubber parts is grinding and subsequent reuse of the particulate rubber as a filler in lower-performance thermoset rubber articles or as a toughening agent in asphalt paving. There is still limited use of devulcanized rubber as reclaim, however, the prospects of reclaim as an outlet for recycling are limited, at best.

Beck and Klingensmith in their chapter of this volume review the pyrolysis of pneumatic tires to generate a carbon black char for non-demanding uses in rubber compounding. This filler application could replace lower-performance carbon blacks and eliminate the need for discarding to a landfill the rubber articles used as raw material.

Perhaps the brightest star on the rubber recycling horizon is TPEs. They are the one hope of recycling rubber articles to a performance level comparable to the virgin rubber part, if proper care is taken during the logistics of recycle. A more practical scenario for TPE recycle is combining different compatible TPEs with each other or with compatible thermoplastics. Thus, a PP/EPDM blend TPE could be combined with a PP/EPDM vulcanizate TPE or with PP thermoplastic to give a useful rubber/PP composition -- lower in performance than the original TPE rubber articles, but still useful and reducing the need for landfill disposal.

This recycle of TPEs is limited to non-tire articles because these materials are not suitable for pneumatic tire applications. Thus, at least for now, the recycle advantages of TPEs are not available for pneumatic tires.

### The Future for Rubber Recycle

As the next 10 to 20 years unfold, a number of positive changes should occur in the recycle of rubber articles. By the turn of the century, the size of the U.S.'s 3 billion plus stockpile of discarded pneumatic tires will be massively reduced and possibly eliminated. The trend toward designing motor vehicles, household appliances and other assembled devices for easy disassembly and subsequent recycle of parts will continue to accelerate and become full blown within the next decade. Marketers of these devices will feel increasing pressure -- and in some cases outright governmental direction -- to take the device back from the consumer at the end of its useful life (6,12). This will generate much incentive for the device manufacturer to design it for easy disassembly.

The use of TPEs offers a ready answer for the recycle of many rubber parts. TPEs, now approximately 12 percent of the non-tire rubber market, should grow to about twice this percentage by the early 21<sup>st</sup> century. Their use in pneumatic tires is highly unlikely during the next decade. Thus, the disposal of scrap tires will continue to be relegated to incineration and certain low performance uses as a rubber compounding material.

As the next century dawns, the reutilization of "spent" rubber articles will progressively grow and become an accepted part of our post-industrial-age lifestyle. This reutilization must, 1) be pragmatic, 2) make good business sense, 3) be based on good science and technology, and 4) be socially and politically acceptable. This will enable the future for posterity to be as worthwhile as our past has been.

### References

1. Goodyear, C., British Patent 2933, December 16, 1853; Miller, G.W., in "Chemistry and Technology of Rubber", C.C. Davis, Ed., Reinhold Publishing Corp., New York, NY, 1937, p. 720.
2. State of Ohio, Environmental Protection Agency, "Recycling of Used Tires in Ohio", June, 1989.
3. Rubber Trends, 3rd Quarter 1994, The Economics Intelligence Unit, London.
4. School, R., in "Elastomer Technology Handbook", N.P. Cheremisinoff, Ed., CRC Press, Inc., Boca Raton, FL, 1993, Chapter 15.
5. Rader, C.P. and Walker, B.M., in "Handbook of Thermoplastic Elastomers, Second Edition", B.M. Walker and C.P. Rader, Eds., Van Nostrand Reinhold, New York, NY, 1988, p. 10.
6. Plastics News, March 16, 1992, p. 6.

7. Purgly, E.P., Gonzalez, E.A. and Rader, C.P., Society of Plastics Engineers, ANTEC '92, Detroit, MI, May 5, 1992.
8. Gonzalez, E.A., Purgly, E.P. and Rader, C.P., Presented at the 140<sup>th</sup> Meeting of the Rubber Division, American Chemical Society, October 8, 1991, Washington, D.C.
9. Alderson, M. and Payne, M.T., Rubber World, May, 1993, p. 22.
10. O'Connor, G.E. and Fath, M.A., Rubber World, January, 1982, p. 26.
11. SAE J 1344, "Marking of Plastic Parts", Society of Automotive Engineers, Warrendale, PA, 1991.
12. Schultz, J., Wards Auto World, December, 1994, p. 21.

RECEIVED July 3, 1995



## Chapter 18

# Rubber Recycling: Emerging Markets and New Technology

Fernley G. Smith

ETA, Inc., 5065 East Sloan Street, Port Clinton, OH 43452

Emerging technology for the production of recycled rubber and a changing market environment more willing to consider recycled rubber as a viable rubber material in product design and applications, supported by acceptable performance and cost effective results, makes the nearly 25% per year projected growth rate a realistic outlook for the expanding rubber recycling industry.

Recycled thermoset rubber has been a standard material of the rubber industry for many years. The early capacity for the manufacture of ground rubber and the processing technologies grew out of the reclaim rubber plant needs for a uniform crumb rubber for devulcanization purposes. (1) Through the years, this ambient temperature grinding technology has been improved and expanded from the original 2mm to .85mm capacity to the .60mm to .425mm sizes now widely used in the rubber industry.

In the 80's the finer grinding technologies emerged via cryogenic and wet grinding systems to generate from vulcanized rubber waste, mesh sizes ranging from .425mm to .150mm and finer.

0097-6156/95/0609-0202\$12.00/0  
© 1995 American Chemical Society

Throughout these years of technical development and improvements, the industry remained relatively stable, with modest annual growth as niche applications for recycled ground rubber were developed. By 1990 sales to this market were estimated at around 160 million pounds annually, produced by a relatively small group of processors with processing capacity totaling between 250 and 300 million pounds. Of this annual sales volume, approximately 65% was ambiently ground material of size .60mm and coarser, with the remaining 35% at .425mm and finer. (2) This shift to finer particle size is continuing.

Ground rubber has historically been dominated by a plentiful supply of tire buffings as the raw material of choice, and has been augmented based on factory waste to meet customer requirements.

The principal uses for ground rubber in 1990 were:

- Pneumatic tires
- Friction materials-brake pads
- Molded rubber goods
- Bound rubber goods
- Athletic surfaces and playgrounds
- Rubber plastic compounds
- Tires/bias ply and retread stocks
- Tire innerliner
- Crack sealer/asphalt
- Asphalt rubber binder

Over a ten year period from 1984 to 1994, forty eight states instituted regulatory scrap tire management legislation with economic incentives to do so, which has resulted in a scrap tire recycling infrastructure with a first stage size reduction capacity capable of producing 50mm to 125mm size chips and a coarse 6-12mm rough crumb from scrap tires.

As of 1994, there are over 150 such new size reduction processors in place capable of initial size reduction of tires.

In a logical progression, many of these new processors are actively planning further particle size reductions to yield 6.3mm and 2.00mm crumb and smaller as they can identify markets for this additional processing investment. This significant new investment in processing capability will urgently seek markets for these materials, to improve the recovery value of the processed scrap tires.

This plentiful supply of feedstock, to supplement the exhausted supply of buffings, is a timely development. Today, we see several emerging trends for new uses of ground rubber. Foremost is the use in asphalt rubber in roads. (Table I) tabulates and

**Table I. Selected Crumb Rubber Modifier Terminology**

<b>Term</b>	<b>Definition</b>
<b>Crumb Rubber Modifier (CRM)</b>	A general term for scrap tire rubber that is reduced in size and is used as a modifier in asphalt paving materials.
<b>Granulated CRM</b>	Cubical, uniformly shaped, cut crumb rubber particles with a low surface area which are generally produced by a granulator.
<b>Granulator</b>	Equipment that shears apart the scrap tire rubber, cutting the rubber with revolving steel plates that pass a close tolerance, reducing the size of the rubber to a crumb particle (generally 9.5 millimeter [3/8 inch to No. 10] sieve)
<b>Ground Rubber CRM</b>	Irregularly shaped torn crumb rubber particles with a large surface area which are generally produced by a crackermill.
<b>Micro Mill</b>	Process that further reduces the crumb rubber to a very fine ground particle, reducing the size of the crumb rubber below a 425 micron (No. 40) sieve.
<b>Rubber Aggregate</b>	Crumb rubber modifier added to hot mix asphalt mixture using the dry process which retains its physical shape and rigidity.
<b>Asphalt Rubber (AR)</b>	Asphalt cement modified with crumb rubber modifier.
<b>Wet Process</b>	Any method that blends crumb rubber modifier with the asphalt cement prior to incorporating the binder in the asphalt paving project.
<b>Dry Process</b>	Any method that mixes the crumb rubber modifier with the aggregate before the mixture is charged with asphalt binder. This process only applies to hot mix asphalt production.
<b>Rubber Modified Hot Mix Asphalt (ROMAC)</b>	Hot mix asphalt mixtures which incorporate crumb rubber modifier primarily as rubber aggregate.

defines the key terms commonly used in the application of ground crumb rubber in highway asphalt paving.

### **Asphalt Rubber: Processes and Related Crumb Rubber Specifications**

**Wet Process.** The wet process (Figure 1) uses ground scrap tire rubber in size ranges from 2.4mm to .7mm.

Through the use of special equipment, the rubber is swollen in the asphalt binder under the high temperatures and agitation of the mix. After a specified residence time, the liquid rubber reinforced asphalt is added to the gravel aggregate at the hot mix plant and the resulting asphalt mix is now ready for placement as paving.

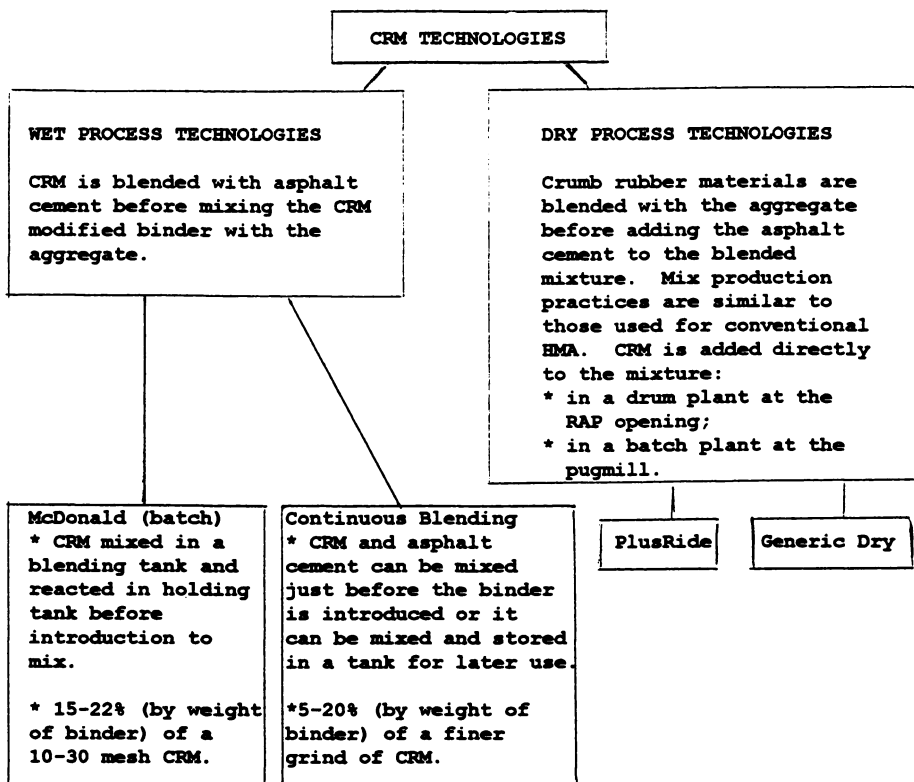
The liquid asphalt rubber binder used in asphalt paving is also widely used for spray-applied surface treatments, where it becomes an effective membrane for controlling adverse sub-base road conditions.

**Dry process.** The dry process (Figure 1) use of scrap tire rubber varies from the wet process in that the rubber is introduced as a partial replacement for gravel aggregate in the asphalt paving application. The dry process, therefore, uses a "coarse granular" crumb material with 6.3mm size combined with a portion of finer ground crumb in the 2mm to .85mm range.

**Polymer Modified process.** This process is based on the use of virgin polymers mixed with the asphalts to achieve improved performance. It can be effectively modified by the partial use of .60mm to .425mm ground scrap tire crumb rubber to effectively replace the polymers at a lower cost and acceptable performance.

**Continuous Blending process.** This process for the production of rubber in asphalt is based on the use of a finer particle ground scrap tire rubber crumb which is blended or blown into the asphalt at the hot mix plant. The mesh size of this crumb rubber ranges in size from .6mm to .18mm.

Of the various processes, work to date has favored the "wet process" which in 1993 represented the majority of asphalt rubber tonnage. However, the relative production infancy of asphalt rubber technology suggests that an increasing number of formulations and materials combinations using scrap tire rubber crumb will be developed. As the knowledge of new highway construction materials and their properties and performance is learned through actual usage, pavement designs and formulations will emerge to improve productivity, performance and cost.



Source: National Center for Asphalt Technology

Figure 1. Comparison of wet and dry processes for incorporating ground rubber into asphalt.

The progress to date is dramatic proof of the technical merits of this new material. Its initial success has been based on its cost and technical performance in service.

While the national debate continues on the mandated uses of asphalt rubber binder in Federally funded highway construction projects, what follow is the 1993 status prior to the effective date of the mandate.

**Current Status - Asphalt Rubber** Asphalt rubber applications are proceeding and gaining acceptance on their technical merits. While the majority of usage through 1993 remained in a group of western states dominated by California, Arizona and Texas, this base of acceptance is growing and now includes strong support in states such as Florida in the Eastern United States.

The preferred technology to date is the wet process with the dominant usage being in a top open graded mix resurfacing layer of asphalt rubber. Costs are rapidly declining with the increased volume and contractor experience from \$400/ton down to \$200/ton over the period 1992-94.

With the original McDonald patents having expired in 1992, more asphalt rubber application contractors are becoming involved and are expanding the capacity base of this new technology with increased bidding resulting. The Charles McDonald patent was based on his work in the 1960's as a materials engineer for the City of Phoenix, Arizona, to use a vulcanized crumb rubber additive in the asphalt cement mix in order to develop a highly elastic material for the repair of asphalt pavement.

Ground crumb rubber in asphalt in 1993 is estimated to total more than 50 million pounds in the USA (Figure 2), dramatically up from the less than 20 million pounds in 1991, with current forecast usage in 1994 of approximately 75 million pounds. This usage is expected to grow to 250 million pounds annually by the end of the 90's.

Thus by 1994, the existing 1990 basic crumb rubber capacity (estimated at 250 million pounds) would have been sold out had the industry's expansion not have been energized by scrap tire legislation events of the late 80's and early 90's. Ground rubber use in "crack sealer" for highway maintenance has now reached a 10 million pounds/year usage and is growing steadily in acceptance, further proof of the versatility of asphalt rubber materials in this application.

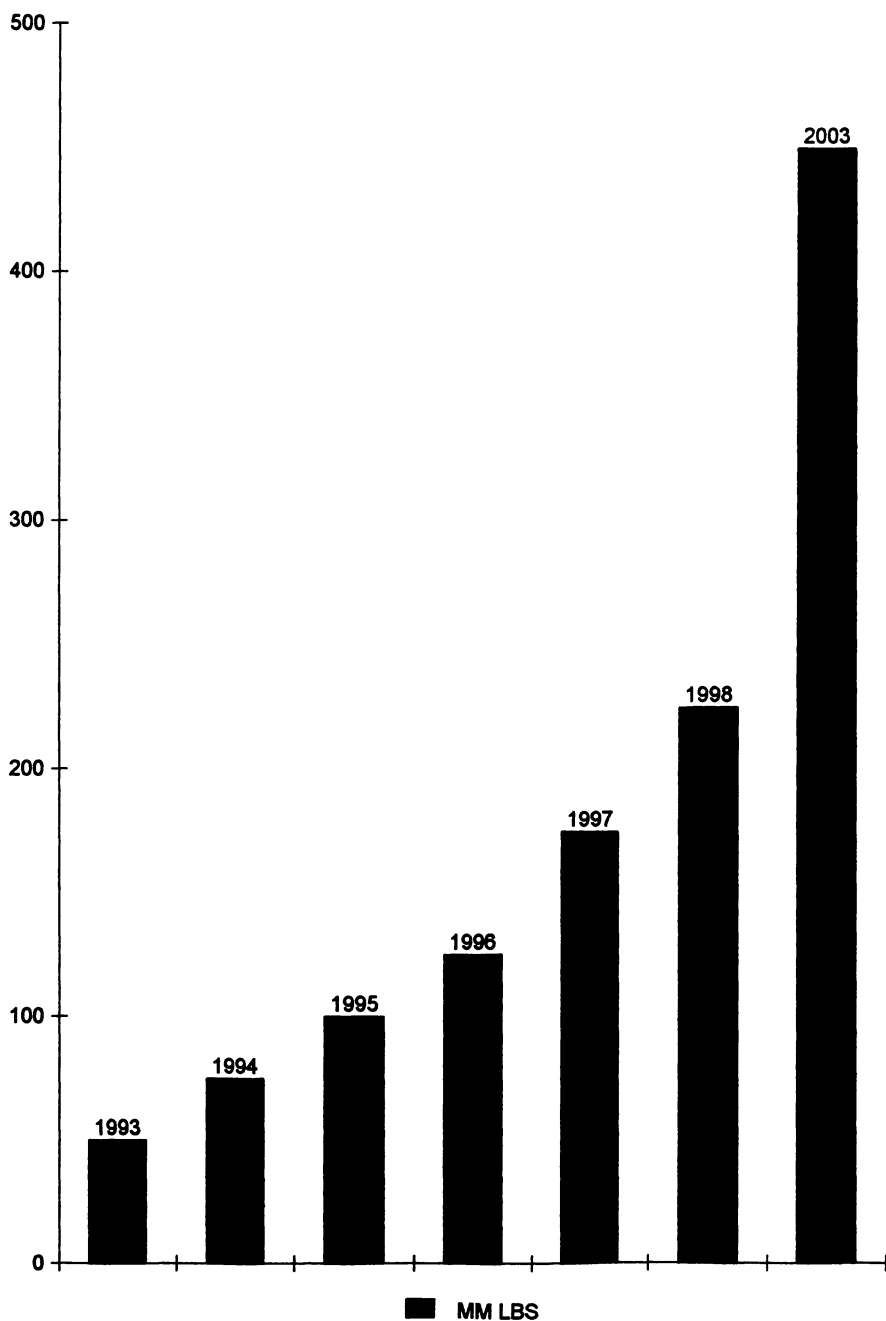


Figure 2. Crumb rubber usage in the United States. Estimated CRM usages (in asphalt rubber applications).

**Automotive Uses**

In addition to the "asphalt rubber" ground crumb requirements, we see additional forces now at work which should add further momentum to this growing usage of ground rubber crumb in industrial applications. These forces are a combination of the growing corporate environmental awareness best defined by the recent commitments by Ford, Chrysler and General Motors to a recycling emphasis exemplified by the following excerpts:

**Ford Motor Company Guidelines** (excerpt)

Protecting the environment has always been important, but today, it is becoming increasingly more important. An area of significant potential benefit to the environment is increased rubber recycling. We are focusing upon the use of recycle in our components and recycling of components at the end of vehicle life.

Ford believes that most of our elastomer material suppliers are already involved in recycling (especially in-process scrap) and will also be recycling more materials in the future. Knowledge about these elastomer recycling efforts is of value to Ford. Consequently, we would like to know the following. A 1993 Ford inquiry of suppliers included the following questions.

- \* Are you recycling rubber now?
- \* What type of material is being recycled?
- \* How much material is being recycled?
- \* Is it post-consumer or in-process scrap?
- \* What is its ultimate utilization?
- \* What are the supplier's future plans for increased recycling?

These questions were to be asked of the appropriate people within the organization to assist Ford in its evaluation.

Ford Motor Company, with supplier help, is striving to be the nation's leader in producing recyclable vehicles and in the use of recycled materials. The purpose of this letter is to ensure that you are aware of Ford's commitment to these objectives, and to provide you with information about some of our initiatives. To aid us in accomplishing our goal, Ford has published the "Ford Worldwide Recycling Guideline". This guideline is intended to provide recycling direction to Ford Engineering activities and Program Managers and is made up of three sections: FASTENERS/MATERIAL SELECTION/COMPONENT DESIGN.



**General Motors Corporation- Material Selection Guideline - GM-1000M (excerpt)**

**Material-** Use recycled materials - select materials for which recycling technologies are currently practiced. Use recycled materials - select materials that have been recycled.

**Material Selection-** Use recycled materials, select rubber materials for which recycling technologies are currently practiced. Consider recycling technologies that produce the greatest material value. Investigate thermoplastic elastomers (TPE) as an alternative to thermoset rubber. TPE's are currently easier to recycle than thermoset rubber. They can be reground and reused.

**Recycling options for thermoset rubber.** Regrind - a percentage of reground rubber can be put into parts that do not have stringent performance requirements. Devulcanization - two methods of devulcanizing rubber (chemical and microwave). The resulting material can be put into virgin material in limited quantities. This technology appears to be still in the development stage.

**Use of recycled materials.** Select rubber materials that have recycled content. Automotive grade thermoset rubbers used for weatherstrips, motor mounts, tires, hoses, belts, seals and gaskets do not currently contain recycled material. Thermoset rubber parts such as mats and truck bed liners can be made with a percentage of reground rubber material. Automotive grade TPE's could contain reprocessed plant scrap.

These excerpts make it clear that, these goals will energize the participants to seek solutions utilizing existing technologies to recover as much as is "currently feasible" using recycling capacities and technologies, and in addition, press for new and innovative solutions from new developing technologies.

There are several emerging recycling technologies now in development that will add significantly to the achievement of pre- and post-consumer rubber recycling goals now being set by the automotive industry. They include new surface treatment technologies applicable to ground rubber particles to substantially improve adhesion, wetting, processing and bonding.

This on-going work includes polymeric surface coatings now being promulgated by both U.S. and European companies, along with a recently developed technology carried out under Department of Energy sponsorship which exposes recycled rubber particulate to a reactive chlorine gas mixture that chemically alters the surface of the rubber particles. At present, surface treatment particulate is being

evaluated for use in a wide variety of automotive applications that, based on initial test results, will most certainly benefit the automotive goals for increased recycled rubber usage in the coming decade.

As can be seen from the "estimated recyclable materials in a 2400 pound vehicle" (Figure 3) we have 140 pounds of post-consumer rubber as a target, plus the manufacturing waste generated to produce these components. If the often stated goal is to achieve 25% rubber recycling content in automotive components (i.e. 35 pounds per automotive unit) this would result in an annual requirement for recycled rubber material supply of approximately 375 million pounds. This will create a substantial new market opportunity for recycled rubber materials and emerging technologies over the next decade.

### **Footwear Uses**

Typical of several newly emerging ground rubber/molded rubber applications in which work is now being successfully completed, is in the footwear industry. Here the emphasis is on the development of both thermoplastic and thermoset compounds utilizing finely ground rubber in a wide assortment of shoe sole and construction components at significant incorporation levels ranging from 20-50% of finely ground scrap tire rubber crumb. This emerging usage is being heralded by the footwear industry as a means to capture USA based market share, in response to a concerned buying public for increased usage of recycled materials in acceptable product applications.

Such a program is exemplified by a new shoe company founded for the purpose of making a product entirely from recycled materials. Figure 4 shows a shoe sole fabricated by the company with the use of up to 50% of post-consumer scrap tire rubber to produce a sole that meets or exceeds all industry standards for wear, comfort and performance. We are currently seeing such activities throughout the footwear industry, suggesting that a major market potential is developing for substantial usage of ground rubber in both thermoset and thermoplastic molded shoe components. The United States' annual market for shoes totals approximately 1.2 billion pairs. The average shoe sole weights between 0.75 and 1.0 pound per shoe sole.

The "comfort shoe" portion of this total USA market is the initial area in which ground rubber is now being incorporated. This market totals between 375 to 425 million pairs. In addition, work is also progressing successfully in "work shoe" applications.

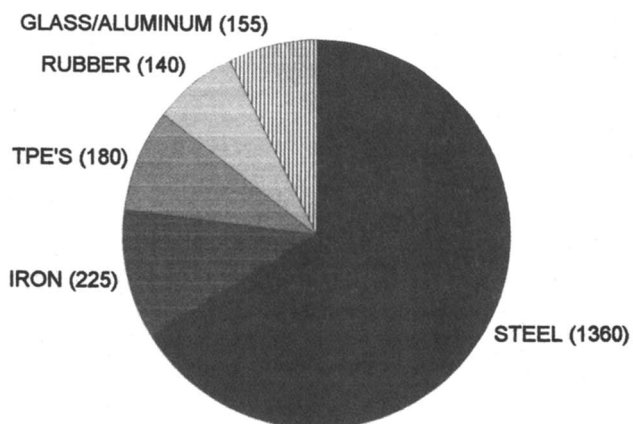


Figure 3. Estimated recyclable material in a 2400 pound vehicle.



Figure 4. Shoe sole derived from post-consumer scrap tire rubber. (Courtesy of Deja Shoe Company.)

With ground rubber incorporation at only a 20% level, this would represent an annual usage of between 120 and 150 million pounds per year. Currently we have reports of a number of shoe sole manufacturers at the 25% level and higher.

The shoe sole in Figure 4 has a 50% incorporation level of recycled rubber and meets or exceeds all abrasion, durometer, scuff-mark, other performance and quality requirements to satisfy the market place for a quality comfort shoe sole at a competitive cost. Thus, the shoe sole market is confirming that the use of recycled rubber particulate can provide excellent results while using a much higher incorporation level without sacrificing quality and performance.

These results truly exemplify the goals of a successful rubber recycling industry.

**Innovation** - utilizing new recycling technology.

**Quality** - maintaining customer demands for quality.

**Performance** - at no sacrifice in performance.

**Cost effective solutions.**

### **Tires**

In further response to these automotive industry goals for recycling, we continue to believe that the tire industry based on work from an earlier study and presented at the Rubber Division, ACS meeting held in Washington, DC (October 1990; Paper No. 15) (3); has an excellent potential for cost savings and increased recycled rubber usage without a sacrifice in overall tire performance (4). We have excerpted from the referenced study, several tables in support of our conclusions.

This data is summarized in the following charts:

Tire Components-Ground Rubber Usage (Table II)

Passenger Tire Usage (Table III)

Cost Savings per Unit (Table IV)

Potential Cost Savings at 5% and 10% (Table IV)

Raw Material Savings (Figure 6)

Table II which sets forth the specific tire construction elements of a passenger tire (Figure 5) in which recycled rubber can be utilized, reflects a consensus of experienced tire manufacturing technologists and current tire performance manufacturing processing capabilities.

The resulting minimum incorporation levels of recycled rubber as applied to the selected components results in a projected usage level per average passenger tire of between 2.3 to 3.6% of the tire weight (Portrayed in Table III). This translates into

Table II. Passenger Tire Components in which a Fine Particle Size Ground Rubber can be used

	<u>Bias</u>	<u>Radial</u>
INNERLINER	YES	YES
PLYCOAT	YES	YES
BEAD INSUL	NO	NO
CHAFER	YES	NO
APEX	YES	NO
COVERSTRIP	NO	NO
BLACK SIDEWALL	YES	NO
WHITE SIDEWALL	NO	NO
BELT	YES	NO
TREADCAP	YES	YES
UNDERTREAD	YES	NO

Table III. Passenger Tire Usage of Finely Ground Rubber at 5%

<u>Component</u>	<u>%</u>	<u>% Ground Rubber</u>	<u>Bias</u>	<u>Radial</u>
TREAD	29	5	1.45	1.45
UNDERTREAD	6	5	-	-
CARCASS	8.5	5	.43	.43
LINER	8.5	5	.43	.43
BLACK SIDEWALL	11	5	.55	-
BEAD INSULATION	1	-	-	-
CHAFER/APEX	8	5	.40	-
BELT	7	-	-	-
			<u>3.26%</u>	<u>2.31%</u>
TIRE WEIGHT			20	20
POUNDS GROUND RUBBER PER TIRE			.65#	.462#

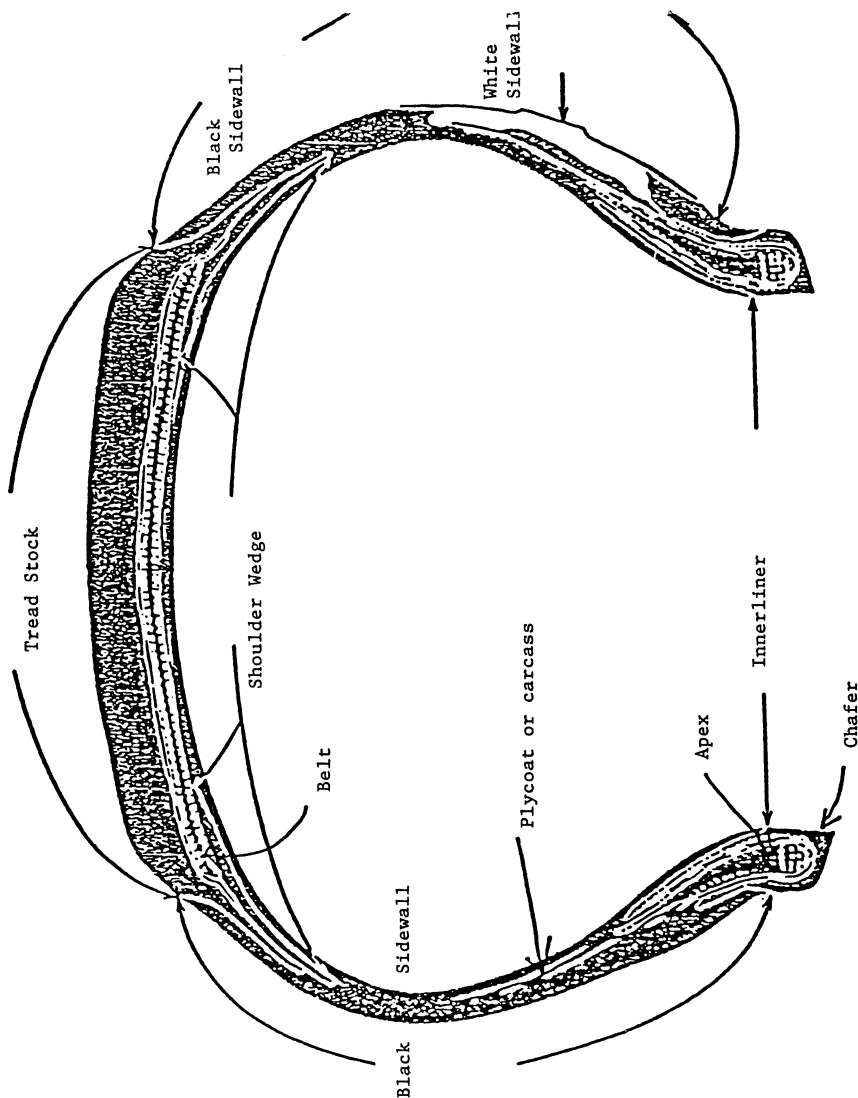


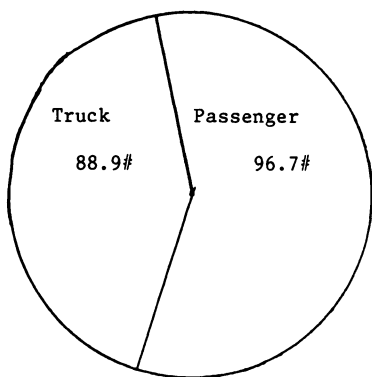
Figure 5. Cross section of passenger tire.

August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch018

**Table IV. Cost Savings per unit using Finely Ground Rubber at 5% & 10%**

<b>Percent</b>	<b>Passenger Tires</b>	<b>Truck Tires</b>
<b>5%</b>	<b>\$0.0980</b>	<b>\$0.5424</b>
<b>10%</b>	<b>\$0.1861</b>	<b>\$1.031</b>

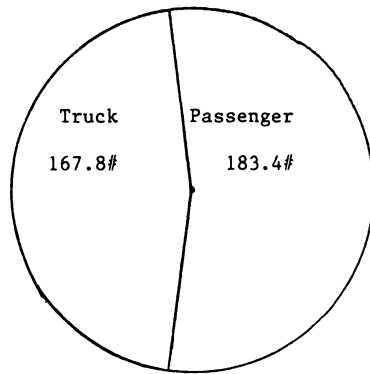
**Based on oil at \$20/barrel**



**AT 5%**

**185 Million pounds**

**Equals approximately:  
15 million tires recycled**



**AT 10%**

**370 Million pounds**

**Equals approximately:  
30 million tires recycled**

**Figure 6. Potential raw material savings using finely ground rubber added at 5% and 10%.**

an economic benefit based on typical costs for the substituted recycled rubber of approximately \$.10 to \$.18 per passenger tire and approximately \$.50 to \$1.00 per truck tire. This cost benefit to the producer could readily support the cost of developing the final compounds, processes and performance tests required to increase the usage of recycled rubber material back into tires and to increase the post-consumer rubber waste recovery being sought by the automotive industry.

Such a program could add some 180 million pounds to the ground rubber annual usage forecast (Figure 6). One very promising and logical place to start would be in the tread area of the mini-spares.

### **Promising New Technologies**

There are several promising new technologies emerging to provide improved recycled rubber choices to the product designer, compounder and manufacturer of rubber goods. These choices now include finer particle sizes, several surface treatments and several thermoplastic elastomer materials which have successfully incorporated recycled rubber at substantial levels using vulcanized finely ground rubber particulate from tires and pre-consumer waste rubber to deliver uniform properties and consistent quality for the manufacture of automotive and footwear components.

Added to these now commercially available technological innovations are several more recent developments in devulcanization of polymers with improved properties over those of the long established "reclaimed" rubbers produced by vintage technologies dating to the 1940's.

The devulcanization technologies employed include both dry and wet chemical processes and ultrasonics. Each of these are claiming improved costs, acceptable environmental operating conditions and higher performance properties than those of the reclaimed materials currently produced.

These preliminary claims will be tested and confirmed by a growing desire to add such material to the recently expanded family of useful recycled rubber materials available to meet a growing demand for recycled rubber materials that can provide quality, performance and potential cost benefits to the markets now served by the rubber industry.

### **Current and Future Market Outlook**

As displayed in Table V, Figures 7 and 8, we foresee a dramatic increase in the usage of ground rubber



**Table V. Forecast of Ground Rubber Crumb Usage in USA by Year 2003**

<b>Category</b>	<b>Millions of Pounds</b> <i>(See Figure 7)</i>	
<b>ASPHALT RUBBER AND HIGHWAY APPLICATIONS</b>	<b>420</b>	<b>38%</b>
<b>TIRES - PNEUMATIC/RETREAD MATERIALS AND OEM AND REPLACEMENT PASSENGER AND TRUCK</b>	<b>115</b>	<b>10%</b>
<b>SHOE SOLES-FABRIC AND COMPONENTS - ALL TYPES OF FOOTWEAR</b>	<b>155</b>	<b>14%</b>
<b>AUTOMOTIVE/APPLIANCE AND OTHER MOLDED GOODS/AUTOMOTIVE, ETC.</b>	<b>165</b>	<b>15%</b>
<b>CARPET, FLOORING, ROOFING, PADDING, ATHLETIC SURFACE AND CONSTRUCTION MATERIALS</b>	<b>155</b>	<b>14%</b>
<b>ALL OTHER APPLICATIONS INCLUDING PLASTIC, RUBBER MATERIALS</b>	<b>105</b>	<b>9%</b>

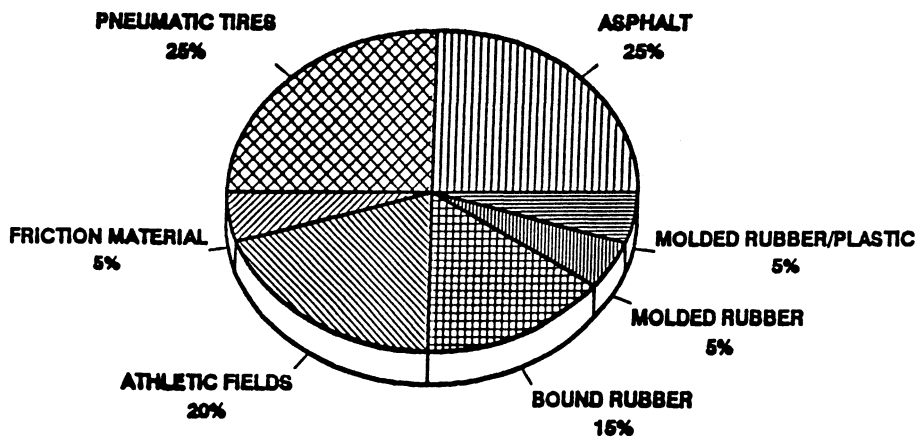


Figure 7. Year 1993 ground rubber usage (est. 200 million pounds volume).

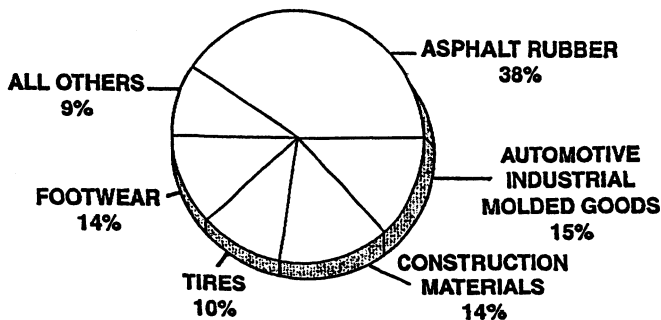


Figure 8. Year 2003 projected ground rubber potential usage.

particulate from the current estimate of 200 million pounds to over 1.1 billion pounds, driven by a diverse set of new technology driven applications in automotive, highway construction, building products, footwear, tires and plastic rubber compounds.

These projected usages clearly display a need for a rapidly expanding quality recycled rubber material to meet the market potential for cost effective and performance driven solutions. This presents both an opportunity and a challenge of substantial proportion to this growing industry.

In summary, as we review the rubber recycling progress being made, most impressive is the broad base of current activity at all levels of the system to promulgate solutions to meet the rubber recycling challenge of our industry and our nation.

### Literature Cited

- 1 Ball, J. M., in *"Vanderbilt Rubber Handbook"*, R. T. Vanderbilt Co., Norwich, Ct., 1978.
- 2 Smith, F. G. and Klingensmith, W., *Paper No. 15*, Presented at the Fall Meeting of the Rubber Division, American Chemical Society, Washington, D.C., October 9, 1990.
- 3 *"Fine Particle Rubber Technology: Butyl Rubber"*, Midwest Elastomers Inc., 1990.
- 4 Eckart, D., *Modern Tire Dealer*, June, 1980.

RECEIVED May 26, 1995

## Chapter 19

# Olefinic Thermoplastic Vulcanizates: Impact on Rubber Recycling

Marc T. Payne

Advanced Elastomer Systems, L.P., 388 South Main Street,  
Akron, OH 44311-1058

Olefinic thermoplastic vulcanizates (O-TPVs) are widely used by manufacturers to produce classical "rubber" parts instead of using thermoset rubbers. The rapid growth of O-TPVs and their widespread use in industries such as automotive, appliance, business machines, medical, fluid delivery and wire & cable, among others has made them an important rubber material. O-TPVs are melt processable and have demonstrated outstanding retention of performance properties after regrinding or recycling of post-consumer parts. As a result, this class of materials offers an excellent opportunity for the rubber parts manufacturer or end-user to produce parts and systems designed for post-consumer recycling into a variety of uses.

### Recycling Background and Importance to Society

**Recycling as an issue for plastics.** The importance of recycling of all consumable materials has intensified in recent years as the cost, ease of access and societal acceptance of throwing consumable trash away in landfills has changed. The EPA reported that within the United States there was 180 million tons of solid waste generated each year. Approximately 80% of this waste goes to landfills (1), 10% is recycled and 10% incinerated. The United States recycled approximately 500,000 tons (2) of the estimated 14.4 million tons (about 8%) (3) of plastics contained within the municipal solid waste stream. By 1998 the number of existing landfills is expected to decline to about 3000 (3) versus 6000 in 1991, 9000 in 1989 and 18,000 in 1976. This decrease in the number of legal landfills has become a driving factor in the increase of recycling post-consumer plastics.

The other factor is societal; throughout the U.S., Europe and Japan, new legislation regarding the banning of plastics, required recycle content, etc. (3) is indicative of the desire by consumers to reduce the amount of solid waste placed in landfills.

0097-6156/95/0609-0221\$12.00/0  
© 1995 American Chemical Society

There has been and continues to be a tremendous investment in the capability to recycle plastic materials. Ernst & Young indicates the U.S. plastics industry will invest more than \$1.2 billion in plastics recycling between 1990 and 1995 (4). However, the focus of much of this effort is in recycling packaging materials, such as plastic bottles, containers, wraps and films made from polyethyleneterephthalate (PET), low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS).

Additionally, people are focusing on recycling polyvinyl chloride (PVC) from non-municipal solid waste streams. Because of the quantity of these plastics in the municipal solid waste stream, visibility of the problem and a developing economic infrastructure to reclaim these materials has developed. As an example, a recovery facility constructed in Medina County, Ohio targeted the following materials for removal from solid waste and marketed as recyclable: newspapers, miscellaneous hi-grade paper, corrugated paper, household cans, aluminum cans, bi-metal cans, HDPE plastic, PET plastic, ferrous metals and miscellaneous copper and aluminum. The collection of these materials is facilitated by the curbside collection programs which now exist in many cities throughout the U.S. The distribution of post-consumer plastic waste is projected to be 87% thermoplastics, 8% thermosets and 5% polyurethanes by the end of the decade (5).

Another source of potentially recyclable materials is contained within durable goods, those items that have useful lives of three or more years. These items include motor vehicles; appliances (including business machines, refrigerators, dishwashers, washing machines, etc.); electronic devices; construction materials such as glazing seals, flooring and wall covering; wire & cable insulation and jacketing; and furniture. The pressure to recycle the plastics materials in these items, especially in vehicles, continues to increase. Some German auto producers were the first to establish an infrastructure for the dismantling of vehicles after their useful life, with the intent to reuse the recyclable materials. A vehicle disassembly center in Highland Park, Michigan, was announced in 1993 by Vehicle Recycling Partnership, a consortium of General Motors, Ford and Chrysler. (6) There are approximately 13 million vehicles (7) scrapped each year in the US. It is estimated there are 700,000 MT of plastics contained (8) within those scrapped vehicles.

These sources and the potential of economically viable recovery methods indicate the time is now to expand the recycling of plastics materials to not only those commodity plastics listed previously but also to any material that possesses the inherent chemistry and stability to be recycled.

**Recycling of thermoset rubbers.** With the potential for recycling plastic materials from durable goods, there also is the problem or opportunity to reuse the thousands of tons of thermoset rubber used to make these goods. Recycling of used tires from vehicles has been practiced to some degree for many years. Although only a small fraction of tires are recycled as tires for retreading. The more common routes of recycling tires consist of some type of processing or pyrolysis step to reclaim the vulcanized rubber as a powder for use in flooring, paving materials, etc. or conversion into fuel (9). Pyrolysis is a useful process only in the reduction of the volume of waste since this process destroys the rubber and leaves only ash and carbon black.

Much less developed is the recycling of all the other thermoset rubber parts used in vehicles and other durable goods. It is estimated that there is an average of approximately 15 kilograms of rubber (excluding tires) on cars and 12 kilograms on light trucks. Forecasters predict that by 1998 (10) there will be more than 41 million cars produced worldwide, with more than 14 million in Western Europe, more than 8 million in North America and at least 9 million in Japan. On a global basis this amounts to 615,000 metric tons of non-tire rubber parts on cars alone.

Unfortunately, recycling of all these rubber parts is impaired by the preponderance of the parts having been produced using thermoset rubbers. Thermoset rubbers have the same difficulty as thermoset plastics, such as melamine or a phenolic resin; a chemical change is necessary to break down the three dimensional network of the material to be recycled.

Therefore, for non-tire thermoset rubber parts the same reclaim outlets that are used for tires are the most viable options. Unlike tires, though, the rest of the rubber parts used in vehicles, appliances and other durable goods tend to be small and are often bonded to other materials such as metal.

There are other problems associated with reclaiming thermoset rubber. (11) The processing to reclaim the rubber involves devulcanization by chemical digestion, which generates some toxic byproducts that must be discarded. The market for rubber reclaim also has declined to 5% of new rubber in 1985 from 32% in 1941. This trend is expected to continue (11). The economical recovery of these parts for useful reclaim value is a much greater challenge.

There is another class of materials used to make rubber parts in vehicles today: thermoplastic elastomers (TPEs). Total TPE usage in the global market is approximately 600,000 metric tons (12), with the automotive market currently using about 200,000 metric tons. About 70% (12) of the TPEs used in autos are thermoplastic olefins (TPOs) and olefinic thermoplastic vulcanizates (O-TPVs). The recycle of thermoplastic elastomers simply requires the material to be melted and resolidified. There is little chemical change, particularly for the majority of olefinic-based TPEs, so the materials are more likely to provide greater utility and value. The major problem with recycling rubber parts of O-TPVs is logistical, not technical, because of the need to disassemble component parts of durable goods, separate and segregate them by composition and clean them. These are challenges, however, that were addressed in the successful recycling of plastic packaging materials. Similar approaches can be used for reclaiming thermoplastic rubber parts.

### **Relative Importance of O-TPVs**

Thermoplastic elastomers have experienced outstanding growth in the last decade with an annual growth rate of 7% to 8% (13). They now have approximately 12% of the non-tire rubber market (or about 600,000 MT). One of the fastest growing of the TPE materials is olefinic thermoplastic vulcanizates (O-TPVs) a class of products first commercialized in 1981 by Monsanto Company. These materials are now widely used in a number of markets, including automotive, appliance, wire & cable, medical, fluid delivery and a variety of industrial rubber parts.

In the automotive market reports suggest that TPE usage will increase to 6.5 kg per car by 1995 (13). The increase in utilization of TPEs has occurred because of design goals by the auto makers to reduce vehicle weight; new safety devices such as air bags; aesthetic changes with soft touch interiors; noise reduction; higher under-the-hood operating temperatures; and a growing understanding of the design capability inherent with thermoplastic elastomers in systems design in combination with rigid thermoplastics. A newer growth opportunity is the greater ease of recycling automotive rubber parts produced from TPEs as compared to conventional thermoset rubber.

Thermoplastic polyolefins (TPOs) and O-TPVs represent the largest segment of TPEs used in the automotive industry (14) and in the appliance, fluid delivery and other durable goods industries. Olefinic plastics such as polypropylene (PP) are also used in increasing quantities in the automotive and other industries. One of the reasons for this increased use is weight savings compared to styrenics such as acrylonitrile butadiene styrene (ABS) and polyamides (nylon). The increased volume of polypropylene and greater worldwide use of TPOs in bumper systems encourages the greater use of olefinic TPVs because of compatibility during reclaiming for recycling.

Table I gives examples of automotive parts that utilize O-TPVs and Table II lists examples of appliance parts.

**Table I. Examples of Automotive Parts Produced with O-TPVs**

Weather-strip (secondary and primary)	HVAC connectors
Air bag door covers	Lamp housings and seals
Acoustic barrier	Body plugs
Rack and pinion steering gear bellows	Strut covers and bellows
Constant velocity joint boots	Clean and dirty air ducts
Wire insulation	Trilobal seals
Interior skins	Suspension bushings
Vacuum connectors	Fuel line covers

**Table II. Examples of Appliance Parts Produced with O-TPVs**

Disk drive seals	Business machine feet
Dishwasher sump boot	Dryer drum roller
Compressor mounts	Door seals
Water line connectors	Button traps

Olefinic TPVs have performance properties that allow them to replace polychloroprene (CR), ethylene-propylene-diene modified (EPDM), natural rubber (NR), styrene butadiene rubber (SBR), epichlorohydrin (ECO), halobutyl rubber and chlorosulfonated polyethylene rubber (CSM). This wide range of performance with a material that has polypropylene as its thermoplastic component make this class of materials extremely important to the future of increasing the recycling opportunity of rubber parts in durable goods.

The Society of Automotive Engineers (SAE) have established a marking and identification system which will facilitate the ease of recycling rubber parts produced from O-TPVs. SAE J 1344 (15), which was developed for classifying rigid thermoplastics, has categories for each generic class of commercial TPE for recycling. Two or more different TPEs or rigid thermoplastics would be compatible for reclaiming together, simplifying the recycling operation. As an example, TPOs and O-TPVs are in the same recycle category, thus it is possible to recycle rack and pinion boots made from O-TPVs with bumpers or fascia made from TPOs. The value of this approach is greater than the ease of reclaiming and recycling the material.

Such a recycled combination can give a range of materials with rubber performance ranging from virgin O-TPVs to enhanced TPO performance. These useful properties are obtained from materials that would otherwise be discarded to the environment.

### **Description of Olefinic Thermoplastic Vulcanizates (O-TPVs)**

**Thermoplastic Elastomers.** Olefinic thermoplastic vulcanizates are one of a class of materials called generically thermoplastic elastomers (TPEs). These materials combine the functional properties of comparable thermoset elastomers with the fabrication advantages of thermoplastics, including the ability to remelt a formed part. Thermoplastic elastomers are defined by ASTM D 1566 as a "family of rubber-like materials that, unlike conventional vulcanized rubber, can be processed and recycled like thermoplastic materials". A rubber is defined (16) as a "a material that is capable of recovering from large deformations quickly and forcibly,..." and "retracts within 1 min. to less than 1.5 times its original length after being stretched at room temperature (18 to 29°C) to twice its length and held for 1 min. before release". There is a variety of TPEs - such as the block copolymers of styrenics, copolyesters, polyurethanes, polyamides, TPOs (blends of EPDM and polypropylene as an example) and TPVs. This chapter will focus on O-TPVs and TPOs.

The elastic properties of a thermoset rubber result from long, flexible molecules that are coiled in a random manner and are crosslinked. When these molecules are stretched they uncoil and have a more specific geometry than the coiled molecules. The uncoiled molecules have lower entropy because of the more restricted geometry and, since the natural tendency is an increase in entropy, the entropic driving force is for the molecules to retract, giving elasticity. (17)

The primary morphological difference between O-TPVs and thermoset rubbers is the presence of soft, crosslinked rubbery domains bonded to hard thermoplastic domains that have a distinct melting point above which the O-TPV is melt fabricable. Most O-TPVs have PP as the thermoplastic matrix and this matrix can be reformed repeatedly through the simple application of heat and shear energy with insignificant or only minor losses in performance. Thus, the "crosslink" sites of the total material are reversible. The completely vulcanized rubber phase behaves as classical crosslinked rubber. When acted upon by an external stress, the initial deformation occurs in the rubber phase because it is softer and requires lower stress for displacement. This behavior gives elastic or rubbery performance up to the point where the strain level is so great that it exceeds the yield stress of the plastic phase. The structure or morphology of O-TPVs is such that quite a large deformation is needed before permanent deformation occurs.



Therefore, O-TPVs perform equivalently or better than thermoset rubbers such as EPDM, CR, NBR, etc. in classical rubber applications.

The primary growth of O-TPVs involves the replacement of conventional thermoset rubbers. Table III shows the replacement opportunities for O-TPVs and TPOs for thermoset rubbers.

**Table III. Substitution Areas of Thermoset Rubbers**

<u>Thermoset rubbers</u>	<u>O-TPVs</u>	<u>TPOs</u>
Styrene-butadiene rubber (SBR)	X	X
Natural rubber (NR)	X	X
Butyl rubber (IIR)	X	
Ethylene-propylene diene modified (EPDM)	X	
Chloroprene (CR)	X	
Chlorosulfonated polyethylene (CSM)	X	
Nitrile rubber (NBR)	X	
Epichlorohydrin (ECO)	X	

In many applications O-TPVs replace thermoset rubbers because they offer equivalent or better performance, generally with a significant cost savings resulting from part-fabrication-cost advantages. There can be even greater cost savings and enhanced ease of recycling by redesigning a thermoset rubber part to exploit the performance of the properties of the O-TPV and when needed combining with a compatible rigid polyolefin.

The design flexibility of O-TPVs has resulted in rubber applications previously nonexistent because of the design and fabrication limitations of thermoset rubbers. The primary design advantages come from the tighter dimensional tolerance capability of O-TPVs, capability of heat welding to a compatible thermoplastic, and/or using fabrication processes such as insert injection molding, dual injection molding, dual (A-B or A-B-A) blow molding, and multi-extrusion.

Olefinic TPVs cannot replace conventional thermoset rubbers in every application. As with any material there are advantages and disadvantages.

**Advantages of O-TPVs Compared to Thermoset rubbers:**

1. There is little to no compounding or mixing required for O-TPVs. Unlike thermoset rubbers that require mixing of curatives, stabilizers, process aids, and other additives, O-TPVs are fully compounded and ready for fabrication into parts. Part-to-part consistency is improved because there is no compound difference that can result from variations in weighing and metering of ingredients. O-TPVs have a better total environmental impact because there is less loss of scrap material compared with thermoset rubber compounding.

2. The total processing operation is simpler for O-TPVs and has fewer steps than the processing operation for thermoset rubber. Because there is no mixing operation or vulcanization step with O-TPVs the cost of a part can be lower. The reproducibility of part fabrication can be better, which potentially reduces the number of reject parts.
3. Thermoplastic fabrication processes typically have shorter cycle times (i.e. injection molding of a thermoplastic vs. compression molding of a thermoset rubber compound) and no need for vulcanization. Generally rubber-processing cycle times are measured in minutes, whereas those for O-TPVs are measured in seconds. The production rate for O-TPV parts is generally much faster than that of a corresponding thermoset rubber part.
4. During the manufacture of the part, O-TPV runners, sprues, start-up material and off-spec parts can be reground and reprocessed with no significant loss in performance. Thermoset rubber process scrap is much less reprocessable and generally requires disposal at landfills.
5. Thermoplastic fabrication processes use less total energy because of more efficient processing, shorter cycle times and the lack of a vulcanization step.
6. Thermoplastic processes are more suitable for high-speed automation and are amenable to robotic assistance vs. thermoset rubber processing which is typically more labor intensive.
7. Thermoplastic fabrication processes such as blow molding, heat welding and thermoforming are not possible with thermoset rubbers. These processes offer the opportunity of better part design, tolerance and the combination of the O-TPV rubber part with a rigid thermoplastic.
8. Because there are fewer steps in part fabrication, part quality can be better and the cost of quality control is less for O-TPV rubber parts.
9. O-TPVs are lower in density than competing thermoset rubber compounds, so a greater number of parts per kilogram of material can be produced, which reduces part cost and facilitates part reclaiming for recycling.

#### **Disadvantages of O-TPVs versus Thermoset Rubbers:**

1. Olefinic TPVs are still a relatively new material so many rubber-parts designers are unfamiliar with the materials' performance and capabilities; therefore there are many parts which could be made from O-TPVs instead of thermoset rubbers which are not today because of a lack of knowledge.
2. Thermoplastic fabrication equipment is different from that typically used by the classical thermoset rubber part producer, which creates the need of a capital investment to process O-TPVs.

3. To replace existing rubber parts made from thermoset rubber, there has to be sufficient volume to recover the investment in a new thermoplastic mold or extrusion die. Thermoplastic injection molds typically cost more than thermoset rubber injection or compression molds because of the higher clamp pressures used and devices for stripping the parts out of the mold automatically.
4. There are fewer O-TPVs below 45 Shore A hardness, although most applications do not require such soft materials.
5. There are upper temperature limits for O-TPVs above which they do not function as rubbers. For O-TPVs based on polypropylene, that temperature varies from about 110°C to 135°C depending on compressive or tensile load, or retention of physical properties.
6. Many O-TPVs require drying before processing into fabricated articles because they are slightly hygroscopic.

The suitability of an O-TPV in any given rubber application must be determined by comparison of these advantages and disadvantages. There are applications that always will require the use of thermoset rubber materials. However, there are thousands of applications that have been converted to O-TPVs and many thousands more that can be converted.

Many of the successful O-TPV applications that exist today are a result of the end-user of a rubber part being convinced of the improved performance, greater design options, lower cost and capability of recycling the post-consumer part than possible with thermoset rubber materials.

**Chemistry of O-TPV.** Olefinic TPVs are a class of TPEs which are a combination of two or more polymers that produce an alloy having better elastomeric (rubbery) properties than that of a simple blend of the two materials (18). Example of blends are found with the class of materials referred to as TPOs. O-TPVs are composed of a rubber phase that is completely vulcanized during a process called dynamic vulcanization, and a plastic phase. A TPO blend either is not crosslinked in the rubber phase or has a very low level of crosslinking.

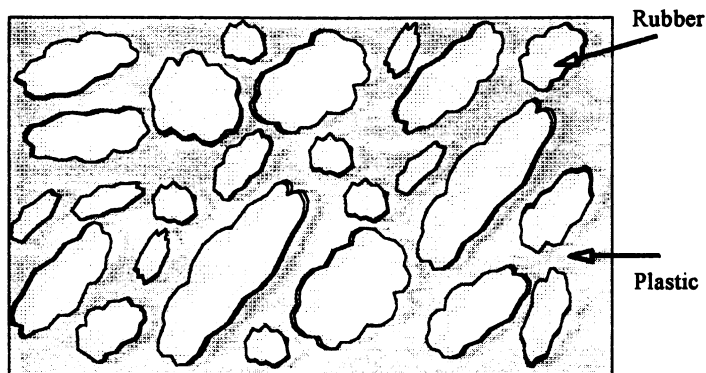
The plastic phase of both the materials is normally polypropylene (PP) but could be HDPE, LDPE or any other polyolefin. Through dynamic vulcanization of the elastomer in the presence of a compatible thermoplastic or an incompatible thermoplastic with a compatibilizer, there is a bonding that occurs between the rubber phase and the plastic phase with the formation of a stable morphology (19). The synergistic result of the alloying of a two-phase system vs. an uncrosslinked blend is shown in Table IV.

These data illustrate the differences between a blend of EPDM and PP and a dynamically vulcanized O-TPV made from the same composition. The crosslinking and alloying process increases the tensile strength by more than three times that of the uncrosslinked TPO system. Similar improvements in performance are seen in compression set, tension set and resistance to oil swell.

**Table IV. Comparison of O-TPV and TPO With the Same EPDM/PP Ratio**

Property	O-TPV	TPO
Hardness, Shore A	84	81
Ultimate Tensile Strength, MPa	13.1	4.0
Ultimate Elongation, %	430	630
100% Modulus, MPa	5.0	2.8
Compression Set, %	31	78
Tension set, %	14	52
Swell in ASTM #3 oil, wt. %	52	162

Another feature of O-TPVs vs. TPOs is the stability of dispersed-rubber-phase morphology. Uncrosslinked or partially crosslinked TPOs have either a dispersed-rubber-phase morphology or, depending on the plastic/rubber ratio, a co-continuous system exists. The uncrosslinked rubber particles of a blend can coalesce after removal of temperature and shear. In an O-TPV the rubber particles have been crosslinked while dispersed in the molten thermoplastic matrix and can not reaggregate. The surface area of the finely dispersed rubber particles enables them to interact intimately and synergistically with the thermoplastic olefin matrix to give a highly elastomeric composition. The vulcanized rubber particles are generally elliptical in shape and range from approximately 1 to 5 micrometers in diameter. A graphical depiction of this morphology is shown in Figure 1.

**Figure 1: Graphical Depiction of O-TPV Morphology**

The smaller the average rubber particle size, the better the stress/strain properties and rubber characteristics of the O-TPV. The mechanics of this system, where there are finely dispersed, fully vulcanized rubber particles with a high packing density in a olefinic thermoplastic matrix, gives true elastomeric performance.

The bulk characteristics of an O-TPV are essentially those of the thermoset rubber used as the elastomeric phase. The elastic limit of the thermoplastic phase only

indirectly limits the elasticity of the O-TPV because of the included rubber phase morphology and the small thickness of thermoplastic material between the crosslinked rubber particles. When a tensile or compressive stress is applied to the O-TPV system, the stress is transferred from the stronger plastic phase to the weaker, but more-elastic rubber particulate, resulting in strain of the rubber particle in the direction of tensile stress or perpendicular to compressive stress. The spatial disturbance of the thermoplastic phase is minimal because of the small thickness of the thermoplastic matrix around the dispersed rubber particles. Because there is sufficient bonding of the rubber particulate to the thermoplastic matrix, there is little or no permanent deformation resulting from deformation at the rubber/plastic interface.

### Case Study of Recycling Olefinic TPVs

A study to determine the practicality of post-consumer recycling of O-TPV rubber parts has been reported (20). That study is an excellent example of actual TPE part recycling.

To study the O-TPV recycle capability, several criteria were established to select an appropriate raw material source:

- the O-TPV rubber part service life was longer than 5 years;
- the part had been exposed to a demanding service environment;  
and
- it was feasible for the part to be dismantled and recovered.

It was decided these criteria could be met in a rack and pinion automotive steering gear bellow, an application that has used olefinic TPVs since 1983.

The part is subjected to the underhood environment, including road dirt, salt, grit, water, etc., and also internally is exposed to a combination of greases necessary for the function of the rack and pinion steering gear. The O-TPV part studied was produced from Santoprene® thermoplastic rubber 103-40, a Shore hardness 40 D, black general purpose O-TPV. The reclaimed steering gear bellows were supplied by TRW Remanufactured Steering Systems Ltd. (UK). To evaluate the potential afforded by O-TPVs and TPOs having the same recycle classification, blends of O-TPV recycle with virgin TPO also were examined.

Once the parts were recovered there were several process steps in order to assess the value of the O-TPE recycle:

- cleaning of the steering gear boots;
- grinding of boots to a usable granulate;
- blending of the granulate with virgin material;
- pre-drying the granulate prior to processing;
- injection molding the dried granulate into test pieces.

Once the parts were gathered a cleaning technique was developed. The parts typically had as much as 20% by weight contamination. In addition, steering gear bellows have a convoluted shape that is a difficult geometry to clean properly. Several part-cleaning techniques were evaluated, including:

- manual cleaning plus various aqueous cleaning agents to 60°C;
- industrial washing machine and cleaning agents at 90°C;
- ultrasonic cleaning bath plus cleaning agent at 60°C; and
- high-pressure hot water and steam at 110°C and 100 bar.

The high-pressure, hot water and steam technique was chosen because there was no need for aggressive cleaning agents or solvents; the process produced minimal effluent and it was the best technique for getting the parts clean, as assessed by visual examination and comparison of physical properties. A comparison of the cleaning techniques is given in Table V.

**Table V: Cleaning Techniques - Comparison by Physical Properties**

<u>Property</u>	<u>Steam + Water</u>	<u>Other Cleaning Techniques</u>
<b>1. Unaged</b>		
Hardness, Shore D	36	37
Tensile Strength, MPa	13.9	13.4
Elongation at break, %	570	540
100 % Modulus, MPa	7.4	7.4
<b>2. Heat Aged</b>		
Hardness, Shore D	41	37
Tensile Strength, MPa	14.5	13.9
Elongation at break, %	530	515
100 % Modulus, MPa	8.7	8.6
<b>3. Oil Aged</b>		
Hardness, Shore D	21	21
Tensile Strength, MPa	10.4	10.0
Elongation, %	330	310
100 % Modulus, MPa	6.4	6.3

Regrinding O-TPV parts is a typical process used in reclaiming in-process scrap such as runners and sprues from injection molding operations and trim pieces from blow molding parts such as the rack and pinion bellow. The type of granulator used in this study is typical and worked well for the 40 Shore D O-TPV.

The granulator used had three rotating blades running at 400 rpm over two fixed blades; feed inlet dimensions of 300 by 150 mm; and a mesh size of 8 mm. Dried and wet boots were satisfactorily ground at a rate of 2 kg/min.

To evaluate the range of recycle potential of incorporating O-TPV recyclate as 100% reclaim into a part and blending the O-TPV recyclate with a TPO, a range of blend compositions were studied. The blend ratios are given in Table VI. The TPO was Vistaflex™ Thermoplastic Elastomer 911B. The virgin hardness and 100% modulus of the TPO and O-TPV were similar.

**Table VI: Blend Test Matrix**

Blend #	Recylate % by weight	O-TPV % by weight	TPO % by weight
1	0	0	100
2	30	0	70
3	70	0	30
4	100	0	0
5	0	100	0
6	30	70	0
7	70	30	0

To properly mix the recylate with virgin material, a dry blending method was used that consisted of using a mixer with a simple two bar mixing blade, low speed and a time of five minutes. All material was dried for 3 hrs. at 80°C in a desiccant dryer.

The materials for evaluation were injection molded into a 2-cavity, 3-mm thick by 100-mm by 150-mm plaque mold. The injection molding machine had a clamp force of 175 tons a shot capacity of 340 grams, and was fitted with a 25/1 L/D thermoplastic processing screw. Melt temperatures were set to standard conditions for the virgin materials, which were 230°C for the TPO and 200°C for the O-TPV. The blends were set at proportional intermediate temperatures. The cycle time was 50 seconds. The mold was maintained at 35°C.

Performance properties for the 100% recycled O-TPV blends with virgin O-TPV and with virgin O-TPV are shown in Table VII.

As can be seen in the data, the 100% recylate O-TPV retained 83% of the tensile strength and modulus and 88% of the elongation of the virgin O-TPV, even after 5 years service as a rack and pinion steering gear boot. This slight deterioration in physical properties appeared not to be a result of degradation of the material, but rather some amount of grease absorbed into the O-TPV over this time. This conclusion is supported by the reduction in hardness from 41 Shore D to 37 and reduction in amount of ASTM #3 oil absorbed during oil aging. The virgin O-TPV gains 58 % weight after immersion in ASTM #3 oil for 168 hrs. at 125°C, whereas the recycled O-TPV gained only 50 % weight. Therefore, recylate obtained from parts not exposed continuously to grease or oil would be expected to retain better than 90% of original physical properties.

Table VIII contains the performance properties of blending the recycled O-TPV with a commercial TPO. As one can see from this data even 30% by weight of the recycled O-TPV significantly improves the performance of the virgin TPO in oil resistance. At a 70/30 ratio of O-TPV/TPO the physical properties are improved as well as a significant enhancement in heat aging performance, oil resistance, and compression set resistance. The property improvement in the TPO is basically proportional to the amount of recycled O-TPV added. Therefore, the O-TPV recylate offers the opportunity to be blended with a TPO with increasing performance for the blend. This result opens up many additional opportunities to utilize the recycled material and/or simplifies the collection and reclaiming of the O-TPV rubber parts.

**Table VII: Performance Property Retention of O-TPV Recyclate**

Recyclate, % by weight	0	30	70	100
Virgin, % by weight	100	70	30	0
<b>Unaged (23°C)</b>				
Tensile, MPa	16.8	15.1	14.4	14.0
Elongation, %	640	600	555	560
100% Mod.	9.0	8.6	8.1	7.5
MPa				
Hardness, Shore D	41	40	39	37
<b>Heat Aged (125°C for 168 hrs.)</b>				
Tensile, (% retention)	103	111	106	101
Elongation, (% retention)	93	98	96	92
100% Mod., (% retention)	113	112	116	116
Hardness change, (Shore D)	+2	+3	+4	+4
<b>ASTM #3 Oil Aged (125°C for 168 hrs.)</b>				
Tensile, (% retention)	73	70	71	72
Elongation, (% retention)	58	58	60	60
100% Mod., (% retention)	75	75	70	74
Hardness change, (Shore D)	-26	-21	-21	-18
Weight gain, (%)	58	55	52	50
<b>Compression Set, % (100°C after 22 hrs.)</b>				
	65	65	65	65



**Table VIII: TPO Performance Property Enhancement by O-TPV Recyclate**

O-TPV Recyclate, % by weight	0	30	70	100
Virgin TPO, % by weight	100	70	30	0
<b>Unaged (23°C)</b>				
Tensile, MPa	9.1	9.3	11.1	14.0
Elongation, %	650	630	570	560
100% Mod., MPa	7.6	7.6	7.7	7.5
Hardness, Shore D	37	38	38	37
<b>Heat Aged (125°C for 168 hrs.)</b>				
Tensile, (% retention)	100	102	107	101
Elongation, (% retention)	69	75	86	92
100% Mod., (% retention)	111	111	116	116
Hardness change, (Shore D)	+2	+3	+4	+4
<b>ASTM #3 Oil Aged (125°C for 168 hrs.)</b>				
Tensile, (% retention)	0	53	60	72
Elongation, (% retention)	0	26	39	60
100% Mod., (% retention)	0	57	62	74
Hardness change, (Shore D)	-37	+4	+16	-18
Weight gain, (%)	340	160	90	50
<b>Compression Set, % (100°C after 22 hrs.)</b>				
	85	80	70	65

This study showed that it is feasible to gain a valuable, usable material by recycling rubber parts made from O-TPV after the original part is used for its lifetime. The recycled O-TPV can be used directly, 100%, to produce other rubber parts, or can be recycled with TPOs to produce products with enhanced performance to virgin TPOs.

Additional work still needs to be done to make post-consumer recycling of O-TPV parts a reality, namely the development of cost-effective and environmentally acceptable cleaning processes on an industrial scale, evaluation of blending recycled O-TPV directly with polypropylene to obtain a usable TPO, and an infrastructure to effectively collect material after dismantling automobiles, appliances and other durable goods. The potential is available with O-TPVs to make rubber part recycling a reality.

### Recovery Methods

The challenge to effectively utilize the potential of recycling rubber parts made from O-TPV is the collection and cleaning of post-consumer parts. Today, most of the polymeric material is landfilled because of problems in separating all types of polymer materials. The emphasis has been on PET, HDPE, LDPE and PS from packaging waste streams. The usual method to separate the various materials in waste streams is based on density differences of the materials. Hydrocyclones and other flotation devices are used to separate lighter materials such as PE and PP from heavier materials such as PVC, thermoset rubber and metal.

O-TPVs usually have densities similar to polyolefins and would be in the lighter fraction; therefore, one could easily separate O-TPV rubber parts from thermoset rubber parts. Further refinement of the density method is possible with the use of heavy liquids. Non corrosive heavy liquids based on dispersions of calcium carbonate in water, have been developed to further segregate the heavier fraction of the lighter materials. (21)

Electrostatic separation of plastics also is making advances. A new method overcomes problems of soiled plastics and enables separation of plastics of equal density such as PE and PP, and potentially O-TPVs. The electrostatic separation method has high throughput levels and uses little energy. Purity levels of more than 99.99% have been claimed. This technique is currently being used to reclaim plastic waste from the electronics and cable industry. (22)

Residual metal content in plastics also is an issue; recent progress in overcoming this problem is reported. (23) A new eddy current separator allows separation of even the smallest non-ferrous particles. In downstream equipment, a new compounding line fitted with a self-cleaning melt-filtration system recently was developed that eliminates collected impurities through secondary discharge. (24)

As the importance, societal pressure, and economic situation of recycling develops, better methods will be developed for separating plastic materials. Therein lies the primary advantage and potential for O-TPVs to have a positive impact on the capability of rubber part recycling. By intention O-TPVs have been similarly classified as TPOs and these materials are similar in density to previously targeted plastics such as PE and PP. As automobile manufacturers, appliance companies and other durable goods producers develop the infrastructure for effective post-consumer reclaim, O-TPV based products are poised to allow a greater percentage of the total materials in the original product to be recycled into valuable new products.

## Acknowledgments

The author wishes to acknowledge Advanced Elastomer Systems, L.P. for permission to publish this work and the many colleagues within AES for the contribution of their work and studies. A special note is made to Dr. Charles P. Rader and his co-editors for their efforts in putting together this important book on recycling.

## Literature Cited

- (1) Rowatt, R.J. *CHEMTECH* 1993, January, pp.56
- (2) "Plastics Issues" *Plastics Engineering* 1994, July, pp. 3
- (3) Nir, M.M, Miltz, J., Ram, A. *Plastics Engineering* 1993, March, pp.78-79
- (4) IBID ref. (2)
- (5) IBID ref. (1) pp. 57
- (6) "NEWSCLIPS" *Plastics News*, 1993, August, pp. 3
- (7) Lebel, M.A. *Plastics Engineering* 1994, January, pp. 23
- (8) Purgly, E.P., Gonzalez, E.A., Rader, C.P. *Rubber and Plastics News* 1992, August
- (9) Nishimura, K. *Kautschuk Gummi Kunststoffe* 1993, December, pp. 990
- (10) "World Automotive Forecast Report" DRI/McGraw-Hill 1993, August, pp. I-7
- (11) Rader, C.P., Wegelin, R.C. "Thermoplastic Elastomers -- A Major Recycling Opportunity" paper presented at the 1994 SPE ANTEC, May
- (12) Eller, R. *Rubber World* 1993, March, pp. 12
- (13) School, R.J., "Markets for Thermoplastic Elastomers" in *Elastomers Technology Handbook*, Cheremisinoff, N.P. Ed., C.R.C. Press, Inc. 1993, pp. 598
- (14) IBID ref. 12
- (15) Society of Automotive Engineers, J 1344, "Marking of Plastic Parts, Recommended Practice", Warrendale, PA 15096
- (16) ASTM D 1566, American Society for Testing and Materials, *Annual Book of ASTM Standards*, Vol. 9.01, 1992
- (17) Allinger, N.L., et. al. *Organic Chemistry*, Worth Publishers, 1971
- (18) Coran, A.Y., Patel, R.P. *Rubber Chem. Technol.*, 1981, Vol. 54, pp. 892
- (19) Coran, A.Y., Patel, R.P., Williams, D. *Rubber Chem. Technol.*, 1982, Vol. 55, pp. 116
- (20) Alderson, M., Payne, M. "Recycling Engineering Thermoplastic Elastomers", Paper No. 218, ACS Rubber Division 142nd Technical Meeting, 1992
- (21) U.S. Patent 5,022,985, Plastic Recovery Systems, Inc., Toledo, OH
- (22) Kali & Salz, *European Plastic News*, 1993, April, pp. 21
- (23) Hopke, B., "The Eddy Current Separatore", *Ingenieur & Industrie* 1993, Vol. 43, pp. 102-105
- (24) *Plastic Technology* 1992, Vol. 12, pp. 38

RECEIVED May 2, 1995

## Chapter 20

# Scrap Tire Recycling: Regulatory and Market Development Progress

John R. Serumgard<sup>1</sup> and Andrew L. Eastman<sup>2</sup>

<sup>1</sup>Scrap Tire Management Council, 1400 K Street, NW,  
Washington, DC 20005

<sup>2</sup>Goodyear Tire & Rubber Company, Akron, OH 44316

The largest problem area for polymer reuse and recycling is the 250 million scrap tires generated annually in the United States. Lacking any possibility of closed loop recycling with this thermoset product, the challenge is to find economically and environmentally sound uses for the tire, whether whole or processed. Since 1990, the beneficial utilization rate for scrap tires has increased from less than 11 % to more than 33% of annual generation. Principal methods of utilization are as a high value fuel in several industrial and electric generating applications, the use of ground rubber to modify asphalt paving materials, the use of ground rubber in other products, and the use of whole and processed tires in civil engineering applications. The outlook for expanding these markets is such that by 1998, virtually all newly generated tires will be reused in some manner.

Two hundred and fifty million tires -- each year, every year -- for the foreseeable future will be discarded in the United States. The search for economically and environmentally sound uses for those tires is a major challenge facing both the solid waste management industry and, equally importantly, all segments of the tire industry. Substantial progress is being made in this effort, although there is still a considerable distance to go before the goal of sound utilization of all scrap tires is realized. The efforts to insure proper handling of scrap tires and to expand their markets involve both responsible regulation at the federal and state government levels and development of private and public sector end uses.

### The Current Scrap Tire Situation

**Volumes.** With tires being scrapped at the rate of nearly 250 million per year, this amounts to roughly one scrap tire for each man woman and child in the country.

0097-6156/95/0609-0237\$12.00/0  
© 1995 American Chemical Society

A state need only look to its population numbers to estimate the number of scrap tires discarded annually. Because all tires are not equal, if the annual generation were converted to passenger tire equivalents, the number would be nearly 350 million, with a total weight of around 3.5 million tons, or slightly more than one and one half percent of the municipal solid waste stream.

Annual generation is only part of the management problem. For many years, one of the major disposal options for tires was the scrap pile. In the absence of good markets, most tires went to landfills or to scrap tire stockpiles. Stockpiles, both legal and illegal, can be found in virtually all states. Some began as entrepreneurial dreams in times of energy shocks that tires would be "black gold" and would someday be worth fortunes for their energy value. Other stockpiles grew out of failed recycling ventures that ended up only with piles of tires and no useful end product. And many stockpiles grew through illegal dumping on out of the way land, or in streams or forests. For the nation as a whole, the United States Environmental Protection Agency estimates there are more than 2 billion stockpiled and landfilled scrap tires.<sup>1</sup>

**Markets.** In 1990, some 25 million scrap tires, or approximately 10% of the annual generation rate, had markets. The most significant market was tire-derived fuel, which consumed 95% of the market share. The remaining five percent was split between rubber modified asphalt and civil engineering applications.<sup>2</sup>

Over the course of the last four years, markets for scrap tires have more than tripled. By the end of 1994 it is estimated that the equivalent of 160 million passenger tires will have markets, or about 46 % of the total annual generation. Whole or processed tire-derived fuel is still the most significant market, consuming almost 103 million scrap tire equivalents. Other major markets are set forth in the following table:

**Table I**

**SCRAP TIRE REUSE/RECYCLING  
as of December 31, 1994**

<i>USE</i>	<i>PERCENT AGE</i>	<i>PASSENGER TIRE EQUIVALENT (000,000)</i>
Energy Recovery	29%	103
Ground Rubber	6%	20
(Asphalt	2.6	9)
(Other	3.4	11)
Fabricated Products	4.6	16
Civil Engineering	2.4	8
Agriculture	1%	3
Export	3%	10
<b>Total</b>	<b>46%</b>	<b>350</b>
<b>Landfill/Stockpile/Monofill</b>	<b>54%</b>	

Projections by the Scrap Tire Management Council show that by the 1997 - 1998 time frame, virtually all annually generated scrap tires will have markets.<sup>3</sup> The three major markets are projected to be whole or processed tire-derived fuel (TDF), rubber-modified asphalt and civil engineering. The remainder should be consumed by a variety of innovative technologies.

### **The Regulatory Picture**

As a solid waste, scrap tires are regulated principally at the state level. There are no specific scrap tire provisions in the Resource Conservation and Recovery Act, the principal federal solid waste law.

Currently 48 of the 50 states have some specific legislation or regulations dealing with scrap tires, Delaware and Alaska being the last two holdouts. At last count, 37 states have enacted specific scrap tire legislation. The balance of the states regulating scrap tires do so under broad solid waste laws. These laws and regulations often have many common features. Among the most common features are:

1. Regulation of the manner of disposing of tires in landfills or at stockpiles;
2. Regulations, including permitting requirements, for scrap tire haulers, processors and end users;
3. Financial responsibility requirements for sites at which scrap tires are collected, stored or processed;
4. Provisions for market development, including financial assistance to end use markets or new entrants into the scrap tire business;
5. Provision for financial support for implementation of the state's scrap tire management program, supported by a state fee or tax at some point in vehicle or tire ownership; and.
6. Provision for cleanup of scrap tire piles.

The actual experiences within several states demonstrate that it is possible to positively affect the management and use of scrap tires. In Oregon, a state law was passed in 1985, just the second state to pass a scrap tire law. By 1992, the state had been successful in cleaning up its scrap tire stockpiles and the private sector had developed markets for all of the newly generated scrap tires, these being principally fuel markets. As a result, the state allowed its special fee for its scrap tire program to expire. Minnesota was the first state to enact scrap tire legislation in 1984, and it has reached the point where it is in the final stages of stockpile cleanup, and has functioning markets for all its new scrap tires. In the process Minnesota has cleaned up more than 12 million stockpiled tires. Illinois has had an aggressive program to assist in developing scrap tire markets, and has seen several major markets develop with state assistance. In Illinois, the use of state funds in the developmental stages of several projects was money well spent when the projects came to operational state.

Where states have focused their attention on identifying, promoting and assisting end use markets, such as in the states just mentioned and in others such as Florida, California, Georgia, and others, steady progress is being made. Some states, however, have taken a different attack, focusing instead on assumption of the burden of basic scrap tire management, and on intermediate processing. In these states, principally Texas and Oklahoma, the development of end use markets has lagged. The Texas program provides payment to processors who collect tires from dealers and process the tires into shreds. The processors have until January 1, 1996 to establish that they have markets for their shreds. As a result, the state now has more than 40 million shredded tires in stockpiles, and very few end use markets. Oklahoma has a similar, if smaller scale problem.

The tire industry has consistently supported sound scrap tire legislation at both the state and federal level to ensure that scrap tires are managed in environmentally responsible ways. Equally importantly, the tire industry has been a consistent participant in the effort to find appropriate markets for scrap tires, and to promote the expansion of those markets.

### Markets for Scrap Tires

Any solutions must address the various sources of scrap tires. Almost 95% are returned by the consumer to thousands of dealers across the country when worn out tires are replaced by new ones. Of the alternatives, immediate recycling/recovery of scrap tire through viable non-subsidized markets is the industry's priority. Feeding stockpiles and landfills -- even with shredded materials -- provides few benefits.

The key to finding solutions to the scrap tire dilemma is the same as it is for any number of other products which society would like to see reused: it's markets, markets, markets.

In addressing any solid waste issue, there is a national public policy which favors consideration of a hierarchy of alternatives. This hierarchy is the now familiar mantra of Reduce, Reuse, Recycle, Recover, Dispose.

For tires, this hierarchy has certain limitations and opportunities. These can be summarized as follows:

**Reduce.** The first most desirable alternative is source reduction. In the case of tires, the objective is to reduce the number of tires that enter the waste stream. The tire industry's efforts during the past twenty years to improve tire life has doubled the mileage and life of a typical passenger tire.

**Reuse.** The next best alternative is to reuse the tire. The tire casing is retreaded or manufactured into miscellaneous products. Significant improvements in retreading permit the average truck tire to be retreaded 2 or 3 times. Airplane tires are retreaded up to 12 times. The casing is often used for miscellaneous products such as muffler hangers and snow blower paddles. Unfortunately, this market represents a small part of the annual take-off and is slow to expand. Grindings or

crumb rubber from tread and sidewalls can be used as a filler for rubber or plastics products and asphalt.

**Recycle.** True recycling of vulcanized rubber products through devulcanization, while technically possible in the laboratory, is highly impractical for large scale use.

**Recovery.** Energy recovery is the best alternative today. There are significant economic and environmental reasons to explain why this alternative is the current best solution.

**Disposal.** Finally, when tires are shredded, they do not create an environmental problem in a landfill or monofill. A recent study by Radian Consultants verified that scrap tires do not create hazardous leachate. Shredded tires take up less space than whole tires and almost eliminate the fire hazard.

In 1994 several regions of the United States will have competitive environmentally sound and economically viable markets that did not exist just a few years before. The additional markets will create competition which will lower scrap tire management costs.

There are several sound markets for scrap tires. The largest current and potential market is the use of scrap tires as fuel, in markets such as electrical generation, industrial boilers, and particularly in energy intensive processes such as cement manufacturing. Ground rubber from tires is finding its way into new applications every day, from an additive to asphalt paving materials, to a wide variety of new products such as flooring and sneakers. Shredded tires are being used as a lightweight fill material in civil engineering applications. Cut tires are used to produce many useful products, including equipment for the commercial fishing industry

**Tire-Derived Fuel.** Tire Derived Fuel, either as whole tires or processed into a chip, is the largest single current and potential market for scrap tires. There are several advantages to using scrap tires in place of most types of coal. Whole scrap tires average about 15,000 Btu per pound. Most coal is in the range of 12,000 Btu per pound. Less carbon dioxide is released to the atmosphere since scrap-tire fuel has more hydrogen than found in coal. NO<sub>x</sub> is reduced because secondary burning of the carbon in tires occurs, and less organic nitrogen exists in tires than in most coals. Additionally, there is less sulfur in tires than in most coals.<sup>4</sup>

Cement kilns are a particularly good fit with tires. As of July, 1994, 24 kilns were using tires on a regular basis, another 13 had conducted test burns and an additional 29 kilns were considering using tires. In cement kilns, tires replace up to 20 percent of the total required fuel. The feed systems for whole tires and TDF are relatively inexpensive. A big advantage of using scrap tires in cement kilns is there is no solid waste disposal. The tire is completely consumed and becomes part of the final product of the kiln called clinker. The clinker is ground with gypsum and the resulting product is Portland cement. Whole passenger tires



can be used as well as coarse tire shreds. Additional success stories in Europe and Japan support the use of scrap tire in cement kilns.

Pulp and paper mills in virtually every section of the US are using tires. Paper manufactures that use stoker grate boilers combine TDF with the wood waste they burn - bark and sawdust - to produce steam. The TDF improves the combustion efficiency and replaces fossil fuels.

Scrap tires can be used in five different types of boilers used in electric generation -- liquid slagging bottom, cyclone, fluidized bed, stoker grate, and dedicated tire boilers. The use of tires in liquid slagging bottom boilers was pioneered by the Goodyear Tire & Rubber Company and further developed by the Ohio Edison Co. at a facility in Toronto, OH. Nearly 50 boilers of this type are currently operational in the US and are potential markets for scrap tire fuel. Several utilities are using tires in various cyclone, fluidized bed and stoker grate boilers. Only two dedicated tires-only plants are operating, although the technology is environmentally sound and the performance is proven. The drawback is the heavy investment needed.

One area of concern is with the potential air emissions from using tires as a fuel. Rather than presenting a problem, extensive emissions testing has shown that the use of tires to replace a portion of coal results in reduced emissions. One example is a test conducted at a Monsanto plant in Sauget, IL. Scrap tires were used to generate steam for electricity generation with 2 inch x 2 inch TDF replacing 20 percent of the plant's coal. The test results proved that TDF is an environmentally sound fuel. Particulate was reduced through lower ash. Volatile organic compound reductions were attributed to TDFs increased volatility when compared to coal, Nitrogen oxide was reduced through reburning. Chlorine reduction was attributed to tires having nearly undetectable levels of chlorine.<sup>5</sup> Sulfur increased slightly because low-sulfur coal was used at the facility. An increased presence of carbon monoxide was corrected after the test by adjusting the TDF chip size and the fuel-to-air mixture ratio. Other metals, such as lead, mercury and cadmium, present when coal is the only fuel, were reduced during the supplement test. Furthermore, the test found that furans and dioxins were non-detectable.

The main components of fuel are fixed carbon and hydrogen-based material. Carbon, when burned, creates carbon dioxide (CO<sub>2</sub>) which is targeted as a major contributor to the greenhouse effect that causes global warming. Coal contains twice the fixed carbon that is in TDF. Conversely, TDF contains much more hydrogen based material than coal. Because TDF has less carbon and more hydrogen than coal, TDF burns much cleaner and hotter, and has over 20 percent more heat value, yet creates less CO<sub>2</sub>.

A fuel potential which has not been developed to date in the US is the use of scrap tire shreds in iron foundries. As in cement kilns, the steel in the tires becomes one of the raw materials required in the foundry operations. The foundries, however, are not as limited with regard to the amount of steel that can be consumed. This technology has an excellent potential to handle truck tires.

Many additional fuel users are expected to be on stream by 1997. Capacity to handle the majority of the scrap tire take-off will exist by this time. In many areas of the country, the capacity will exist to make significant reductions in the tire piles. The competition that develops will be favorable to disposal costs and will weed out noncompetitive markets.

Growth in tire usage has also increased in other areas. In many of these cases, subsidies and legislation have played an important role in developing these markets. Nonetheless, usage in these areas has increased, and all of these options combine to help address the scrap tire problem.

Civil engineering uses have increased primarily in the area of highway construction. Tire shreds used as lightweight fill have gained acceptance and will be further driven by the asphalt rubber mandate in the Intermodal Surface Transportation Efficiency Act of 1991 (ISTEA). Whole tires have been used on some projects to form walls and barriers as part of road projects. Soil modifiers are gaining acceptance and use in athletic fields.

California, Florida and Arizona are the most active in promoting the use of crumb rubber in asphalt. Most states are running tests to decide how to deal with the mandate of ISTEA. Section 1038 of ISTEA requires that Crumb Rubber Modifier (CRM) for asphalt paving be used in a percentage of each states roads constructed using federal funds. Studies required by the Act were released in 1993.<sup>6</sup> State governors and others challenged the wisdom of the mandate, and Congress chose to delay its implementation. Changes to the law are being proposed to allow wider use of scrap tire rubber in road construction and to delay implementation until 1995. The cost of using crumb rubber is a major drawback. Consistent improvements in test results, reduction in pavement thickness and market volume increases could reduce costs. However there is only limited evidence of this in the last several years. This continues to be a technology that should continue to be developed and utilized where found to be cost effective.. Laws that mandate scrap tire technology, however, interfere with development of free market solutions.

Crumb rubber in plastics is being driven by many recycling entrepreneurs, In general, this material enhances the economics more than the quality of the end product.

Finally, fabricated products from scrap tires continues to show slow growth; however, entrepreneurs are looking for conventional (non-radial) tires to fill their production requirements.

Some believe that scrap tires could be reused in new tires in quantities of 5 percent or more. However, there is a serious problem in this concept since ground rubber from scrap tires is not chemically the same as natural rubber or synthetic rubber. In the grinding process, the rubber is broken down, but no chemically combined sulfur has been removed. The rubber has not been devulcanized. An analogy can be made with baked bread. Yeast and flour cannot be removed from the final product and reused again. Old bread cannot be recycled into new bread.

Reclaim or ground material used as a filler in tires causes lower tensile strength, heat buildup and oxidative aging. Therefore, in a new tire, for each

percent of reclaim that is used, there is approximately a 1 percent reduction in tread life. The rolling resistance of a tire containing reclaim is increased, which results in lower fuel economy. Also there is increased lug cracking in large tires. The conclusion -- these use of reclaim rubber in new tires is very limited.

### Conclusion

The tire industry continues to work at all levels to find balanced solutions to the scrap tire issue. This includes working with legislators and regulators at the federal, state and local level on a nearly continuous basis. In addition, extensive efforts continue to promote sound, effective markets.

Using scrap tires for fuels is a true win/win opportunity. Overall, solid waste and air emissions are reduced, natural resources are conserved, and energy independence is enhanced. In most cases, it is the cost effective solution.

There are many viable, higher uses for scrap tires that exist today and will evolve in the future. Each should be developed, even if individually it does not have a major impact on the waste stream. Together they will.

Support must be given to existing technologies. As other solutions develop, they will be encouraged. The tire industry is acting now to enable scrap tires to be handled in an environmentally sound way at the lowest cost to the tire consumer.

### References

1. U.S. Environmental Protection Agency, *Markets for Scrap Tires*, EPA/530-SW-90-074B, 1991.
2. A.T. Kearney, *Scrap Tire Use/Disposal Study*, Scrap Tire Management Council, 1990.
3. A.T. Kearney, *Scrap Tire Use/Disposal Study*, Scrap Tire Management Council, 1992.
4. Malcolm Pirnie, *Air Emissions Associated with the Combustion of Scrap Tires for Energy Recovery*, Ohio Air Quality Development Authority, 1991.
5. U.S. Environmental Protection Agency, *Burning Tires for Fuel and Tire Pyrolysis*, EPA-450/3-91-024, 1991.
6. Federal Highway Administration, *State of the Practice - Design and Construction of Asphalt Paving Materials with Crumb Rubber Modifier*, 1992.

RECEIVED May 2, 1995

## Chapter 21

# Chemical Methods of Devulcanizing Thermoset Rubber

Walter C. Warner

Rubber World, 1867 West Market Street, Akron, OH 44313-6901

The literature records numerous methods which have been used to reverse vulcanization. Many have long been used, for purposes of analysis or studying mechanisms of vulcanization and have become commonplace in large laboratories. Possibly certain ones may be worth considering for eventual recovery of rubber and other ingredients on a commercial basis. Any such process would have to be studied from the standpoint of fine-tuning reactants, solvating media, conditions of least degradation and minimizing toxic exposure, as well as economic viability.

Thermoset plastics or rubbers degrade and/or depolymerize when subjected to heat and lose their valuable polymeric properties. Therefore any serious effort for recovery must take every advantage of the fact that crosslink bonds can be more reactive than the chemical bonds of the backbone.

Included in a list of the chemical probes which were found in this search are propanethiol, hexanethiol, sodium-di-n-butyl phosphite, triphenyl phosphine, lithium aluminum hydride, methyl iodide and phenyl lithium. Related methods include microbial action, grafting reactions, catalysis, microwaves, sonics and solution by orthodichlorobenzene.

The rubber industry faces a major challenge in this decade to find a satisfactory way to deal with the enormous quantity of rubber goods, particularly tires, which reach the end of useful life each year. The variety of topics being addressed at a recent symposium (1) attests to the importance to our industry of finding a good long-range solution. Some have described the current dilemma as "the synthetic rubber problem all over again." Fifty two years ago the reserves of rubber in the United States were lower than ever before or since. Thanks to the dedicated efforts of many rubber chemists, engineers, management teams and enlightened cooperative programs between government and the private sector, the problem was solved within a few years.

Significant reviews of the technical aspects of reprocessing of vulcanized rubber have been published by Makarov and Drodzdovski (2), of disposal by Crane,

0097-6156/95/0609-0245\$12.00/0  
© 1995 American Chemical Society

Elefritz, Kay and Laman (3) and Beckman, Crane, Kay and Laman (4) and of recycling by D. Smith (5) and Klingensmith (6). Excellent perspectives on the whole problem are currently provided by Dunn (7), an anonymous article in the *European Rubber Journal* (8), Paul (9) and other papers in Klingensmith's symposium (1). In a current review of the rubber industry as a whole, Reisch (10) concluded that the dilemma of used tires is "...one that will require action on the part of the entire rubber industry."

### Definition of Devulcanization

For the purpose of this literature review, the subject may be defined in the following way: "Devulcanization in a sulfur cured rubber is the process of cleaving, totally or partially, the poly-, di- and monosulfide crosslinks which were formed during the initial vulcanization." Partial devulcanization is useful in the analytical laboratory in the study of crosslinking mechanisms and structure. For any commercial purpose of reuse or recycling total devulcanization would be the primary goal. The treatment of cleavage of carbon-carbon crosslinks created by peroxide or radiation curing is outside the scope of this paper.

ASTM D 1566 (11) currently defines vulcanization in a phenomenological way without reference to cure system, and omits any definition of devulcanization, except by implication. ASTM STP 184A (12) earlier defined devulcanization as a combination of depolymerization, oxidation and increased plasticity as they usually occur during the process of reclaiming. Earlier definitions, especially those in the reclaim industry, tend to use the concept of ASTM STP 184A (12).

### Chemical Probes

The use of chemical probes for sulfur-cured natural rubber was pioneered and refined to a high state of usefulness in the 1960s at the Malaysian Rubber Producers Research Association (MRPRA), then called Natural Rubber Producers Association (NRPRA). Saville and Watson (13) wrote a masterful and extensive review. To paraphrase, they defined a chemical probe as an analytical reagent which will react in some useful way with a specific network feature, which is capable of being homogeneously introduced into the network, and which can be easily extracted after the chemical reaction has been completed without side reactions. Their abiding goal evidently was to study thoroughly the most intimate details of the exact chemistry of the process of vulcanization with sulfur using commercially important curing systems, and also to characterize the network completely. Their review specifically mentions triphenyl phosphine, sodium di-n-butyl phosphite, thiol-amine reagent, lithium aluminum hydride, phenyl lithium and methyl iodide.

Saville and Watson (13) provided an ample bibliography of much laboratory work on low molecular weight compounds to leave little doubt about the specificity of each chemical probe discussed. This approach opened the way for them and subsequent workers to distinguish among polysulfide, disulfide and monosulfide bonds in carbon black filled NR vulcanizates. The use of swelling measurements before and after treatment with the probes was used to establish crosslink density. Chapman and Porter (14) provided a concise perspective on the approach and a good bibliography prior to 1988. In general, laboratory glassware at atmospheric pressure was used to perform the necessary reactions.

Russell (15) early applied these techniques to the very important practical problem of improving the life of truck tires. He studied various portions of truck tires as a function of time on the road and was able to relate the content of poly-, di- and monosulfide with blow-outs and tread separation. Thus the probes mentioned above were shown to have great practical as well as theoretical significance in

addition to our present concern with methods for devulcanization. The chemical probes identified by Saville and Watson (13) will now be described in more detail and related to devulcanization.

**Triphenyl Phosphine and Sodium di-n-Butyl Phosphite.** Moore and Trego (16, 17) early described the use of triphenyl phosphine and sodium di-n-butyl phosphite as chemical probes to establish the structural features of sulfur links in vulcanizate networks from a variety of compounds of natural rubber (NR) cured with sulfur. Their studies included also a cis-1,4-polyisoprene-TMTD-zinc oxide system and a system of NR and ethylene-propylene rubber (EPDM) crosslinked with dicumyl peroxide and sulfur. The triphenylphosphine converts the polysulfide links into monosulfide and, to a lesser extent, disulfide links. Sodium di-n-phosphite cleaves di- and polysulfide crosslinks but leaves monosulfide and carbon-carbon crosslinks intact. They stated that "...thus determination of the degree of chemical crosslinking before and after treatment with this reagent yields estimates of these two different classes of crosslinks." Moore and Porter (18) and Lal and McGrath (19) also reported the successful application of triphenyl phosphine to network studies.

**Thiol-Amine Reagent.** Saville and Watson (13) and Campbell (20) described the use of propane-thiol/piperidine to cleave polysulfide linkages while leaving disulfide, monosulfide and carbon-carbon bonds intact. Campbell (20) found hexane-1-thiol to be more reactive and capable of cleaving both polysulfide and disulfide linkages while leaving monosulfide intact. Parks, Parker, Chapman and Cox (21) used hexane-1-thiol to study networks and were particularly interested in sorting out the sulfur in pendant groups. Onouchi, Inagaki, Okamoto and Furukawa (22) found that bond scission mainly took place on disulfide and polysulfide linkages by the binary mixture of thiols and amines which they used. Saville and Watson (13) (p 140) described the laboratory glassware useful for using the thiol-amine reagent.

**Dithiothreitol.** Goethals, Tossaert, De Vos and De Clercq (23), in a discussion of decrosslinkable networks, reported that dithiothreitol quantitatively cleaves disulfide bonds into two thiol groups.

**Lithium Aluminum Hydride.** Studebaker (24,25) pioneered the use of lithium aluminum hydride as a chemical probe. This reagent cleaves disulfide and polysulfide bonds, leaving monosulfide intact. For this reason the latter are determined by difference. A good perspective on the approach of Studebaker (24, 25) is given in the review article of Saville and Watson (13). Their only other reference, simultaneous with Studebaker's article, (24) was that of Gregg and Katrenick (26), to be discussed next.

**Phenyl Lithium.** Gregg and Katrenick (26) and Gregg (27) found that treatment of a polybutadiene vulcanizate with phenyl lithium in benzene cleaved the polysulfide and disulfide bonds. They generalized that, based on their work, phenyl lithium does not cleave monosulfide crosslinks.

**Methyl Iodide.** The action of the chemical probes discussed so far really constitutes, at most, partial devulcanization, because, in general, the probes cleave polysulfide, disulfide and the combination of polysulfide and disulfide linkages. Any combination of chemical methods or probes which is to be considered seriously for devulcanization on a large scale will of course have to cleave *all* sulfide linkages, either in a single or multistep process. Saville and Watson (13) discussed at length (pp 122-124) the ability of methyl iodide to cleave monosulfide linkages and

provided significant references. They observed that methyl iodide has properties ideally suited to a chemical probe.

Selker and Kemp (28) and Selker (29) early reported work on both model low molecular weight compounds and vulcanizates to show the specificity of methyl iodide to break monosulfide bonds. Moore (30) treated tetramethylthiuram disulfide/ZnO vulcanizates with methyl iodide and found that most of the crosslinks were broken. Manik and Banerjee (31) used the method of Moore (30) to confirm the results of a study of the mechanism of acceleration with N-cyclohexyl-2-benzothiazole sulfenamide. Selker and Kemp (32) even applied methyl iodide to reduce the amount of combined sulfur in ebonite. Unfortunately Lewis (33) recently reported methyl iodide to be a carcinogen.

### Other Chemical Methods

**Catalysis.** Nicholas (34,35) reported on interesting work to improve the properties of reclaim. To quote from his first page: "The main goal of this study was to find low cost chemistry for converting scrap rubber into a material more nearly resembling the structure of new rubber. Specifically, we have examined phase transfer catalysis as a means of transporting hydroxide ions from water into rubber particles to cleave polysulfide crosslinks and derivitized monosulfide crosslinks, with little main chain scission." The transfer of an anion from water into the organic phase (finely divided rubber) was made possible by means of a quaternary ammonium chloride catalyst having a large hydrocarbon radical attached to nitrogen. Hydroxide ions transported by onium ions from water rapidly break polysulfide crosslinks with little or no main chain scission. Methylated monosulfide crosslinks do not cleave under these conditions. A U.S. patent (36) to B.F. Goodrich has been granted on the process. Certainly the possibility of working in an aqueous medium toward the goals eloquently summarized by Nicholas make further experimentation attractive. Evidently, rates of diffusion and residual traces of accelerating residues are problems.

In another reference, Nikolinski and Mirtscheva (37) removed sulfur in swollen vulcanizates as well as aqueous dispersions with the aid of Raney nickel whereby C-S bonds are replaced with S-H bonds.

**Grafting and Related Reactions.** Adam, Sebenik, Osredkar, Ranogajec and Vekslil (38) reported on work done to modify rubber granulate chemically for the purpose of enlarging the quantity of waste rubber to be possibly reused in the rubber industry. They grafted ethyl acrylate onto waste rubber consisting of ground polybutadiene vulcanizate using a redox method and also by use of gamma rays. Unfortunately, the properties of the waste rubber were found to have worsened by the treatment. The quantity of grafted monomer was larger when gamma irradiation was used.

Wagener and coworkers (39) have developed the technique of acyclic diene metathesis (ADMET). They claimed that the technique is capable of modifying elastomer structures, and through the depolymerization reaction should offer opportunities for recycling unsaturated polymers. In another publication, O'Gara, Portmess and Wagener (40) found that sulfur does not intrinsically inhibit the ADMET reaction.

**Solution by Orthodichlorobenzene.** Dinsmore and Smith (41) reported that orthodichlorobenzene (ODCB) dissolves a variety of vulcanizates including hydrocarbon, nitrile and chloroprene rubbers. Their purpose was to prepare a film for use in identifying vulcanizates by applying infrared spectrophotometry. The procedure involves cutting the vulcanizate into small pieces with scissors, refluxing

(approximately 180 degrees Celsius), centrifuging out the carbon black, and then casting a film. Some prefer to bubble oxygen through to hasten the process. Some find Celite useful to help clarify the solution from the carbon black. The final film definitely acts like a piece of unvulcanized rubber as observed in at least one laboratory. It is interesting to speculate on what has happened during refluxing, but it can be strongly inferred that most or all of the poly-, di- and monosulfide crosslinks originally present were cleaved, and without excessive degradation. Clark and Scott (42) also used boiling orthodichlorobenzene successfully to devulcanize mixtures of SBR and polybutadiene for purposes of identification. They found that the addition of a small amount of 2,2'-dibenzamidodiphenyl disulfide substantially decreased the time for dissolution.

### Wave Methods

**Microwaves.** Novotny, Marsh, Masters and Tally obtained a U.S. patent (43) assigned to Goodyear on the microwave devulcanization of rubber. The main claim consisted of applying a controlled dose of microwave energy at specified frequency and energy level in an amount sufficient to sever substantially all carbon-sulfur and sulfur bonds and insufficient to sever carbon-carbon bonds. The examples included EPDM hose end trim, butyl tire bladders and a tire tread material. Thus they proposed that elastomer waste can be devulcanized without depolymerization to a material capable of being recompounded and revulcanized and having physical properties essentially equivalent to the original vulcanizate.

Fix (44) and an article in *Plastic and Rubber News* (45) discussed advantages of this method in subsequent publications. They pointed out that the cost to devulcanize hose and inner tube material is only a fraction of the cost of the original compound. Also, the transformation from waste to refined stock ready for remixing takes place in only five minutes with usually 90 to 95% recovery of the rubber. Makarov and Drozdovski (2) discussed the microwave method (p 69), especially the work of Novotny et al (43).

**Ultrasonics.** Serious efforts to devulcanize rubber in this manner have long been discussed in technical circles. A significant contribution was reported recently by Okuda and Hatano (46). They subjected a natural rubber vulcanizate to ultrasonic waves at 50 kHz for twenty minutes to devulcanize it, and then they revulcanized it. The properties of the revulcanized rubber were found to be very similar to those of the original vulcanizate.

Senapati and Mangaraj (47) of Battelle obtained a U.S. patent on vulcanization of rubber with ultrasonic waves. Dr. Mangaraj (48) stated that, in general, higher intensities of energy than those covered in the patent for vulcanizing will cause devulcanization or reversion in the case of NR. Conditions must be carefully controlled and there must be substantial back pressure to prevent cavitation.

Isayev (49) at the University of Akron has been granted a U.S. patent for devulcanizing rubber with ultrasonics. He uses an extruder into which the ultrasonic field is focused. Zimmer (50), in a news release from the University, described the marketing arrangements and general concept.

### Other Methods

**Microbial Action in Vulcanized Rubber and Coal.** Beckman, Crane, Kay and Laman (4) included in their 1974 review a thorough treatment of biodegradation of rubber. Surprisingly, microorganisms are reported and referenced which metabolize rubber hydrocarbon, but these are killed by the toxic substances usually present in compounded rubber. Regarding our current interest in the possibility of



devulcanizing sulfur cured vulcanizates, they reported that: "The utilization of unbound sulfur in rubber vulcanizates by microorganisms has been previously reported. However, no reports of utilization of bound sulfur have been recorded." In agreement with that observation, Bos, Boogerd and Kuenen (51) discussed the use of microorganisms to remove sulfur from coal. There was difficulty in removing organically bound sulfur. Borman (52), in an article on bacteria which flourish above 100°C, stated that "Because some thermophilic bacteria can transform sulfur into hydrogen sulfide, the organisms are being considered for potential use in desulfurization of coal." Haggin (53) reported that up to 90% of organic sulfur may be removable from coal by appropriate cleaning technology, including the use of biological agents.

**Use of the Steam Autoclave for Vulcanizates.** Devulcanizers are commonly listed in the directories used in the rubber industry. Their purpose is to devulcanize certain rubbers by subjecting scrap rubber to superheated steam. Sverdrup and Wendrow (54) summarize the technique, and point out that it is also called the thermal process or Palmer (high pressure) process depending on the pressure of the steam. Schaefer and Berneking (55) used the steam autoclave method for NR, Schaefer (56) for butyl rubber and Bowers, Barber and Allinger (57) for silicone.

### Comparison of Probes and Reclaiming

Some of the chemicals mentioned in the literature on reclaiming are comparable with those used as probes. In 1937, Miller (58) mentioned the use of a solution of aniline-sodium as a method for removing combined sulfur, which is similar to phenyl lithium used by Gregg and Katrenick (26) and Gregg (27). Le Beau (59) mentioned phenol alkyl sulfides and disulfides, aliphatic and aromatic mercaptans, amino compounds and unsaturated compounds as active reclaiming agents. Some of these bear a similarity to the thiol-amine reagents described by Campbell (20). Sverdrup and Wendrow (54) provide a thorough discussion of the chemistry of reclaiming. They refer to the same chemicals as Le Beau, who is referenced in their bibliography.

The literature on reclaiming reveals a number of articles describing the science and technology from various points of view and over a long period of time. Miller (58) in a classic work in 1937 described the methods of manufacture, theory of reclaiming (considered synonymous with devulcanization at that time), compounding, advantages, selection and testing. Ball (60) in 1956 prepared a manual on reclaimed rubber which included compounding procedures specific for SBR, IIR and NR. He included a discussion of commercial uses in tires, automotive goods, industrial rubber products and footwear. Appropriate physical and chemical tests were also discussed. Nourry (61) edited a comprehensive text on aspects of reclaimed rubber through 1962. Szilard (62) described the essential technology and uses of reclaim from approximately 120 patents issued from 1955 through 1973 for rubber and other polymers. He provided indexes by company, and author as well as contents and subject. He included more than 20 additives for reclaiming. F. Smith (63) discussed the reclaiming field from the production standpoint in 1978. He covered processing advantages, economics, compounding and important uses. Schaeffer and Isringhaus (64) described in 1987 the early history of reclaiming, including a comparison of mechanical and chemical processes. They were unusually careful to define terms. They also covered processes, advantages and included a section on rubberized asphalt. LaGrone (65,66) provided recent encyclopedic perspectives on the field of reclaiming rubber.

One paramount consideration for both of these disciplines is to create the finest

particle size of vulcanizate that is possible. In the analytical laboratory this is usually accomplished by cutting samples as finely as possible with sharp scissors, or putting the sample through a laboratory rubber mill. LaGrone and Lynch (67) describe the critical importance of extreme fineness, as do many authors in the literature of reclaim. Swor, Jensen and Budzol (68) reported a process for producing 90% of the particles below 20 micrometers in diameter (approximately 500 mesh), which may be helpful on a production scale.

### Summary and Conclusions

- 1) Methods have been reported in the literature which reverse the vulcanization process for sulfur-cured rubbers, and with minimal degradation.
- 2) Further experimental work would seem appropriate in ultrasonics, which is already occurring, using microbial action, solution by orthodichlorobenzene and the phase transfer catalysis technique.
- 3) A useful purpose may well be served by looking at homologs and other chemicals related to those described in the literature of polymer science as chemical probes and those described in the literature of reclaiming as devulcanizing agents. (Possibly homologs of methyl iodide would devulcanize and yet be non-carcinogenic.)
- 4) It is hoped that some of the ideas and literature assembled here may be helpful to the rubber industry as we enter the era of life cycle management and responsibility for all products to perform flawlessly *and* to be reused effectively.

### Acknowledgement

My profound thanks and gratitude go to my wife, Henrietta, to my boss, Don Smith, and to many, many others who generously and patiently supported and encouraged me in the preparation of this paper.

### Literature Cited

1. William A. Klingensmith, Symposium on Recovery and Reuse of Rubber, Rubber Division, American Chemical Society, Orlando, Florida, October 26-29, 1993.
2. Vladimir M. Makarov and Valerij F. Drozdovski, *Reprocessing of Tyres and Rubber Wastes*, Ellis Horwood, New York, 1991.
3. G. Crane, R.A. Elefritz, E.L. Kay and J.R. Laman, *Rubber Chem. Technol.* 51, 577-599 (1978).
4. J.A. Beckman, G. Crane, E.L. Kay and J.R. Laman, *Rubber Chem. Technol.* 47, 597-625 (1974).
5. Don R. Smith, *Rubber World* 179, No. 3, 46-49 (Dec. 1978).
6. Bill Klingensmith, *Rubber World* 203, No. 6, 16-21 (Mar. 1991).
7. John R. Dunn, presented at Recycle '93 Davos International Forum and Exposition, "Recycling, Resource Reduction, Sustainable Developments, Global Actions," Davos, March 22-26, 1993.
8. *European Rubber Journal*, July/August 1993, pp 22-30.
9. John Paul in *Encyclopedia of Polymer Science and Engineering*, H.F. Mark, Ed., John Wiley & Sons, New York, 1988, Vol. 14, 787-804.
10. Marc S. Reisch, *C&EN*, May 10, 1993, p 33.
11. *Annu. Book ASTM Stand.* 09.01, 307 (1992); ASTM D 1566-92, "Standard terminology relating to rubber."

12. American Society for Testing and Materials, *Special Technical Publication 184A*, "Glossary of Terms Relating to Rubber and Rubber Technology," 29 (1987).
13. B. Saville and A.A. Watson, *Rubber Chem. Technol.* 40, 100-148 (1967).
14. A.V. Chapman and M. Porter, in *Natural Rubber Science and Technology*, A.D. Roberts, Ed., Oxford University Press, New York, 1988, ch. 12, pp 511, 515, 526-527, 600.
15. R.M. Russell, *Br. Polym. J.* 1969, 53-58 (Vol. 1, Mar. 1969).
16. C.G. Moore and B.R. Trego, *J. App. Polymer Sci.* 8, 1957-1983 (1964).
17. C.G. Moore and B.R. Trego, *J. App. Polymer Sci.* 5, 299-302 (1961).
18. C.G. Moore and M. Porter, *Rubber Chem. Technol.* 36, 547-557 (1963); *ibid.* 36, 1173 (1963).
19. Joginder Lal and James E. McGrath, *Rubber Chem. Technol.* 36, 1159-1172 (1963).
20. D.S. Campbell, *Rubber Chem. Technol.* 43, 210-221 (1970); *J. Appl. Polymer Sci.* 13, 1201-1214 (1969).
21. C.R. Parks, D.K. Parker, D.A. Chapman and W.L. Cox, *Rubber Chem. Technol.* 43, 572-587 (1970).
22. Yukio Onouchi, Shinji Inagaki, Hiroshi Okamoto and Junji Furukawa, *Polymer Preprints* 20, No. 1, 943-944 (Apr. 1979).
23. E.J. Goethals, G. Tossaert, R. De Vos and R. De Clercq, *Makromol. Chem., Makromol. Symp.* 1991, 48-49 (Eur. Polym. Fed. Symp. Polym. Mater., 3rd, 1990, 427-429 [Eng.]).
24. M.L. Studebaker, *Rubber Chem. Technol.* 43, 624-650 (1970).
25. Merton L. Studebaker and Lester G. Nabors, *Rubber Chem. Technol.* 32, 941-961 (1959).
26. E.C. Gregg, Jr. and S.E. Katrenick, *Rubber Chem. Technol.* 43, 549-571 (1970).
27. Earl C. Gregg, Jr., *Rubber Chem. Technol.* 42, 1136-1146 (1969).
28. M.L. Selker and A.R. Kemp, *Ind. Eng. Chem.* 36, 16-28 (1944).
29. M.L. Selker, *Ind. Eng. Chem.* 40, 1467-1470 (1948).
30. C.G. Moore, *J. Polym. Sci.* 32, 503-506 (1958).
31. S.P. Manik and S. Banerjee, *Rubber Chem. Technol.* 40, 1311-1326 (1970).
32. M.L. Selker and A.R. Kemp, *Rubber Chem. Technol.* 22, 8-15 (1949).
33. Richard J. Lewis, *Hazardous Materials Desk Reference*, Van Nostrand Reinhold, New York, 1991.
34. Paul P. Nicholas, *Rubber Chem. Technol.* 55, 1499-1515 (1982).
35. Paul P. Nicholas, *ACS Symp. Ser.* 1987, 326, (Phase Transfer Catal.: New Chem., Catal., Appl.), 155-168 (Eng.) (Chapter 13).
36. Paul P. Nicholas (to the B.F. Goodrich Company), U.S. 4,161,464 (July 17, 1979).
37. P.D. Nikolinski and V.V. Mirtscheva, *Kautschuk, Gummi, Kunstst.* 22, 298-299 (1969).
38. G. Adam, A. Sebenik, U. Osredkar, Z. Veksli and F. Ranogajec, *Rubber Chem. Technol.* 63, 660-668 (1990); *ibid.* 64, 133-138 (1991).
39. K. Wagener, J.G. Nel, R.P. Duttweiler, M.A. Hillmyer, J.M. Boncella, J. Konzelman, D.W. Smith, Jr., R. Puts and L. Willoughby, *Rubber Chem. Technol.* 64, 83-95 (1991).
40. J.E. O'Gara, J.D. Portmess and K.B. Wagener, *Macromolecules* 26, 2837-2481 (1993).
41. H.L. Dinsmore and Don C. Smith, *Anal. Chem.* 20, 18-24 (1948).
42. J.K. Clark and R.A. Scott, *J. Appl. Polymer Sci.* 14, 1-9 (1970).
43. Donald S. Novotny, Richard L. Marsh, Frank C. Masters and David N. Tally, (to The Goodyear Tire & Rubber Company), U.S. 4,104,205 (August 1, 1978).

44. S.R. Fix, *Elastomerics* 112, No. 6, 38-40 (1980).
45. *Plastic and Rubber News*, p 9 (September 1979).
46. Masayuki Okuda and Yasuo Hatano (to Yokohama Rubber Co.), JP 62,121,741 (June 3, 1987). (CA 107: 200,131h).
47. Nagabhusan Senapati and Duryodhan Mangaraj (to Battelle Memorial Institute), U.S. 4,548,771 (Oct. 22, 1985).
48. Duryodhan Mangaraj, Personal Communication.
49. Avraam J. Isayev (to the University of Akron), U.S. 5,258,413 (to be issued Nov. 2, 1993).
50. Phil Zimmer, News Release, The University of Akron, (received Sept. 2, 1993) "Massillon Firm to Use UA's Technology for Tire Recycling."
51. Peter Bos, Fred C. Boogerd, J. Gijs Kuenen in *Environmental Microbiology*, Ralph Mitchell, Ed., Wiley-Liss, Inc., New York, 1992, ch.15, pp 375-403.
52. Stu Borman, *C&EN*, Nov. 4, 1991, pp. 31-34.
53. Joseph Haggin, *C&EN* June 17, 1991, pp. 32-35.
54. E.F. Sverdrup and B.R. Wendrow in *Encyclopedia of Polymer Science and Technology*. Norbert M. Bikales, Ed., John Wiley & Sons, Inc., New York, 1970, Vol. 12, pp 341-355.
55. R. Schaefer and R. Berneking, presented at the meeting of the Rubber Division, Atlanta, Georgia, October 7-10, 1986 [Symposium: Reclaiming and Recycling of Elastomeric Products]; abstract in *Rubber Chem Technol* 60, No. 1, 205 (1987).
56. Roger A. Schaefer [same symposium and abstract as ref. 55].
57. Bruce Bowers, Dennis Barber and Richard Allinger [same symposium and abstract as ref. 55].
58. George W. Miller in *The Chemistry and Technology of Rubber*, Carroll C. Davis and John T. Blake, Eds., Reinhold Publishing Corporation, New York, 1937, ch. 22, pp 720-738.
59. D.S. Le Beau, *Rubber Chem. Technol.* 40, 217-237 (1967).
60. J.M. Ball, Ed., *Manual of Reclaimed Rubber*, Rubber Reclaimers Association, Inc., New York, 1956.
61. A. Nourry, Ed., *Reclaimed Rubber: Its Development, Application and Future*, MacLaren & Sons, London, 1962.
62. J.A. Szilard, Ed., *Reclaiming Rubber and Other Polymers*, Noyes Data Corporation, Park Ridge, NJ, 1973.
63. Fernley Smith in *The Vanderbilt Rubber Handbook*, Robert O. Babbit, Ed., R.T. Vanderbilt Company, Inc., Norwalk, CT, 1978, pp 319-336.
64. Roger Schaefer and R.A. Isringhaus, in *Rubber Technology*, Maurice Morton, Ed., Van Nostrand Reinhold Company, New York, 1987, ch. 18, pp 505-517.
65. B.D. LaGrone in *Advances in Materials Science & Engineering* comprising *Supplementary Volumes to the Encyclopedia of Materials Science & Engineering* and *Concise Subject Encyclopedias*, Robert W. Cahn, Ed., New York, 1986, Review Article No. 12.
66. B.D. LaGrone in *Concise Encyclopedia of Polymer Processing & Applications*, Patrick J. Corish, Ed., Pergamon Press, New York, 1992, pp 607-609.
67. B.D. LaGrone and Jerry Lynch [same symposium and abstract as ref. 55].
68. R.A. Swor, L.W. Jensen, and M. Budzol, *Rubber Chem. Technol.* 53, 1215-1225 (1980).

RECEIVED May 2, 1995

## Chapter 22

# A Black Filler for Rubber from Tire Pyrolysis Char

Michael R. Beck<sup>1</sup> and William Klingensmith<sup>2</sup>

<sup>1</sup>Polymer Valley Chemicals, Inc., 1872 Akron Peninsula Road,  
Akron, OH 44313

<sup>2</sup>Akron Consulting Company, Akron, OH 44319

The purpose of this paper is to review the requirements that need to be met by a black filler.

This paper reviews two major aspects of rubber technology. The first is a review of the black fillers used in rubber compounding. The second is a discussion of the scrap tire generation and disposal issue and how a black reinforcing filler can be generated using scrap tires and pyrolysis, grinding and beneficiation to produce a useful product. There is over 3 billion pounds of carbon filler used in North America. Over 90% of this is as a reinforcing and/or extender filler for rubber. The three types of black, furnace, thermal, and channel are reviewed and their benefits presented. A typical production specification for several grades of carbon black are shown and the actual production results for over 40 lots of carbon black are analyzed for consistency. In addition a brief history of carbon black development and the specific plant and processing needs of carbon black are discussed.

Carbon black is the major reinforcing agent for rubber. Most rubber articles require the incorporation of reinforcing agents to be useful. Other reinforcing agents that are used include silica, clay and ground carbonates. The rubber compounder selects the reinforcing agent or filler to impart the properties to the rubber compound that make it serve its' intended purpose at the lowest possible cost.

Carbon black is made in many different types and grades. These include thermal black with little reinforcing power to N110 furnace black with high reinforcing ability. These are discussed in detail in another part of this paper. The total amount of carbon black consumed in the US is estimated at 3.0 billion pounds. About 90% of this is used by the rubber industry with the remaining 10% divided between inks, plastics, coatings, paper and electrodes. These are summarized in Chart 1 (1).

0097-6156/95/0609-0254\$12.00/0  
© 1995 American Chemical Society

There is a significant amount of work being done to recover the carbon black from used rubber goods, especially tires. This has not happened as quickly as many recyclers have desired. This paper will review some of the efforts that have been tried to recycle carbon black from tires. The purposes of the paper are the following:

- 1.0 Review the properties of carbon black used in tire compounding.
- 2.0 Review the tire disposal needs and properties of a black filler produced from tire pyrolysis char
- 3.0 Assess the potential for black filler from tire pyrolysis char to meet carbon black reinforcing requirements.

### Carbon black types

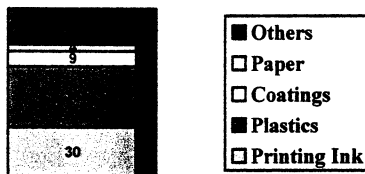
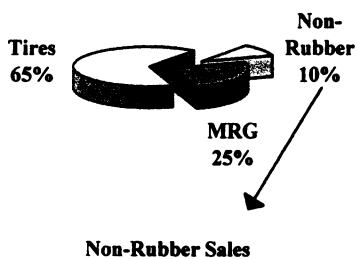
There are twenty five to thirty grades of carbon black that are commonly used. These are broken into the following classes: N100, N200, N300, N500, N600, N700 and N900. Chart 2 shows the various % of each of the blacks used overall (2). The lower the number the more reinforcing the carbon black. The N100, N200 and N300 series blacks generally used in treads for abrasion resistance while N300 and N500 series are used in carcasses of radial tires.

The N600 and N700 series are also used in carcasses and sidewalls of less critical performance bias and slow speed tires. As a result when tires are pyrolyzed a mixture of all the blacks occur along with zinc oxide, titanium dioxide, silica and silicates like clay and talc. The result is a black colored char with a carbon content around 88-90% and an ash of 8-12%. These vary depending on the tire composition used in the pyrolysis operation.

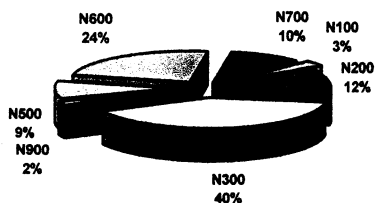
The major types of carbon black and the typical applications in which they are used is as follows:

<u>Designation</u>	<u>General Rubber Properties</u>	<u>Typical uses</u>
N110, N121, N166	High Abrasion Resistance	Special Tire treads, airplane, off-the-road racing
N220, N299, N234	High Abrasion Resistance, Good processing	Passenger, off-the-road, special service tire treads
N339, N347, N375, N330	High Abrasion Resistance, easy processing	Standard tire treads, rail pads, solid wheels, mats, tire belt, sidewall, carcass, retread
N326	Low modulus, good tear strength, good fatigue, good flex cracking resistance	Tire belt, wire carcass, sidewall, bushings, weather strips, hoses
N550	High modulus, high hardness, low die swell, smooth extrusion	Tire innerliners, carcass, sidewall, innertubes, hose, extruded goods, V-belts

**CHART #1**  
**Total Carbon Black Sales**



**CHART #2**  
**US CARBON BLACK PRODUCTION**



<b>N650</b>	<b>High modulus, high hardness, low die swell, smooth extrusion</b>	<b>Tire innerliners, carcass, belt, sidewall, seals, friction, sheeting</b>
<b>N660</b>	<b>General purpose, low die swell, smooth extrusion</b>	<b>Carcass, sidewall, bead compounds, innerliners, seals, cable jackets, hose, soling, flooring, MRG</b>
<b>N762</b>	<b>High elongation and resilience, low compression set</b>	<b>Mechanical goods, footwear, innertubes, innerliners, mats</b>

### Carbon black properties

The properties of virgin carbon black are closely controlled. They are monitored and the purchaser of the carbon black is provided with a specification sheet. The values reported typically are ash content, heat loss, 325 mesh sieve residue, pellet crush strength, iodine absorption, DBP absorption and physical properties compared to an IRB Reference black in the ASTM D3192 or D3191 recipe (3). A sample of the technical data for a lot of N550 and N762 are shown in Chart 3.

As mentioned previously the properties of the black filler obtained from tire pyrolysis char vary widely due to differences in composition of the tires being processed and lack of control of the tire pyrolysis process where temperature and time variations will cause differences in composition. These effects have been studied in great detail in several other studies.

To show how consistent carbon black composition can be, lot analysis sheets for 24 lots of N550 and N762 were obtained. These were analyzed and summarized for ash content, pour density, DBP absorption and iodine number. These are all critical composition or performance criteria for carbon black and closely monitored by the end user. These values are all shown in Charts 4 through 11.

As the data shows the carbon black properties are very consistent. The quality and consistency of the black along with low grit are considered critical to the carbon performance in rubber. The variations in compositions of black filler from tire char have caused many rubber companies to be cautious in supporting the use of such a filler. It will be necessary to get the composition under control and within acceptable limits for black filler from char to be used by the general rubber industry.

### History

Carbon black has been the major reinforcing filler in the rubber industry for well over 100 years and it will continue to be so for years to come. It has historically been made from natural gas and oil feed stocks using the channel, thermal and furnace processes.

The production of carbon black is also possible using a pyrolysis process with worn scrap tires as the feed stock.

This paper is not intended to sell the tire pyrolysis process per se, but to review the technology, economics, and business factors that currently affect its development. It will not go into non-tire or plastics pyrolysis potential.

It will also show that pyrolysis carbon black can be accepted as a viable alternative reinforcing filler for many rubber applications if properly produced.



## CHART # 3

## Physical Chemical Properties

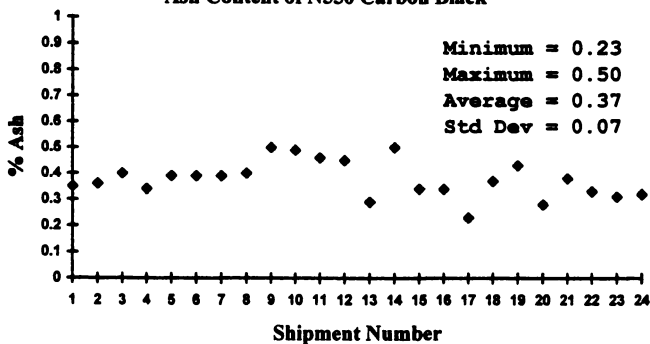
	<u>N762</u>	<u>N550</u>
Ash, D1506	.26 %	.34 %
Heat loss, as packaged D1509	0.1 %	0.1 %
35 Mesh Sieve Residue, D1514	.000 %	.000 %
325 Mesh Sieve Residue, D1514	.003 %	.002 %
Toluene Discoloration 425 m $\mu$	83 %	95 %
Pellet Crush Strength, min	14 grams	8 grams
Pellet Crush Strength, max	41 grams	32 grams
Pellet Crush Strength, avg	27 grams	20 grams
Fines 5' Rotap, D1508	4.4 %	3.6 %
Pour Density, D1513	31.2 lb/ft <sup>3</sup>	22.6 lb/ft <sup>3</sup>
Iodine Absorption, mg/gm D1510	28.3	43.3
DBP, cc/100gm D2414	64.4	119.9

## Properties in NR Formula ASTM D3192

	<u>Cure 30'@143°C</u>			<u>IRB#6 Sample Difference</u>			<u>IRB#6</u>
	<u>Sample</u>	<u>Difference</u>					
300% Modulus	1790	1586	-204	1765	1933	168	
Tensile	3627	3591	-36	3740	3459	-281	
Elongation	546	543	-3	561	496	-65	

## CHART #4

## Ash Content of N550 Carbon Black



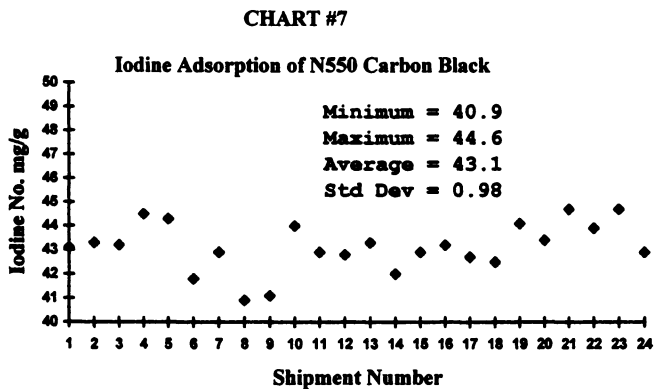
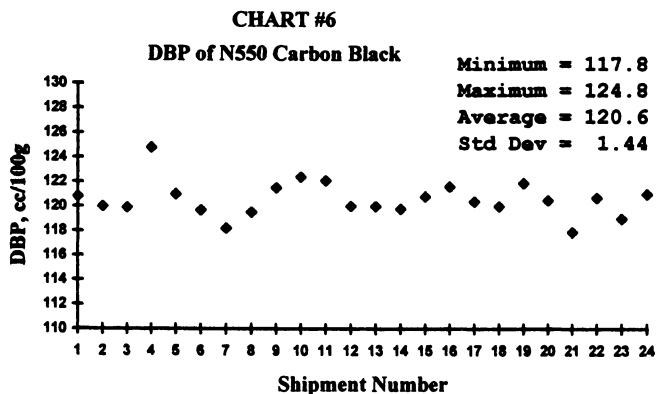
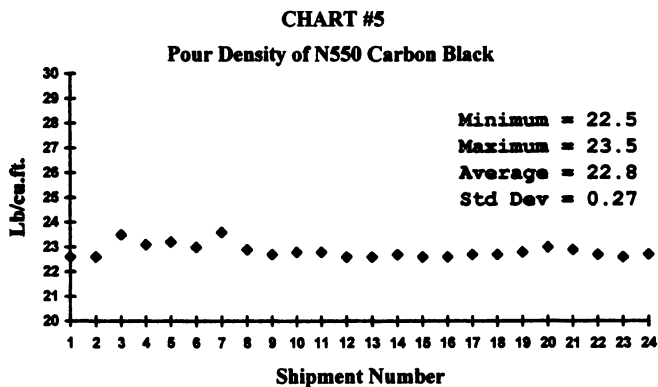


CHART #8

## Ash Content of N762 Carbon Black

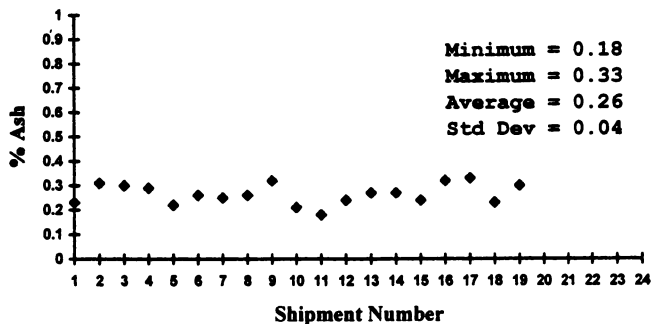


CHART #9

## Pour Density of N762 Carbon Black

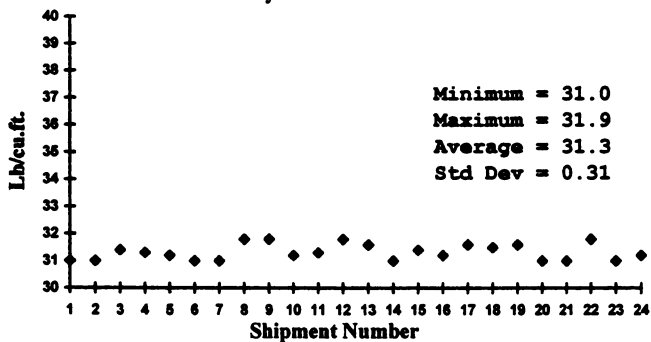
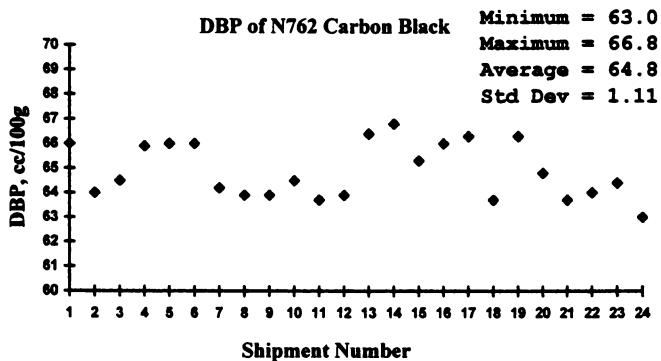


CHART #10

## DBP of N762 Carbon Black



In America today, we have in excess of two billion scrap tires stockpiled. Regulations have been passed in several states to regulate collection, storage, and disposal of scrap tires. This issue is also being addressed at the federal level.

We are recovering less material from our scrap tires today than we did back in 1960 (4). (Chart 12)

In 1960, when reclaimed rubber was widely used, there was 36.4% in recovered material obtained from the 1.1 million tons of scrap tires produced. With the advent of the radial tire, compounders removed reclaim rubber to improve green strength and durability. Recovered material dipped to 5.6% in 1988 and is now at 11.6% for 1.8 million tons of scrap tires in 1990 (5).

We are currently scrapping 250 million passenger tires per year at an average weight of 20 pounds or 9.1 kilograms each. This equate to a fuel value of 300,000 Btu's per tire (6). (Chart 13)

It is evident that the scrap tire disposal problem must continue to be addressed and given more priority. I won't go into detail regarding other alternative disposal measures such as ground rubber as an asphalt additive, or burning as fuel. This paper will show that tire pyrolysis is a viable technical alternative to producing a carbon filler, in essence a new process for carbon black manufacturing.

### **Manufacturing Processes**

The channel, thermal and furnace processes are the three basic methods used to make carbon black.

The century old channel process burns natural gas where the burners impinge on long iron channels depositing the carbon. This is an inefficient and environmentally poor process and is no longer utilized in the U.S.A. Channel black is still made in some parts of the world, with EPC being the most recognized grade to the rubber chemist. (Chart 14)

The thermal process was introduced in the 1920's and is still used today to manufacture a coarse particle size black used predominately in non-tire applications. In this process natural gas is introduced to a pre-heated brickwork furnace and thermally decomposes to release hydrogen and carbon. The resulting products are the familiar N800 and N900 series carbons. (Chart 15)

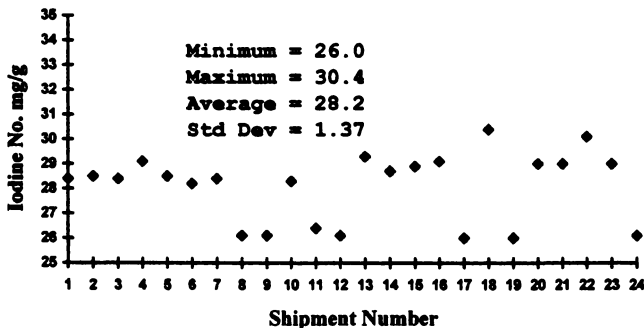
The oil furnace process is the most widely utilized and commercially diverse method for making carbon black. Oil feed stocks are injected into heated, refractory lined furnaces where the oxygen content, burner type and furnace geometry are precisely controlled to generate the large number of grades now available ranging from the N100 through the N700 series (7). (Chart 16)

With pyrolysis, tires are heated to extremely high temperatures in the absence of oxygen until the components separate yielding oil and carbon "char." (Chart 17)

The typical yield for an average passenger tire is: One gallon of oil, seven pounds of carbon, two pounds of steel, two pounds of methane gas, and about one-half pound of fiber. All of these recovered materials can be re-utilized. (Chart 18)

The pyrolysis process will generate a new and different filler material. Pyro black will compete with current materials in narrow, select segments of the market and on a cost performance basis.

**Chart #11**  
**Iodine Adsorption of N762 Carbon Black**



**Chart #12**  
**SCRAP TIRE DISPOSAL HISTORY**

	<u>Tons</u>	<u>% Recovered Materials</u>
1960	1,100,000	36.4%
1988	1,900,000	5.6%
1990	1,800,000	11.6%

From: Characterization of Municipal Solid Waste in the U.S. 1992 Update

**Chart #13**

We are currently scrapping 250 million passenger tires per year at an average weight of 20 pounds or 9.1 kilograms each.

**Fuel Value = 300,000 Btu's / tire**

**Chart #14**

**CHANNEL BLACK PROCESS**

- **Burn Natural Gas**
- **Impinge on iron channels**
- **Inefficient: 1% to 5% yield**

## Chart #15

**THERMAL BLACK PROCESS**

- **Thermal decomposition of natural gas**
- **Preheated brickwork furnaces**
- **Yields 40% to 50%**

## Chart #16

**FURNACE BLACK PROCESS**

- **Oil Feed Stock Injected**
- **Refractory Lined Furnaces**
- **Controlled Conditions**
  - **Oxygen Content**
  - **Burner Type**
  - **Furnace Geometry**

## Chart #17

**PYROLYSIS BLACK PROCESS**

- **Tire Collection System/ Scrap Tires**
- **Tire Preparation**
  - **Sorting and Classifying**
  - **Shredding**
- **Pyrolysis Furnace - Absence of Oxygen**
- **Yield**
  - **Gas**
  - **Oil**
  - **Steel and Fabric**
  - **Char**
- **Post Treatment**

### Carbon Black Market

The North American market uses about (1.5 million tons) three billion pounds of carbon black per year that is split almost equally between hard (N100, N200, N300 series) and soft (N500, N600, and N700 series) grades.(Chart 19)

Of the three billion pounds (1.5 million tons), about 70% is consumed in tires and tire related products. The remaining 30% is used in non-tire applications such as Molded MRG, Extruded MRG, Foam & Sponge, Wire & Cable, Flooring, Matting, Solid Wheels, and Roofing Membrane.(Chart 20)

It is in this non-tire segment, using 450,000 tons of carbon black per year and which is virtually all soft black and thermal black, that pyrolysis blacks will first find a home. (Chart 21)

This is because the pyrolysis blacks generated with current technology have a broad particle size distribution that yields reinforcement properties in between the SRF (N762) and MT (N990) range. (Chart 22)

It is also quite possible that certain tire applications such as innerliner, carcass and sidewall would be able to utilize pyrolysis carbons in blends with virgin furnace grades..

The fact is that pyrolysis blacks will provide the compounder with an alternative compounding material, and should be viewed accordingly. Pyrolysis blacks are not channel, thermal, or furnace blacks.

In order for pyrolysis black to gain initial acceptance, the market will have to overcome a pre-conceived opinion that it is of inferior quality and lacks uniformity.

This posture is not unfounded. The many small companies that, in the past have tried and, in some cases, are still producing pyro blacks, have fueled this perception. These blacks are very coarse and contain much extraneous material, and as a result, have limited market potential. They have failed to recognize the quality level that must be achieved through additional processing techniques after they generate the initial char.

### Technical Requirements

A pyrolysis black, when properly produced, will meet the following specification and provide reinforcement as shown in the two ASTM test formulations.

The key points to observe in this specification are the low volatiles, the low sieve residue, the soft pellets, the fact that densification is required, and the minimum tensile requirements. (Charts 23 and 24)

In the ASTM D3191 SBR formula note that the minimum tensile is achieved and that reinforcement is indeed between that of N774 and N990. (Chart 25)

In the ASTM D3192 NR formula the modulus and tensile values exceed those of N990 at equal loading. (Chart 26)

These test results reflect data generated from actual pyrolysis carbon produced to the previous specification in pilot plant quantities under current patented processes (Beck, M.R., Polymer Valley Chemicals, unpublished data).

The keys to attaining the acceptable reinforcement levels are two-fold. First, the time temperature relationship during pyrolysis must be controlled to produce a black with minimum volatile content on the surface. Secondly, the physical screening, grinding, and classifying techniques employed must remove the extraneous materials and meet the 325 mesh sieve residue specification. (Chart 27)

Chart #18

TYPICAL PYROLYSIS YIELD (%) - AVERAGE PASSENGER TIRE

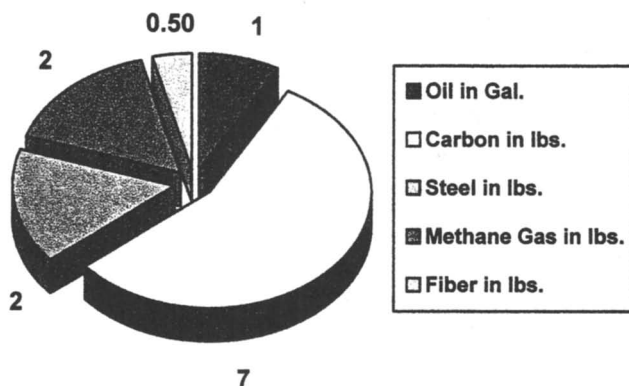
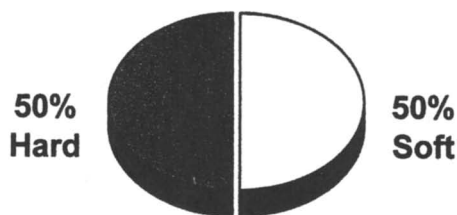


Chart #19

NORTH AMERICAN CARBON BLACK MARKET

3.0 Billion Pounds = 1.5 Million Tons



August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch022



**Chart #20**  
**NORTH AMERICAN CARBON BLACK MARKET**

3.0 Billion Pounds = 1.5 Million Tons



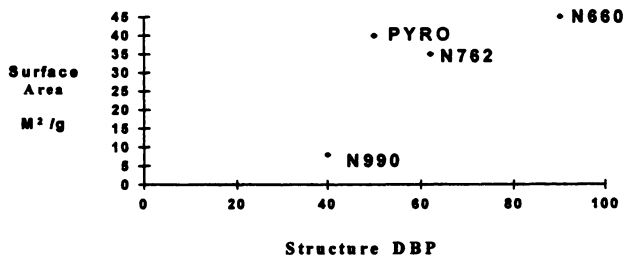
**Chart #21**

**NON - TIRE SEGMENT**

- **450,000 Tons of Carbon Black per Year**
  - **Predominately Soft Blacks & Thermal Black**
  - **Pyrolysis Black Target Segment**

**Chart #22**

**Relative Carbon Black Classification**



## Chart #23

**PYROLYSIS CARBON  
TARGET SPECIFICATION  
RUBBER INDUSTRY**

<u>PROPERTY</u>	<u>RANGE</u>	<u>ASTM TEST</u>
Form	Black Pellet	---
Specific Gravity	2.0	---
Bulk Density	25 lbs./ft <sup>3</sup> . ( $\pm$ 1.0 lb.)	D1513
pH	7.5 ( $\pm$ 0.5)	D1512
Ash	9% - 15%	D1506
Volatiles	0.20% - 0.30%	---
Carbon Content	80.0% Min.	---
Total Sulfur (Non-Reactive)	3.0% Max.	D1619

## Chart #24

**PYROLYSIS CARBON  
TARGET SPECIFICATION  
RUBBER INDUSTRY**

<u>PROPERTY</u>	<u>RANGE</u>	<u>ASTM TEST</u>
Particle Size, Measured	40 - 50 Micron	---
Particle Size, Effective	0.06-0.1 Micron	---
325 Mesh Sieve Residue	0.20 % Max.	D1614
Individual Pellet Hardness		D3313
- Average	50 Grams	
- None Higher Than	70 Grams	
Heat Loss	1.0 % Max.	D1609
6' Pelleted Fines Content	8.0 % Max.	D1608
Minimum Tensile - SBR	2600	D3191
Minimum Tensile - NR	3100	D3192

## Chart #25

**PYROLYSIS CARBON  
FORMULA: ASTM - D3191 SBR RUBBER**

	<u>PYRO</u>	<u>N-774</u>	<u>N-990</u>
<u>Rheometer @293° F, 3° Arc.</u>			
Max. Torque MH, Lbf.,in.	71.2	78.1	67.0
Min. Torque ML, Lbf.,in.	12.9	11.8	9.9
Scorch Time, TS2 Min.	6.9	6.0	7.1
Cure Time, TC 90% Min.	19.0	16.1	17.3
<u>Physical Properties 50' @293° F</u>			
Tensile, PSI	2640	3110	2070
100% Modulus, PSI	270	450	230
300% Modulus, PSI	960	1830	740
Elongation, %	620	450	660
Hardness, Shore A	58	63	52

### Requirements for Market Acceptance

It is evident that pyrolysis carbon of this quality level can and should be used in many applications. Utilization of carbon recycled from old tires has obvious benefits to the environment and permits the tire manufactures to become part of the solution to the scrap tire problem.

Even a modest acceptance in non-tire applications would generate an initial market of over 50,000 tons for pyrolysis carbons with growth potential in both tire and non-tire applications. (Chart 28)

So what is preventing the development of pyrolysis carbons? The problem to date has been the lack of recognition by the entrepreneurs and investors that carbon production is much more than simply burning the tires. The job is not done when the char is obtained, it is only just beginning as far as rubber applications are concerned. The cost to move on to this next level and the technical know-how required to achieve it are main factors which have prevented the production of a pyrolysis grade suitable for the rubber industry.

Successful pyrolysis black producers will develop post treatment techniques to further beneficiate the char by a combination of grinding, screening, classifying, pelletizing and drying techniques. (Chart 29)

Their goals should be to:

- eliminate hard particles and magnetics
- reduce particle size to improve tensile
- fraction out large non-reinforcing particles
- maintain even particle size distribution
- produce an easy to handle product (densification)
- assure quality and uniformity with a defined program (Chart 30)

In conclusion there are several marketing factors that will eventually lead to the acceptance of pyrolysis black as a filler in the rubber industry. These factors require joint recognition by both potential producers as well as end users.

The first will be to overcome initial resistance based on concerns over quality, uniformity, that it is a recycled or "waste" product, continuance of supply, and simply the fact that it is different. (Chart 31)

Secondly recognize and utilize the inherent advantages:

- There is a basic movement to use recycled products in our everyday lives. One may be able to take advantage of beneficial legislation that provides incentives or tax breaks for using recycled products. Marketing and sales advantages may exist by being a concerned corporate citizen and generating a good public relations image by being a part of the solution for scrap tire disposal.
- There will most likely be a competitive price advantage for pyrolysis blacks versus standard furnace or thermal blacks. Pyrolysis black producers will also be able to market the other by-products or re-use the gas and oil as fuel for their process. This will affect their overall profitability and pricing policies.
- Pyrolysis carbons may actually provide unique properties that are desirable. A wide particle size distribution would contribute to lower hysteresis as well as higher loading capability. It is also possible that surface modified versions could be produced with enhanced properties as the technology grows.

## Chart #26

PYROLYSIS CARBON  
 FORMULA : ASTM - D3192 NATURAL RUBBER

	PYRO	N-990	IRB #8
<u>Rheometer @ 293° F., 3" Arc.</u>			
Max. Torque Lbf. in.	74.80	69.50	88.70
Min. Torque Lbf. in.	21.10	15.40	24.10
Cure Time 90 % Min.	26.00	25.75	29.75
Scorch Time TS 2, Min.	10.00	9.50	10.25
<u>Physical Properties</u>			
<u>15'/293° F</u>			
Tensile, PSI	3800	3450	3990
300% Modulus, PSI	1320	730	1870
Elongation, %	560	660	550
Hardness	57	50	65
<u>30'/293° F</u>			
Tensile, PSI	3300	3250	3950
300% Modulus, PSI	1560	950	2170
Elongation, %	510	610	510
Hardness	60	52	69

## Chart #27

## KEYS TO REINFORCEMENT

- Time - Temperature Relationship
  - Minimum Volatiles
- Physical Post Treatment

## Chart #28

## NON - TIRE SEGMENT

- 450,000 Tons of Carbon Black per Year
  - Predominately Soft Blacks & Thermal Black
  - Pyrolysis Black Target Segment

INITIAL MARKET: 50,000 Tons plus Growth

## Chart #29

## POST TREATMENT REQUIREMENTS

- Grinding
- Screening
- Classifying
- Pelletizing
- Drying

**Chart #30****POST TREATMENT GOALS**

- **REDUCE GRIT**
  - **Must be Free from Hard Particles & Magnetics**
- **OPTIMIZE TENSILE**
  - **Reduce Particle Size**
    - **Maximize Reinforcement**
  - **Fraction Out Large Non-Reinforcing Aggregates**
- **MAINTAIN UNIFORMITY**
  - **Maintain Consistent Particle Size Distribution**
    - **Important for Product Acceptance**
    - **Determines Approval & Repeat Orders**
- **PROVIDE EASE OF HANDLING**
  - **Produce Pelleted Form - High Bulk Density**
    - **Facilitates Packaging in Poly Bags or Bulk**
    - **Fluffy Black Will Not Easily Disperse**
  - **Control Pellet Hardness**
    - **Cannot Have Hard Pellets**
    - **Dispersion Affected**
    - **Minimal or No Binder**
- **DEVELOP QUALITY PROGRAM**
  - **SPC Techniques for Product Uniformity**
  - **Provide COA With Shipments**

**Chart #31****MARKETING FACTORS**

- **Initial Resistance**
  - **Quality Perception**
  - **Concern Over Uniformity**
  - **Concern That It Is a Waste Product**
  - **Concern Over Continuance of Supply**
  - **It's Different**

- Being a new supplier is often advantageous, especially when the product is new and different. (Chart 32)

Thirdly, become part of the solution for disposing of scrap tires before legislative actions dictate solutions for us. This will require end users to be open minded and amenable to supporting tire pyrolysis efforts. (Chart 33)

Finally, a plant must be built large enough to bypass the economical barriers experienced by the small operators and entrepreneurs that have been involved in pyrolysis to date. A large scale plant on the order of fifty million pounds per year is needed to define and refine the process.

Given a chance, pyrolysis carbon suitable for rubber applications should become a compounding material during this decade.

Chart #32

**MARKETING FACTORS**

- **Advantages**
  - **Desire to Use recycled Products**
    - **Legislation May be Beneficial**
    - **Good Public Relations**
    - **Concerned Corporate Citizen**
  - **Competitive Pricing**
  - **Unique Properties**
    - **Wide PSD = Lower Hysteresis**
    - **Use Higher Loadings**
    - **Potential to Surface Modify**
  - **New Supplier**

Chart #33

**MARKETING FACTORS**

- **Public Awareness**
  - **Become Part of the Solution**
  - **Avoid or Preempt Legislative Mandates**
- **LARGE SCALE PLANT NEEDED**

**“Literature Cited”**

- (1) Current market conditions and product requirements for Carbon Black Worldwide - personal communications - Alan McNeish, Degussa Corporation.
- (2) *“Carbon Black”, Encyclopedia of Chemical Technology*, John Wiley.

- (3) ASTM D3192 and D3192, *Volume 9*, ASTM Standards, 1993.
- (4) Characterization of Municipal Solid Waste in the US: 1992 Update.
- (5) Beckman, Crane, Kay, and Laman, "*Scrap Tire Disposal*", 1975 RCT, pp. 597-603.
- (6) Crane, Elefritz, Kay, and Laman, "*Scrap Tire Disposal Procedures*", 1978 RCT, *Vol. 51*, pp. 577-599.
- (7) Donnet, Bansal, and Wang, *Carbon Black*, Marcel Dekker, 1993, 2ed.

RECEIVED May 2, 1995

## Chapter 23

# Cellulose and Paper Recycling: A Pragmatic View

Sheryl D. Baldwin

Packaging Design and Development, Philip Morris Research Center,  
P.O. Box 26603, Richmond, VA 23261

Cellulose, as the most abundant polymer, is also the most extensively recycled. This overview chapter for cellulose and paper recycle describes the importance of cellulose recycle as central to the overall recycle of materials. After developing a conceptual framework for the sustainable recycle of cellulose and paper, the critical elements of cellulose and paper recycling are identified as raw material supply, fiber and product quality issues (strength and cleanliness), the availability of infrastructure, and the ability to sustain growth. The critical issues of sustainability and the infrastructure are discussed at some length.

Cellulose is the most abundant polymer on earth. It is nature's polymer and is the key structural component of grasses, shrubs, and trees, as well as nearly all other plants, including many microorganisms. In its various embodiments, cellulose has been adapted for use by mankind to produce materials for writing, housing, tools, textiles, tennis racquets, weapons, and works of art.

As a food additive, it is found in fat free salad dressings and various sauces and confections. As a binder or thickener, cellulose is also widely used in the pharmaceutical industry. The derivatives of cellulose are used as thickeners for sauces and gravy (for both human and canine consumption), as well as for frozen whipped toppings. Cellulose derivatives are also used in tooth paste formulations, paint, ink, and coating formulations. Ethylcellulose is commonly used as a coating on bowling balls. Cellulosics make good adhesives, and are also used as binders in cement, and for various other applications in the construction industry.

Cellulosic polymers are also used in the oil drilling industry as the "mud" used to lubricate drill bits and for tertiary recovery in older oil fields. Cellulose derivatives serve as the absorbent fibers in disposable diapers and other personal products. Cellulose derivatives can be used, like cellulose, as filtration media. Cellulosic materials are used for coffee filters, locomotive engine oil filters, as well as cigarette filter tow.

0097-6156/95/0609-0274\$12.00/0  
© 1995 American Chemical Society



The preponderant application for cellulose, however, is in the manufacture of paper products. Paper is used for writing, printing and publishing, as well as for packaging. The list of uses for cellulose is virtually endless, since new uses are constantly being developed. Indeed, cellulose is ubiquitous. In nearly every area of human activity, cellulose plays a role. Its importance to us is unquestionable. Ironically, however, because it has become so integral a part of our experience, it has become nearly transparent to us. Perhaps this is the highest mark of success for a material. It has been so extensively and creatively utilized in our lives that we often are completely unaware of its presence. When considering the subject of recycling, cellulose once again appears at the top as the most widely recycled polymer in the world. Because the range of applications for cellulose is so extensive, it is necessary to limit the scope of this section on recycling to address the areas which are most critical in terms of the role which cellulose plays.

Cellulose is the most widely recycled polymer in the world, largely as a consequence of paper recycling. Papermaking began with the Egyptians who produced papyrus from the inner fibrous component of the stem of the papyrus plant. Papyrus used in this manner was prepared as a mechanical pulp. The modern method of papermaking, in which an aqueous slurry of cleaned and beaten fibers drains through a screen to produce a sheet, essentially began in China in the first century AD. Ts'ai Lun, an official in the court of Emperor Ho Ti, is credited with its invention. Although cellulose has been widely recycled by modern papermakers because of the relative expense of the fiber, the economic importance of cellulose recycle can be traced to the development of the printing press. With the advent of this new technology, the demand for printing material grew rapidly, causing shortages in the supply of paper. Cotton and linen rags were recycled for the manufacture of paper, as they imparted additional strength to the sheet due to the length of the cotton or flax fiber and the high degree of polymerization of the cellulose derived from those sources. The issue of strength of recycled cellulose in its varied forms is still critical to us today.

### **Sustainable recycle of cellulose and paper**

This section of the book will address cellulose and paper recycle. Because the subject is so broad, only key factors currently reflecting the greatest challenges have been selected for treatment here. Additionally, most of the contributors to this section of the book are practitioners in the field. They represent the industrial leaders in the area of paper recycle, and were chosen because of their extensive knowledge and experience. What we wish to identify are the technical hurdles and logistical issues having the greatest practical significance in the field. We wish to draw on the successful experiences of those industrial leaders who have risen to meet these challenges. That knowledge and experience, focusing on what has worked for their businesses, is presented here for the reader who wishes to effectively plan for development work involving recycling. That work may involve development of recycling processes, of recycled or recyclable materials or products, or the judicious management of any solid waste. Clearly for the recycle of paper and cellulose fiber, cleanliness and strength are critical issues. Consequently, three chapters are dedicated to those issues. Additionally, raw material supply, procurement, and quality issues are covered in another chapter that addresses the marketing aspects of the subject. An

abundance of facts and statistics about the global situation for cellulose and paper recycle is provided by Dr. Keith Hall, of International Paper Company, who is also a past president of TAPPI. We also wish to inform the reader about both existing state-of-the-art technologies and longer range innovative approaches with potential for the future.

This section is structured to reflect the principles of sustainable development. By applying some of the most effective and results oriented strategies used by different industries to approach the issue of cellulose and paper recycle, we can point the way to make steady and sustainable gains in that area. These examples model solid approaches to sustainable development, each demonstrating how to attain substantial improvements in the recycle of cellulose and paper, as well as how to do so cost effectively. At the presidential plenary session inaugurating the American Chemical Society national meeting in Washington, D. C. in August 1994, Dr. Leo Jansen of the Netherlands described a framework for planning and assessing progress in environmental protection called "sustainable technology development" (1). That framework defines three major levels of attainable progress (2), (3).

The first level of progress involves environmental care or improved environmental management practices (1, 3-4). Initiatives of this type reflect improved efficiencies obtained by prudent management of current situations and practices. For example, during the energy crisis of the early 1980s many manufacturing plants found that considerable energy could be saved (along with dollars) simply by taking more care to plug steam leaks in the existing piping network. This type of easily attainable improvement not only met the energy conservation goals intended, but also increased profitability. In terms of the recycle of cellulose and paper, as well as in other areas of manufacturing, waste minimization is both cost effective and environmentally sound. Many companies, such as Du Pont, have recognized this fact and have established programs committed to reducing and minimizing waste as an integrated part of developing environmentally sound manufacturing practices. It is simply good business to do so.

The second level of progress can be attained by utilizing existing environmental technologies or management practices in innovative ways. Some such practices include the recycle of solid manufacturing wastes. Instead of sending scrap material to the landfill, it is sold to commercial recycle providers. Weyerhaeuser has now (early 1995) built or purchased 29 recycling facilities across the country and is developing a thriving business buying and reselling solid manufacturing wastes (Friberg, T., Weyerhaeuser Co., January 1995). Major manufacturing companies, including Philip Morris and Kraft Foods, began this practice several years ago, selling recyclable scrap instead of sending it to the landfill (McAndrews, P., Kraft Foods, presentation, June 21, 1994). This type of recycling practice not only reflects responsible care, but also is an innovative and cost effective method of managing solid waste. Tom Friberg, et al, of Weyerhaeuser Co., describe some of the practical issues and obstacles encountered in commercial recycling in their chapter on raw material supply and procurement. Moving on into "process-integrated" environmental technologies, we find the most sophisticated advances possible with existing technologies. An excellent example of

this type of innovative application of process technology is reflected in Bruce Janda's description of process innovations implemented by James River Paper to develop a 100% recycled fiber paper board with significantly improved cleanliness and print quality compared to typical 100% recycled board.

These types of gains have been attained by industrial leaders in realistic time frames, i.e., two to five years. All these levels of progress move us toward our goal, but there are limits to that which can be attained with existing technologies. The final stage of advancement toward the desired environmental goals can only be attained by longer range research and breakthrough technologies. The time frames in this category of endeavor are much longer, but the long range research is essential for sustainability. It is the key to sustainable development, which must be more than simply cleaner production. We must develop the breakthrough technologies.

### **The Critical Issues**

#### **Recycled Paper and Fiber Critical Properties**

Three categories of critical fiber and product properties are purity, strength, and surface characteristics. Purity is important for safety and toxicological reasons, as well as for performance. Strength is important principally in the packaging area, in which product protection is critical. Strength is also a safety issue. Of paramount importance in printing, writing, and communication papers, as well as for printed board materials, are the surface properties. These include smoothness, wettability, absorbency, printability, linting, optical properties, brightness and dirt. The surface free energy of recycled fibers and the corresponding paper and board differs from that of virgin materials, and these differences may have an impact on the printing and adhesion attributes of the finished paper or board product. The subsequent chapters rather extensively address fiber cleaning techniques, including some discussion of surface treatment of fibers during deinking. Strength and cleanliness are addressed as a processing issue in Janda's chapter. The last two chapters in this section present new concepts in and approaches to the recycle of cellulose. Of particular interest is Rowell's concept of the agro-refinery as a recycled cellulose processing facility. The discussion in this chapter will focus on the critical issues of infrastructure and sustainable development.

#### **The Infrastructure and Sustainability**

Roget's International Thesaurus, Fifth Edition, cites the word recover as a synonym for the word recycle. Indeed, recovery of valuable goods or materials is always preferable to waste and loss. Our point here is to note that the process of recycling implicitly denotes the recovery of goods or materials of value. Indeed, in order to gain a greater understanding of the broader issues associated with cellulose and paper recycle, it is helpful to consider the entire process of recovery. Recovery may be defined as the process of separating materials of value from other wastes at the point of origin of the waste, collecting and transporting the materials, sorting the materials into categories for processing, and finally processing the materials to produce a usable feed stock for other manufacturing processes.

Breaking this down further into the component steps will help to develop an understanding of the infrastructure required to effect the desired rates of recycle of cellulose and other materials recommended by the Environmental Protection Agency (5-6). Collection of the materials usually takes place at the point of generation. Alternatively, it may be collected at a drop-off site or buy-back center. Occasionally, collection may take place at the processing facility itself. Sorting simply involves separating the materials into appropriate categories. This step can be done by the source generator. The generator may be residential, commercial, or public. Sorting can also take place at the processing facility. With curbside collection, sorting options include household sorting, truckside sorting, or commingling of recoverable items. The materials may then go to recyclable materials processing facilities (RPFs) or materials recovery facilities (MRFs). Low-tech MRFs rely on manual labor for sorting, while the high tech variety are mechanized. In China, teams of 2000 people separate municipal solid waste into its component categories for recycling. Such a scenario is only conceivable in a country with a billion people. There is also no welfare in China, since everyone is a worker, and all forms of work are respected.

After additional sorting and preparation for processing, the material is ready to go to the processing facility. The entire recovery process is described for waste paper in the following chapters, with the focus on cleanliness and strength of the resulting product.

### **Infrastructure for Recycling**

Given this description of the process of recycle, let us consider once more the issue of infrastructure. Infrastructure, by definition and for our purposes here, is comprised of the facilities and installations necessary for the effective accomplishment of all the component steps of the recycling process described above. Table I shows the number and distribution of existing and planned programs and facilities for recycling in the U.S. The recycle of cellulose is inexorably linked to the overall recycle of all solid waste, since cellulose comprises more than 50% of the total solid waste stream, particularly for municipal wastes (calculated from data given in reference 7). Consequently, if we are designing or developing products made from or packaged in cellulose containing materials, we need a clear understanding of the location and nature of recycling centers in our marketplace, along with the extent of household and individual participation in recycling programs in order to make effective business decisions. This discussion is intended to benefit these readers, as well as those engaged in research or planning in the cellulose and paper industries.

The infrastructure to support recycling has changed over the past 20 years. In the past, cities could not give away recycled waste. In the last two years the situation has reversed itself, with recycled materials gaining marketplace respectability by being added to the Chicago Board of Trade's list of commercial commodities (8). Curbside collection of recyclable items has also increased rapidly since 1990. The total number of curbside programs in the United States nearly doubled between 1990 to 1992. The Northeast region led in number of programs in operation in 1990, with 56 percent of the total. That region also established the most new programs between 1990 and 1992.

Table 1

**EXISTING AND PLANNED SOLID WASTE RECYCLING AND PROCESSING FACILITIES AND LANDFILL SITES, 1992\*\***

Recovery/Processing of Recyclable Materials	Northeast	Southeast	Central	Mountain	Pacific	Totals
<b>Curbside collection</b>						
Number of programs	2,939	570	1,122	111	662	5,404
% of population served	42%	25%	10%	14%	50%	31%
<b>Materials recovery facilities (MRF)</b>						
Number of facilities	123	33	26	8	32	222
Capacity (tons per day)	15,310	5,197	1,423	2,331	4,127	28,388
% of population served	36%	23%	5%	21%	25%	24%
<b>Mixed waste processing facilities</b>						
Number of facilities*	13	5	3	3	11	35
Capacity (tons per day)	11,639	1,900	570	435	10,443	24,987
% of population served	5%	1%	1%	6%	19%	2%
<b>Landfilling</b>						
Landfills Number of facilities	1,054	852	1,449	25	453	4,633
Average tipping fees (\$/ton)	49	34	19	13	28	31
Population density (persons/sq. mi.)	255	167	56	16	45	70

\* Existing and planned

\*\* Reprinted with permission from Keep America Beautiful, Inc., from "The Role of Recycling in Solid Waste Management to the Year 2000", Franklin Associates, Ltd., 1994, Prairie, KS.

In most regions of the country, collection is voluntary. In the Northeast, however, approximately two thirds of the programs are mandatory participation programs, including 100 percent of the programs in New Jersey and Connecticut. Few states outside the Northeast have mandatory programs. The overall participation rate for curbside recycling programs in the US is about 70%(9). Recent reports comparing recycling rates in London and Hamburg indicate that the extent of participation in recycling programs is significantly higher in Hamburg than in London. This can be accounted for primarily by the greater density of recycling facilities combined with the use of more sophisticated systems such as dual or multi-bin collection containers. For either system, cost of the programs was a central issue (10).

Recyclable materials recovered through curbside collection are processed for materials markets at a recyclable materials processing facility (RPF) or a materials recovery facility (MRF). The extent of separation either by the generator or the collector determines the type of processing facility required. Recyclable materials processing facilities (RPFs) accept only separated recyclable materials. At these facilities, there is little or no processing of materials prior to their resale to end users or material brokers. RPFs also accept materials from buy-back centers and handle presorted industrial scrap as well as municipal solid waste (MSW). The number of recyclable materials processing facilities and the amount of material processed is market driven. The number of such facilities is growing and companies such as Weyerhaeuser, which, as noted earlier, recently purchased its twenty-ninth paper recycling facility, are taking advantage of the demand for recycled cellulose fiber by expanding rapidly in an area in which they already have great expertise. This type of action makes profound business sense and is an exemplary marketplace response directed toward filling the need for a more fully developed infrastructure for recycle.

MRFs are divided into two categories--low or high technology (relatively speaking), depending on the degree of mechanical processing done. In 1992, there were 172 MRFs in operation in the continental US, of which 56 were considered high-tech operations. These facilities have a total capacity of 18,200 tons of recyclable papers and other goods per day. The Northeast has over 50 percent of the recyclable materials processing capacity and 43 of the 56 high-tech MRFs. On the basis of the most recent data available, about two thirds of the MRFs are privately owned and nearly 90 percent are privately operated (11). The majority of the publicly owned and operated facilities are in the Northeast. Table II shows the number and distribution of materials recycling centers in the U. S. by region, based on information published last fall.

## **Sustainability of Recycling**

### **The recent view**

Between 1985 and 1992, recycling became an important part of municipal solid waste management. Since paper and cellulose comprise over two thirds of the materials recycled by some estimates, the following data assume importance for the purpose of this discussion. Municipal solid waste (MSW) recovered for recycling in the United States doubled in tonnage during this period, also doubling the rate of recovery from 10 percent to 21 percent of total MSW (12). In 1988 75 million tons of cellulose fiber were recycled; by 2001 approximately 130 million tons will be recycled

**Table II**  
**Materials Recovery Facilities 1992 (\* \*)**

Region *	<u>Technology</u>		<u>Ownership</u>		<u>Operation</u>		Capacity (tpd)
	Low	High	Public	Private	Public	Private	
<i>North and east</i>							
<i>East North Central</i>							
Illinois	6	3	1	8		9	934
Michigan	3	1	1	3	1	3	548
Ohio	1	4		5		5	544
Wisconsin	<u>3</u>	<u>1</u>	<u>1</u>	<u>3</u>	<u>1</u>	<u>3</u>	<u>160</u>
Subregion Total	13	9	3	19	2	20	2,186
<i>Middle Atlantic</i>							
New Jersey	5	6	6	5	3	8	2,007
New York	16	10	16	10	10	16	2,800
Pennsylvania	<u>14</u>	<u>10</u>	<u>4</u>	<u>20</u>	<u>3</u>	<u>21</u>	<u>1,683</u>
Subregion Total	35	26	26	35	16	45	6,490
<i>New England</i>							
Connecticut		4	2	2		4	954
Maine	1		1		1		2
Massachusetts	2	2	1	3		4	734
New Hampshire	1	1		2		2	80
Rhode Island	<u>—</u>	<u>1</u>	<u>1</u>	<u>—</u>		<u>1</u>	<u>210</u>
Subregion Total	4	8	5	7	1	11	1,980
<i>Region Total</i>	52	43	34	61	19	76	10,656
<i>Southeast</i>							
<i>South Atlantic</i>							
Delaware	1			1		1	40
Florida	7	2	2	7		9	1,417
Georgia	2			2		2	470
Maryland	4	3	2	5		7	655
North Carolina	1	1		2		2	155
South Carolina	1		1		1		80
Virginia	<u>1</u>	<u>1</u>		<u>2</u>		<u>2</u>	<u>250</u>
<i>Region Total</i>	17	7	5	19	1	23	3,067
<i>Central</i>							
<i>West North Central</i>							
Iowa	2	1	3		3		50
Minnesota	7	2	5	4	3	6	416
Missouri	<u>1</u>			<u>1</u>		<u>1</u>	<u>48</u>
Subregion Total	10	3	8	5	6	7	514
<i>East South Central</i>							
Alabama	1	1	1	1		2	63
Tennessee	<u>2</u>			<u>2</u>		<u>2</u>	<u>115</u>
Subregion Total	3	1	1	3		4	178

*Continued on next page*

**Table II**  
**Materials Recovery Facilities 1992 ( \* \*)**

Region *	<u>Technology</u>		<u>Ownership</u>		<u>Operation</u>		Capacity (tpd)
	Low	High	Public	Private	Public	Private	
<i>West South Central</i>							
Louisiana	1		1		1		70
Texas	<u>6</u>		<u>6</u>		<u>6</u>		<u>161</u>
Subregion Total	<u>7</u>		<u>7</u>		<u>7</u>		<u>231</u>
<i>Region Total</i>	20	4	9	15	6	18	923
<i>Mountain</i>							
Arizona	4		4		4		261
Nevada	<u>1</u>		<u>1</u>		<u>1</u>		<u>1,000</u>
Region Total	5		5		5		1261
<i>Pacific</i>							
California	20	1	21		21		1,769
Washington	<u>2</u>	1	<u>3</u>		<u>3</u>		<u>528</u>
Region Total	22	2	24		24		2,297
US Total	116	56	48	124	26	146	18,204

\* Regions and subregions are those used by the Bureau of the Census

\*\* Reprinted with permission from Keep America Beautiful, Inc., from "The Role of Recycling in Solid Waste Management to the Year 2000".



(13). Despite this rapid growth, the way to the year 2001 has many hurdles to be surmounted, because recycling based on current technologies has practical limits that will soon be reached. Even as recycling continues to grow in both the public and private sectors, the population and economy continue to grow, so that we rapidly reach the limits of sustainability within the scope of existing technologies.

There are even practical limits to increasing recycling from residential sources. Successful communities achieving recovery levels above 30 percent of generation have comprehensive programs in place, which combine many different existing practices. To attain an average recovery rate approaching 30 percent nationally, curbside collection would need to double by 2001. Expanding curbside programs to double the 1992 coverage of about 80 million people would be likely to require more expensive programs. The increased costs may be partially offset by rising prices for recycled materials (14), but the prices are likely to be highly cyclical.

Although a report in *The Wall Street Journal* implied that curbside recycling had only a minimal impact on reduction of the total solid waste stream (15), based on figures quoted from the executive summary from the Franklin Associates report on recycling, a more careful assessment of those data reveals that the curbside programs do recover a substantial portion of household wastes (excluding yard trimmings), about 20%. While the figures quoted are correct (2.5% of total recovered materials come from curbside programs, while over 11% come from commercial and industrial sources, as calculated from data in reference 16), the actual benefit of these programs is understated by such an interpretation. Because commercial and industrial solid wastes provide greater quantities of cleaner and more uniform recovered materials than that derived from residential sources, the relative contribution of those sources is greater overall, without question. The capacity to recover 25% of the recyclable items from household wastes and nearly 20% of all household waste (non yard waste) is not insignificant for our cities. Curbside recycling programs also result in higher individual participation rates than that obtained using only drop-off or by-back programs for residential waste. Curbside recycling programs are not, however, a panacea; but neither are they without overall benefit. Also, they will add cost, approximately \$1 to \$3 per household per month, according to some reported estimates (17). It is clear, however, that materials recovered from commercial, institutional, and government sources must play the greater role in our approach to recycling. While a majority of municipal solid waste generation is from residential sources, recovery of recyclable materials from commercial, institutional, and governmental sources of MSW is absolutely essential, because these sources are expected to comprise nearly half the recovered materials in 2000. Cellulose and paper products will comprise over two thirds of that total (18).

The central role of paper recycle in the whole story of recycling is amply documented. In the two comprehensive reports by Franklin Associates, one on paper recycling and the other on solid waste recycling, many overlapping trends emerged from each analysis, all leading to the conclusion that cellulosic materials lend themselves more readily to recycling than do other materials in the solid waste stream. When considering the various types of waste materials, paper and cellulose products provide the greatest flexibility in terms of the methods of recovery. If we include

composting and energy generation as part of the picture, nearly every recovery option is applicable to cellulose and paper products. Further, the sheer volume of waste which is cellulosic in origin adds to the importance of cellulose in the whole of the recycling scheme.

The recovery of paper and other solid waste material by salvaging them from the waste stream and recycling them does save energy and reduce landfill costs overall. Additionally, there is reduced dependence on landfills for regions where this is an issue. The most significant energy savings and environmental benefits are obtained when the recovered materials are utilized in place of virgin materials in manufacturing processes. There are often significant cost savings to be realized by the use of recycled paper or packaging materials as well. The use of landfills will still be a necessity for the foreseeable future. Overall, however, to realize effective utilization of our resources, an integrated approach is necessary. We must develop practices combining source reduction, waste minimization, and other diversion techniques along with recycling, to sustain us until the new technologies can be developed.

### **The Long View**

What will really work over the long haul for recycling cellulosic materials? As we have seen, the most readily realizable gains in recycling can be made by emphasizing increased recycling of commercial wastes. An integrated approach to the management of resources is also necessary. This means approaching recycling and source reduction (including waste minimization) concurrently, as part of a comprehensive materials management strategy that should also include cost reduction wherever possible. This is the only approach that makes sound business sense. Measures that are cost effective will be the most readily embraced. Responsible care and environmental technologies will help us get there. For the longer term, however, toward the year 2001 and beyond, we must invest in longer range research to develop new methods, new materials, new processes, and new infrastructure. To sustain development, we must extend beyond our current capabilities in each of those areas. To approach and sustain the cellulose and paper recycle levels recommended by the Environmental Protection Agency will require investment with a long view. More effective management of existing practices, responsible care, and innovative applications of existing technologies are needed now, to solve the near term problems, but these practices will not sustain our ability to meet these recycling goals as both the economy and population grow. These approaches will only buy us the time to invent the future solutions. We must, however, be working on those solutions now if we are to progress. To do otherwise is to compromise our ability to sustain both economic and population growth.

### **Literature Cited**

1. Jansen, L.; presentation, Presidential Plenary Session, "Environmental Technologies for the Future", ACS National Meeting, August 21, 1994, Washington, D.C.
2. Jansen, L.; Don, A; Programme STD internal document, "Chemistry in Sustainable Development", Programme Bureau, Dutch Government for Sustainable Technology Development (STD), Delft, The Netherlands, 1994.

3. "Looking Back From the Future", Programme Bureau, Dutch Government for Sustainable Technology Development (STD), Delft, The Netherlands, February 1994.
4. Freeman, C; Perez,C., "Structural Crises of Adjustment, Business Cycles, and Investment Behavior", in *Technical Change and Economic Theory*, Pinter, London and New York, 1988.
5. Flanders, L.; *Pulp & Paper*; 1994,7,p.53.
6. Environmental Protection Agency, "Comprehensive Procurement Guideline", quoted in *Recycled Paper News*, May 1994, pp. 1-3.
7. Franklin Associates, Ltd., "The Role of Recycling in Integrated Solid Waste Management to the Year 2000", report for Keep America Beautiful, Inc., Stamford, CT, September, 1994, 2, pp.11-12.
8. Stipp, D.; *The Wall Street Journal*, September 19, 1994.
9. Franklin Associates, Ltd., "The Role of Recycling in Integrated Solid Waste Management to the Year 2000", report for Keep America Beautiful, Inc., Stamford, CT, September, 1994, 3, p 10.
10. Gandy, M.; *Waste Management & Research*, 1994, 12, pp 481-494.
11. Franklin Associates, op.cit., Appendix G.
12. Franklin Associates, ibid., Appendix A.
13. Panchapakesan, B.; *Pulp & Paper*, 1994, 6, pp 105-107.
14. Stipp, D.; op.cit.
15. Bailey, J.; *The Wall Street Journal*, October 4, 1994.
16. Franklin Associates, op.cit., Appendix A.
17. Bailey, J.; *The Wall Street Journal*, January 19, 1995.
18. *The Outlook for Paper Recycling to the Year 2000*, Franklin Associates, Ltd., Prairie Village, KS, 1993.

RECEIVED May 11, 1995

## Chapter 24

# Paper Recycling and the Environment

F. Keith Hall

Corporate Research Center, International Paper, Long Meadow Road,  
Tuxedo, NY 10987

Cellulose-based paper and board constitute the largest component in the solid waste stream and these materials are extensively recycled. The problems and benefits of recycling paper and board are discussed in terms of the impact on product quality and the environment. Some limitations of recycling are identified and several alternative approaches based on renewable resources and energy recovery are presented. The importance of careful cost-benefit analysis is emphasized.

Recycling is unquestionably politically correct. It may even be regarded by some as patriotic, and almost every one has a "warm and fuzzy" feeling that when we are reusing some of our waste products, we are thereby benefitting mankind. I will address many of these points in this chapter, but first let us consider a few relevant facts. The United States generated about 200 million tons of municipal solid waste, henceforth called "MSW." From this waste stream, recovered materials were collected as follows: (1)

- ▶ In 1993, nearly 36 million tons of paper were recovered in the United States -- twice as much as in 1980.
- ▶ Paper and paperboard account for more than 60% of all materials diverted from the MSW stream.
- ▶ More than one of every two newspapers, nearly 60% of all corrugated material, and one third of all paper and paperboard packaging (compared to 12% of all other packaging) are being recovered.
- ▶ One third of all the paper collected in the world is recovered in the United States, where an average of 267 pounds is now recovered annually by each citizen.
- ▶ Overall, Americans now recover 40% of all paper used -- achieving a goal the industry set for 1995 two years ahead of schedule.

0097-6156/95/0609-0286\$12.00/0  
© 1995 American Chemical Society

This material is recycled and reused and here again progress is impressive.

- ▶ Every day, U.S. papermakers recycle enough paper to fill a 15-mile-long train of boxcars.
- ▶ 75% of the more than 500 U.S. paper and paperboard mills recycle some recovered paper -- and 200 depend on it entirely.
- ▶ In the year 2000, an estimated 78% of recovered paper will be recycled domestically; 15% will be exported to foreign recyclers; and the remaining 7% will be reused to make products such as animal bedding, insulation, hydromulch, and compost.
- ▶ At the turn of the century, recovered paper is expected to supply 40% of all fiber used domestically to make paper and paperboard products -- up from 25% in 1988. (3)

All this recovered fiber is, of course, diverted from the solid waste stream with the following effects. (2)

- ▶ Even though paper consumption has increased, significantly less paper is going to landfills -- 11 million fewer tons in 1993 than 1987.
- ▶ In all, U.S. paper recovery last year saved more than 90 million cubic yards of landfill space.
- ▶ In 1993, for the first time in history, more paper was recovered in the United States than was landfilled.
- ▶ When the new industry goal of 50% is achieved, twice as much paper will be recovered as is landfilled. (6)

### **Regulation Versus Market Forces**

These achievements are significant. The question, however, is whether these actions which result from legal directives and not from market forces are ultimately beneficial. In this environment, one has to be very concerned about the cost/benefit analyses of recycling, and whether such dedication to collection and reuse is beneficial or inimical to the country's economy overall. (7)

The nation's forest products industry will be using recyclable paper products costing hundreds of dollars a ton to collect and process, while ignoring virgin fiber supplies which are in oversupply on world markets and underutilizing disposal capacity which can be had for a fraction of the cost of recycling. To date, public policy has failed to discriminate between recycling that makes economic sense and recycling that does not make economic sense. Therefore, the politics of recycling is really over who will decide the fate of certain industrial raw materials -- the marketplace or government mandates. (8)

We must ask the basic questions as to why we are recycling. Is it worth the cost? What are the benefits? What are the alternatives?

## Waste Management Options

There are five basic waste management options: recycling materials into new products; landfilling; waste-to-energy, i.e., burning residues to recover their energy value; source reduction, or minimizing the material used in manufacturing; and composting organic materials. Consideration of all five options is encouraged in comprehensive, locally tailored, integrated waste management programs, since no one option is the single answer to managing solid waste. According to current estimates by the EPA, today approximately 67% of MSW is sent to a landfill, 17% is recycled, and 16% is burned. (3)

**Landfilling.** Landfilling is the low-cost option, but environmental advocates and NIMBY supporters insist that we need to conserve landfill space. This premise is based upon the fact that we in the U.S. have closed over two thirds of all earlier, more primitive landfills in the last two decades. This was undoubtedly the correct thing to do. However, with the emergence of large regional landfills, there is currently abundant landfill capacity and tipping fees have stabilized or even decreased in the last several years. (9)

Except, perhaps, for the Northeast, most places in the United States have plenty of land for landfills, and well-engineered disposal facilities have little in common with the open dumps that predominated until the 1970s. Modern landfills are designed to minimize potential hazards to public health and the environment. They typically include natural and synthetic liners, groundwater monitoring, leachate collection, methane gas recovery systems, and effective capping procedures when capacity is reached. With careful planning, landfills can be turned into nature reserves or recreation areas after they are closed. Methane gas can be collected from landfills and converted into electricity.

At the present rate of landfilling, all the MSW generated by the United States over the next one thousand years could easily be contained within a single 30 by 30 mile area using current technology. This is three one hundredths of one percent of the land area of the contiguous 48 states. (10)

Although mandated recycling policies are designed to save landfill space (or trees, or whatever), for many cities they actually require the expenditure of more resources at a time when municipal budgets are already strained. In New Jersey, one study showed recycling programs sometimes cost cities \$200 per ton of materials collected, more than the highest amount charged to simply landfill trash. (11) Even low-priced recycling programs, at \$40 per ton, cost more than the average landfill fee of \$28 per ton. Landfill location is, of course, a highly emotional issue. As Bill Ruckelhaus, formerly of the EPA and now CEO of Browning-Ferris, said, "everyone wants you to pick up the garbage and no one wants you to put it down."

**Recycling.** Recycling sometimes makes economic sense, of course, and the marketplace stimulates recycling under these conditions. The recycled aluminum can, for example, requires less than 10% of the energy necessary to transform bauxite into aluminum. These savings have given industry an incentive to purchase recycled aluminum which, in turn, gives entrepreneurs an incentive to collect used cans.

Recycling has symbolic appeal -- it makes us feel virtuous and frugal. Product bans and waste-reduction mandates seem to put the environment first, efficiency second. But the two -- environmental protection and economic efficiency -- aren't really competitors. In a market economy, prices reflect information about the relative scarcity of all resources, including labor, land, materials, capital, and energy. The search for cost-effectiveness thus drives us toward, not away from, environmental conservation.

The near-term paper recycling problems facing American industry are more economic than technical. Perhaps a whole new set of recycling paper mills located in or near big cities will provide some of the necessary economic incentive for recycling.

**Waste-to-Energy.** In the third MSW management option, modern waste-to-energy plants burn refuse at high temperatures and reduce its volume by as much as 90%, producing an ash residue that must be landfilled. Like landfilling, burning has been used for centuries to dispose of waste. In the United States, combustion of MSW to recover energy in the form of saleable electricity was first practiced in about 1902 in New York City.

Until the 1970s, MSW waste-to-energy facilities operated with little, if any, air pollution control equipment, thereby creating an unacceptable image with the American public. Although the technology has improved, public perception continues to be a significant barrier in waste-to-energy facility siting. Energy recovery is fighting an uphill battle to be fully utilized as an effective solid waste management technique.

In a sense, combustion of paper as a fuel completes a cycle. Carbon dioxide (CO<sub>2</sub>) is released from the paper during burning, which is the same CO<sub>2</sub> released had the paper, or the wood, naturally decomposed. This CO<sub>2</sub> was absorbed from the atmosphere while the tree was growing and producing cellulose. Unlike burning fossil fuels, no "new" CO<sub>2</sub> is added to the earth's atmosphere. (4)

In the United States, there are currently some 140 operating waste-to-energy plants. An additional 40 incinerators simply burn waste materials without capturing energy.

Approximately 29 million tons of waste (16 percent of MSW) are incinerated annually, generating enough electricity to supply the needs of more than 1.2 million homes. The EPA estimates that by the year 2000, over 300 waste-to-energy facilities will handle 25 percent of the nation's waste.

Regulatory requirements for control of MSW combustion have grown increasingly stringent since first implemented in the 1970s. Federal regulations governing all facilities with capacities greater than 250 tons per day set limits on a range of pollutants. The EPA is developing comparable requirements for units with capacities of less than 250 tons per day. Current regulations for the larger plants are more stringent than those governing fossil fuel plants.

In fact, recovering energy from garbage is a much cleaner process than using traditional fuels such as oil or coal because of strict air pollution control requirements.

Japan, short of land, already combusts 70% of its solid waste streams.

**Source Reduction.** The fourth MSW management option is "source reduction." Recognizing the value of source reduction, I'd like to digress a moment and discuss the general benefits of packaging in relation to waste minimization. Packaging, in conjunction with storage (including refrigeration) and distribution systems, plays an important role in reducing food waste: developed countries with sophisticated packaging, storage, and distribution systems waste much less food than undeveloped countries. Studies show that for every ton of paperboard packaging that winds up in the waste stream, about 20 tons of refuse (husks, rinds, shells, etc.) have been kept out of households and landfills and used instead as animal feed and ground mulch when this crop-related waste is kept nearer agricultural operations.

Packaging helps the United States maintain one of the world's lowest rates of waste food. (7)

Two thirds of all packaging is used to protect food: it contains products in a sanitary manner, provides tamper-resistant seals, and includes information on the contents, directions, and appropriate warnings for the consumer. Packaging provides two other major functions: an advertising vehicle and a deterrent to pilferage. (12)

In most cases, packaging is an accepted and necessary practice. The only thing worse than overpackaging is underpackaging and a ruined or broken product.

Now back to source reduction. We are actively involved in developing products and technologies with this goal in mind. When multiplied by the billions of units of consumer goods that are purchased and repurchased, the actual reduction in size or weight of each package is extremely significant. In addition to less garbage, fewer resources are extracted and processed and less weight is transported, saving fuel consumption and shipping costs. Some examples include folding cartons that hold moisture-sensitive materials without a plastic liner, recyclable paper cartons capable of containing hard-to-hold liquids, reusable corrugated containers, and paperboard packaging spacers that replace plastic and styrofoam materials.



**Composting.** Composting, the fifth waste management option, has been widely advocated as an effective means of reducing the solid waste stream. It can yield a useable soil amendment product for agricultural purposes. Composting requires presorting to eliminate metal, glass, and plastic contamination. Energy recovery is not possible.

### **Forest Productivity**

One of the most frequently promoted reasons for recycling is to "save trees." This is based on the false assumption that trees are a diminishing resource, and that is patently not true as I shall discuss in the following paragraphs. I tend to view this reason as analogous to a suggestion that we should all eat one slice of bread less to "save wheat."

Let us look at forest productivity. Reforestation, afforestation, and advanced silviculture offer benign opportunities that yield many ecological and climatic benefits, as well as increasing the fiber supply. (13) Concern over the possibility of global warming has caused us to study the use of trees to alleviate the problem, and I will discuss this later.

About one third of the United States -- 731 million acres -- is forested, of which 483 million acres are commercial forest. Net annual growth exceeds harvest and losses to insects and disease by 27% each year in the commercial forests. Private owners account for 57% of the commercial forests, government owns 28%, and the forest industry owns 15%.

More than 244 million acres of federal land are set aside currently by various government agencies. In total there are some 13.2 million acres of old-growth forest remaining, equivalent to a band of trees five-miles wide stretching from coast to coast. Eight million acres of this old growth is already within set-aside areas.

**Reforestation.** Reforestation in the United States has had a major impact this century and was the result of two significant economic factors. First, American agriculture moved west to take advantage of the rich prairie soils, and the eastern states reverted to forests when agriculture was no longer viable. Second, numerous individual landowners and forest products companies realized that tree farms were an economically attractive option and provided a cost-effective source of trees for papermaking. Today, America's tree farms cover more than 95 million acres -- an area larger than the nation of Japan -- and contain some 95 billion trees. In 1991, 1.7 billion seedlings were planted (6 for each American), of which the forest industry planted 43%, private landowners 35%, and government 18%.

This extensive replanting program has an important side effect: young, healthy, rapidly growing forests are actually oxygen factories that help slow global warming. A typical tree uses nearly a pound-and-a-half of carbon dioxide and gives off more than a pound of oxygen to "grow" a pound of wood. (16) An

acre of trees might grow 4,000 pounds of wood a year, using 5,880 pounds of carbon dioxide and giving off 4,280 pounds of oxygen in the process. (14)

In Europe, forest resources are also increasing, with the standing volume being 25% larger in 1990 than in 1971.

**Silviculture.** Although real differences exist between agriculture and silviculture, the biological parallels are equally real, and silviculture can benefit from the applicable technology developed by the agriculturists. In the past we in the forest industry were largely hunter-gatherers of wood. This practice is now reaching its end as the last harvestable virgin forests in North America are used up. So we have become farmers, albeit tree farmers.

The increasing productivity of U.S. forests is illustrated in Figure 1. The first four levels reading up from the bottom show progress to date in improving forest productivity. (15)

The top four steps move us into the future and illustrate the gains predicted through five generations of genetic improvement. Additional gains are predicted through asexually propagating the best trees produced in our genetic program.

The judicious use of both conventional and less-conventional genetic approaches can yield a 3.7-fold increase in productivity, simultaneously improving our raw material supply and the environment.

We should not lose sight of the emotional appeal of trees since a negative but very human reaction to cutting frequently gets in the way of doing the right thing to ensure the sustainability of our industry (and perhaps of our climate), including the refusal to accept the proven "farming" concept for tree crops.

**Carbon Sequestration.** Couldn't we grow enough trees to sequester all the fossil fuel carbon entering the atmosphere? A number of estimates have been made recently of the additional forest area necessary to offset all or a portion of the annual buildup of atmospheric CO<sub>2</sub>. (14) In the temperate U.S. with its lower growth rates, Roger Sedjo estimates that 465 million hectares would be required to sequester 2.9 billion tons of carbon, an area which is equivalent to all the states west of the Mississippi. This is equal to about 10% of the world's forested areas. Sedjo further estimates that the cost of establishing these plantations would be \$372 billion in the Temperate zones or \$186 billion in the Tropics. While this latter figure is almost 3% of the U.S. GNP, it is much lower than the Temperate Zone figure.

I have not attempted to address the question of what to do with all this wood as it matures. Certainly, a forest plantation effort large enough to significantly affect the prospects for global warming would be at a scale that would dwarf all previous forest plantation efforts and would provide a major new renewable energy resource, since its productivity greatly exceeds the world's need for fiber. (17)

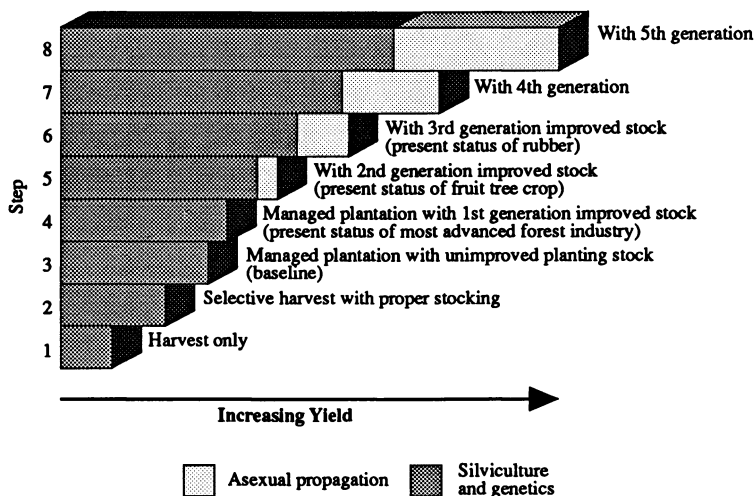


Figure 1. Progression from tree gathering to silviculture.

### Forest Products Industry

Turning from the speculative to the real world of today, in the U.S. the forest products industry employs some 1.6 million people and produces wood and paper products valued at more than \$200 billion each year. This makes our industry the 5th or 6th largest in the United States. We are an economic giant, but an almost unknown and invisible giant as far as much of the public is concerned. Most of the good that we do has gone largely unnoticed. On the other hand, the unsightly visual appearance of a clear-cut, or environmentally inspired misinformation about spotted owls, or the supposed impact of our processes on the receiving waters, etc., has gained great prominence.

**Endangered Species Preservation.** A few facts can perhaps dispel some of this negative image. In the 1970s, scientists knew of only 200 pairs of spotted owls. By early 1992, they had found 3510 owl pairs, many in second growth managed forests, so the species is hardly endangered.

The white-tail deer population has grown from 4.5 million to over 16 million in the past 30 years, in part because of the reforestation of the Northeast. Parenthetically, as a keen gardener, I have suffered a great deal of damage from these herbivores and, therefore, personally regret this particular "success" story.

Wild turkeys have increased from near extinction to over 4 million today.

My company has worked extensively for more than 20 years to protect the gopher tortoise, the Red-Hills salamander, and the red cockaded woodpecker, all of which are on the "endangered species" list.

**Clearcutting.** With respect to clear-cutting, it must be realized that several important tree species will only grow in full sunlight so clear cutting is the only possible way of reestablishing the forest. Douglas fir is preeminent among these species, and without clear cutting, either man-made or induced by cataclysms such as major forest fires or the explosion of Mount St. Helens, there would be no same-age stands of mature Douglas fir in the Pacific Northwest.

**Process Modifications.** On the process side, the increase in environmental awareness following "Earth Day" in the early 1970s caused the industry to take stock of its contribution to pollution and to start to do something about it. Since our industry was based on fairly unchanging technologies -- kraft pulping and chlorine-based bleaching -- for more than 100 years, we knew that no major health hazards were extant, or they would have shown up earlier in the epidemiological evidence or as unusual diseases amongst the stable and unchanging populations of small mill towns. Nevertheless, the industry installed aerated sludge basins for its liquid effluents and scrubbers, etc., for our gaseous streams without knowing whether the results would be cost-effective in terms of human health or reduced environmental impact. Pollution was reduced, in many cases by 70-80%.

In 1985 when improved analytical techniques showed for the first time the presence of minute quantities of chlorinated dioxins in our effluents, the industry again responded voluntarily and changed the bleaching sequence at considerable expense so as to reduce the concentration of these compounds down to the "non-detectable" level. The key question for all of us to face concerns the balancing of cost vs. benefit in these environmental actions. Obviously, dioxin in our daily lives is a nonserious issue, but we have spent hundreds of millions of dollars on it already. Our more recent environmental policies models continue that trend. The toxic pollution control provisions of the Clean Air Act amendments will cost \$5 to \$10 billion/yr without any clear cost/benefit analysis. It is hard to imagine that this expenditure could not be put to better use elsewhere in the U.S. More globally, William Ruckelshaus, who was a major contributor to the Bruntland report entitled *Our Common Future*, finds "something unsettling about a world where every day twenty-five thousand people die from easily preventable waterborne diseases. And yet we continue to argue in America about even smaller increments of pollution abatement with diminishing health benefits." (4)

### Cost/Benefit Analysis

Descartes coined the immortal phrase "I think therefore I am." I have modified this for modern times to "I am therefore I pollute." We must all realize that we, the American public at large, are the polluters, and we are indeed the ones who will be footing the bill. We need to pay more attention to the costs - and benefits - of antipollution measures. (18) Only then will demands for totally chlorine-free products or utopian recycling laws become less popular. The forest products industry will continue to pursue the research and investment efforts that have already been sustained over many years, and hopefully the day will come when it will not be attacked for the minute and insignificant pollution remaining in its ef-

fluents. We look forward to the day when environmentally friendly forest management measures, long ago adopted by the forest industries, will be appreciated and the intrinsic environmental value of producing goods from wood, such as paper and lumber, will be recognized as the most sustainable, recyclable, and beneficial of all industrial products.

### Literature Cited

- (1) *Fast Facts*; American Forest & Paper Association: New York, NY; 1994.
- (2) National Solid Wastes Management Association: May 1992.
- (3) EPA Reusable News 530-SU 90-055; Washington, D.C.; Summer 1990.
- (4) The World Commission on Environment and Development; *Our Common Future*; Oxford University Press: New York, NY, 1987.
- (5) *The Bridge Technology and the Environment*; NAE News & Notes: Summer 1990; Vol. 20.
- (6) *The Outlook for Paper Recovery to the Year 2000*; Franklin Associates; Prairie Village, KS, 1993.
- (7) Stein, M. *Los Angeles Times*; August 18, 1989.
- (8) Schneider, K. *New York Times*; January 20, 1992.
- (9) Resources for the Future: Winter 1992; No. 106.
- (10) Wiseman, A.C. Resources for the Future: Washington, D.C., 1991; No. 105, pp 9.
- (11) Scarlett, L. *Wall Street Journal*; January 14, 1991.
- (12) *Solid Waste Disposal Overview*; National Solid Wastes Management Assn: Washington, D.C.
- (13) Hall, F.K. *Global Resources and Markets: Issues and Trends*; Editor, D. F. Root; Univ. of Washington: Corvallis, WA, 1990; pp. 163.
- (14) Sedjo, R.A. *The Comparative Economics of Plantation Forests*; John Hopkins University Press: Baltimore, MD, 1983.
- (15) Hall, F.K. Paper Science and Technology - The Cutting Edge; Institute of Paper Chemistry: Appleton, WI, 1979.
- (16) Trabalka, J.R. USA Dept. of Energy DOE-ER 0239. Atmospheric Carbon Dioxide and the Global Carbon Cycle; United States Dept. of Energy: Washington, D.C., 1985.
- (17) Sedjo, R.A. *Journal of Forestry*, 1989, Vol. 87.
- (18) Hall, F.K. *Tappi J.* 1993, Vol. 76, pp. 57.

RECEIVED June 26, 1995

## Chapter 25

# Recycled Paper: Raw Material Supply and Other Considerations

Tom Friberg<sup>1</sup>, Gordon Cawker<sup>2</sup>, and Jan Huston<sup>3</sup>

<sup>1</sup>Corporate Research and Development, <sup>2</sup>Recycling Business, and <sup>3</sup>Paper Company Engineering, Weyerhaeuser Company, Tacoma, WA 98477

Presently, close to 40 million tons of waste paper is recovered each year in the U.S. This is expected to grow to 50 million tons by the year 2000. During this time, there will be significant changes in the sources and methods of paper recovery. Recovered paper grades will change in response to papermaking and end-product requirements. Much of this will be cost-driven though government regulation will continue to impact collection and utilization.

### Conceptual Model for Recycling

A convenient model for evaluating recycling has three parts. The first is the **raw material supply**. Where does it originate, what is its character and quality? What kind of volumes, prices and costs are associated with its procurement? The second area is the **production capacity**. This is the technical conversion of the raw material into the final product. For recovered paper, this is the repulping, cleaning, screening, and deinking (if necessary) to produce a recycle pulp, paper or paperboard product. The third area is **market demand**. This area deals with the end-use requirements and specifications for a recycle content product. It also includes volumes and prices. In this paper, we will talk only about raw material supply and market demand.

### Raw Material Supply

**Recovered paper specifications.** Over the years, a set of "origin-based" recovered paper grades have developed. There are approximately 50 standard grades and 30 special grades based upon the type of paper collected. Table I has aggregated these grades into their major categories. The definitions used in stipulating these grades are very brief descriptions of the recovered paper (see Figure 1). In addition to the brief description, limits are placed on the level of contamination that is acceptable. The first are **outthrows** which are contaminating papers other than those indicated in the description. An example outthrow would be old corrugated when

**Table I: Major Categories of Waste Paper (1)**

- Pulp Substitutes
  - High quality pre-consumer white
- Ledger
  - High quality post-consumer white
- Office Waste Paper (OWP)
- Old Newspaper (ONP)
- Old Corrugator Containers (OCC)
- Old Magazines (OMG)
- Mixed Waste Paper
  - Office (MOW)
  - Residential (MRW)

**Outthrows**

The term "Outthrows" is defined as "all papers that are so manufactured or treated or are in such a form as to be unsuitable for consumption as the grade specified."

**Prohibitive Materials**

The term "Prohibitive Materials" is defined as:

- a. Any materials which by their presence in a packing of paper stock will make the packaging unsuitable as the grade specified.
- b. Any material that may be damaging to equipment.

**EXAMPLES:****News**

Consists of baled newspapers containing less than 5% of other papers.

- Prohibitive materials may not exceed 1/2 or 1%
- Total Outthrows may not exceed 2%

**Corrugated Containers**

Consists of baled corrugated containers having liners of either test liner, jute or kraft.

- Prohibitive materials may not exceed 1%
- Total Outthrows may not exceed 5%

Figure 1. Grade definitions (1).

found in a newsprint bale. The second limit is prohibitives which are materials that are not paper (metal, rocks, etc.). (1)

**Sources of recovered paper.** Traditionally, recovered paper has been collected from easily available, larger volume sources. These include commercial operations, retail stores, offices and residences. Examples are wholesale and retail operations for old corrugated containers, residences for old newsprint, and larger office buildings and commercial institutions for ledger grade paper.

These "low-hanging plums" of relatively easy to access recovered paper are generally collected with varying degrees of source separation. In the future, we will see sourcing of smaller generators of recovered paper, such as small offices, multi-tenant buildings, and residences. There is a trend toward commingled collection. This will impact quality, consistency and cost. The smaller generators will require more innovative sourcing methods to reduce unit procurement costs.

**Types of collection.** Because of logistical and cost advantages, most traditional recovered paper sourcing has been "source separated." This provides larger volumes of discrete grades which are sorted at time of pick-up or drop-off. We are seeing a trend toward commingled collection of waste paper. This is because many of the collectors are waste haulers/handlers and, for them, moving volume is important. Many cities and counties attempting to comply with state mandated recovery goals view commingling as an efficient means to satisfy these numerical quotas. When viewed in the context of the paper industry and their requirements for sustainable recovery, it is clear that such efforts may only serve to shift the burden of "disposal" from one group to another unless we can cooperatively design recovery to meet end-user requirements and existing technological capabilities. Commingled collection can have lower initial cost in collection and handling. It also has the potential for more flexibility in responding to market opportunities by selectively sorting the commingled collection. It generally has higher processing costs.

**Collection and processing.** Recovered paper may be picked up in large, presorted batches from commercial organizations; small, presorted batches as from some residential collection; or in large and small batches from commingled collection. Paper may also be dropped off at specified sites or brought directly to a material recovery facility or packing plant. In none of these cases is garbage included with the recovered paper. With commingled collection, it may include many varieties of paper and has a higher level of contamination.

Regardless of the method of collection, all recovered papers are received, weighed and categorized. There may or may not be sorting, depending upon the purity of the collected material and the immediate market demands for the various grades. Sorting may vary from simply dumping the paper on the floor and pushing it around to highly mechanized systems of screens, magnets, and picking conveyors. After processing through the plant, most recovered paper is baled. The "bale" is the common commercial and transportation unit and weighs about 1600 pounds (range 500-2000). Bales may vary considerably in size, but are generally 4 ft square by 5-6 ft long and are wire banded. Tight, uniform bales permit relatively easy loading,



transportation, and unloading. In cases where there are large volumes and steady customers, bulk compaction into trailers may be used.

**Government influences.** Free market conditions are not the only factor that are influencing recovered paper collection and utilization. Government is playing a significant role. This has been a difficulty for most in the commercial collection and recycling business because recycling is an "incremental" business. Recovered paper supply is inelastic in the short term because of the required infrastructure for collection. With the large step jumps in supply that government regulation can trigger, recovered paper prices may be extraordinarily volatile. The very low prices during the 1991-1993 period were largely the result of the collection systems fostered by governments during the late 1980's.

We are seeing government intervention in the area of recycling and recovered paper collection because jurisdictions have set goals for waste diversion from landfill. To accomplish these goals, governments are using a variety of tools: recovery rates, bans from landfill and advance disposal fees. Most every state established recycle goals that ranged from 25-70%. Some states even enacted landfill bans that prohibited the disposal of paper.

### Market Demand

**The market...a tale of two cultures.** On the waste paper supply side, we have the collectors, haulers/handlers, and recyclers, and on the utilization side, we generally have the pulp and paper mills. Therein lies a tale of two cultures. The waste haulers and handlers are interested in the collection and low-cost transportation of material from one location to another. This is very different from the requirements of the pulp and paper mills, which strive toward constant and controlled raw material characteristics.

**Utilization of recovered paper.** The bulk of the 38 million tons of paper recovered in 1994 was used as a raw material for new paper products. It also went to other uses such as insulation, molded pulp, fuel compost, etc. Recovered paper is used domestically as well as exported to markets throughout the world.

For perspective, the percentage of recyclable paper used in overall fiber furnishes in the US did not change appreciably in the decades of the 70's and the 80's. Recovery rates really began to climb in the late 80's and reached 40% in early 1993. The new goal of 50% recovery is set for the year 2000. Figures 2 and 3 show overall US recovery and utilization data. (2)

Recycled fiber usage varies by type of paper production. For instance, tissue and containerboard producers utilize a much higher percentage of recovered paper than fine paper producers. See Figure 4.

**Re-use considerations.** So far, the discussion has dealt with where the paper has "come from." Re-use considerations depend upon where the paper is "going to." In general, waste paper fibers are either mechanical (from groundwood, thermomechanical, or semi-chemical/mechanical) or chemical (kraft or sulfite pulping). The chemical fibers will be either unbleached or bleached. While the

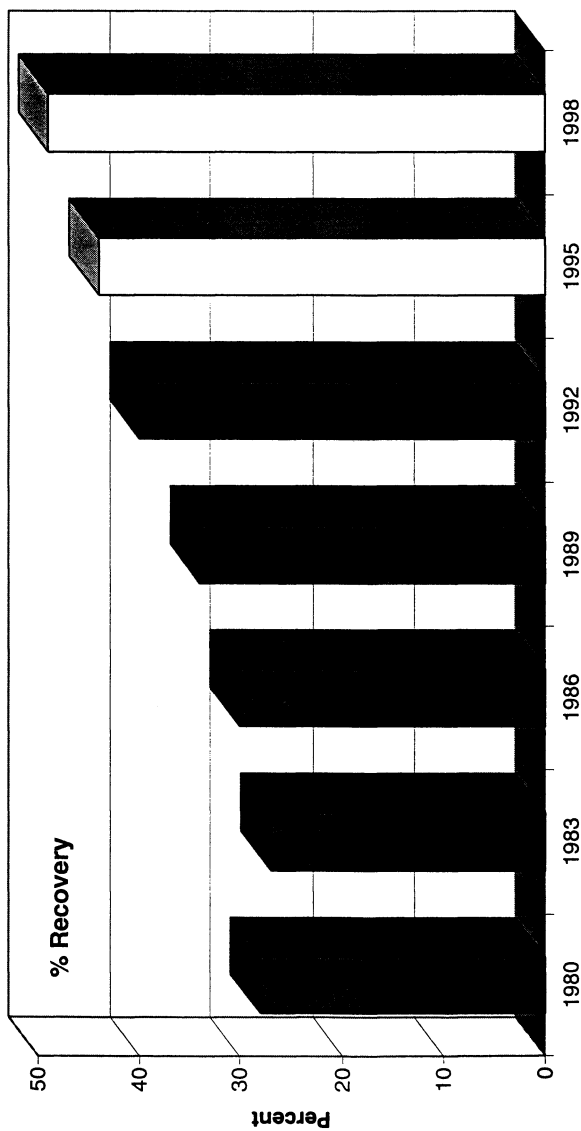


Figure 2. U.S. paper industry recovery rate (2). Historical and projected recovery of paper and paperboard.

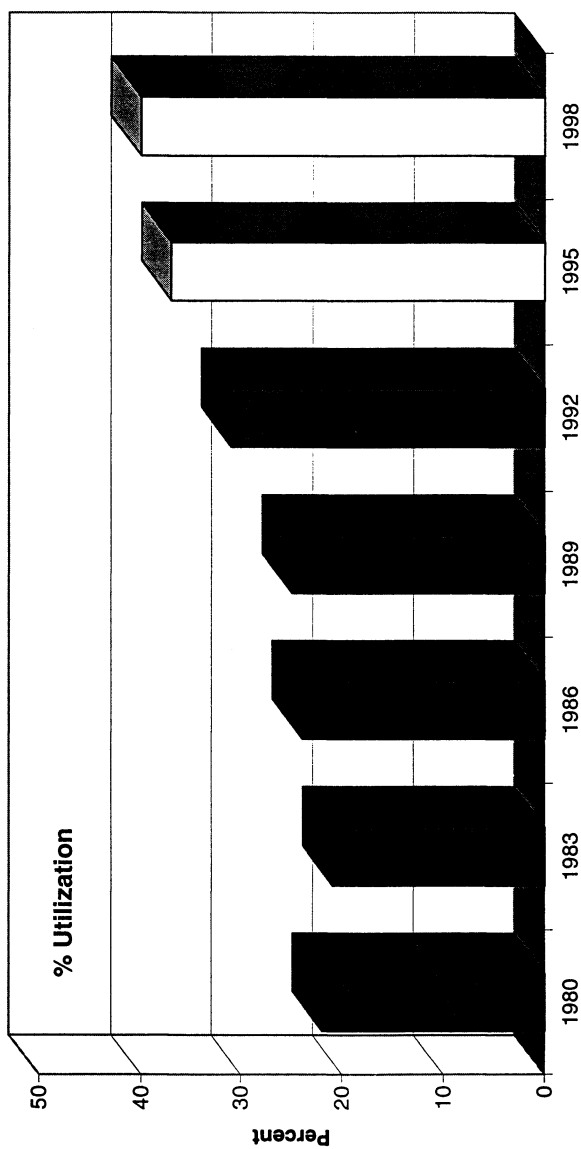


Figure 3. U.S. paper industry recovered paper usage (2). Historical and projected utilization rate.

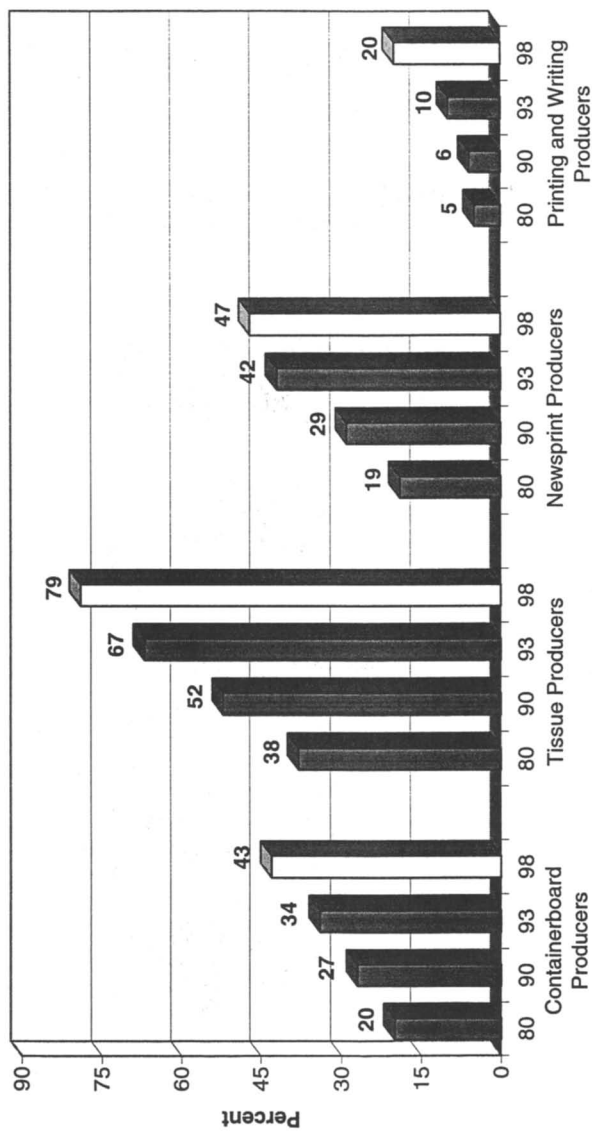


Figure 4. U.S. paper and paperboard industry recovered paper utilization (2). Historical and projected rates by major industry segment.

species of origin for waste paper fibers may vary dramatically, this is of less importance in recycled fiber use. Once fibers are recycled, they tend to perform as though they are hardwood fibers.

While far beyond the scope of this paper, it is important to note that there are other considerations beyond the waste paper fiber itself. They include the coatings and sizings that are used in paper and the inks, coatings and varnishes that are used on paper. There are also the impacts of contaminants such as glues, binders, adhesives, staples, and other tramp material that can be inadvertently or otherwise included with the waste paper.

**Recycled paper properties.** Three general property areas are strength, bulk, and surface characteristics. Strength (tensile, tear, compression, internal bond, etc.) is important principally in packaging, exemplified by the use of recycle fiber in liner and medium linerboard for corrugated packaging. Recycle fiber tends to be stiffer than virgin fiber, so this contribution to the bulk of a sheet may be useful. Lastly, and particularly important in printing, writing and communication papers, are the surface properties. These include smoothness and linting and the optical properties like brightness and dirt.

There is a common misperception that all recycle fibers lose strength and other properties upon recycling. Some of the strength properties of chemically pulped recycle fibers are diminished. Interestingly, select optical and printability properties are generally improved through recycling of chemical fibers. With the case of mechanical fibers, such as fibers originating from newspapers, strength properties are not lost.

**Fiber flows.** Traditionally, waste paper has been used in direct substitution for like products or it has been "downcycled." Examples of direct substitution are old newspapers (ONP) going back to newspapers or old corrugated containers (OCC) going back into the liner or medium of new corrugated containers. Downcycling is exemplified by white office paper going into tissue use.

We are now seeing interactions and substitutions of waste paper. This is the start of a transition from basing waste paper use on where it has "come from" toward using waste paper based on where it is "going to." The four major grades involved in interaction and substitution are old newsprint (ONP), old magazines (OMG), old corrugated containers (OCC), and office waste paper (OWP). Increasingly, old magazines are incorporated into the production of newsprint. Also, we are seeing mixed waste paper coming from offices and residences utilized in the production of liner and medium for corrugated containers. One of the most dramatic changes is the use of old corrugated containers for white paper and bleach board. This "upcycling" is the mild chemical repulping and bleaching of old corrugated containers to produce a white fiber that is a higher value than the original fiber.

**Government influences.** The market side of waste paper utilization is also affected by government regulation. At present, governments are driven to develop markets for materials collected through recycling. The most common tool used by government is recycle content. An example at the Federal level is the procurement guidelines for printing and writing paper. This establishes general levels of 25% by

**Table II: Alternative Uses for Recovered Paper, 1990 and 2000 (5)**  
(tons per year)

	1990	2000
Molded Pulp	500,000	1,000,000
Insulation	300,000	600,000
Fillers and Fibers	260,000	(1)
Animal Bedding	125,000	300,000
Internal Packaging	100,000	(1)
Hydromulch	100,000	250,000
Wallboard	90,000	(1)
Medium Density Board	80,000	(1)

(1) No information.

1995 and 35% by 1998. It is expected that these guidelines will be reflected by state and local governments. (3)

**Alternative uses for waste paper.** Not all waste paper that is collected finds its way back into paper or paperboard. Presently, more than one million tons annually is used in products such as molded pulp, insulation, hydromulch, animal bedding, and filler fibers. Please see Table II. This does not include fuel which is a growing use of paper that is too low in quality to be recycled into paper.

### Challenges and Opportunities for Recycle Paper

1. Going deeper into the waste stream – We are seeing trends toward wider varieties of paper collection and smaller volume sources. We are also seeing substitutions in utilization of the waste paper.
2. Develop wider "scaled" operations – We are seeing both smaller and simpler recycled paper mills, as well as larger volume use by existing and new mills using recycle paper.
3. Preserve or recover recycled fiber properties – Recycling does change the properties of chemically pulped fibers. We need to see improvements in strength, bulk, and surface and optical properties.
4. Develop improved recycling processes – Existing processes need to be streamlined, upgraded, and better understood for repulping, decontamination, and deinking of waste paper.

### Summary

With life cycle considerations and resource conservation, recovered paper will play an ever increasing role. As a raw material, it can serve in many ways. It can be reused, recycled, burned for energy, composted, and, what does go to landfill, will ultimately degrade.

With 29 existing recycling plants, Weyerhaeuser expects to grow by a factor of four by the year 2000. Innovative sourcing coupled with increased sorting will be required to meet the logistical issues of the increased volume flow. Finally, paper and paperboard process and market requirements will demand informed procurement, grading, and supply of recovery paper.

### References

1. Institute of Scrap Recycling Industries; *Scrap Specifications Circular*; Institute of Scrap Recycling Industries: Washington DC; 1994.
2. *Options Review for Recycling Division Information Package*; Weyerhaeuser Company: Tacoma, WA; 1994.
3. Alig, Joanne; *State Legislation Focus on Market Development*; *Recycled Paper*. Vol. 4, No. 5, 1994, January, 1-8.
4. *Recycled Fiber in North America; Changing and Emerging Opportunities in the 1990s*; Jaakko Poyry: Tarrytown, NY; 1992.
5. Friberg, T.; *Resource Recycling*. 1993, January, 26-33.

RECEIVED July 13, 1995

## Chapter 26

# Advances in Paper Fiber Recycling: Meeting the Challenge

Bruce W. Janda

Neenah Technical Center, James River Corporation, P.O. Box 899,  
Neenah, WI 54957-0899

Cellulose fiber (paper) accounts for 34% of the weight of materials sent to landfill in the United States. The paper industry recently exceeded its goal of recovering and reusing 40% of the fiber produced and has set a new goal of 50%. This high recovery level presents both challenges and opportunities. It requires using a much wider variety of materials, while improving product performance and value. James River is meeting the challenge with several projects now on-line. A new process for using 100% waste paper to produce recycled paperboard for packaging provides capability to independently process multiple sources of recovered materials to remove contaminants without the costs of a deinking system. These highly cleaned feedstocks are delivered to a multilayer paper machine designed to get the maximum performance from recovered fiber.

Paper products ranging from newspapers and packaging materials to towels and tissues are the most familiar disposables. Paper is the most common packaging material, utilized in 48% of all packaging (1) and is made from a renewable raw material that is in abundance in North America. However, concern has grown over the ability to site new landfills to sustain the rate of trash generation and disposal. Cellulose fiber, in the form of paper and paperboard, accounted for 34% by weight of municipal solid waste discards in an 1988 EPA study (2). In a time of increased concern over landfill disposal, it is not surprising that recycling of paper fiber should receive so much attention from consumers, the paper industry, producers of packaged goods, and municipalities.

Consumers have begun to expect that their paper products and paper packaging be made, at least in part, from recycled fiber. The American Forest and Paper Association has responded by meeting its initial goal of recovering and reusing 40% of the fiber produced. Recovery rates for different paper products range from more than 50% of newspapers published and 60% of old corrugated containers to 33% of all paper and paperboard packaging (3). A new goal of 50% recovery by the year 2000 has been set.

It is expected that achieving these high recycling rates will result in fiber strength degradation and increased levels of contaminants in the new waste paper

0097-6156/95/0609-0306\$12.00/0  
© 1995 American Chemical Society



sources. At the same time, consumer expectations for product and packaging performance continue to increase. Increased performance in packaging often means maintaining strength and function at lower basis weights to reduce the amount of packaging waste at its source. Packaging performance is important to prevent waste, damage or spoilage of the protected product. Increasing both the fiber recovery rate and the performance of recycled products presents a significant challenge. The purpose of this paper is to review the practical complexity of one area of paper fiber recycling and how James River Corporation is meeting this challenge by implementing projects with improved technology.

## Challenges

**The Effect of Recycling on Fiber Properties.** Paper fibers have a tubular structure that results in a higher strength to weight ratio than steel, aluminum, or glass. One challenge to increasing the recovery rate of paper fibers is the tendency of the fibers to be weakened with repeated recycling. Some processors avoid the recovery of corrugated cartons from electronics packaging originating in Asia as they have already been recycled four or five times and exhibit a noticeable strength loss. The recycling process rehydrates the fiber and then mechanically stresses it as it is cleaned, refined, formed, pressed, and redried. Each recycling process results in loss of some polysaccharides, and the breakdown of some cellulose into low molecular weight fragments and fine pieces of the fiber that cannot be formed into a web and are lost in the process water (4). In addition, many of the additives contained in paper, such as clay coatings and inks, must be removed in the recycling process. This tends to reduce fiber strength and increase the volume of rejected material destined for the landfill.

A recent study of the effect of recycling on chemical properties of pulp concluded that repeated recycling results in only minor chemical changes in the fibers. This means that chemical analysis cannot be "used as a tool for differentiating between virgin and recycled fibers" (5). The loss of strength properties with repeated recycling is better associated with physical changes to the fibers. Howard and Bichard conducted a study of recycling effects on pulp physical properties showing that fiber length was little affected. Repeated recycling generated fines that when included in an arithmetic average of fiber length, tended to unfairly skew results found in the literature (1). The individual strength of fibers was unaffected by recycling, again indicating little structural change in the cellulose polymer. However, the bonding potential of the fibers was affected by recycling resulting in changes to the strength of paper produced. This bonding strength is controlled by the fiber-to-fiber contact area and is a result of hydrogen bonding.

Figure 1 shows a comparison of 100% recycled fibers with typical virgin chemical pulp fibers. These are light microphotographs at 100 times magnification. Increased fiber damage and debris are seen in the recycled furnish.

The fiber physical changes associated with paper recycling were found to depend on the class or source of the fiber. Chemical pulps in products such as white office papers or brown corrugated boxes tend to lose their natural high bonding potential as the swelling or rehydration of the fibers is reduced with recycling. The fibers experience "hornification," tending to close up and become less conformable with repeated recycling, interfering with fiber-to-fiber hydrogen bonding. Sheet bulk may increase when recycling chemical pulps.

Mechanical pulps found in products such as newsprint tend to increase their otherwise low bonding potential with recycling as the fibers are flattened and become more flexible. Sheet bulk using these pulps tends to decrease with recycling. These opposite effects for chemical and mechanical pulps do not cancel each other out in the production of a recycled product containing both classes of

pulps. Chemical pulps are much stronger than the mechanical, and therefore a net strength loss is expected with repeated recycling. The ability to handle the different fiber classes separately represents an advantage to minimizing fiber damage and strength loss expected with increased recycling. The paper forming systems must be optimized to get the most performance possible out of the weaker fiber furnish. As we move to meet the challenge of recovering 50% of the fiber produced, we will be increasingly recycling already recycled fibers.

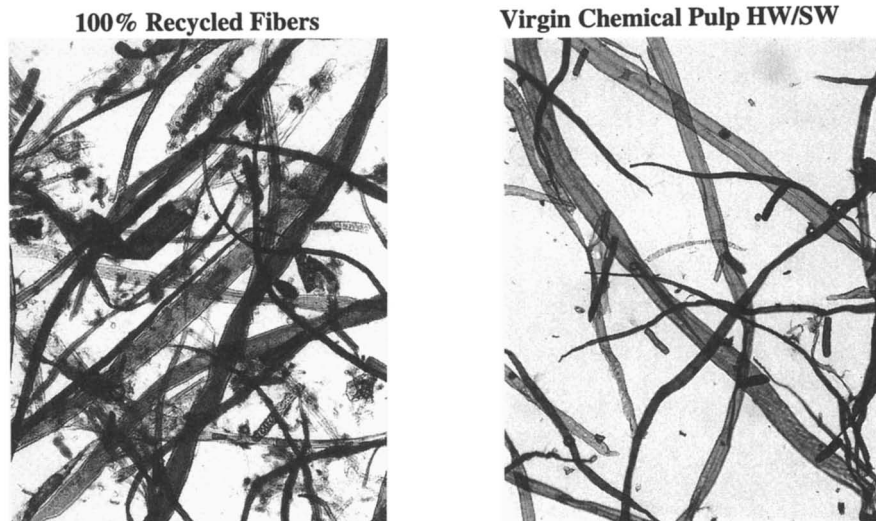


Figure 1. 100X Microphotographs

**Fiber Contamination.** Recycled paper mills have long had to deal with staples, paper clips, glue, tape, plastics, dirt, and many other unwanted contaminants. Increased recovery rates also can be expected to increase the amount of contaminants in the waste paper supply stream. Recycling processes work best on a steady supply of clean and homogeneous materials. In the past, recycled paper materials were obtained from industrial sources as overrun stock, misprinted materials, and box clippings. They are homogeneous, in that the contaminants are consistent and in small amounts. These relatively clean “pre-consumer” waste materials are already included in the national recovery rates achieved. Increasing the fiber recovery rate requires additional use of “post-consumer” or post-use waste that is contaminated with a wide variety of materials and requires more extensive treatment and cleaning. Competition for clean fiber sources will require the use of more contaminated materials. Meeting the 50% fiber recovery challenge will require improved systems for cleaning. Again, separate processing and treatment for the different fiber classes is needed to achieve the best cleanliness with the least fiber damage.

**Recycled Product Quality.** Traditionally, products made from recycled materials carried the connotation of inferior quality and performance as opposed to products made from virgin or new materials. Recycled products were used where lower performance and cleanliness could be tolerated in return for lower costs. Now

consumer expectations of recycled products are changing dramatically toward equal performance to virgin materials. Experience in consumer paper goods shows consumers interested in recycled products demand both high recycled contents and high performance. This is a challenge as waste paper sources become increasingly contaminated and recycled fibers become weaker.

Packaging design is also affected as concern over waste generation from packaging leads to "source reduction." This is an attempt to reduce the amount of packaging material required through increased material performance and corresponding reductions in basis weight. Again, this is a challenge for paper based packaging as recycled fibers lose their strength. As a result, recycled paperboard is often 20% heavier than virgin paperboard to maintain the same strength specification. A study by Arthur D. Little, Inc. stated this challenge clearly: "The challenge for the paper packaging industry is to use as much waste material as possible in packaging while still meeting the user's requirements for strength, protection, and other criteria. ... To be successful over the long term, products and packaging made from wastepaper must compete with virgin fiber products. Short-term 'fad' sales to exploit the green marketing trend will not secure long-term markets." (7).

**Recycling Benefits.** Recycling of paper fibers offers many benefits in spite of the abundant supply of wood resources in North America. The Arthur D. Little, Inc. study also found that recycling a unit of paper can reduce air pollution by 74% and water pollution by 35% over producing virgin fibers. Recycling and deinking can save 15% of the water required for virgin production. A recycling process that does not require deinking can save 50% of the water. These are average results that can vary widely at individual sites.

Not all forms of paper recycling are economically effective. The costs of processing some fibers into high performance products can be higher than producing virgin products. Some government recycled purchasing mandates allow a 10-15% price premium for recycled products in competitive bidding. The challenge is to improve the recycling process to reduce costs and to focus on paper grades that fit well with recycled fiber.

Recycled paperboard is a special case. This product has been produced from old newspapers and corrugated boxes for a long time. Over half of the folding cartons or boxes on the supermarket shelf are made from 100% recycled fiber. The cost is lower than virgin as there is no deinking process step required, and the recovered materials are used efficiently. The white printing surface is generated by applying a pigmented coating. However, the challenges stated still apply. Maintaining cleanliness and strength performance while reaching deeper into the pool of waste material requires process upgrades. Meeting the increased demand for high performance 100% recycled packaging requires an improved paperboard for items that have traditionally relied on virgin fiber.

### **K-1 Recycler Project**

**Project Description.** James River approved funding of a project to rebuild the K-5 paperboard machine at Kalamazoo, Michigan, in August of 1990. The new paperboard machine components were built around the existing K-5 multiple cylinder machine, allowing its operations to continue for 75% of the construction time (8). The new process began operations in November of 1992 as the K-1 Recycler. This \$120 million rebuild added major capabilities to meet the challenge of providing a world class system for the production of high performance 100% recycled paperboard. A state-of-the-art facility for processing and cleaning recycled fiber was constructed that allows each class of recycled fiber to be treated separately. A triple fourdrinier forming section replaced the cylinder formers to

provide improved control over formation and resultant physical properties of the paperboard. The pressing and drying systems were replaced to support the increased productivity of the new system. A networked computer system for process control and quality data was added to provide the operators with real-time data, graphical representations of the process, and the ability to implement advanced controls. A simplified flow diagram of the K-1 paperboard production process is shown in Figure 2. This conceptual view of the process does not show the multiple fiber processing streams and the three layer forming systems.

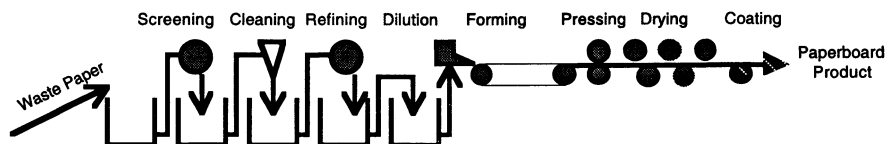


Figure 2. K-1 Recycler Simplified Process Flow Diagram

The new K-1 Recycler is capable of producing up to 680 metric tons per day of PaceSetter® 100% recycled paperboard. Two main grades are produced: a grayback product with a light gray color from newspaper in the bottom liner, and a whiteback product with office paper in the bottom liner. Top coatings and surfaces are formulated for both gravure and lithographic printing applications. The product basis weights and thicknesses produced range from 254 g/m<sup>2</sup> (52 lb/1000 ft<sup>2</sup>) and 305 μm (12 pt) to 469 g/m<sup>2</sup> (96 lb/1000 ft<sup>2</sup>) and 610 μm (24 pt).

**Fiber Sources.** Fiber is received in a 9,000 square meter processing center located almost one half kilometer from the K-1 former. An average production day requires the unloading of 26 semitrailers. Production of a quality product begins with prescreening of material by fiber brokers at their facilities. Communication between plant operators and the brokers as to runnability and contaminants results in continuous improvements in waste paper quality. A contract with a large food store chain to recover "OCC" or the old corrugated containers used for food shipment and storage provides a consistent source of quality fiber. Similar arrangements exist for the delivery of old newspapers.

The K-1 complex has four separate process systems to receive and process waste fiber. Each system is tailored to process and clean a specific fiber class. This increased versatility allows the process to be optimized to get the most effective cleaning while minimizing fiber damage and losses. The fiber sources and properties for each of the four processing systems are shown in Table I. The freeness (ml CSF units) is a measure of the tendency of the stock to drain or release water with a higher value indicating faster drainage. The Kajaani fiber length (mm) is an optical measurement of the fiber length in dilute solution. The Kajaani fines is the percentage fibers with a length less than 0.2 mm.

The topliner process system provides a smooth and white colored surface for coating application. The top liner fiber furnish is also used for the back side in whiteback production. Typical sources are envelopes, computer forms, catalogs, sales literature, and other office papers.

TABLE I. K-1 Recycler Fiber Sources

Fiber Class & Sources	% Furnish	Average Fiber Properties		
		Freeness ml CSF	Kajaani Fiber Length mm	Kajaani Fines %
<b><i>Top Liner Process System</i></b>				
Colored Envelope Cuttings	25	398	2.1	7.4
Manifold White Ledger	25	327	2.0	—
Groundwood Computer Output	25	248	2.1	7.5
Unprinted Bleached Kraft	25	503	1.6	8.8
<b><i>News Process System</i></b>				
Old Newspapers	100	151	2.1	9.3
<b><i>OCC Process System</i></b>				
Old Corrugated Containers	100	588	2.5	6.8
<b><i>Boxshop - Process System</i></b>				
Baled Carton Plant Waste (Paperboard Cuttings)	100	430	2.1	8.5

The news system processes old newspapers. This is a one-component system optimized for this feed source. The news furnish is split and used for both the middle filler and back side (backliner) of the product. The ink is not removed providing a uniform light gray color. The mechanical pulps used in the production of newsprint provide a low freeness pulp with relatively high fines content. These fibers tend to be rigid, kinked, and curled providing some product bulk.

The OCC process system is also optimized for one furnish. The old corrugated containers are made from chemical fibers that drain more quickly. The increased fiber length and good bonding characteristics of this fiber source make this fiber class important for strength generation in the product. OCC is used in the middle filler layer. The boxshop system processes returned product cuttings from the paperboard converting process. This paperboard recycle stream is used in the middle filler ply.

**Fiber Preparation and Cleaning.** Mixed in with the fibers received are contaminants, such as sand, metal, tapes, waxes, plastics, glues, adhesives, and dirt. These contaminants could be from the original paper product, picked up in use, or from the collection process. They must be removed to produce a clean, high strength product and maintain productivity in the forming and coating process. The challenge of the fiber preparation process is high efficiency separation of the contaminants from the fiber while minimizing fiber losses. The intensity of the cleaning process must be controlled to prevent fiber damage and strength degradation. The K-1 process meets this challenge by providing four different fiber preparation processes.

The fiber entering each of the four systems is repulped at about 4-5% solids with water in large continuous pulpers. Mechanical action of the pulper rotor and

associated hydraulic forces separate the waste paper into individual fibers in preparation for screening and cleaning. High density cleaners after the pulpers remove heavy contaminants. The fiber is then sent to the screening system to remove contaminants based on size and shape. The fiber and water slurry is pumped through a series of hole and slotted screens at 2-4% solids where debris larger than the screen size is concentrated into a reject stream for further processing. Hole screens tend to remove long debris, and the slotted screens remove cubical debris while allowing fiber to pass. The screens are arranged in a cascaded flow system to rescreen rejects and minimize fiber losses. Figure 3 shows the screen size and process flow for the topline system.

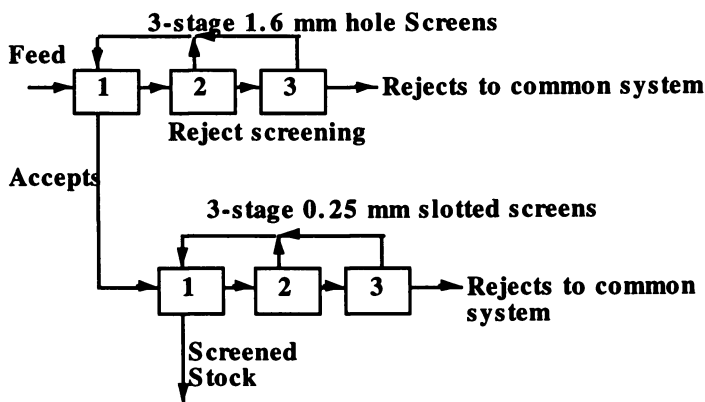


Figure 3. Topliner System Screening Process

Fiber and debris would tend to block the holes or slots with time and blind the screen, restricting flows if counter measures were not available. To facilitate debris removal, the screens contain a rotating foil to create a temporary back pulse in the screen flow to remove debris blocking the screen and move them to the reject line (9). A conceptual diagram of the cleaning foil is shown in Figure 4.

The OCC system has additional equipment to remove small lightweight contaminants that may pass the screens. These contaminants include polystyrene foams (e.g., Styrofoam™), wax, pressure sensitive adhesives, and fine plastics. Cleaning technology for separating the fiber from these materials relies on the density difference between cellulose fibers and the contaminants. The specific gravity of fiber is about 1.2 when the cellulose is swelled by water. The contaminants listed typically have a specific gravity less than 1.0. Two Gyrocleaners are used to separate contaminants from the OCC fiber. A conceptual diagram of a Gyrocleaner is shown in Figure 5. A high speed rotating drum imparts a high centrifugal force to the slurry, allowing separation of the lighter contaminants. The Gyroclean system generates separation forces up to 700X gc, resulting in much greater cleaning efficiency at much higher solids and lower fiber losses than traditional reverse cleaners (10).

Rejected material from the screening processes is sent to a common reject processing system. A series of hole and slotted screens separate good fiber from the contaminants. The contaminants are removed from the process for disposal, and the recovered fiber is sent back to be reprocessed by the OCC screening system. This extra cleaning step insures that good fiber is not discarded while maintaining product cleanliness.

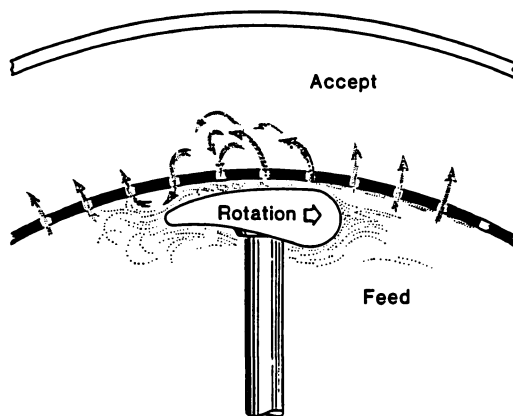


Figure 4. Foil Action in a Pressure Screen  
(Reproduced with permission from ref. 9. Copyright 1993 TAPPI Press)

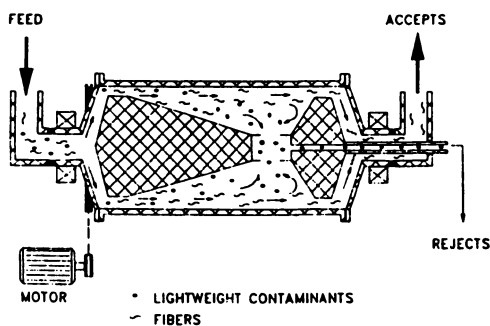


Figure 5. Gyrocleaner  
(Reproduced with permission from ref. 10. Copyright 1993 TAPPI Press)

August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch026

**Stock Preparation.** The cleaned fibers from the four processing systems are then sent to the stock preparation area of the paperboard machine and blended into three systems that supply the three layers of the forming process. The filler ply or middle layer process is shown in Figure 6. This process stream uses a blend of newspaper, boxshop, and OCC fibers to provide both product bulk and strength. Each of the fiber classes is refined separately. The refining process works the fibers in a high shear zone to increase swelling or rehydration. This improves the bonding potential of the fibers and resultant product strength and stiffness. The flexibility of the K-1 Recycler process allows the refining processes to be optimized for each fiber source for improved strength while avoiding damage that weakens the fibers. After refining, the fibers are blended and diluted to about 0.75% solids and screened again in preparation for forming.

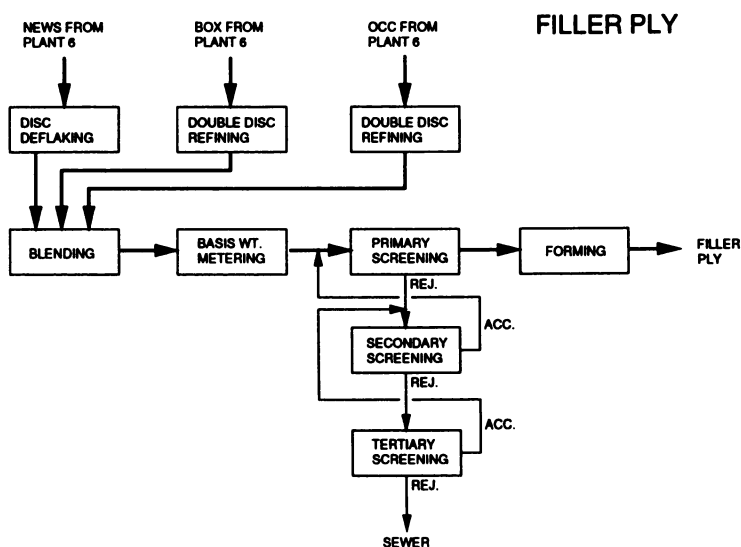


Figure 6. Filler Ply Stock System

The top liner and back liner stock systems are fed a single source of fiber. The back liner is 100% news, and the top liner uses the light blend described in the fiber cleaning section. Process flow diagrams for both of these systems are shown in Figures 7 and 8. These systems also have refining capability and then dilute the fibers to about 0.2% solids in preparation for further cleaning. A series of centrifugal cleaners on both systems removes contaminants using a similar principle to the Gyrocleaners used at higher solids in the OCC fiber system. These cleaners use hydraulic flow to create the separation forces. The centrifugal force on a particle tending to move it outward is balanced by the drag and buoyant forces. A drawing of the principle of cleaner operation is shown in Figure 9.



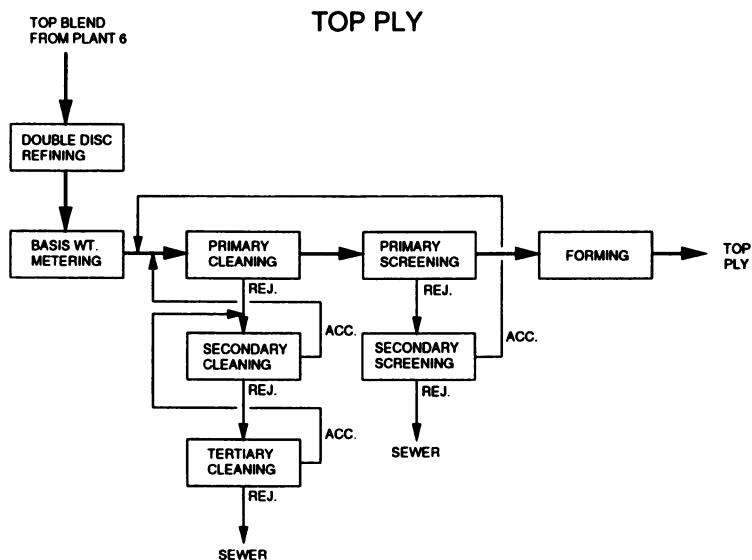


Figure 7. Top Liner Process

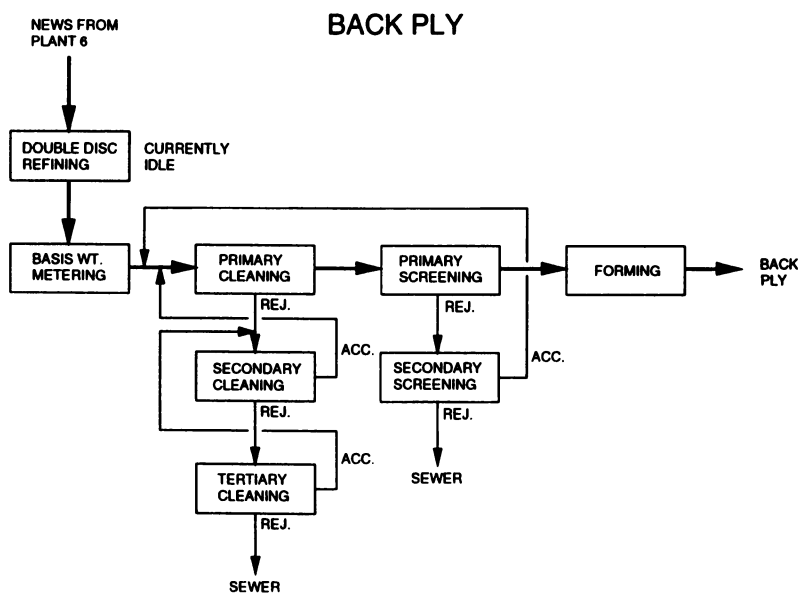


Figure 8. Back Liner Process

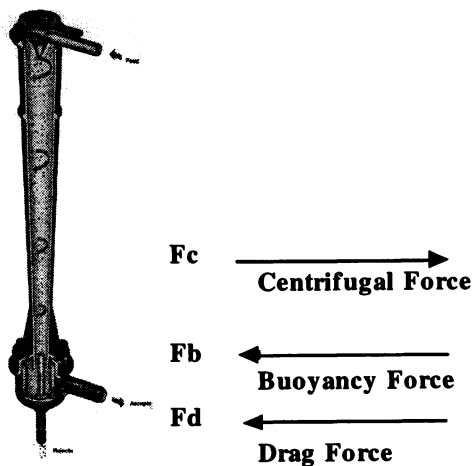


Figure 9. Cleaner Operation  
(Adapted from ref. 11.)

A vortex flow pattern is created by the shape of the cleaner body, and the contaminants are separated from the fiber by differences in specific gravity (11). A table of typical contaminants and their specific gravity ranges is shown in Figure 10. The larger the difference in specific gravity from that of fiber and water, the easier it is to get a good separation.

<u>Type</u>	<u>Specific Gravity</u>
Sand	2.0 – 2.2
Metal	6.0 – 9.0
Clay	1.8 – 2.6
Wax	0.9 – 1.0
Polyethylene	0.91 – 0.97
Styrofoam	0.3 – 0.5
Polystyrene	1.04 – 1.1
Latex/Rubber	0.9 – 1.1
Hot Melt Glues	0.95 – 1.1
Pressure Glue	0.9 – 1.1
Asphalt	1.1 – 1.5
Ink	1.2–1.6

**Separation by Density Difference**  
**Forward Cleaner – Remove Specific Gravity > 1**  
**Reverse Cleaner – Remove Specific Gravity < 1**

Figure 10. Contaminants Specific Gravity  
(Adapted from ref. 11.)

**Contaminant Analysis.** Chemical analysis of the contaminants that make it through the system is used to manage and improve the fiber cleaning process. The Analytical Chemistry Research Lab at the Neenah Technical Center provides analysis of composition and structure of these materials. Analytical methods used for paperboard and machine deposit samples are FT-IR spectrometer with a microscope to examine small contaminants, Mass Spectrometer with fast atom bombardment, and C-13 NMR.

This information is used by process engineers to continue to improve product and process cleanliness by adjusting the process systems for better removal. Contaminant information allows the operators to look for offending materials in incoming materials. Fiber suppliers also can use the information to screen their sources.

**Forming System.** Papermaking on the K-1 Recycler begins with three fourdrinier forming systems that each produce a separate paper web. Unlike the cylinder type formers traditionally used in the production of recycled paperboard, the multiple former concept provides increased flexibility in how each fiber component is treated and used. Figure 11 is a schematic drawing of how the three layers are formed and then combined to get one multilayer web.

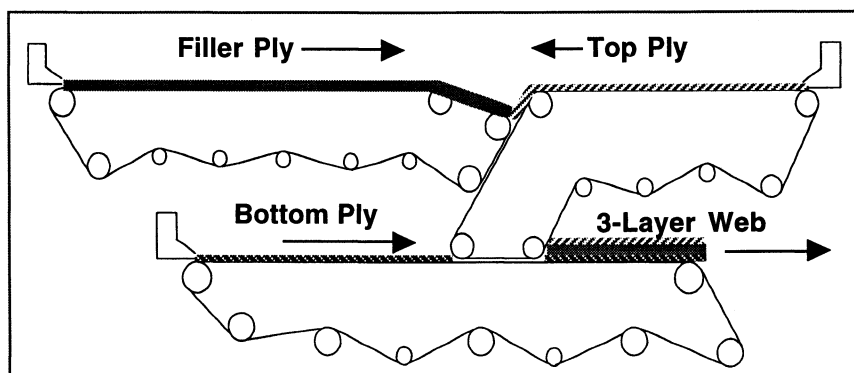


Figure 11. Multiple Layer Fourdrinier

This increased flexibility provides the potential to engineer the paperboard product to use each recycled fiber class in the furnish to get maximum product performance. This capability is key to meeting the challenge of providing maximum product performance while using recycled fibers. The photo in Figure 12 shows the scale of the triple former unit. Retention aids and sizing to control moisture pickup are added to the dilute slurries from the top liner, filler ply, and back liner stock systems before forming. The amount of filler ply is adjusted to control the thickness and final basis weight of the product. The dilute slurries are pumped to their respective headboxes where they are distributed across the width of the moving drainage surface with a precision orifice called a slice. The velocity of the slurry exiting the slice is adjusted to nearly match that of the moving drainage fabric or wire. The relative orientation of the fibers is controlled by adjusting this velocity difference (12). This in turn effects the directional orientation of the physical properties in the paperboard produced.

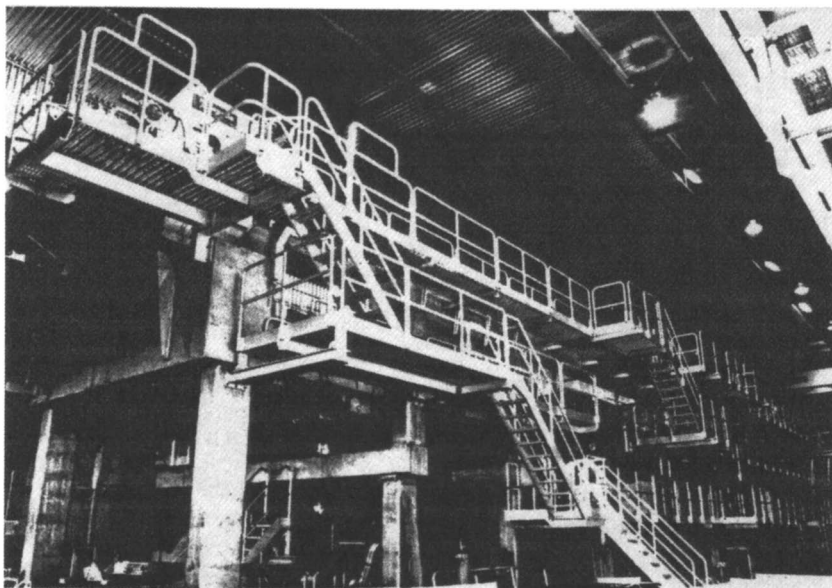


Figure 12. K-1 Recycler Multiple Ply Former

A key measure of paperboard performance in folding cartons is the resistance to bending called Taber stiffness (13). Britt states: "In many instances the basis weight (*of the paperboard*) is determined by the stiffness required, and means to increase stiffness would permit lower basis weight and saving of material" (14). Preserving and enhancing the stiffness of the paperboard is important to the efficient use of recycled fibers that tend to be weaker as a result of repeated recycling. The use of potentially weaker recycled fibers sometimes conflicts with the goal of packaging source reduction (packaging weight reduction). The **K-1 Recycler** is designed to meet the challenge of both recycling and source reduction. While fibers in a paper web tend to lie parallel to the paper plane, the tendency of all machine-made papers to orient the fibers in the direction of the moving wire can be minimized, and the stiffness of the product in the weakest or cross machine direction can be maximized (15).

Process trials on the forming section have shown the capability to control the ratio of machine direction to cross direction Taber stiffness from 3.5 to 1.8. The capability to make this adjustment is used to improve the paperboard stiffness in the cross machine direction. Since many applications of paperboard depend on the minimum strength or stiffness, this capability is key to producing a high performance paperboard while using a furnish of 100% recycled fibers that tend to be weakened by repetitive recycling.

Each fourdrinier table has drainage elements consisting of vacuum boxes and foils that speed water removal from the web of fibers. The drainage table for each layer is specially adjusted to improve the formation of the class of recycled fiber on that table. Formation is a descriptive property of paper which includes the "degree of fiber dispersion, the extent and type of fiber orientation, and the degree of packing or solid fraction (16)." Kershaw states that the formation of a paper web can influence other sheet properties, such as sheet strength, appearance, and the

anisotropy or directional distribution of paper properties (17). Good formation is key to effective and efficient use of fiber materials, especially for meeting the challenge when using recycled fibers.

The middle filler layer drainage system has a top wire system that allows two-sided drainage. This insures a uniform distribution of fiber lengths and fines to each drainage surface. The similarity of the top and bottom sides of the middle layer insures that it will bond to both the top liner and back liner in the same way, producing a superior multilayer product. A schematic drawing of a top wire unit is shown in Figure 13.

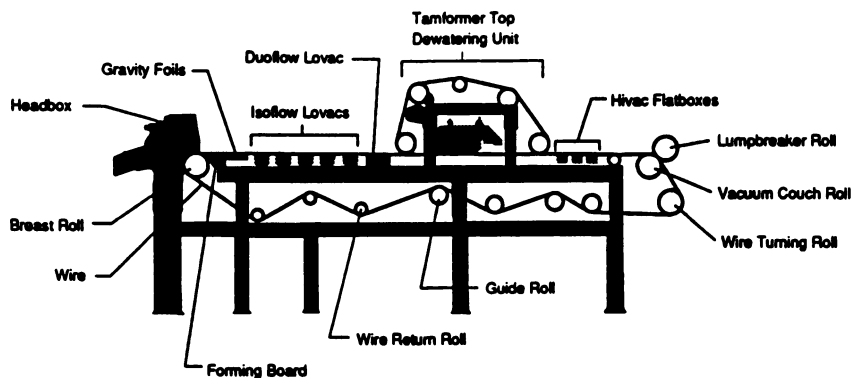


Figure 13. Top Wire Former

Each web is drained to about 9% solids. The separate top liner, middle filler layer, and back liner webs are then pressed or “couched” together to form one strong multilayer paperboard web.

**Paperboard Process.** The multilayer web is then transported to the press section where multiple nips mechanically remove water from the web until it is about 50% solids. The damp web then passes through the dryer section where water is thermally removed resulting in a raw paperboard sheet at 96% solids.

The raw web is calendered and treated to smooth the surface and prepare for the coating process. The top side is double coated to provide a smooth and white uniform surface for coating. The coating is a blend of clay and titanium dioxide in a synthetic binder. The coating make-up system is completely automated and controlled by the same distributed control system that controls the fiber preparation and papermaking systems.

The two-step coating application consists of a base bar applied coat followed by an air knife application. The coating is then dried and the paperboard recalendered to achieve a glossy surface. It is then wound in large reels and slit and rewound to the customer’s request.

**Product Applications.** K-1 PaceSetter® 100% recycled paperboard is used in a wide range of packaging and printing applications. These applications range from cereal boxes and other folding cartons to the backing for blister packaging and labels and tags.

A cross-section microphotograph of the product at 125X magnification is shown in Figure 14. The two coating layers show up as light and dark layers. Unfortunately, this technique does not show the difference among the different fiber classes, fiber orientation, or multilayer construction.

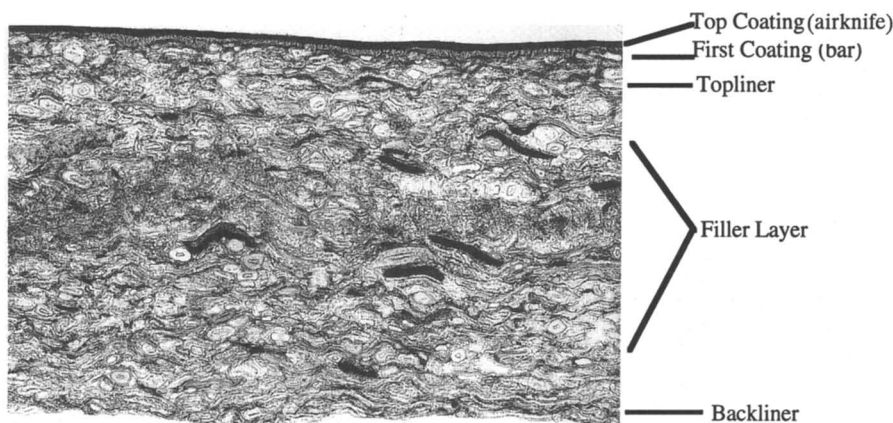


Figure 14. 125 X microphotograph of Paperboard Cross Section

**Continued Advances.** Improvements to the K-1 Recycler process are being planned to continue meeting the challenge. Studies are under way to identify projects to improve the fiber preparation area to increase contaminant removal and improve fiber strength. Similar programs are also under way for the forming and coating section to insure K-1 maintains its technology advantage.

### Comparison to Deinking Process

James River Corporation is also meeting the recycling challenge with processes for recovering and deinking fiber for the production of high quality white office papers and towel and tissue products. James River's newest deinking recycling plant is the Halsey, Oregon, facility. The Halsey plant was started up in March of 1992 at a cost of \$70 million. It processes about 400 metric tons of waste paper daily to produce about 275 metric tons of recycled pulp. A comparison of the K-1 recycled paperboard process to the Halsey deinked pulp process provides insight into the specific challenges faced in each process.

**Fiber Sources.** The Halsey Mill processes office paper waste including white and colored ledger grades and coated book papers. This material is collected and sorted from large sources and tends to be more homogeneous in fiber properties than the materials used in coated recycled paperboard.

**Fiber Cleaning and Bleaching.** The Halsey waste paper is contaminated with materials associated with office or desk use, such as ink, fillers, paper clips, staples, glue, and dirt. The fiber cleaning process begins with similar repulping and screening systems to the K-1 system. However, there is only one process stream, and the waste paper is blended together. A two-stage bleaching process using

hydrogen peroxide and sodium hydrosulfite is used to remove color. This achieves high pulp whiteness and brightness without using chlorine.

**Deinking.** Ink is removed from the fibers using a foam flotation process. Air is injected into a diluted solution of the fibers, dispersed ink particles, and surfactant. The hydrophobic ink particles are adsorbed or trapped by the rising air bubbles and skimmed off the top. This process is effective in eliminating dark spots from pulp at a cost of increased waste water volume and increased fiber losses. The Halsey plant has an advanced water treatment system to handle this load.

**Products.** The deinked pulp is then thickened and pressed to about 50% solids for use at the Halsey Tissue Mill and transported to the James River Camas, Washington, and Wauna, Oregon, mills. Final products are Eureka!™ copy paper, Renaissance™ commercial tissue and towel products, Quilted Northern® bath tissue, and Brawny® paper towels.

**Key Process Differences.** The K-1 and Halsey processes show the range of challenges in recycling paper fiber. The K-1 fiber source is heterogeneous, representing several different fiber classes. These fiber classes are processed separately to achieve the highest performance. The contaminants found in the K-1 system represent the different end uses and collection systems associated with these different fiber classes. The Halsey furnish is relatively homogeneous with predictable contaminants from offices and office collection systems. Fiber losses and treatment costs are much higher in a deinking and bleaching process. A deinking plant like Halsey tends to supply several paper machines and paper mills while the K-1 fiber system is integrated with the single paperboard machine. The capital cost of the deinking process per ton of pulp produced is much greater than that of a recycled paperboard fiber system.

## Conclusion

James River Corporation is meeting the challenge of increasing paper fiber recycling rates while maintaining and improving recycled product performance. Both the K-1 process for producing PaceSetter® 100% recycled paperboard and the Halsey fiber deinking plant process represent the application of state-of-the-art technology in the processing and use of recycled fiber to meet a wide range of product needs.

## Acknowledgments

I would like to thank my coworkers at James River's Neenah Technical Center and the Kalamazoo Paperboard Mill for their assistance in preparing this paper. Specific assistance was provided by:

Dr. Kim Robinson - Recycled fiber mechanics

Dr. John Litvay - Microphotographs

Mr. Mike Schmitt - K-1 fiber cleaning

Mr. Rex Robertson - K-1 stock preparation and forming

Mr. Robert De Jong - Halsey Fiber Plant

Mrs. Pamala Tackman - Document preparation and editing

Mr. Mike Henderson - Macintosh computer network support

**Literature Cited**

- 1 Stilwell, E. J.; Canty, R. C.; Kopf, P. W.; and Montrone, A. M., Packaging For The Environment, (Author D. Little: 1991), p. 47.
- 2 Alexander, J. H., In Defense of Garbage, (Praeger Publishers: 1993) p. 24.
- 3 Paper Recovery Programs Continue to Grow, The Official Board Markets "The Yellow Sheet", March 19, 1994; (Advanstar Communications, Vol. 70, No. 12, Cleveland, OH), p. 1.
- 4 Alexander, J. H., p. 119
- 5 Bouchard, J., and Douek, M.; The Effects of Recycling on the Chemical Properties of Pulps, Journal of Pulp and Paper Science, Vol. 20, No. 5, May 1994, p. J136
- 6 Howard, R. C., and Bichard, W., The Basic Effects of Recycling on Pulp Properties, PAPRICAN Report PPR 864, May 1991, p. 4
- 7 Stilwell, E. J.; Canty, R. C.; Kopf, P. W.; and Montrone, A. M., p. 55
- 8 Zirngibl, P., RPTA Production-Technical Seminar, Proceedings May 1993, p. 11-2.
- 9 Bliss, T., Secondary Fiber Recycling; Spangenberg, R. J. ed., (TAPPI Press, 1993), p. 127
- 10 Ibid., p. 120
- 11 Ibid.; p. 103
- 12 Kershaw, T. N., Pulp and Paper. Chemistry and Chemical Technology, Casey, J. P. ed., 3rd Edition Vol. 2, (John Wiley & Sons, Inc.: 1980) p. 1027.
- 13 Brandon, C. E., Pulp and Paper. Chemistry and Chemical Technology, Casey, J. P. ed., 3rd Edition Vol. 3, (John Wiley & Sons, Inc.: 1980) p. 1810.
- 14 Britt, K. W., Handbook of Pulp and Paper Technology, Britt, K. W., ed., 2nd Edition, (Van Nostrand Reinhold Co., 1970) p. 677.
- 15 Kershaw, p. 1027
- 16 Kershaw, p. 965.
- 17 Ibid.

RECEIVED June 20, 1995



## Chapter 27

# Chemistry of Unit Operations in Paper Deinking Mills

John K. Borchardt

Shell Chemical Company, P.O. Box 1380, Houston, TX 77251-1380

Unit operations in paper deinking mills encompass a range of mechanical and chemical processes. Pulping begins the process and is used to convert wastepaper into dispersed cellulose fibers. Pulping, kneading, and dispersion are unit operations in which ink is detached from cellulose fibers and the size and geometry of the dispersed ink adjusted for efficient removal in other unit operations. These unit operations include washing, flotation, screening, and mechanical cleaning. Additional unit operations such as bleaching, refining, and fractionation are used to impart the desired optical and physical properties to the recycled paper. The choice and sequence of unit operations is determined by the types of wastepaper being processed, the types of paper products being produced, and economic factors. Other unit operations critical to efficient and environmentally responsible mill operation include process water treatment and sludge handling.

Paper deinking mill unit operations encompass everything from sorting collected paper to treatment to solid and liquid wastes. The sequence of unit operations is determined by:

- \* the types of wastepaper being processed
- \* the types of paper products produced
- \* availability of process water and
- \* decisions regarding the financial trade-offs between higher initial capital costs/lower mill operating costs and lower initial capital costs/higher operating costs.

Important unit operations include:

- \* pulping
- \*\* high density cleaning

0097-6156/95/0609-0323\$12.00/0  
© 1995 American Chemical Society

- \*\* screening
- \*\* forward cleaning
- \*\* reverse cleaning
- \*\* washing
- \*\* flotation
- \* dispersion and kneading
- \* water treatment
- \* sludge handling

The unit operations for removing ink and other contaminants from the cellulose fibers are indicated by \*\*. The effectiveness of these operations is determined by particle size, geometry, density, and surface chemistry (Figure 1).

### Pulping

Pulping is a physical process that disaggregates paper into individual fibers dispersed in water. Pulping may be a batch or continuous process. Newsprint deinking mills commonly use continuous pulping. Most mills producing tissue products or printing and writing paper from deinked pulp use batch pulping. Low pulping consistency (3-6% solids) is common in newsprint and many tissue mills. High consistency pulping (8-18% solids) is common in mills deinking mixed office paper (MOW). MOW contains substantial amounts of photocopied and laser printed paper. The

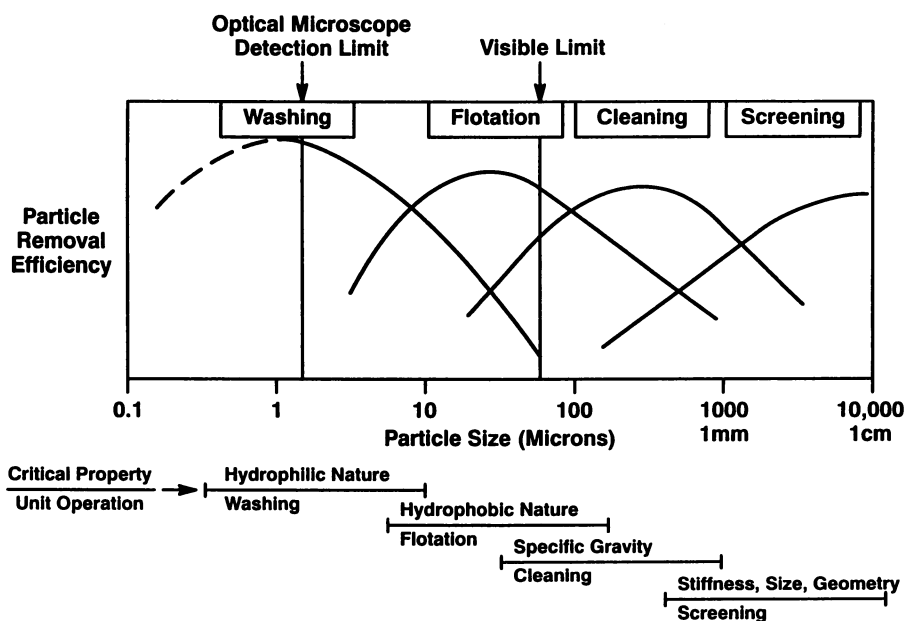


Figure 1. Removal Efficiency as a Function of Particle Size for Different Unit Operations.

inter-fiber abrasion forces associated with high consistency pulping assists in ink particle detachment and breaking toner inks apart (1-3). Fiber flexing and bending also promote ink detachment.

Ink detachment from fibers occurs by chemical processes as well as the mechanical processes mentioned above. Added chemicals can promote ink detachment from fibers and adjust the dispersed ink particle size. Fiber swelling is promoted by high pH. For this purpose, sodium hydroxide is often added to the pulper to raise the pH to 8-10. Usage levels are up to 3% of the weight of the dry paper being pulped (1). Occasionally in office paper deinking, even higher pH's, 10-11, are used. Sizing agents and toner inks render paper surfaces less hydrophilic and can retard cellulose fiber swelling and paper disaggregation (2). Added surfactants and extended pulping times can overcome adverse effects of sizing agents and toner inks.

Since high pH can promote yellowing of lignin-containing pulps, a bleaching agent, usually hydrogen peroxide, is often added to the pulper. Concentrations up to 2% of the dry recovered paper weight are used (1). Complexing agents such as ethylenediamine-tetraacetic acid (EDTA) and diethylenepentaminetetraacetic acid (DPTA) to retard hydrogen peroxide decomposition promoted by multivalent metal ions present in the process water.

Surfactants are added to the pulper to promote ink particle detachment from fibers and dispersion of the detached ink in the process water. Recently, mechanisms similar to those proposed for liquid soil removal from fabrics have been theorized (3). Other recent papers suggest that toner inks behave similarly to solid soils on fabric (3,4). Recent results suggest that enzymes promote detachment of various types of ink from cellulose fibers and could be useful in deinking (5).

Surfactants also can provide some control over the particle size of dispersed ink. The effectiveness of different deinking unit operations in separating dispersed ink from cellulose fibers varies with ink particle size (see below). Thus, optimum dispersed ink particle size and therefore the type of surfactant used in the pulper is determined by the deinking process engineering. By "matching" pulper chemistry and deinking process engineering, mill operators can improve ink removal efficiency. For example, washing is most effective on relatively small ink particles. So strongly dispersing surfactants are used during pulping in wash deinking mills. Some mills remove toner ink particles using fine screens and mechanical cleaners. These unit operations are most effective on relatively large ink particles (Figure 1). Operators of these mills prefer deinking agents which agglomerate ink particles into large aggregates or convert flat toner flakes into 3-dimensional particles.

Exploitation of the ability to have some control over ink particle size is discussed in the various sections on ink removal unit operations below. However, recovered paper can be highly variable, even on an hour-to-hour basis, in deinking mills. Variation in the ink compositions of the paper being pulped reduces the precision of some pulper additives in controlling ink particle size. This is particularly true for many of the agglomeration chemicals.

Ink particle redeposition on cellulose fibers is an important concern. Ink particle redeposition reduces deinked paper brightness. Should larger ink particles redeposit on fibers, visible ink specks may result. Sodium silicate is often added to the pulper to act as a dispersant and reduce this redeposition (5,6). Up to 5% (relative to the weight of the dry recovered paper) may be used (1). Ink redeposition may be most severe with flexographic newsprint ink because of the very small particle size of the dispersed ink (7). These very small ink particles are not difficult to detach from cellulose. However, they are known to redeposit on fibers readily (8). Use of laundering anti-redeposition agents such as carboxymethyl cellulose and sodium poly(acrylate) has been shown to increase deinked sheet brightness (7). Presumably, these chemicals function by reducing dispersed flexographic ink particle redeposition onto cellulose.

Anti-redeposition agents increase the steric hindrance and electrostatic repulsion between dispersed particles. These forces prevent the approach of dispersed ink particle and cellulose fibers to within the distance at which the onset of attractive van der Waals forces occurs.

### **High Density Cleaning and Screening**

High density cleaning is usually the first step after pulping (9). Its purpose is to remove high and medium density large objects found in wastepaper. These include rocks and dirt, nuts, bolts, nails, paper clips, and assorted other objects. High density cleaners rely on centrifugal forces to separate the less dense cellulose fibers from these heavy objects. These large objects can damage expensive downstream process units. So their removal is important.

Screening usually follows high density cleaning (10). Its purpose is to remove large contaminants (usually low density) from the pulp slurry. These contaminants include unpulped paper, plastic, and large adhesive particles from envelopes and labels. Removal of adhesive particles from pulp is most efficient using a combination of the narrowest screen slot with and the highest pulp consistency practical for that slot width (11). Recent developments in improved screen design and operation have been reviewed (1-2).

### **Washing**

Washing is used to remove dispersed ink particles from the pulp slurry. Washing is discussed in detail in reference 13. This process is comparable to home laundering in many ways (3,13). Unlike laundering, washing is a continuous process. In mills relying only on washing and not on flotation, strong dispersants such as alcohol ethoxylates and alkylphenol ethoxylates perform well as deinking surfactants. Washing is most effective on small, dispersed ink particles such as letterpress, offset, and flexographic newsprint inks (Figure 1). It is less effective on large, poorly dispersed ink particles such as toner inks from photocopiers and laser printers and ultraviolet- and heat-set inks. Therefore, the most effective wash deinking surfactants promote ink particle dispersion by increasing the hydrophilic nature of the ink particles on which they adsorb. These strong dispersants are high HLB

surfactants, usually nonionic. (HLB is the hydrophilic: lipophilic balance and indicates the emulsifying behavior of a surfactant. The HLB is described and methods for its measurement discussed in reference 14.)

**Wash Deinking Surfactants.** Alcohol ethoxylates and alkylphenol ethoxylates are the most commonly used wash deinking surfactants. More recently, proprietary, formulated products have been developed to increase deink effectiveness and improve surfactant handling properties.

Effective washing chemistry begins in the pulper with efficient ink detachment from fibers. Both mechanical and chemical forces promote this detachment. Deinking surfactants with a hydrophilic - lipophilic balance (HLB) of about 14.5 provide the highest deinked sheet brightness when wash deinking newsprint inks (15). The optimum deinking surfactant HLB for wash deinking is dependent on ink composition. The optimum alcohol ethoxylate HLB for wash deinking toner printed paper is 10-11 while the optimum for ledger inks is 13-14 (16). However, the optimum alkylphenol ethoxylate HLB for wash deinking ledger inks is 11.5-12 (17). So, when dealing with different chemical classes of surfactants, HLB alone may not define the best deinking agent to use.

Colloidal particles such as finely dispersed ink and mineral particles used as fillers in paper are removed in proportion to the water removal in the washing step. However, as more water is removed from the pulp slurry, the tendency of ink particles to redeposit on fibers increases. This is why washing is often conducted with simultaneous removal and addition of water. The effluent from washers is heavily laden with ink, mineral fine particles, and small cellulose fibers. As a result, it can be difficult to clarify.

**Pulp Washing.** As more water is removed from the pulp, the pulp consistency at the washer discharge increases. Ink removal efficiency decreases with increasing pulp consistency at the washer discharge. Ink particle redeposition on cellulose fibers is the probable cause of decreased ink removal efficiency. Several different types of washers are used. They can be classified on the basis of their discharge pulp consistency:

- \* low consistency - up to 8% consistency
  - sidehill screens
  - gravity deckers
- \* intermediate consistency - 8-15% consistency
  - high speed belt washers
  - inclined screw extractors
  - vacuum filters
- \* high consistency - >15%
  - screw presses
  - belt presses

Cellulose fiber loss is a function of washer design and pulp discharge consistency (Table I).

Table I. Fiber Losses in Typical Commercial Washing Units<sup>a</sup>

Washer Type	Consistency (% by weight)			1 Stage Fiber Loss, %
	Washer Inlet	Washer Outlet	Effluent	
Sidehill screen	0.6 - 1.0	3 - 4	0.15 - 0.25	12 - 18
Gravity decker	0.7 - 1.0	4 - 6	0.04 - 0.09	6 - 8
Inclined screw extractor	3.0 - 4.0	8 - 12	0.25 - 0.35	8 - 12
Screw press	3.0 - 4.5	24 - 28	0.1 - 0.2	2 - 5

a. Data taken from reference 18.

The higher the fiber yield loss, the less deinked pulp the mill can produce. Washers are often used in series. The ink-containing reject water from a later washing stage is used as the pulp dilution water for an earlier stage of washing. This counter-current washing recovers fibers lost in the reject water of later washing stages thus reducing overall fiber loss.

Washers also differ in their relative purchase and operating costs (Table II).

Table II. Relative Capital and Annual Operating Costs of Washers<sup>a</sup>

Washer Type	Relative Capital Cost	Relative Operating Cost
Sidehill screen	0.60	1.00
Gravity decker	1.00	0.62
Inclined screw extractor	0.97	0.40
Screw press	0.93	0.22

a. Data taken from reference 13.

Typical papers processed using wash deinking are 100% old newspaper and sorted office paper containing no toner ink-printed paper. (During pulping, toner-printed paper produces many ink particles too large to be efficiently removed by washing (Figure 1). Flotation is more efficient in removing these larger ink particles.)

### **Flotation**

Flotation is used alone or in combination with washing and cleaning to deink mixtures of old newsprint and old magazines and office paper. Unlike washing, the

office paper can contain toner ink-printed paper. Figure 2 illustrates a simple flotation cell. An effective flotation process must fulfill three functions:

- \* efficiently entrain air. Air bubble volume is about 1,000 microns<sup>3</sup>. Typically air bubbles will occupy 25-60% of the flotation cell volume. Increasing the air:liquid ratio in the flotation cell is said to improve ink removal efficiency (19). Air bubbles must have sufficient residence time in the cell for ink attachment to occur.
- \* ink must attach to air bubbles. This is primarily a function of surfactant chemistry. The mechanism proposed by Thompson and coworkers provides a theoretical framework to consider flotation physics and chemistry (20). To attach to an air bubble, an ink particle must approach to within the distance (critical gap) at which van der Waals attractive forces overcome repulsive effects. Within the critical gap, ink particle attachment to the hydrophobic air bubble surface occurs. Agents that modify ink particle surface chemistry to increase hydrophobic character result in an increase in the critical gap. Attractive forces overcome repulsive forces at a greater ink particle - air bubble distance. The result is that ink particle attachment to air bubbles occurs more readily.
- \* minimal trapping of cellulose fibers in the froth layer. This depends on both cell design and surfactant chemistry.
- \* efficiently separate froth layer from the pulp slurry before too many air bubbles collapse and return ink particles to the pulp slurry.

Flotation is discussed at length in reference 21. Substitution of carbon dioxide, nitrogen, and oxygen for air does not improve flotation ink removal efficiency (22). Solids content of the pulp slurry during flotation is typically 0.7-1.0%. Air enters the pulp slurry as bubbles. Surfactant promotes attachment of ink particles to bubble surfaces. As air bubbles rise to the top of the flotation cell, ink particles, mineral fine particles from paper fillers, and small cellulose fibers are trapped in the froth layer. The surfactant stabilizes air bubbles long enough for the froth to be removed before many bubbles collapse allowing ink re-enter the pulp.

High flotation cell microturbulence and small air bubbles are said to favor removal of small ink particles while low microturbulence and larger air bubbles are more effective in removing larger ink particles that can form visible specks in the pulp (23). At least one commercial cell has been designed to have zones of different microturbulence and produce a wide range of bubble sizes (23).

**Flotation Deinking Surfactants.** These surfactants render ink particle surfaces more hydrophobic. This increases ink particle aggregation and retards dispersion

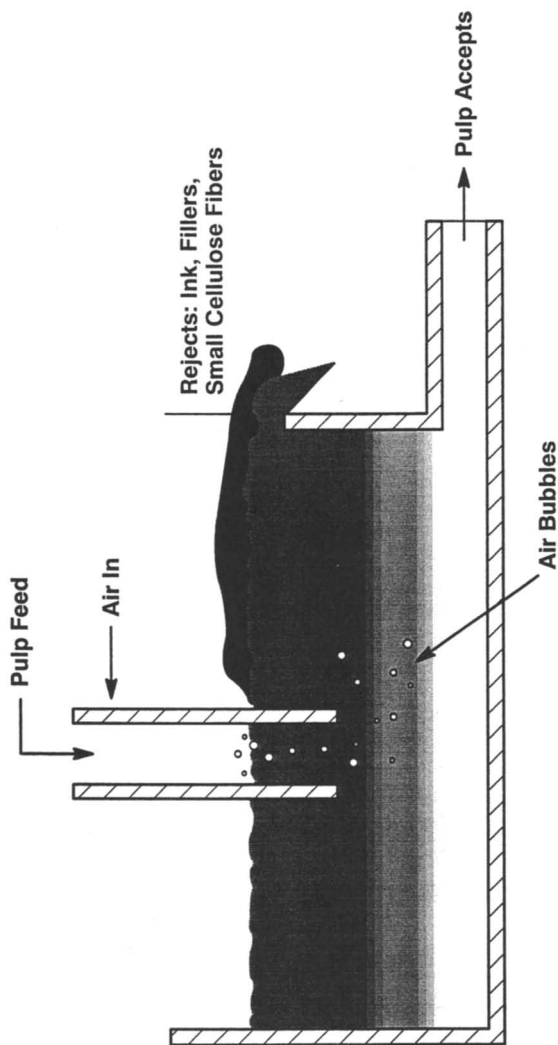


Figure 2. Generic Flotation Cell (figure adapted from Figure 15.1, reference 10 and used with permission).



during pulping. Flotation is most effective on somewhat larger particles than is washing (Figure 1). Thus, the larger ink particle size is an advantage. Increasing the hydrophobic character of ink particles promoting their attachment to air bubbles (see above). In contrast, wash deinking surfactants render ink particle surfaces hydrophilic promoting ink particle dispersion. Thus, optimum HLB values are significantly lower than for flotation deinking surfactants than for wash deinking surfactants. These surfactants are added either to the pulper or to the pulp immediately before flotation.

Early flotation deinking surfactants were fatty acids. Fatty acids require calcium ions to function. A minimum water hardness of 5°dH is needed (1). The calcium salt can be generated in situ, usually by addition of a soluble  $\text{Ca}^{+2}$  salt such as calcium chloride. Process water naturally containing high levels of hardness ions may not require addition of a calcium salt. Calcium carbonate filler particles in magazine paper can also serve as a calcium source. (This is why about 30% old magazines are added to the newsprint being deinked by flotation.) Fatty acids are added just before flotation. These are usually used at higher concentrations (2-4 times) that of more recently developed flotation deinking surfactants.

More recently commercialized flotation deinking surfactants are alkoxyates of fatty alcohols or fatty acids containing both ethoxy units (EO) and propoxy (PO) units (24,25). Little chemical structure information is available on these proprietary products. Patent references suggest optimum products are synthesized by adding an approximately 2:1 by weight mixture of EO and PO to a fatty alcohol such as hexadecanol or fatty acid such as stearic acid (26,27). However, the situation is complex as EO:PO ratios ranging from 1:2 to 4:1 have been claimed (28,29). Alkoxyates in which the EO and PO are added separately to form two or more blocks are also described in the patent literature (30).

Recent results suggest that more effective, lower foaming deinking agents are synthesized when EO and PO are added sequentially to a fatty alcohol than when they are added simultaneously to form a chain with a random distribution of EO and PO units (31). Deinking efficiency of twin-tailed hydrophobe alkoxyates are said to be superior to single chain hydrophobe alkoxyate surfactants (24).

Ethylene oxide-propylene oxide copolymers (28) and proprietary formulated products are also used in flotation deinking operations.

When pulping office paper containing toner ink printed paper, certain proprietary deinking agents promote formation of 3-dimensional, often spherical, ink particles (33-35). These are more hydrodynamic than the flat ink flakes usually formed when pulping toner-printed paper. Flotation of these more hydrodynamic particles may be more efficient than flotation of flat ink flakes. Other deinking agents are designed to agglomerate toners into very large particles (36).

**Laboratory Flotation Deinking.** Laboratory results indicate that surfactants providing lower interfacial tension against model newsprint ink vehicles provide more efficient ink removal (24,31). Contact angle studies indicate that surfactants providing better wetting of ink surfaces also provide more efficient flotation ink removal (24,31). Surfactants that provide better wetting of toner inks also are more efficient flotation deinking agents (37). The correlations of ink removal efficiency with lower interfacial tension and better wetting of ink surfaces is probably related to more efficient ink detachment from fibers during pulping. Surfactants providing a less negative ink particle *zeta*-potential, provided improved flotation ink removal efficiency (24,31).

When using sodium silicate as a pulper additive, its surface active properties: wetting, emulsification, and penetration, of liquid into solids, do not appear to impact ink removal efficiency in subsequent flotation deinking (38).

Flotation can also remove paper filler and coating particles dispersed in the pulp. Like ink, these particles can become attached to air bubbles and be trapped in the froth layer. Addition of certain cationic organic polymers such as poly(diallyldimethylammonium chloride) to pulp improves the removal efficiency of mineral fine particles during flotation (39,40). (These mineral fine particles are formed from paper fillers and coatings.)

### **Mechanical Cleaning**

A cleaner is a hydrocyclone device utilizing fluid pressure to create rotational fluid motion (9). Operation of a forward cleaner is illustrated in Figure 3. Contaminants denser than water such as toner inks remain in the center of the cleaner and exit the cleaner in a separate stream. For most forward cleaners, optimal ink removal efficiency is obtained at a pulp feed consistency of 0.2-0.3%. Most forward cleaners' deinking efficiency declines at pulp feed consistencies greater than 0.4%. Recently a cleaner said to be efficient at 1.2% pulp consistency has been developed (41).

Reverse cleaners operate on the same principles as forward cleaners (9). Contaminants less dense than water exit the cleaner as a separate stream from the pulp slurry. Reverse cleaners are used to remove adhesive and plastic particles as well as paper filler particles and light weight particles formed from paper coatings.

Cleaners are most efficient on relatively large particles (Figure 1). One report indicates that in pilot mill tests ink removal efficiency toner ink particles greater than 100 microns in diameter was 70% (34). For toner ink particles less than 30 microns in diameter, ink removal efficiency was 35%. Since the tendency is for toner ink

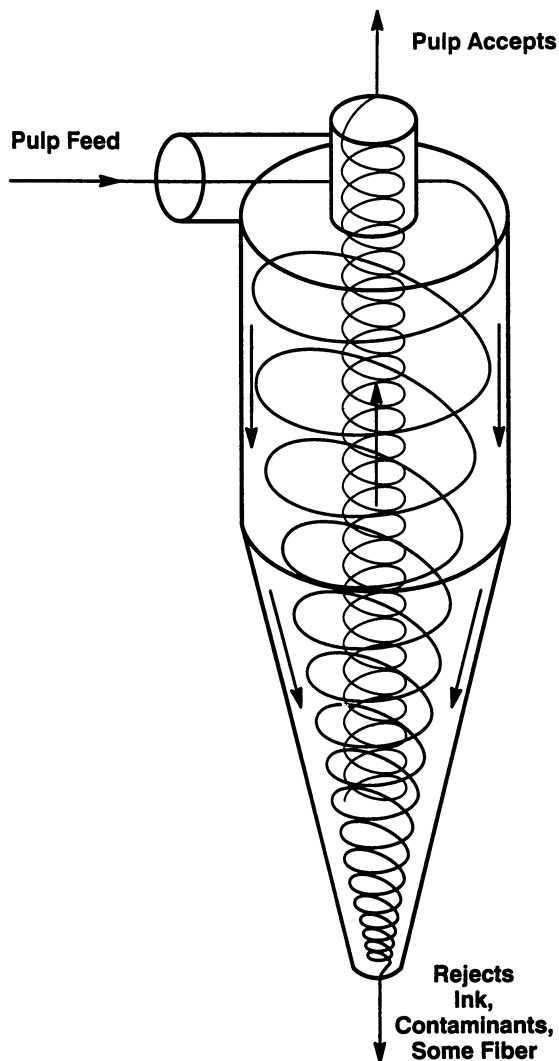


Figure 3. Schematic Diagram of a Forward Cleaner (adapted from Figure 13.2, reference 9 and used with permission).

particles to fragment during processing, it is probably best to locate mechanical cleaners early in the sequence of deinking unit operations (42).

**Chemistry and Mechanical Cleaning.** Forward and reverse cleaning are considered to be purely mechanical processes. However, using fatty alcohols (35) or certain proprietary deinking agents (36) can facilitate the later removal of toner inks in forward cleaners by aggregating them in the pulper to the size range at which forward cleaners are most effective (Figure 1). Scanning electron microscopy/energy dispersive X-ray analyses clearly indicate that some ink particles are formed by the fusion of different ink particles rather than the detachment of toners from paper in the form of very large particles (34). Confocal laser scanning microscopy indicates these particles have a 3-dimensional, often spherical geometry (33). In contrast, flat flakes form when using no surfactant or when using many deinking agents. The more 3-dimensional particles are have a higher apparent density. This and their more hydrodynamic shape compared to flat ink flakes can increase forward cleaner ink removal efficiency.

Pilot mill results indicate that, over most of the ink particle size range studied, use of certain proprietary deinking surfactants (33) resulted in higher ink removal efficiencies for a given particle size compared to use of no surfactant (43). However, at a given ink particle size, the different toner ink agglomeration chemicals used in another report (44) did not alter toner surface properties or geometry in such a manner as to increase ink removal efficiency. (The standard of comparison was removal of the same size ink particles using no agglomeration chemical.)

### **Dispersion and Kneading**

Dispersion and kneading (44) are mechanical processes designed to reduce dispersed ink particle size through fiber - ink abrasion processes. Fiber - fiber abrasion can detach additional ink particles from fibers. Dispersion is performed at elevated temperatures above the softening point of toner inks (ca. 65°C), UV-cured inks (85-120°C), and adhesive particles (85°-110°C). Particle softening can aid in reducing particle size. Kneading may be performed using pulp at ambient temperature. However, frictional processes in kneading can significantly increase pulp temperature. Both kneading and dispersion are performed at high consistency, up to 30% by weight cellulose fiber (45).

Dispersion and kneading are often used for pulp containing toner inks. These inks often form large particles during pulping. Dispersion and kneading reduce the toner ink particle size below the visible range. Recently developed proprietary chemical agents can be added to the pulper to reduce toner ink particle size substantially (37). These agents, by reducing toner resin glass transition

temperature, could promote greater ink particle dispersion during pulping. This reduction in ink particle size could permit a shorter pulp residence time in kneaders and dispersion units permitting a higher pulp throughput rate. Contact angle studies indicate that effective wetting of toner particle surfaces is required for efficient deinking.

With pulp made from old newsprint and magazines, dispersion is sometimes used after flotation and washing to improve optical homogeneity of paper made from the deinked pulp. By reducing particle size to less than about 40 microns, dispersion and kneading reduce pulp brightness while eliminating visible ink specks. Washing or flotation are often performed after dispersion or kneading. These unit operations remove the small ink particles formed in these processes (Figure 1) and thereby increase deinked pulp brightness (45).

### **Bleaching**

Bleaching has a long history since it was first developed for bleaching cellulose fibers prepared directly from wood. In paper recycling, bleaching agents are used both during pulping and in separate bleaching operations performed after removal of inks and other contaminants from the pulp. Addition of bleaching agents during pulping to retard fiber darkening at high pH is discussed above. Addition of bleaching during kneading takes advantage of the high (ca. 30%) solids content of the pulp and conversion of mechanical energy into heat that occurs during kneading. These factors increase the rate of reaction of bleaching chemicals with dyes and pigments that reduce pulp brightness.

Bleaching as a separate operation whitens fibers and removes the coloring effect of dyes. As practiced in paper mills, bleaching is a multi-stage operation using different bleaching agents in each stage. There is a vast literature describing bleaching chemistry (46).

There are two types of bleaching: oxidative and reductive. Oxidative bleaching cleaves carbon-carbon double bonds thus destroying chromophores. Reductive bleaching which reduces carbon-carbon double bonds to single bonds. The loss of extended conjugation in the chromophore leads to loss of color.

The most common oxidative bleaches are:

- \* hydrogen peroxide
- \* sodium hypochlorite
- \* chlorine dioxide
- \* oxygen
- \* ozone

Although it is a very cost-effective bleaching agent, sodium hypochlorite is not used extensively to whiten deinked pulp due to environmental concerns. Reductive bleaches include sodium hydro- sulfite and formamidine sulfinic acid (FAS). Improved cost effectiveness is claimed when FAS is generated in the pulp slurry by reaction of hydrogen peroxide and thiourea (47).

In deinking mills, ink removal and bleaching are intimately related. Microscopic ink particles have a more adverse effect on deinked sheet brightness than visible ink particles (48). Bleaching will not alleviate the negative impact of small black ink particles on deinked sheet brightness. The presence of many microscopic ink particles can be a gray-looking paper sheet. More bleaching agent is required to whiten fibers to obtain a required deinked sheet brightness. Thus, poor ink removal efficiency can increase bleaching costs.

### **Refining and Fractionation**

Refining and fractionation are processes used to alter and select cellulose properties so the final sheet has the desired properties. Properties of recycled fibers differ from those of fibers prepared directly from wood. Recovered fibers have:

- \* lower freeness (related to the rate of water drainage from pulp on paper machines)
- \* increased apparent density
- \* lower sheet strength (burst, tensile, etc.)
- \* increased sheet opacity
- \* inferior fiber - fiber bonding properties
- \* lower fiber swelling
- \* lower fiber flexibility
- \* lower water retention
- \* reduced fiber fibrillation
- \* much lower internal fiber delamination

Refining is used to develop the desired pulp drainage properties and improve the following sheet properties:

- \* bulk and density
- \* strength
- \* surface smoothness
- \* porosity
- \* printing characteristics

The double disk refiner is most commonly used in modern mills (49). Its function is to increase fiber flexibility while reducing fiber length.

Fractionation separates pulp is separated into two more homogeneous fractions significantly different from each other. Fractionation is used to separate fines and short, weak cellulose fibers from longer, stronger cellulose fibers.

A recent review of fractionation technology is available (50). The primary application of both refining and fractionation is in processing paper, particularly old corrugated containers into new packaging products, particularly linerboard.

### Water Clarification

Process water needing to be clarified comes from several different sources in the recycling mill:

- \* rejects from screens and mechanical cleaners
- \* rejects from washers, thickeners, and flotation cells
- \* water that drains from the pulp as it is converted into paper on the paper machine (white water)
- \* water from felt washers

These waters contain different dissolved chemicals and suspended solids and are processed separately.

Water from screens, cleaners, washers, thickeners, and flotation cells contain relatively high levels of ink. These waters also contain valuable chemicals: sodium hydroxide and surfactants. Recycle of this water can save up to 10% in chemical costs. Customarily combinations of cationic and anionic flocculants are used in deinking process water clarification. The nature of the deinking surfactant can have a major effect on the efficiency of flocculants in clarifying deinking process water (25). The selection of cationic flocculant appears less critical than the anionic flocculant when deinking newsprint (25) and office paper (50). However, the cationic flocculant can have a major effect on the optimum dosage of anionic flocculant (25).

The nature of the deinking surfactant can have a major effect on the efficiency of flocculants in clarification of deinking process water (25). When deinking office paper, deinking agents with a HLB of 12-13.5 gave the best process water clarification in terms of the smallest flocculant dosage and the lowest water turbidity (51). When using a fatty acid alkoxyate containing both EO and PO, addition of free fatty acid to the surfactant formulation did not improve water clarification (51).

The types of ink and paper being processed and can also influence process water clarification. The amount of anionic/cationic dual polymer treatment chemical needed for office paper deinking process water clarification is only about 20% of that required for newsprint deinking process (51).

Paper machine white water contains suspended fillers, pigments, and short cellulose fibers. Recycling this water back to the paper machine can recover these valuable materials.

Mills have three major options in handling their process water. The first is to discharge the water to a municipal treatment facility. The second is to use sedimentation tanks to allow solids to settle out of the liquid. The third is dissolved air flotation. Dissolved air flotation is faster than settling and the water loses less

heat before being returned to mill operations. The sludge removed from the flotation unit is higher in consistency than sludge from settling tanks.

Removal of small solid particles suspended in the process water is critical to successful water recycling. Two-stage polymer treatments are typically used (25). First a low molecular weight cationic polymer is added to neutralize negative charge on suspended solids. For economic reasons, the polymer is typically an ammonium salt. Then a high molecular weight anionic polymer is added to flocculate the suspended solids. This is usually a copolymer of acrylamide or a chemically modified polyacrylamide.

Inorganic chemicals may also be used. Bentonite may be used as a flocculant in combination with polymer treatment. Alum, once a common coagulant is less used now because its concentration can build up in recycle water. Alum can bind ink to fibers and increase the difficulty of deinking.

Removal of the very small flexographic ink particles in process water is difficult. Ultrafiltration has been proposed to remove these very small dispersed ink particles (52).

### **Rejects and Sludge Handling**

Sludge from water clarification contains:

- \* water
- \* inks and solid pigments
- \* dispersed adhesive particles
- \* small plastic particles
- \* short cellulose fibers
- \* paper filler and coating particles

Efficient dewatering minimizes sludge volumes sent to landfills thus reducing hauling costs and tipping fees. Efficient sludge dewatering also increases the efficiency of heat utilization during incineration. Inclined screw thickeners are often used to thicken the rejects from dissolved air flotation clarifiers. Reciprocating piston presses are also used.

Heavy-weight rejects include rocks, metals, ceramics, wire, and dirt. These are discharged from high density cleaners and forward cleaners. These incompressible rejects have no fuel value and are usually landfilled (after gravity drainage increases the solids content to 40-80%).

Lightweight rejects include plastics, wax, and adhesive particles. These are discharged from coarse screens, fine screens, and reverse or throughflow cleaners. Highly compressible, these rejects have a high fuel value if they are dewatered sufficiently. Lightweight rejects usually contain significant amounts of cellulose fibers.



Ink and mineral particles (originating from paper coatings and fillers) are discharged from flotation cells, washers, and forward cleaners. These are also often accompanied by cellulose fibers.

Sludge applications under investigation include use in bricks and as a fertilizer spray on fields and roadsides.

### **Technical Challenges in Paper Recycling**

Many challenges remain for scientists and engineers in paper recycling. As more wastepaper is collected, a wider variety of inks and other contaminants must be removed from the paper. Sorting wastepaper is expensive. So deinking agents must be effective on a wide variety of ink types. Increased collection and processing also means the quality of recycled paper fibers is decreasing. Increasingly, the collected paper will contain cellulose fibers that have already been recycled. Residual ink content and fiber weakening can cause product quality problems when this paper is recycled. Scientists and engineers must compensate for this to produce paper of adequate strength. More information is needed on the effect of deinking surfactant chemical structure and usage levels on recycled fiber properties.

Demands for higher ink removal efficiency and the processing of more heterogeneous wastepaper grades are increasing the need for additional unit operations in recycling mills. This will increase mill capital cost. New types of unit operations requiring lower capital costs and reduced operating expenses are being developed. Equipment manufacturers are developing new, more effective models of equipment currently used in recycling mills.

The same demands have resulted in a continuing search for more effective deinking chemicals. Ink detachment processes, aggregation of dispersed ink particles, and flotation mechanisms are under active investigation. Enzymes may assume an important role in detachment of ink from fiber as they have in soil detachment from fabric during laundering. Results of this basic research can assist in the design of improved chemicals and process equipment.

### **Literature Cited**

1. Renders, A. Proceedings TAPPI Pulping Conference, TAPPI Press: Atlanta, GA, 1992; 233.
2. Dorris, G.M.; Sayegh, N.N. Proc. TAPPI Pulping Conference, TAPPI Press: Atlanta, GA, 1994; 1273.
3. Borchardt, J.K. Coll. Surf. A.: Physiochem. Eng. Aspects, 1994, **88**, 13.
4. Morsink, J.B.W.; Daane, G.J.R. Proc. TAPPI Pulping Conference, TAPPI Press: Atlanta, GA, 1992; 963.
5. Putz, H-J.; Renner, K.; Gottching, L.; Jokinen, O. Proc. TAPPI Pulping Conference TAPPI Press: Atlanta, GA, 1994; 877.
6. Ali, T.; McLellan, F.; Adwinata, J.; May, M.; Evans, T. J. Pulp and Pap. Sci., 1994; J3 (January).

7. Borchardt, J.K.; Raney, K.H.; Shpakoff, P.G.; Matalamaki, D.W.; Denley, D.R. Proc. TAPPI Pulping Conference, TAPPI Press: Atlanta, GA, 1994; 1067.
8. Gottsching, L. Putz, H-J. Proc. TAPPI Recycling Symposium, TAPPI Press: Atlanta, GA, 1994; 207.
9. Merriman, K. In Secondary Fiber Recycling; Spangdenberg, R.J., Ed.; TAPPI Press: Atlanta, GA, 1993; 101.
10. Bliss, T. In Secondary Fiber Recycling; Spangdenberg, R.J., Ed.; TAPPI Press: Atlanta, GA, 1993; 125.
11. Vitori, C.M. Pulp Pap. Can., 1993, 94 (12), 109.
12. Winkler, J.; Kelly, A. Proc. TAPPI Recycling Symposium, TAPPI Press: Atlanta, GA, 1994; 415.
13. Horacek, R.G.; Forester, W. In Secondary Fiber Recycling; Spangdenberg, R.J., Ed.; TAPPI Press: Atlanta, GA 163.
14. Marszall, L. In Nonionic Surfactants: Physical Chemistry; Schick, M.J., Ed.; Surfactant Science Series No. 23; Marcel Dekker, Inc., New York, NY, 1987; 493.
15. Turai, L.L.; Williams, L.D., Tappi J., 1977, 60 (11), 167.
16. Borchardt, J.K.; Rask, J.H. Proc. TAPPI Pulping Conference, TAPPI Press; Atlanta, GA, 1993; 839.
17. Suwalo, D.W., Proc. TAPPI Pulping Conference, TAPPI Press; Atlanta, GA, 1983; 533.
18. Horacek, R.G. Tappi J., 1979, 62 (7), 39 and references therein.
19. Gilkey, M.W.; Seifert, P.; Conte, T.O. Proc. TAPPI Recycling Symposium," TAPPI Press; Atlanta, GA, 1994; 163.
20. Pan, R.; Paulsen, F.G.; Johnson, D.A.; Bousfield, D.W.; Thompson, E.V. Proc. TAPPI Pulping Conference, TAPPI Press; Atlanta, GA, 1993; 1155.
21. McCool, M.A. In Secondary Fiber Recycling; Spangenberg, R.J., Ed.; TAPPI Press: Atlanta, GA, 1993; 141.
22. Marchildon, L.; Castro, C.C.; Lapointe, M.W.; Daneault, C. Tappi J., 1993, 76 (3), 207.
23. Britz, H. Wochenbl. Papierfabr., 1993, 121 (10), 394.
24. Masamizu, K.; Tai, Y.; Hagiwara, M.; Ukigai, T. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1994; 39.
25. Hsu, N.N.-C.; Vazquez, I.J. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1994; 79.
26. Ishibashi, Y.; Myauchi, Y.; Inoe, M.; Edo, T. Jpn. Kokai Tokkyo Koho 06 49 790, 1994.
27. Shiroishi, T.; Edo, T.; Inoe, M.; Miyauchi, Y.; Ishibashi, Y.; Takahashi, H. Jpn. Kokai Tokkyo Koho 05 222 686, 1993.
28. Ishibashi, Y.; Urushibata, H. German Patent 4 217 907, 1992.
29. Ishibashi, Y.; Urushibata, H. Jpn. Kokai Tokkyo Koho 04 289 287, 1992.
30. Kato, K. Jpn. Kokai Tokkyo Koho 05 263 379, 1993.
31. Masamizu, K.; Egawa, J.; Hagiwara, M.; Ukigai, T. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1995; 317.
32. Okamoto, Y.; Hirakouchi, Y.; Hagiwara, M. Canada Pat. Appl. 2 076 308, 1993.

33. Borchardt, J.K.; Matalamaki, D.W.; Lott, V.G.; York, G.A. Prog. Paper Recyc., 1994, 4 (1) 44.
34. Borchardt, J.K.; Rask, J.H., Proc. TAPPI Pulping Conference, TAPPI Press, Atlanta, GA, 1994; 485.
35. Borchardt, J.K. U.S. Patent 5 258 099, 1993.
36. Darlington, W.D. Tappi J., 1989, 72 (1), 35.
37. Borchardt, J.K. and Lott, V.G. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1995; 17.
38. Mathur, I. Proc. TAPPI Pulping Conference, TAPPI Press, Atlanta, GA, 1991; 1015.
39. Gottschalk, H. Papier (Darmstadt), 1990, 44 (10), 538.
40. Liphard, M.; Schreck, M.; Hornfeck, K. Proc. TAPPI Pulping Conference, TAPPI Press, GA, 1991; 1031.
41. Sutman, F.J.; Phillippe, I.; LeBlanc, P. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1994; 399.
42. Dessureault, S.; Michaud, G.; Tremblay, S.; Massicotte, C., Proc. TAPPI Pulping Conference, TAPPI Press, GA, 1993; 875.
43. Borchardt, J.K.; Matalamaki, D.W.; Lott, V.G.; Rask, J.H. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1994; 449.
44. Alexander, A.C.; Kurtz, R.; McBride, D.H. In Secondary Fiber Recycling; R.J. Spangdenberg, Ed.; TAPPI Press: Atlanta, GA, 1993; 197.
45. Kotani, Y., Prog. Paper Recyc., 1993, 3 (3), 110.
46. Angulo, J.E. In Secondary Fiber Recycling; Spandenberg, R.J., Ed.; TAPPI Press: Atlanta, GA, 1993; 229.
47. Fallon, C.K. Proc. TAPPI Pulping Conference, TAPPI Press, Atlanta, GA, 1994; 263.
48. Walmsley, M.; Yu, C.Y.; Silveri, L. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1993; 417.
49. Carty, B. In Secondary Fiber Recycling; Spangdenberg, R.J., Ed.: TAPPI Press: Atlanta, GA, 1993; 185.
50. Yu, C.J.; DeFoe, R.F.; Crossley, B.R. Proc. TAPPI Pulping Conference, TAPPI Press, Atlanta, GA, 1994; 451.
51. Hsu, N.N.; C.; Vazquez, I.J. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1995; 217.
52. Upton, B.H.; Krishnagopalan, G.A.; Abubakr, S. Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, GA, 1994; 17.

RECEIVED July 7, 1995

## Chapter 28

### Office-Paper Deinking

#### Environmental Scanning Electron Microscopy Studies of Interactions of Toner Inks and Deinking Agents

John K. Borchardt and James H. Rask

Shell Chemical Company, P.O. Box 1380, Houston, TX 77251-1380

Environmental scanning electron microscope (ESEM) analyses demonstrated differences in ink morphology for electrostatic inks compared to letterpress, offset, and flexographic inks. The conventional inks existed as relatively thin films coating cellulose fibers. In contrast, electrostatic inks formed a thick layer of fused beads on top of the cellulose fibers. ESEM imaging of ink particles indicated certain deinking agents promote conversion of ink particles from flat flakes into larger spherical particles. Energy dispersive X-ray spectroscopy of ink particles formed by pulping mixed office papers in the presence of certain surfactants were performed. This pulping resulted in the formation of ink particles that are the fusion products of toner and non-toner ink particles.

Toner inks, those used in photocopiers and laser printers present a difficult problem for paper mills that want to recycle office paper. Office waste paper collection programs are increasing the supply of xerographic and laser-printed paper. In addition, laser printers continue to replace impact printers thus decreasing the supply of laser-free computer printout (CPO). Sorting to remove sheets printed with toner inks from mixed office waste is expensive.

Cost-effective, efficient deinking of used paper containing substantial amounts of photocopier- and laser-containing inks is essential to produce printing and writing paper from recovered office paper. Developing effective deinking agents for these inks is an important, challenging goal. Understanding the interactions between toner inks and deinking agents is important in developing improved deinking chemistry.

**Electrostatic Ink Composition.** Excellent descriptions of the xerographic photocopying and laser printing processes are available (1-3). Differences between

0097-6156/95/0609-0342\$12.00/0  
© 1995 American Chemical Society

toner inks and conventional inks and the effect of these differences on de-inking have been discussed elsewhere (4,5). Contrasting ink chemistry results in differences in ink particle size and geometry after pulping (6). A major means of differentiating toners is the binder resin used. The most common toner ink binder resins are: copolymers of styrene and acrylate esters such as 2-ethylhexyl acrylate or butyl acrylate, copolymers of styrene and butadiene, and polyesters. Broadly speaking, similar ink types are used in laser printing and in photocopying.

The difficulties in deinking office papers containing toner inks are well known. It is difficult to disperse the thermoplastic binders used in laser and xerographic ink (7). The use of high consistency kneaders has been proposed to reduce ink particle size mechanically (8-11). Dispersion units have also been used to reduce toner ink particle size mechanically (1,12-16). An alternative approach is to use chemicals to agglomerate the ink. The larger particles can be removed by centrifugal cleaning and fine screening.

Toner inks differ from conventional inks in another important way: at a certain temperature they change from a brittle solid to a sticky, rubber-like material. This temperature is called the glass transition temperature,  $T_g$ . The  $T_g$  is dependent on the chemical composition and molecular weight of the toner binder resin and the presence of other chemicals such as plasticizers in the ink composition. The  $T_g$  of toner inks is typically considered to be 150°-160°F (2). By absorbing on and intermixing with the ink, surfactants and solvents can reduce the  $T_g$  of toner inks (17).

Differences in ink chemistry and ink particle morphology result in differences in ink particle size after pulping old paper (Table I) (6). Without carefully designed de-inking agents, pulping paper printed with toner inks results in formation of flat ink flakes. Many of these ink flakes are both too large to be removed by flotation and too small to be removed by screens and mechanical cleaners (8,18). (Figure 1 of the chapter on "Chemistry of Engineering of Unit Operations in Paper Deinking Mills" elucidates this point.)

**Deinking Agents for Toner Inks.** The differences between toner and conventional inks result in different deinking agent performance requirements. As a result, effective toner ink deinking chemicals differ in composition from most conventional deinking agents. However, to be used commercially, deinking agents used on old office paper need to be effective on all ink types found on mixed office papers. In addition to toner inks, these include offset, flexographic, and gravure inks. Sorting paper to removed the toner-printed sheets is usually too expensive to be economically feasible. The availability of recovered toner-free office paper is declining due to widespread use of laser printers and photocopiers (19). This

Table I. Ink Particle Size After Repulping Old Paper<sup>a</sup>

Printing Process	Average Ink Particle Size (microns) for	
	Uncoated Paper	Coated Paper
Letterpress	2-30	10-100
Offset	2-30	5-100
Flexography	0.3-1	0.7-2
Gravure	2-30	5-30
Laser, Xerographic	40-400	40-400

a. Data taken from reference 6.

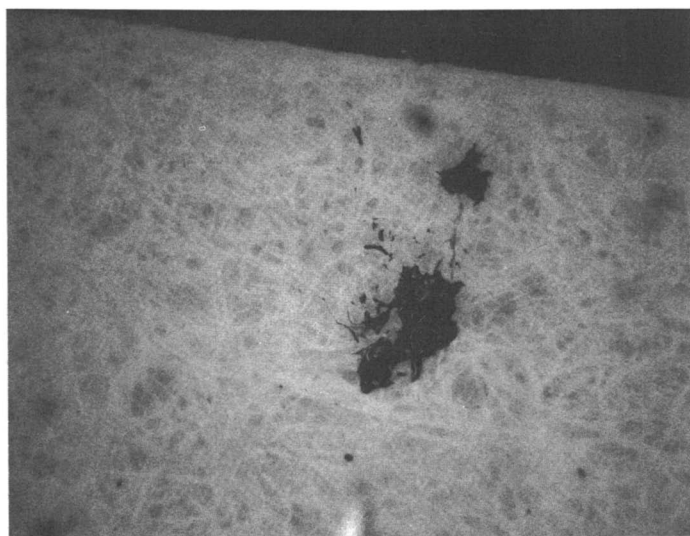


Figure 1. Optical microscopy image of a residual ink particle after pilot scale deinking of mixed office paper.

decline is forecast to continue. Improved deinking surfactant effectiveness on different ink types will enable mills to deink cheaper grades of recovered paper and improve their profits. Results for several proprietary products claimed to be effective on toner inks and other inks found in recovered office paper have been reported (20-33).

Experts have classified toner deinking agents into various types (8,34,35). By combining these classification schemes, deinking agents can be grouped into three classes by their effect on dispersed toner particles: agglomeration (8), densification (34), and dispersants (35). These terms are self-explanatory. Agglomeration agents soften ink particles and fuse them into larger masses more easily removed by fine screens or forward cleaners. Densification agents increase the apparent density of ink particles making them easier to remove in centrifugal cleaners. Dispersants can reduce ink particle size to the size range at which flotation deinking is most effective.

These classifications are not rigid. For example, pulper temperatures equal to or greater than the toner ink  $T_g$  are required to facilitate ink densification by some deinking agents. Particle agglomeration can also occur at these temperatures. Some results suggest that toner agglomeration and dispersion are competitive processes during pulping (see below). Ink particles that are clearly fusion products of separate ink particles are present even when image analysis indicates no increase in the average longest ink particle dimension (5).

**Environmental Scanning Electron Microscopy.** ESEM provides an excellent method to study ink particle morphology before and after de-inking. ESEM has also been used to study fiber behavior before and after recycling operations (36). A recent bibliography of ESEM technical papers is available (37). The principles of the Environmental Scanning Electron Microscope are described in detail in reference 38.

The principal difference between the ESEM and conventional scanning electron microscopes is that the ESEM does not require test samples to be under high vacuum. The typical vacuum in a scanning electron microscope is  $1.0 \times 10^{-5}$  torr. The pressure in the ESEM sample chamber is typically 2-20 torr. Another advantage of the ESEM is in studying insulating samples such as cellulose. In conventional scanning electron microscopy, insulating samples must be given a conductive coating to prevent charging. This is not necessary when using the ESEM. Thus the natural surface properties of samples can be studied using the ESEM technique.

The size and geometry of ink particles after pulping used office paper are important factors in determining ink removal efficiency. ESEM has advantages over optical microscopy for imaging these ink particles. This can be seen in comparing

Figures 1 and 2. These are images of the same ink particle obtained by optical microscopy and ESEM. The lower resolution of the optical micrograph is due in part to enlarging the original Figure 1 image. The greater depth of field of ESEM microscopy is apparent. The ink particle surface appears black and almost featureless in the optical micrograph (Figure 1). However, surface morphology is apparent in the ESEM image (Figure 2). The small bright specks in Figure 2 are iron mineral particles. (Magnetite is a common ingredient in toner inks.) The energy dispersive X-ray spectrometer (EDS) attachment of the ESEM clearly indicates the presence of iron minerals in some ink particles after pulping used paper (4,5,33,36).

The ESEM micrographs shown in Figures 1,2, 5-10, and 11 are of ink particles that have been detached from cellulose fibers while pulping printed paper. The ink particles are redeposited on the surface of a bed of cellulose fibers during sheetmaking. Thus, the background of the micrographs are a bed of cellulose fibers.

EDS helps elucidate the mechanism of ink particle agglomeration during pulping (see below). Some toner compositions contain iron minerals while others do not. Conventional (offset, letterpress, gravure, etc.) black inks also do not contain iron minerals. Mixed office paper containing both toner inks and conventional inks was de-inked in a pilot scale paper mill (5,32,33). EDS identifies many ink particles in which iron minerals are localized in only part of the particle. This indicates such ink particles are fusion products of ink particles containing iron minerals with ink particles that do not (see below). (Such localization of iron mineral content in ink particles was not apparent after laboratory pulping of paper printed only with a toner ink containing iron minerals. EDS and microscopy indicated the dispersed ink particles formed after pulping containing no such localization of iron mineral content.)

### **Experimental Section**

Laboratory and pilot mill test procedures are detailed in references 5,32,33 and 39. The ESEM instrument is described in references 40 and 41.

The deinking agents tested are referred to as Synthetic Deinking Agents (SDA). These are available from Shell Chemical Company (Houston, Texas) under the tradename NONATELL surfactant.

### **Results of Microscopic Analysis**

Environmental scanning electron microscope (ESEM) imaging results indicate the morphological differences between conventional inks and toner inks. The cellulose fibers are visible beneath the thin ink film of flexographic printed paper (Figure 3). Letterpress and offset inks are similarly present as thin films on printed fiber surfaces. In contrast, toner inks form a thick layer of partially fused beads over the



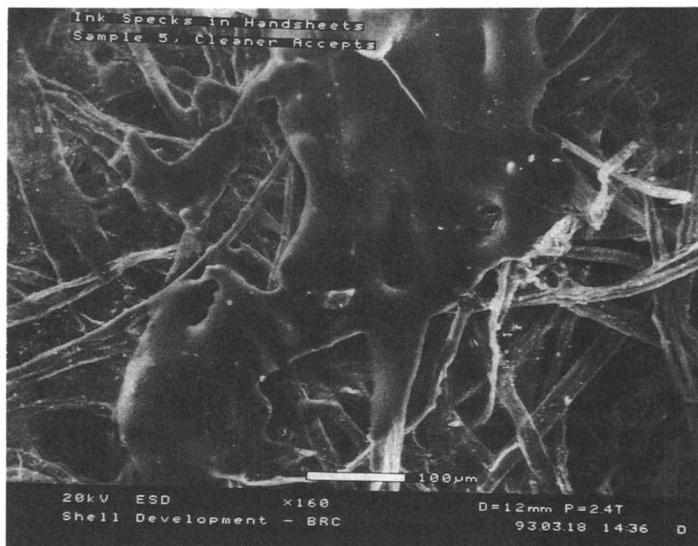


Figure 2. ESEM image of the Figure 1 ink particle.



Figure 3. ESEM image of flexographic printing on newsprint.

cellulose fibers during printing (Figure 4). Comparison of the printed portions of Figure 4 with Figure 3 clearly indicates the morphological differences between toner ink print and conventional inks.

ESEM micrographs were made of deinked pulp cast into sheets using a Buchner funnel procedure (33). Pulper experiments were performed at temperatures above (200°F) and below (110°F) as well as at the nominal toner glass transition temperature (160°F). The micrographs (exemplified by Figure 5) indicate that, without any deinking agent, most toner ink particles are relatively thin, flat flakes. Carefully chosen deinking agents result in larger, more spherical ink particles (Figure 6, photocopier ink, and Figure 7, laser ink). More spherical particles have a lower surface area:volume ratio and thus are more hydrodynamic (move more readily in the direction of pulp slurry flow). Also, the change from flake to sphere increases the apparent density of the ink particles. These factors render the ink particles easier to remove in centrifugal cleaners. These ink particles are hard objects to the touch. This indicates they should not form stickies (adhesive particles which can cause severe problems during paper making and during printing).

**Toner Ink Particle Surface Features.** The indentations in the Figure 6 photocopier ink particle appear to be due to cellulose fibers originally bound to the ink. The deinking process temperature for Figure 6 was approximately equal to the glass transition temperature. Ink softening could have aided ink particle detachment from cellulose fiber. Similar results were observed at 200°F, substantially above the toner glass transition temperature (approximately 160°F). However, apparently the toner resin softening was insufficient for resin to flow into and fill the indentations left by the cellulose fibers.

Some particles also exhibit pitting (Figure 7, laser printer, and Figure 6, photocopier ink) suggesting partial solubilization or emulsification of the toner ink. Other ink particles (Figure 9) remained at least partially bonded to cellulose fibers. A large groove in the ink particle is indicated by the upper arrow (Figure 9). This groove is believed to be due to a detached fiber. Nearby is a cellulose fiber indicated by the lower arrow in Figure 9. It is partially embedded in the ink particle. Figure 9 supports the interpretation that the grooves observed in the ink particles are where cellulose fibers were attached to the ink.

The pulping temperature for the Figure 9 ink particle was 110°F, substantially below the nominal ink glass transition temperature. The ink particle could have been softened by chemical action (see below). Then vigorous agitation during pulping could have embedded this cellulose fiber into the ink particle. However, it seems more likely that such impressions are where the ink was originally attached to the paper.

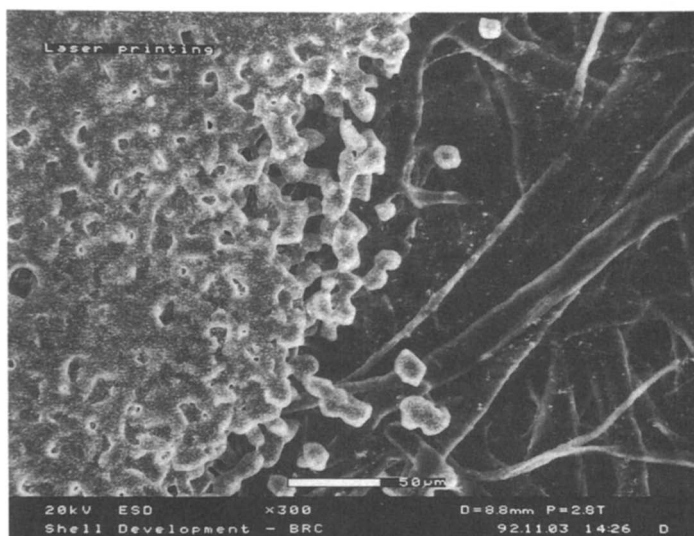


Figure 4. ESEM image photocopier printing using a toner ink.

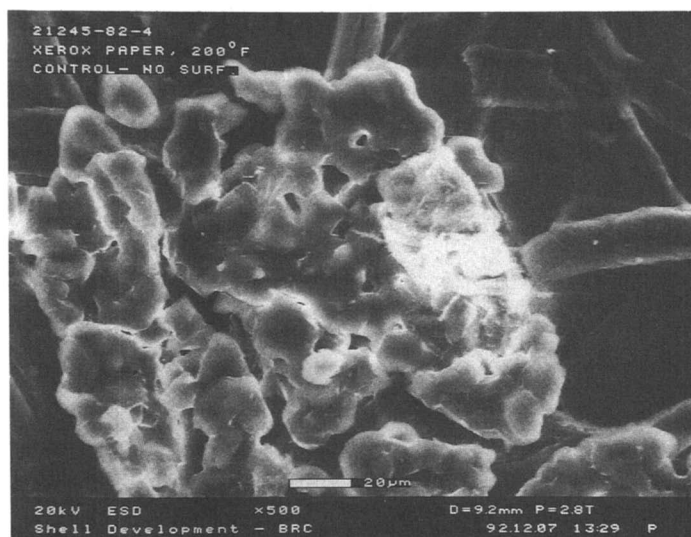


Figure 5. ESEM image of styrene-acrylate toner ink particles after pulping photocopies without a surfactant.

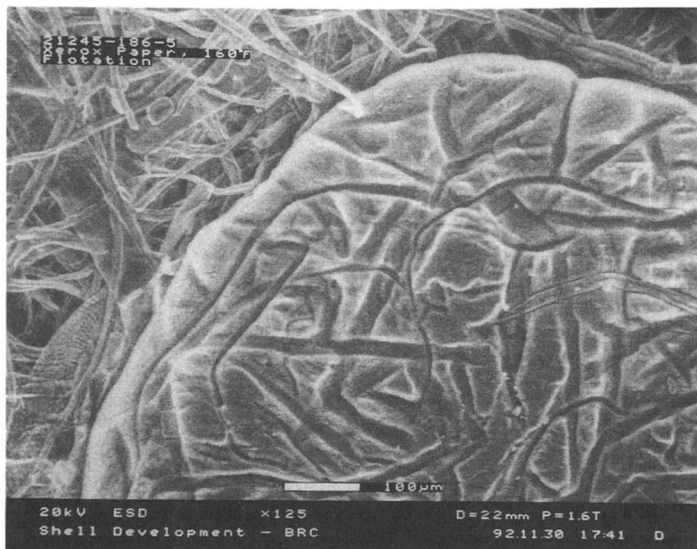


Figure 6. ESEM image of a styrene-acrylate toner ink particle after pulping photocopies in the presence of a proprietary surfactant.

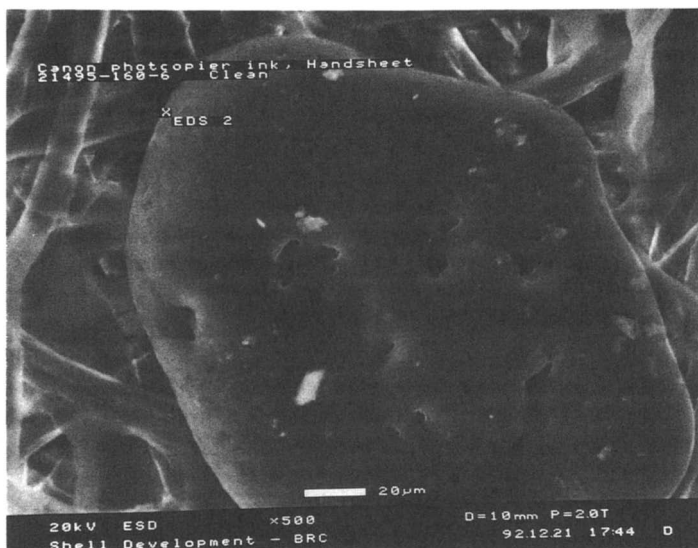


Figure 7. ESEM image of a residual polyester resin toner ink particle after deinking photocopyer paper using a proprietary surfactant.

These impressions imply a deinking mechanism in which a large, somewhat softened ink particle is detached from the cellulose surface. Softening during pulping is sufficient to assist ink particle detachment but not sufficient to erase the grooves left by cellulose fibers once in contact with the ink. Chemical and mechanical action during pulping promote conversion of flat flakes (Figure 5) to more spherical objects (Figures 6-8). The hydrophobic nature of toner ink surfaces (as indicated by contact angles studies reported in reference 42) is a driving force to minimize ink surface area exposed to water. This driving force assists conversion of flat ink particles into more three-dimensional objects.

**Toner Ink Particle Softening Below  $T_g$**  Figure 10 represents an experiment performed at 110°F. This is well below the nominal ink softening point. Grooves apparently due to detached cellulose fibers are present in the ink particle. Fiber detachment would be assisted by softening of ink particle surfaces. Did ink softening occur? Figure 10 does not assist in establishing this. Some protruberances on the ink particle are apparent. These are due to individual toner beads that are only partially fused into the ink mass. Has ink softening taken place? At the higher pulping temperatures, 200°F and 160°F, these partially fused toner particles are not observed. This indicates ink softening is more complete at the higher pulping temperatures.

Other evidence clearly indicates that some toner ink particle softening did occur at 110°F. During a 160°F deinking experiment using a styrene-acrylate photocopy ink and SDA 24, ink particles were carefully separated from the flotation rejects. The glass transition temperature of these ink particles was determined to be 104°F (40.0°C). The deinking agent, acting like a plasticizer, appears to have reduced the glass transition temperature of the toner ink. This is consistent with an earlier proposal in the literature (17). However, despite this softening, these ink particles are hard at both room and mildly elevated (about 90°-100°F) temperatures.

### **Presence of Iron Mineral Particles in Toner Inks**

The ESEM micrographs of photocopy or laser paper often exhibit sub-micron sized bright spots in the ink images. Many residual toner ink specks also exhibit bright spots but they are more sparsely dispersed (Figures 5, 7 and 8). Energy dispersive X-ray spectroscopy (EDS) analysis of the ink images (Figure 11) indicate these bright spots are due to iron minerals present in the particles. (Magnetite is present in many toner inks.) When a portion of the handsheet containing no ink particles is imaged, no iron peaks are observed in the EDS spectrum. In handsheets, iron is only found associated with ink particles containing the sub-micron sized bright spots.

**Toner Ink Particle Agglomeration And Dispersion** Figure 12 is representative of many ink particles formed when pulping used office paper in two pilot scale paper

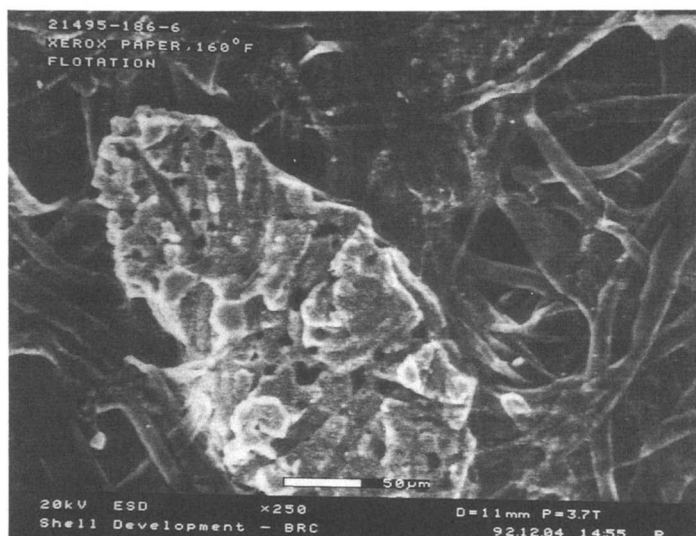


Figure 8. ESEM image of a residual styrene-acrylate toner ink particle after deinking photocopies using a proprietary surfactant.



Figure 9. ESEM image of a polyester resin toner ink particle containing attached fibers after pulping in the presence of a proprietary surfactant.



Figure 10. ESEM image of a styrene-acrylate toner ink particle after pulping photocopies in the presence of a proprietary surfactant.

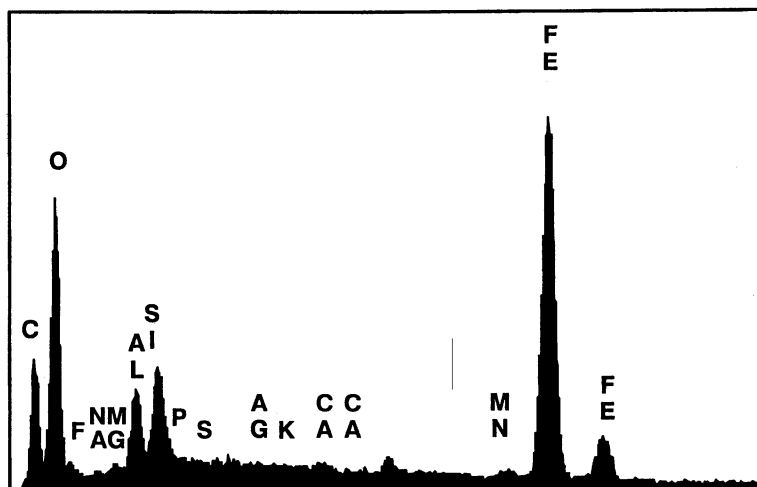


Figure 11. Energy dispersive X-ray spectrogram indicating the presence of iron compounds in the toner ink. The elements are identified in solid capital letter versions of their standard symbols used in the Periodic Table of the Elements.



**Figure 12. ESEM image of an ink particle resulting from agglomeration of an iron-containing toner ink particle and another ink particle containing no iron compounds.**

mills (5,32,33). EDS analysis indicates the left-hand portion of this ink particle contains high levels of iron compounds. In contrast, the right-hand portion of this ink particle did not contain iron compounds. The two portions of the ink particle can be distinguished visually in Figure 12. They are completely fused together indicating ink particle agglomeration has occurred.

During pulping of toner printed paper, ink particle agglomeration and dispersion occur simultaneously. Without a SDA surfactant, dispersion processes dominate and toner inks form flat flakes (Figure 3). Using certain deinking agents, more spherical toner ink particles are formed during pulping. Image analysis provides a measure of the longest ink particle dimension. Image analysis can indicate a flat ink flake and a more spherical ink particle have the same longest particle dimension (10). However, the more spherical ink particle will contain substantially more ink.

Using fine screens, flat ink flakes are more difficult to remove than spherical ink particles. The smallest dimension of the flat ink flake can align with the hole or slot. This allows relatively large ink particles to pass through screens and not be removed from the pulp.



ESEM provides enough depth of field to indicate the more spherical character ink particles shown in Figures 6,8,7 and 10 ink particles compared to the ink particle shown in Figure 5. (Confocal microscopy also indicates the more spherical nature of particles formed when pulping toner printed paper in the presence of certain deinking surfactants (32,36).)

### **Conclusions**

ESEM micrographs indicate toner ink particles are detached from fibers in the form of thin flakes when no deinking agent is used. Carefully chosen deinking agents promote formation of more spherical toner ink particles. EDS analyses indicate some ink particles observed after pulping mixed office papers were formed by fusion of iron-free and iron-containing (toner) ink.

### **Acknowledgements**

The authors thank Shell Chemical Company for permission to publish this work. The laboratory deinking experiments were performed by S.B. Akpaudo.

### **Literature Cited**

1. Quick, T.H.; K.T. Hodgson, *Tappi J.*, 1986, **66** (3), 102-106.
2. Gruber, R.J.; Ahuja, S.; Seanor, D., "Xerographic Materials," in "Encyclopedia of Polymer Science and Engineering" (J.I. Kroschwitz, ed.), John Wiley & Sons, New York, 1989, Vol. 17, pp. 918-943.
3. Shrinath, A., Szewczak, J.T., and Bowen, I.J., *Tappi J.*, 1991, **74** (7), 85-93.
4. Borchardt, J.K.; Rask, J.H., "Proc. TAPPI Pulping Conference," TAPPI Press, Atlanta, GA, 1993, Book 3, pp. 839-873 and references therein.
5. Borchardt, J.K.; Matalamaki, D.W.; Lott, V.G.; Rask, J.H., *Prog. in Paper Recycling*, 1994, **3** (4), pp 47-62.
6. Ferguson, L.D., "Introduction to Printing Technology and Ink Chemistry," 1992 TAPPI Deinking Seminar Course Notes, TAPPI Press, Atlanta, GA, pages not numbered.
7. Meersman, T., "Achieving Paper Product Quality with Post-Consumer Waste," presented at Wastepaper II, Chicago, IL, May 21-23, 1991.
8. Rhodes, T.; Ferguson, L.. "Proc. TAPPI Recycling Symposium, TAPPI Press, Atlanta, 1993, pp. 123-129.
9. McBride, D.H., "Proc. TAPPI Recycling Symposium," TAPPI Press, Atlanta, 1993, pp. 173-188.
10. McBride, D., *Pulp & Paper*, 1992, **66** (5) 149-152.
11. Galland, G.; Brun-Chevalier, G.; Vernac, Y., *Prog. Paper Recyc.*, 1993, **2** (3), 105-114.
12. Rangamannar, G.; Silveri, L., "Proc. TAPPI Pulping Conference," TAPPI Press, Atlanta, GA, 1989, pp. 381-390.
13. Shrinath, A.; Szewczak, J.T.; Bowen, I.J., *Tappi J.*, 1992, **74** (7), 85-93.
14. Doshi, M.H., *Prog. in Paper Recycling*, 1991, **1** (1), 72-75 and references therein.

15. Matzke, W.; Selder, H., "Proc. TAPPI Pulping Conference", TAPPI Press, Atlanta, GA, 1986, pp. 597-605.
16. Carr, W.F., "Proc. TAPPI Pulping Conference," TAPPI Press, Atlanta, 1990, pp. 111-121.
17. Darlington, W.B., Tappi J., 1989, 72 (1), 35-38.
18. Rhodes, T.; Ferguson, L., "Proc. TAPPI Recycling Symposium," TAPPI Press, Atlanta, GA, 1993, pp. 123-129.
19. Iannazzi, F.D. "Outlook on Supply, Demand, and Future Prices for Office Wastepaper," in "Sorted Office Paper: Markets, Technologies, and Trends," Miller-Freeman, Inc., San Francisco, CA, 1994, pp. 4-9.
20. Greer, C.S.; Cosper, D.R., "Proc. 80th Ann. Meeting, Technical Section, CPPA," Canadian Pulp and Paper Association, Montreal, Quebec, 1994, pp. A203-210.
21. Marchildon, L., Bonnelly, B., and Lapointe, M., 1993, J. Pulp Pap. Sci., 1993, 19 (4), J156-J160.
22. Quick, T.H., U.S. Patent 4 276 118, 1981.
23. Richman, S.K.; Letscher, M.B., U.S. Patent 5 302 242, 1994.
24. Olson, C.R., Hall, J.D., Phillippe, L.J., Prog. Pap. Recycl., 1993, 2 (2), 24-34.
25. Green, C.J., Jr., U.S. 3 635 789, 1972.
26. Ortner, H.; Pfalzer, L.; Bergfield, D.; Fischer, S., German Patent 3 200 893, 1983.
27. Wood, D.L.; Wood, D.C., U.S. 4 561 933, 1985.
28. Cosper, D.R., Can. Pat. Appl., 2 105 829, 1994.
29. Chu, K.; Kitagawa, T., Jpn. Kokai Tokkyo Koho JP 06 136 677, 1994.
30. Srivatsa.; Wesolowski, R.R.; Kerstanski, D.J., U.S. Patent 5 259 969, 1993.
31. Borchardt, J.K., U.S. Patent 5 258,099, 1993.
32. Borchardt, J.K.; Matalamaki, D.W.; Lott, V.G.; York, G.A., Progress in Paper Recycling, 1994, 4 (1), 44-56.
33. Borchardt, J.K.; Matalamaki, D.W.; Lott, V.G.; Rask, J.H., "Proc. TAPPI Recycling Symposium," Atlanta, GA, 1994, 449-475.
34. Ferguson, K.H., Pulp & Paper, 1992, 66 (12), 57-64.
35. Jones, W.S. "Proc. TAPPI Pulping Conference," TAPPI Press, Atlanta, GA, 1993, pp. 1005-1016.
36. Borchardt, J.K. TODAY'S CHEMIST at Work, 1994, 3, 20-23.
37. G.D. Danilatos, Microscopy Research and Techniques, 1993, 25, 529-534.
38. G.D. Danilatos, Advances in Electronics and Electron Physics, 1988, 71, 109-250.
39. Borchardt, J.K.; Rask, J.H. Tappi J., 1994, 77 (9), 161-169.
40. Danilatos, G.D., Adv. Electronics Electron Phys., 1988, 71, 109-250.
41. Borchardt, J.K., Tutunjian, P.N., Rask, J.H., and Prieto, N.E., "Proc. TAPPI Contaminants Problems and Strategies in Waste Paper Recycling Seminar," TAPPI Press, Atlanta, GA, 1992, pp. 85-112.
42. J.K. Borchardt and V.G. Lott, "Proc. TAPPI Recycling Symposium," TAPPI Press, Atlanta, 1995, 17-36.

RECEIVED July 7, 1995

## Chapter 29

# Utilization of Recycled Agriculture-Based Fiber for Composites

Roger M. Rowell

Forest Products Laboratory, Forest Service, U.S. Department of Agriculture, 1 Gifford Pinchot Drive, Madison, WI 53705-2366

Approximately 60 percent of the volume of solid waste in an average municipal waste stream consists of agro-based resources such as paper and paper-based products, wood, and yard wastes. These resources, along with a vast quantity of agricultural residues, can be utilized in natural fiber-based composites. These composites include geotextiles, filters, sorbents, structural and non-structural, molded, packaging, and combinations with other resources such as plastics, glass, and metals. Collection of these resources can be done through an agro refinery concept where breakdown, sorting, cleaning and processing into products can be done based on market needs.

A reduction is urgently needed in the quantities of industrial and municipal solid waste materials that are currently being landfilled. Major components of municipal solid waste (MSW) stream include waste wood, paper, and other agriculture wastes. There are also potentially millions of tons of wood fiber in timber thinnings, industrial wood waste, demolition waste, pallets, and pulp mill sludges not to mention the millions of tons of agricultural wastes generated each year. These resources offer great opportunities as recycled ingredients in natural fiber-based composites.

Source separation and recycling not only extend the life of landfills by removing materials from the MSW stream but also make available large volumes of valuable raw materials for use by industry in place of virgin resources. Industrial use of such materials reduces both costs for raw materials and the energy it takes to make a finished product. The main requirement is that the recycled ingredients meet the quality and quantity requirements of the consuming production operation.

This chapter not subject to U.S. copyright  
Published 1995 American Chemical Society

### Challenges in Recycling of Waste Agro-Based Resources

A comprehensive waste management program must rely on the aggregate impact of several courses of action: waste reduction, recycling, waste-to-energy schemes, and landfill [1]. The greatest impact that is likely to result from further research is in the area of recycling. Increased use of recycled agro-based resources will allow the markets for fiber composites to grow without increasing the use of virgin timber. Therefore, forest products industries will benefit from such research because less expensive raw materials will be available for producing value-added composites [2].

In 1986, the United States generated almost 158 million tons of solid waste, almost 50 percent of the world's total [3]. It is projected that this total will increase to approximately 193 millions tons by the year 2000 [4,5]. In 1986, only about 17 million tons, or 9 percent of the total solid waste was recycled [6]. This is a waste of resources, energy, space, and labor.

The word "waste" projects a vision of a material with no value or useful purpose. However, technology is evolving that holds promise for using waste or recycled wood, paper products, and other forms of agro-resources into an array of high-performance composite products that are in themselves potentially recyclable.

When fibers, resins, and other resources are used as raw materials for products such as paper, they require extensive cleaning and refinement. When recovered fibers, resins, and other resources are used for the manufacture of composites, these materials do not require extensive preparation. This greatly reduces the potential cost of manufacturing.

A case-in-point is the making of composites from recycled paper. In the United States, nearly 80 million tons of 6,000 different paper and paper board products are produced and over 70 million tons are discarded each year [7,8]. Few of the paper products found in the MSW stream are produced solely from fiber and water. Each product consists of a fiber matrix to which some inorganic or organic chemical compound is added to enhance the utility of the product. Thus, many forms of wastepaper contain contaminants (extraneous materials). Whether they are adhesives, inks, inorganics, dyes, metal foils, or plastics, these contaminants may need to be separated from the wastepaper before the fiber can be recycled into another useful paper product. This is not the case with fiber-based composites. In many uses, natural fiber composites of varying types are opaque, colored, painted, or overlaid. Consequently, recovered fibers, resins, or other resources used for composites do not require extensive cleaning and refinement. Thus, composites provide an unusually favorable option for the recycling of several highly visible and troublesome classes of MSW.

A considerable amount of data is available regarding the inventory of the U.S. MSW stream (Table 1). In 1988, paper and paper board, wood, and plastics in the MSW stream accounted for approximately 71.8, 6.5, and 14.4 million tons respectively. By the year 2000, these figures are expected to increase to 96.1, 8.4, and 21.1 million tons annually [8]. In addition to the wood fiber in the MSW stream, vast quantities of low-grade wood, wood residues, and industry-generated

wood waste in the form of sawdust, planer shavings, and chips are now being burned or disposed of in other ways.

Table 2 shows the data on the agro-based resources in the MSW as of 1988 [8]. The data includes all the residential waste products but not the industrial waste resources such as pallets, timber thinnings, production wastes, bark, and sawdust. There is also no data available on the total amount of potential agricultural wastes such as bagasse (from sugar cane) and seed hulls which are collected in central locations. There is also a vast amount of agricultural residues that are currently left in the fields. These could also be utilized for fiber.

Many steps are associated with the use of waste resources, including collection, analysis, storage, separation, clean up, breakdown, uniformity, form, and processing into products. There are many different plans to handle these steps, but no matter how they are done, or in what order, they must be done economically. Desire does not drive markets! Markets are driven by economics.

There are at least three issues that have caused great concern in the recycling industry. One is the cost of landfilling which has been one of the strong driving forces in the economics of recycling as the cost to landfill has risen sharply in the last few years. Another concern, is the inconsistency in the markets for recycled products. Many schemes have been proposed to use such wastes as old newspapers, plastic milk and soda pop bottles, etc., but the markets using these waste products have not been reliable. The final concern is the actual cost of recycled resources versus virgin resources. In most cases, the recycled resource is more costly to use than virgin so the use of recycled resources is not economically feasible. There is little indication that the majority of the consuming public is willing to pay more for products made from recycled resources compared to virgin resources.

The purpose of the research presented in this paper is to describe the potential for producing structural composites from waste wood [9], paper [10-12], agricultural residues [13], and other forms of agro-resources [14]. For comparison, a mixed hardwood fiber [10-11] and hemlock fiber [9] are included. The properties of all boards are compared to minimum standards as outlined by the American Hardboard Association [15].

### **Processing of Fiber Into Boards**

**Materials** The following recycled and agro-fibers were used to make fiberboards for testing:

**Hardwood** - Mixture of several hardwood species processed from pulp-grade chips through a defibrator digester at 690 KPa steam pressure for 4 minutes and refining through a Bouer 400 refiner.

**Old Newspaper** - Old newspaper hammer milled using a 25.4 mm screen, placed into a repulper for further fiberization, and then hammer milled again using a 6.3 mm screen.

**HW-ONP** - 50-50 Percent by weight of hardwood and old newspaper fiber. Newspaper fiber was re-hammer milled using a 1.6 mm screen.

**Table 1.- Estimated distribution of resources in the municipal solid waste stream in the United States in 1988 [2]**

Source	Amount in MSW stream	
	Percent	Weight (x10 <sup>6</sup> tons)
Paper and paper board	40.0	71.8
Yard waste	17.6	31.6
Metals	8.5	15.3
Food waste	7.3	13.2
Glass	7.0	12.5
Plastics	8.0	14.4
Textiles	2.2	3.9
Wood	3.6	6.5
Rubber-leather	2.6	4.6
Miscellaneous inorganics	1.5	2.7
Other	1.7	3.1
(Total)	100.0	179.6

NOTE: Some data from ref. 2.

**TABLE 2 - Estimated portion of agro-based resources in municipal solid waste in 1988 [8]**

SOURCE	AMOUNT IN MSW	
	PERCENT	WEIGHT (million tons)
PAPER/PAPER BOARD	38.8	61.2
NEWSPAPER	(6.3)	(9.9)
CORRUGATED	(7.9)	(12.5)
MIXED	(21.9)	(34.5)
MAGAZINES	(0.7)	(1.1)
YARD WASTE	18.2	28.7
WOOD	2.6	4.2
TOTAL	59.6	94.1

NOTE: Some data from ref. 8.

Hemlock - Pulp grade chips, steamed for 2 minutes at 0.759 MPa disk refined, and flashed dried at 160 C.

Demolition wood - Wood shredded, hammer milled, cleaned and processed as given for hemlock.

Mixed Office Waste - Mixed white office waste paper including envelopes was hammer milled using a 3.75 cm screen.

Colored Paper - Mixed colored office waste paper including envelopes hammer milled using a 3.75 cm screen.

Magazine Paper - Mixed magazine paper hammer milled using a 3.75 cm screen followed by a 1.25 cm screen.

Bagasse - Fiber from a countercurrent diffusion extractor with a five-roller dewatering mill in Hawaii was screened to remove fines and dried to 30% moisture. The fiber was then hammer milled using a 1.25 cm screen.

Kenaf - Kenaf bast fiber was separated from the core using an air separation system. The bast fiber was then hammer milled using a 1.25 cm screen.

### **Resin Application and Board Fabrication**

The different fibers were sprayed separately in a laboratory blender with a water-soluble, 50% solids content, liquid phenolic resin. Different levels of resin were used for each board. A final fiber moisture content of approximately 10% was obtained for all fibers. The fiber was then hand-formed into a 508 mm x 508 mm randomly oriented mats and the mats pressed to a maximum pressure of 75 kg, with press platens at 190 C for 10-12 minutes.

### **Testing of Board Properties**

**Static bending** Static bending tests were conducted on board specimens (50 by 200 mm) conditioned to 65% relative humidity (RH), according to ASTM standard D 1037 [16] using a 150 mm span. Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined. Fifteen specimens for each cycle were tested and the results averaged.

**Tensile strength parallel to board surface** Tensile strength parallel to the board surface was determined on board specimens (50 by 250 mm) conditioned to 65% relative humidity (RH), according to ASTM standard D 1037 [16]. Fifteen specimens for each cycle were tested and the results averaged.

**Water tests** Oven dried, weighed specimens (5 by 5 by 1.27 cm) were placed in a 28 x 36 cm container, 5 cm deep. Thickness measurements were taken on a flatbed micrometer. Water was added to the container and the board thickness recorded as a function of time. Measurements were taken in time increments of 15, 30, and 45 minutes for the first hour, every hour for the first 6 hours, then once a day for 5 days. After 5 days, each specimen was again oven dried for 24 hours at 105 C and weights and thickness determined. Fifteen specimens for each cycle were tested and the results averaged.

**Relative humidity tests** Oven dried, weighed specimens (5 by 5 by 1.27 cm) were placed in constant humidity rooms at 30%, 65%, and 90% RH and 27 C . After 31 days, the specimens were weighed to determine the equilibrium moisture content (EMC) and thickness measured to determine thickness swelling. Fifteen specimens for each cycle was tested and the results averaged.

**Linear expansion tests** Tests were conducted according to ASTM standard D 1037 [16] on specimens 1.25 by 15 by 0.6 cm. Each specimen was conditioned at 50% RH, 27 C and length measured. The specimens were conditioned at 90% RH, 27 C for 21 days and length again measured. Linear expansion from 50 to 90% RH was then calculated. Five specimens of each type of board were tested and the results averaged.

### Results of Board Testing

Because of the limited number of specimens per individual test, statistical analysis of the data was not appropriate. The results presented here should be considered as indicative of trends that a larger, statistically valid experiment should confirm.

The results shown in Table 3 show that the fiberboard with the highest modulus of rupture was the boards made from mixed hardwood fiber followed closely by the 50/50 mixture of hardwood fiber and old newspaper fiber. The highest modulus of elasticity came from boards made from the 50/50 mixture of hardwood fiber and old newspaper fiber followed by the mixed hardwood fiber. Tensile strength was about the same for boards made from the 50/50 mixture, hardwood fiber alone and hemlock fiber. All boards made from recycled fiber alone had lower MOR, MOE, and TS as compared to boards made from non-recycled fiber. All boards met the minimum ANSI standard for MOR except the boards made from mixed office waste, colored paper, and magazine paper. MOE and TS values are also very low for these same boards.

The data in Table 4 show that thickness swelling was above the ANSI standard for all boards except for the boards made from mixed hardwood, 50/50 mixture, and bagasse fiber. The boards made from mixed office waste, colored paper, and magazine paper elongated in the water almost twice as much as all other boards.

Part of the reason fiberboards made from magazine paper have such poor strength properties may be due to the inorganics present in the paper. Recycled resources that are only dry hammer milled before board formation result in particles of fiber bundles which are held together by hydrogen bonding. These particles are then bonded together with a thermosetting matrix to form the boards. The mechanism of failure in these boards may be in the hydrogen bond matrix while the rest of the boards fail through the fiber cell wall or the resin matrix.

The primary objective of this research was to show that structural fiberboards can be made from recycled resources. While the strength properties of most of the boards made from 100% recycled fiber are lower than fiberboards made from virgin fiber, strength properties can be improved by changing the method of fiber processing and the type and amount of resin used. There are also many other non-structural applications for recycled fiber in other types of composites.



**Table 3 -  
Modulus of rupture (MOR) and modulus of elasticity (MOE) in bending and tensile strength (TS) parallel to the board surface of fiberboards made from recycled fiber**

Fiber Source	Level of Adhesive		MOR MPa	MOE GPa	TS MPa
	.....	% .....			
HARDWOOD	7		96.7	4.83	38.7
OLD NEWS PAPER	7		44.1	2.14	21.3
HW-ONP	7		88.3	5.44	39.4
HEMLOCK	10		50.6	3.66	33.0
DEMOLITION WOOD	10		43.2	3.23	28.3
MIXED OFFICE WASTE	8		13.2	0.48	11.6
COLORED PAPER	8		12.1	0.36	10.0
MAGAZINE PAPER	8		7.0	0.31	5.2
BAGASSE	5		13.9	1.4	----
KENAF	8		47.1	4.6	31.0
ANSI STANDARD			31.0	----	----

**TABLE 4  
- Thickness swelling (TSw) and linear expansion (LE) in water of fiberboards made from recycled fiber**

Fiber Source	Level of Adhesive		TSw . % ..	LE 50-90 % RH . % ..
	.....	% ....		
HARDWOOD	7		13.4	0.26
OLD NEWS PAPER	7		35.0	0.32
HW-ONP	7		20.3	0.39
HEMLOCK	10		25.2	----
DEMOLITION WOOD	10		29.8	----
MIXED OFFICE WASTE	8		29.8	0.64
COLORED PAPER	8		33.7	0.60
MAGAZINE PAPER	8		30.3	0.44
BAGASSE	5		24.1	----
KENAF	8		37.3	----
ANSI STANDARD			>25	----

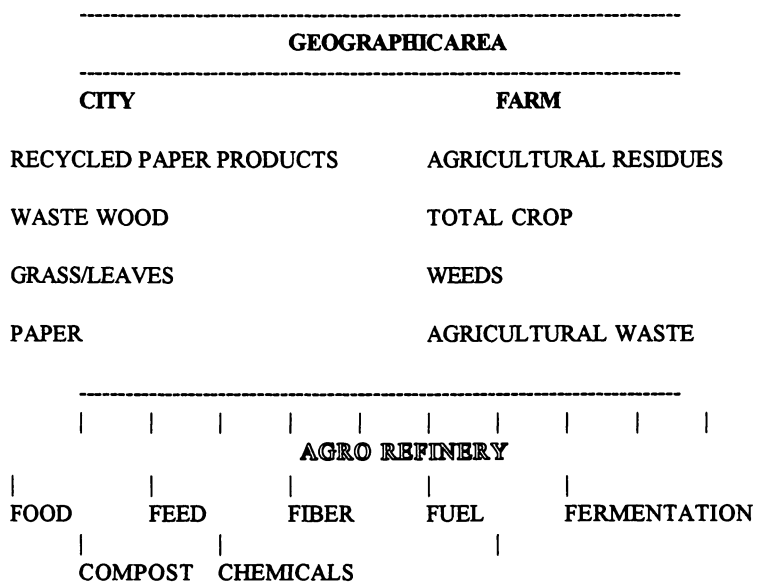


Figure 1. Concept of an agrorefinery.

### Collection of Recycled Resources

One of the key issues in the recycling arena is how to collect recycled resources. We offer a system for collection and processing based on the same principal as a petroleum refinery. In a refinery based on petroleum, crude oil is brought into the refinery and the computer decides what products will be made based on market demand. The same principal could be applied to the agro-based industry.

Figure 1 shows the basic concept of an agro refinery. In any geographic area, all agro-based resources are brought to the refinery. No predetermined markets are assumed and, as with the petroleum refinery, decisions as to processing and final product selection are made by market demands. From the cities within the geographic area comes recycled paper products, waste wood, grass, leaves, and other agricultural wastes. From the rural area comes these same resources along with all agricultural products. No separation of grain from cob or stock is made on the land. Everything is cut off at the ground and brought in. The refinery then has many options to produce food, feed, fiber, fuel, or used as a media for fermentation, produce chemicals, or convert part to compost. The market structure determines what processing will be done and the best decisions based on total needs will be made. Since it has been shown that farm land must have some of the crop residue left on the land, it is important that part of the products produced include some type of compost. The compost produced can be better than the original plant residues as it can be enriched with other needed ingredients.

Our present paradigm in the food growing industry is to grow grain for food and use the residue for feed. In many parts of the United States, however, there is excess grain and there are schemes to burn grain for fuel. Plants, such as kenaf, are now grown for fiber on lands that once were used to grow grain. We have, for generations, used herbicides to remove weeds from food and feed crops, but, if we are after fiber, the "weeds" may be the best crop. There are schemes to ferment grains to ethanol to be used as an additive to gasoline. There are also schemes to convert agro-based resources to methanol, phenols, and other chemicals.

Instead of all of these product decisions made in advance, the agro refinery would be the central processing and decision making hub for the entire agro-based industry. It will lead to many more options for the use of this valuable resource.

### Literature Cited

1. Kovacs, W.L. *Ecology Law Quarterly*, 1988 15(4),537-625
2. Rowell, R.M., Spelter, H., Arola, R.A., Davis, P., Friberg, T., Hemingway, R.W., Rials, T., Luneke, D., Narayan, R., Simonsen, J., and White, D. *Forest Prod. J.*, 1993, 43(1) 55-63
3. New York Legislation Commission on Solid Waste Management. *The economics of recycling municipal waste*, 1986.

4. U.S. Environmental Protection Agency, *Report EPA/530-SW-90-042*, 1990, Washington, DC.
5. U.S. Congress, *Facing America's trash: What's next for municipal solid waste*, 1989, Office of Tech. Assessment, OTA-0-424, Washington, D.C.
6. U.S. Environmental Protection Agency, *Characterization of municipal solid waste in the United States, 1960 to 2000*, 1988, EPA, Washington, D.C.
7. Focus '95+. *Landmark paper recycling symposium*, 1991, Atlanta, GA,
8. Franklin Associates, Ltd. Environmental Protection Agency Report, NTIS No PB87-178323, 1988, Prairie Village, KS
9. English, B., Youngquist, J.A., and Krzysik, A.M., Lignocellulosic composites. In, *Cellulosic polymers, blends and composites*, R.D. Gilbert, Ed. Hanser Publishers, 1994, New York, NY, 115-130
10. Krzysik, A.M., Youngquist, J.A., Muehl, J.M., Rowell, R.M., Chow, P., and Shook, S.R. Dry-process hardboards from recycled newsprint paper fibers. In, *Materials interactions relevant to recycling of wood-based materials*, R.M. Rowell, T.L. Laufenberg, and J.K. Rowell, eds, 1992, Materials Research Society, Pittsburgh, PA, Vol 266, 73-78.
11. Krzysik, A.M., Youngquist, J.A., Rowell, R.M., Muehl, J.M., Chow, P., and Shook, S.R., 1993, *Forest Prod. J.*, 43(7/8) 53-58.
12. Rowell, R.M. and Harrison, S. Fiber based composites from recycled mixed paper and magazine stock, In, *Materials interactions relevant to recycling of wood-based materials*, R.M. Rowell, T.L. Laufenberg, and J.K. Rowell, eds. Materials Research Society, Pittsburgh, PA, 1992, Vol 266, 65-72.
13. Rowell, R. M., and Harrison, S. E., 1993, *Proceedings, Fifth Annual International Kenaf Conference*, Bhangoon, M. S., Ed., California State University Press, Fresno, CA, 129.
14. Rowell, R.M. and Keany, F. *Wood and Fiber Sci.*, 1991, 23(1) 15-22
15. American National Standard. Basic hard board. ANSI/AH A 135.4, American Hardboard Association, 1982, Palatine, IL.
16. American Society for Testing and Materials Standard D 1037-38, Standard methods for evaluating properties of wood-based fiber and particle panel materials, 1982, Philadelphia, PA.

RECEIVED August 2, 1995

## Chapter 30

# Recycling of Mixed Plastics Using Cellulosic Reinforcement

P. Gatenholm<sup>1</sup>, P. Hedenberg<sup>1</sup>, and C. Klason<sup>2</sup>

<sup>1</sup>Department of Polymer Technology and <sup>2</sup>Department of Polymeric Materials, Chalmers University of Technology, S-412 96 Göteborg, Sweden

The aim of this research was to create novel structural composites based on waste paper and plastics that show good mechanical properties and long-term exposure properties. In this report, we summarize the results of a model study on the effect of combining chemithermomechanical pulp (CTMP) fibers and MAH-SEBS compatibilizer (maleic acid anhydride-grafted styrene-ethylene/butylene-styrene block copolymer) with a simulated waste plastic fraction composed of LDPE and HIPS (70:30). Experimental work demonstrated that an essential improvement of the mechanical properties of waste plastics can be obtained by the presence of cellulose fibers. Achieving proper strength in a material of this kind, composed of several phases, requires the addition of a compatibilizer.

Growing environmental awareness has brought about great activity in the field of plastic recycling. Plastic waste is now being collected in many countries and, after being sorted, is added to feed stock of virgin materials. Other concepts for plastic recycling include plastic product re-use and the conversion of material into monomers (chemical recycling). However, a substantial part of the municipal solid waste stream is composed of paper-contaminated plastics that are difficult to separate (1-2). Such a waste stream is a potentially inexpensive source of materials that can be converted into valuable composites.

Cellulose fibers offer several advantages when combined with the plastic. Among them are low density, high modulus and high strength (3-5). The most important requirement for a discontinuous fiber to be able to act as reinforcement in a composite material is that the fiber have a sufficient length to diameter ratio (fiber aspect ratio) (4-7). Cellulose fibers in a typical paper product used together with synthetic polymer in a typical packaging material originate often from wood and exhibit a typical length of 0.2-2 mm (8). During processing, fibers are often

0097-6156/95/0609-0367\$12.00/0  
© 1995 American Chemical Society

broken into smaller fragments, which commonly makes them too short to be useful as reinforcement (9). As the critical fiber length is dependent on the efficiency of the stress transfer from the matrix to the fibers, one way to overcome the problem of fibers that are too short is to improve interfacial adhesion between the cellulose fibers and polymeric matrix. There are several possible strategies for improving adhesion between cellulose and thermoplastic matrices. Surface treatments of cellulose with coupling agents, plasma, corona and ozone are among the most extensively used methods for improving the properties of cellulose-polymer composites (10-13).

Another technical problem associated with plastic waste, such as the household plastic fraction of waste, is a heterogeneous composition. Instead of one well defined polymer, a blend of incompatible polymers is present. Owing to the lack of compatibility of different polymers, the properties of blends are inferior when no addition of a compatibilizing agent has been made (14).

In this paper, we summarize the results of a model study on the effect of combining chemithermomechanical pulp (CTMP) fibers with a simulated waste plastic fraction composed of LDPE and HIPS (70:30). Maleic acid anhydride-grafted styrene-ethylene/butylene-styrene block copolymer (MAH-SEBS) is used as a compatibilizer.

### Experimental Methodology

**Materials.** Low density polyethylene (LDPE), NCPE 1800, was supplied by Borealis AB, Stenungsund, Sweden. High impact polystyrene (HIPS), Polystyrol 456M, was supplied by BASF. Maleic acid anhydride-grafted styrene-ethylene/butylene-styrene block co-polymer (MAH-SEBS), Kraton FG 1901X, was supplied by Shell Chemical Co. Chemithermomechanical pulp (CTMP) composed of 95% spruce and 5% pine was from S.C.A., Sundsvall, Sweden. Regenerated cellulose fibers (rayon) were supplied by Svenska Rayon AB.

**Preparation of composites and mechanical testing.** LDPE and HIPS were blended in a 70:30 weight proportion together with the CTMP fibers in a Buss-Kneader PR 46. After homogenization, the samples were injection-molded in an Arburg 221E/170R. The mechanical properties of the test bars (DIN 53455) were evaluated by tensile testing (Instron 1193) with the deformation rate  $4.5 \times 10^{-3} \text{ s}^{-1}$ . The fractured surfaces of the test bars were examined in a scanning electron microscope (Jeol JSM-5300). Impact strength tests were performed using a Frank KMO 79, pendulum type tester. The dynamic mechanical properties were evaluated in the bending mode using a Rheometrics RSA 11 dynamic mechanical analyzer. The frequency of the forced oscillation was kept at 1 Hz.

**Single fiber fragmentation test.** Specimens for the single fiber fragmentation test were prepared by placing rayon fibers between thin LDPE films, which were melted together in a press at 140°C for 2 minutes at a maximum pressure of 8 MPa. An optical microscope equipped with crossed polarizers was used to study the fragmentation process in the specimens when elongated in a Minimat Miniature Materials tester (Polymer Labs Thermal Sciences). Modification of regenerated fibers

took place in 100°C toluene, where MAH-SEBS was dissolved. The fibers were reacted for 10 minutes with a concentration of MAH-SEBS in solution calculated as 5% by weight, relative to the rayon fibers. All fibers were Soxhlet-extracted in toluene for 12h prior to specimen fabrication.

### Results and Discussion

**Mechanical properties of composites.** The plastic fraction of municipal solid waste (PFMW) was simulated in this study by mixing 70% LDPE with 30% HIPS. Figure 1 shows the effect on the tensile modulus of the presence of various amounts of cellulose fibers (CTMP) and compatibilizer (MAH-SEBS) in the simulated plastic waste fraction. The stiffness of the plastic composite is almost linearly increased with an increased amount of fiber. Samples with 30% fibers and 5% MAH-SEBS had an elasticity modulus 180% higher than that of samples without cellulose and MAH-SEBS. The presence of 30% cellulose in an LDPE/HIPS 70:30-blend offers a load bearing capability to rather low-value materials, making them comparable with a lower range of engineering plastics. The stiffness of samples with no compatibilizer added was even higher (13). This can be explained by the mechanical characteristics of the compatibilizer (MAH-SEBS) itself, which decrease the tensile modulus. The elastic modulus of the MAH-SEBS modified material was determined to be 0.15 GPa, and the elongation at break was over 300%. However, the higher stiffness of the unmodified samples will be at the expense of a loss of impact strength. The impact strength for unnotched samples containing 30% cellulose fibers was measured as 14,4 kJ/m<sup>2</sup> and 19,9 kJ/m<sup>2</sup> for unmodified and MAH-SEBS-modified composites, respectively.

Figure 2 shows the effect of cellulose with and without the addition of compatibilizer on the tensile strength of composites. Without the addition of compatibilizer, cellulose fibers act only as a filler, and do not reinforce the plastic blend. The tensile strength increased by 77% when both 30% fibers and compatibilizer were present. The improvement in tensile strength is the result of the reinforcing effect of the cellulose fibers that is achieved when the cellulose fibers are surface-modified with MAH-SEBS. The surface modification will most probably increase compatibility and adhesion between the plastic phase and cellulose fibers, which is necessary to achieve such improvement of tensile strength.

Dispersion of fibers is another important point to consider in respect to the mechanical performance of the cellulose fiber/waste plastic composite materials. In samples without MAH-SEBS, the high fiber content yields agglomeration and causes fractural impressions, whereas improved compatibility between the fibers and the matrix in MAH-SEBS-modified samples will be expected to improve the dispersion of fibers. Agglomeration may explain the decreased tensile strength registered for unmodified composites, containing 30% CTMP fibers.

The earlier reported effect of SEBS-based compatibilizers of improving dispersion in pure polyethylene/polystyrene blends is also likely to take place in the MAH-SEBS modified composites. This consequently would have a number of positive effect on the mechanical properties (15,16). Hence, as shown in Figure 2, the tensile strength for the LDPE/HIPS material without fibers is increased by the addition of MAH-SEBS.

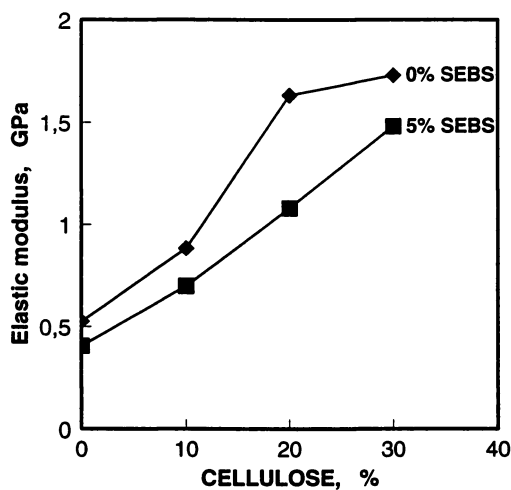


Figure 1. The effect of the incorporation of cellulose and compatibilizer on the E-modulus of simulated plastic waste.

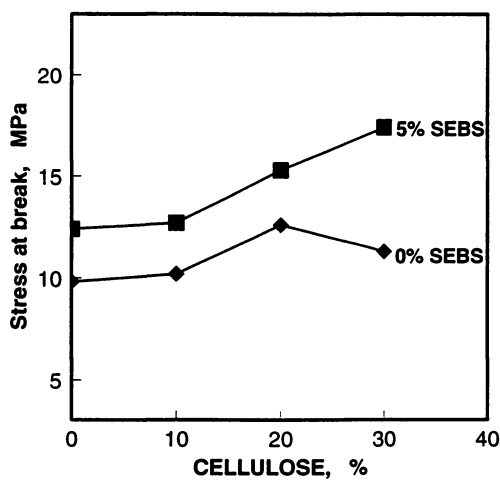


Figure 2. The effect of the incorporation of cellulose and compatibilizer on the tensile strength of simulated plastic waste.

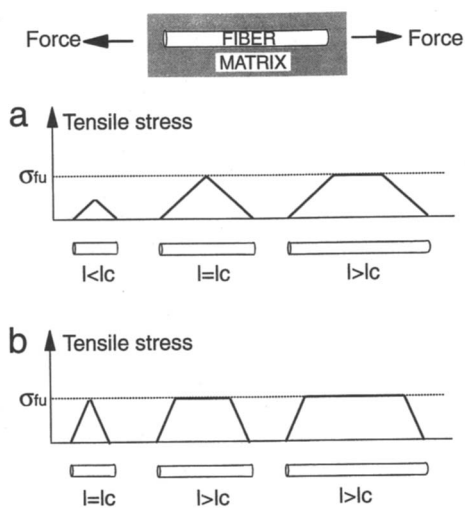


**Role of adhesion in short-fiber composites.** Short fibers have the ability to reinforce a thermoplastic matrix material by carrying load that is applied to the composite. However, load can only be carried when the applied stress is transferred from the matrix to the fiber by shear along the fiber/matrix interface. Consider an isolated short fiber as in Figure 3a. If the matrix is extended by tension along the fiber axis, then, according to the shear law, the tensile stress builds up from zero at the fiber ends to a maximum in the center portion of the fiber. To understand the relationship between the fiber length and the load bearing capability, consider now a fiber *longer* than some specific length,  $l_c$ . The length of this fiber is sufficient to allow the transferred stress that builds up along the fiber axis to reach the ultimate stress in the fiber before break. A fiber that is *shorter* than  $l_c$  will be too short to have the ability to build up enough tensile stress to reach the fracture point. In other words, the fiber does not fully utilize its strength. The limiting length for which the stress that builds up can reach the maximum strength of the fiber is called the critical fiber length and is denoted  $l_c$ . Thus, in a composite with a fiber length distribution surrounding the critical fiber length, improved fiber/matrix adhesion will lead to a more efficient stress transfer, which consequently will be seen as a decreased critical fiber length as compared with the earlier case. This is illustrated in Figure 3b.

The critical fiber length for native cellulosic fibers in a common thermoplastic matrix is difficult to establish owing to the natural inhomogeneity of the fibers. Therefore, in order to perform such studies with cellulose, it is common to use regenerated cellulose fibers (rayon), which offer a route to achieve reproducible measurements. The critical fiber lengths that have been determined for rayon fibers and cotton fibers in thermoplastic matrices (LDPE, PP) have typically been around 0.5-1 mm (11,17). As mentioned earlier, the length of wood fibers in thermoplastic composites have a broad range, typically between 0.2 and 2 mm (18). This means that some proportion (large or small) of the fibers in the LDPE/HIPS/CTMP composites will have lengths that are below the critical fiber length, as a woodfiber also normally has a higher tensile strength as compared with a rayon fiber. Increasing the fiber/matrix adhesion in such a system would thus inevitably increase the composite strength, as a larger fraction of fibers can utilize their maximum strength.

To establish that the surface modification has indeed improved the cellulose fiber/waste plastics adhesion and that the critical fiber length is lower in the MAH-SEBS-modified composites, we utilized the single fiber fragmentation (SFF) test (11). The test involves a dogbone-shaped specimen of the matrix material in which a fiber is embedded, aligned in the direction of elongation. When the specimen is elongated, stress that builds up in the matrix is transferred to the fiber via shear at the fiber/matrix interface, as described earlier in Figure 3. When the stress in the fiber reaches the ultimate strength of the fiber, the fiber breaks. Further elongation of the specimen will give rise to new stress build-up in the fiber and cause additional fractures. Finally, the fiber consists of fragments all shorter or equal to the critical fiber length, and no further breakage occurs. At this stage, the fragment length distribution is used to determine the critical fiber length.

In our study, we used regenerated cellulose fibers (rayon) as a model system instead of CTMP in order to achieve reproducible measurements. The important



**Figure 3.** Stress distribution along the fiber axis.

issue in this type of comparison of the effect of the surface modification is that the surface chemistry is similar, which indeed is the case with these two types of cellulose. Also, the model system involved pure LDPE as matrix material, as it is the component in excess in the composite and therefore will be the major component in contact with the fibers. This is seen on the SEM micrograph shown below.

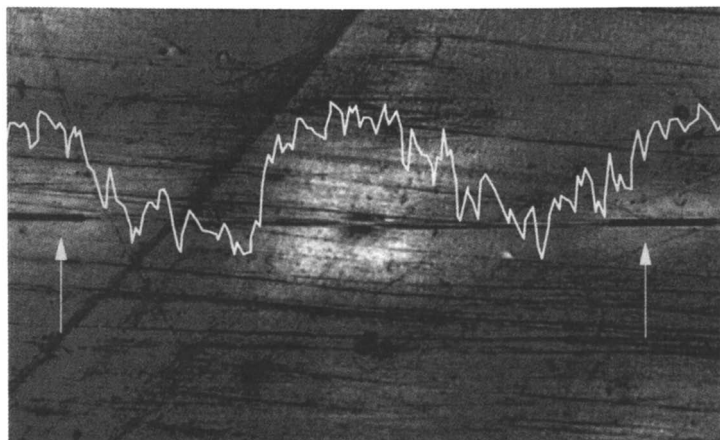
Unmodified and MAH-SEBS-modified fibers embedded in an LDPE matrix were subjected to the SFF test and the result was followed in an optical microscope equipped with crossed polarizers, which made it possible to study the stress patterns that developed in the matrix. Figures 4a and b are representative for several tests made. The figures show the fiber fragments in the matrix and the light intensity curves obtained from the birefringence patterns that develop from stress concentrations in the LDPE. The fracturing process is completed for both samples, and the matrix is at equal elongation.

In Figure 4a, the unmodified rayon fiber, the stress in the matrix is concentrated to the center portion of a relatively long fiber fragment. There is also stress surrounding the fractures, indicated by arrows, where no fiber prevents the flow of the matrix material. Between these two light intensity maxima, there is a rather extensive distance of low light intensity, indicating a low stress level. The low light intensity may be interpreted in terms of insufficient stress transfer to the fiber owing to a lack of adhesion. It is even possible that there is delamination between the fiber and the matrix at this point.

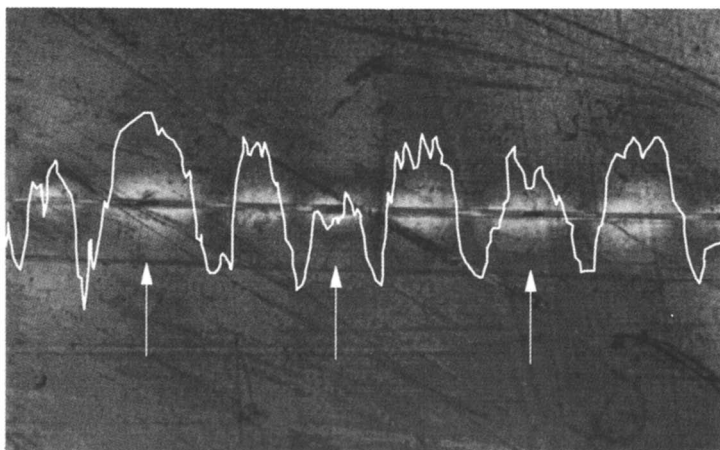
When comparing the unmodified rayon fiber with the MAH-SEBS-modified fiber shown in Figure 4b, the effect of the compatibilizer becomes obvious. In the modified, sample there is an intense fluctuation between nodes and maxima in the light intensity curve. Again, stress concentrations are located at the center portion of the fiber fragments and at the fractures, but the part of the fiber that is surrounded by low light intensity is dramatically shorter than the unmodified sample in Figure 4a. Thus the stress transfer between cellulose fibers and LDPE seems to be more efficient, and this will naturally be a consequence of an improved adhesion.

Determinations can also be made of the length of the fragments in order to achieve a measurement of the interfacial adhesion. Obviously, the length of the modified fragments in Figure 4b are only about 30% of the unmodified fragments represented in Figure 4a. However, it is not of major importance to present numerical values of the critical fiber length, as the system chosen is merely a model of the actual, more complicated system containing wood fibers in an LDPE/HIPS mixture. Still, it is obvious that the adhesion between cellulosic fibers and LDPE can be improved considerably with the use of MAH-SEBS.

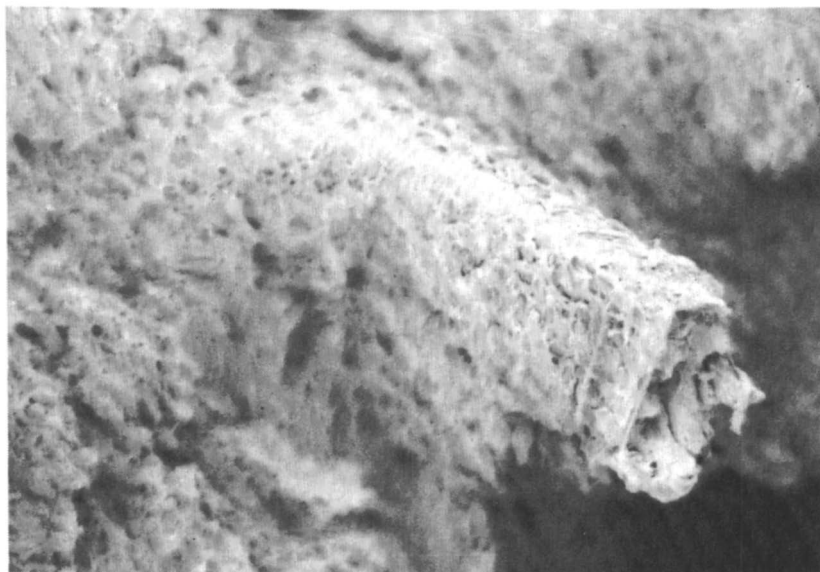
**Fractured surfaces.** The fracture surfaces of composites were investigated using Scanning Electron Microscopy. Figure 5 shows a typical fracture surface of a fiber containing composite sample without the addition of compatibilizer. This figure supports the earlier discussed results of the SFF test. It shows the ability of MAH-SEBS to yield a more intimate contact between the cellulose fiber and the LDPE/HIPS matrix. The plastic matrix covers the cellulose fiber surface, when, normally, the wetting of cellulosic fibers with thermoplastic melts is inferior, resulting in a poor coating of the material on the fibers (19).



**Figure 4a.** Unmodified rayon fiber in LDPE during SFF testing. Light intensity curves from birefringence patterns are overlaid on the picture.



**Figure 4b.** MAH-SEBS modified rayon fiber in LDPE during SFF testing. Light intensity curves from birefringence patterns are overlaid on the picture.



*Figure 5. SEM micrograph of a fractured surface in an LDPE/HIPS/CTMP composite with MAH-SEBS.*

The effect of MAH-SEBS on composite properties can probably be explained on an elementary chemical level on the basis of SFF and SEM results. The following mechanism has been proposed to be responsible for the enhancement of adhesion: Maleic acid anhydride grafted on SEBS chains is highly reactive towards hydroxyl groups at the cellulose surface and, when compounding at elevated temperatures, both covalent and hydrogen bonds develop between the functionalized compatibilizer and the cellulose surface (14). Furthermore, MAH-SEBS covers the cellulose surface and, thus, wetting by the polyolefinic LDPE and HIPS phases is simplified, and better contact between cellulose and plastics is achieved.

**Dynamic Mechanical Properties.** One of the limitations of thermoplastic materials is their heat sensitivity. Samples of composites with various fiber contents were evaluated with regard to their thermal response using DMTA. Investigation of the dynamic elasticity modulus, shown in Figure 6, confirms the overall stiffening effect of cellulose fibers. In fact, measurements at 60°C show that the stiffness of a composite containing 30% fibers is comparable with that of a composite without fibers at 10°C. This also proves that cellulose preserves the stiffening effect under the influence of heat.

### Conclusions

Experimental work demonstrated that an essential improvement in the mechanical properties of waste plastics can be obtained by the presence of cellulose fibers.

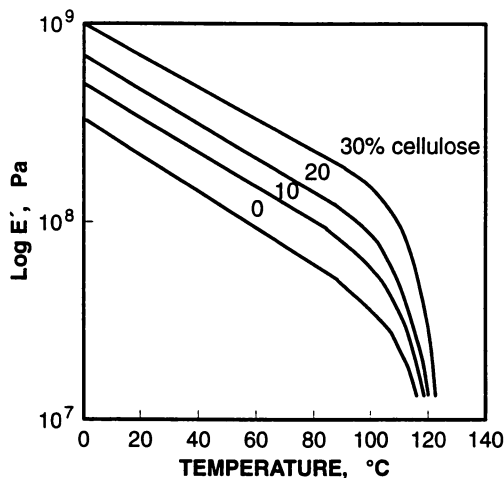


Figure 6. Dynamic Elasticity Modulus for samples with various fiber contents.

Achieving proper strength in a material such as this, composed of several phases, requires the addition of a compatibilizer. Not only does a reactive compatibilizer improve compatibility between the phases, but also improves adhesion between cellulose fibers and the waste matrix. Improved adhesion is maintained by the formation of covalent bonds between the maleic acid anhydride group of the compatibilizer and the hydroxyl groups at the cellulose surface.

Hence, cellulosic fibers can act as reinforcement and provide both strength and stiffness to mixed waste plastic matrices. Furthermore, the cellulosic fibers also preserve the stiffness of the material over a wider temperature range than is seen for the pure waste plastic blend.

#### Acknowledgments

The authors are grateful to Dr. A. Mathiasson for his assistance in the experimental work. Financial support from the Swedish Waste Research Council is gratefully acknowledged.

#### Literature Cited

1. Klason C.; Kubat J.; Gatenholm P. In *Viscosity of Biomaterials*; Glasser W.; Hatakeyama, H., Ed.; ACS Symposium Series; American Chemical Society: Washington D.C., 1992.
2. Mathiasson A., PhD. Thesis; Chalmers University of Technology: Göteborg, Sweden, 1992.
3. Zadorecki P.; Mitchell A.J. *Polym. Compos.* **1989**, *10*, 2.
4. Maldas D.; Kokta B.; Daneault C. *Intern. J. Polymeric Mater.* **1989**, *12*, 297.
5. Dalvåg H.; Klason C.; Strömvall H.-E. *Intern. J. Polymeric Mater.* **1985**, *11*, 9.

6. Cox H.L. *Br. J. Appl. Phys.* **1952**, *3*, 72.
7. Felix J.M.; Gatenholm P. *J. Appl. Pol. Sci.* **1993**, *50*, 699.
8. Mitchell A.J.; Vaughan J.E.; Willis D. *J. Appl. Polym. Sci.* **1978**, *22*, 2047.
9. Gatenholm P.; Mathiasson A. *J. Appl. Pol. Sci.* **1994**, *51*, 1231.
10. Bataille P.; Ricard L.; Sapiha S. *Polym. Comp.* **1989**, *10*, 103, (1989)
11. Felix J.; Carlsson G.M.; Gatenholm P. *J. Adh. Sci. Technol.* **1994**, *8*, 1.
12. Felix J.M.; Gatenholm P.; Schreiber H.P. *J. Appl. Pol. Sci.*, **1994**, *51*, 285.
13. Gatenholm P.; Felix J.M. In *New Advances in Polyolefins*; Chung T.C., Ed.; ACS Symposium Series; American Chemical Society: Washington D.C., 1993.
14. Hedenberg P.; Gatenholm P. *J. Appl. Pol. Sci.*, in press.
15. Welander M.; Rigdahl M. *Polymer*, **1989**, *30*, 207.
16. Brahami B., Ait-Kadi A.; Ajji A.; Fayt R. *J. Polym. Sci., Part B: Polym. Phys.*, **1991**, *29*, 945.
17. Felix J.M.; Gatenholm P. *J. Mater. Sci.*, **1994**, *29*, 3043.
18. Gatenholm P., Bertilsson H.; Mathiasson A. *J. Appl. Polym. Sci.*, **1993**, *49*, 197.
19. Felix J.M.; Gatenholm P. *J. Appl. Polym. Sci.*, **1991**, *42*, 609.

RECEIVED June 20, 1995

## Chapter 32

# Recycled Plastics for Food-Contact Applications

## Science, Policy, and Regulation

P. M. Kuznesof and M. C. VanDerveer

Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, Washington, DC 20204

The use of recycled plastics for food packaging raises concerns about unregulated substances that may migrate into food and the possible adulteration of the food. In May, 1992, the Center for Food Safety and Applied Nutrition made available a document entitled "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations." The document highlighted those issues that manufacturers of recycled plastic should consider during the evaluation of a recycling process to produce material suitable for food-contact applications. This paper briefly reviews the highlights of the "Points," discusses the basis for some recent opinions that the Center has given for specific recycling applications, and comments on the agency's developing regulatory policy on the use of recycled plastic for construction of food-contact articles.

"A Guilt-free Guide to Garbage" was the headline for an article in the February, 1994, issue of *Consumer Reports* magazine (1), and the August, 1993, issue of *ASTM Standardization News* featured an article entitled "From the Garbage Heap to Your Home" (2). The interest in recycling municipal solid waste (MSW) has taken a firm hold in the public's mind because recycling is viewed as a "green" technology. Over the last several years, local, state, and federal government activity aimed at developing legislation mandating recycling of various components of MSW has provided a strong incentive for many industry groups to enter the recycling business. Among the industries, the food and food-packaging sectors have also recognized that use of recycled packaging may be a valuable adjunct to their marketing and public relations strategies.

Glass, paper, aluminum, and ferrous metals have been recycled at relatively high efficiencies for some years. Only recently has plastic, principally plastic

This chapter not subject to U.S. copyright  
Published 1995 American Chemical Society



packaging, begun to be recycled to any significant degree. The composition of MSW based on 1992 information is illustrated in Figure 1, which is based (1) on Franklin Associates' report prepared for the US Environmental Protection agency. According to Franklin Associates (1), the recycling rate for 1992 was highest for aluminum cans/foil - 68%. Paper, container glass, and steel cans were also being recycled at reasonably high rates: 38%, 33%, and 41%, respectively. However, only 6.5% of plastic packaging was recycled in 1992. The major plastics currently recycled are polyethylene terephthalate (PETE) - 450 million pounds recycled, high-density polyethylene (HDPE) - 450 million pounds, and low-density polyethylene (LDPE) - 110 million pounds (3) (figures are for 1993), all of which are extremely important to the food-packaging industry.

Recycle feedstock from food-packaging material included approximately 360 million pounds of PETE soda bottles, 30 million pounds of PETE "custom" containers, i.e., for liquor and other foods, cosmetics, toiletries, and pharmaceuticals and 285 million pounds of HDPE milk and water jugs (3). Recyclate used to manufacture food-contact articles was limited essentially to PETE soda bottles in 1993. Only 25 million pounds was produced from post-consumer recycled bottles. This represents 2.5% of PETE soda bottle poundage for 1993. These figures suggest that plastic material fabricated for food-contact use and recycled for additional food-contact purposes is currently having little effect on mitigating the MSW crisis. However, this effect is not insignificant with respect to issues that relate to the safety of the US food supply. The purpose of this paper is to highlight these issues and to describe the efforts of the US Food and Drug Administration (FDA) to ensure the safe use of post-consumer recycled plastics for food-contact applications.

The desire to use post-consumer recycled plastics to manufacture food-contact articles raises concerns about adulteration of the food by contaminants and unregulated substances that may migrate into the food from the articles. For example, how does one address the potential for consumer misuse or abuse of plastic containers or packaging through storage of household, garden, or automotive chemicals, and how can the potential risk to the public health from exposures to these toxic substances be assessed if post-consumer recycled plastics are to be used in food-contact applications? In May, 1992, FDA's Center for Food Safety and Applied Nutrition (CFSAN) made available an informal document entitled "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations." (Copies are available from the Office of Premarket Approval, HFS-220, Center for Food Safety and Applied Nutrition, US Food and Drug Administration, 200 C Street, SW, Washington, DC 20204.) This document (the "Points") was intended to provide manufacturers of articles from recycled plastics with CFSAN's initial thoughts on the important issues that need to be addressed during the evaluation of a recycling process to produce material suitable for food contact. Before discussing the "Points" and the developments following their release, it seems useful to first outline the current regulatory framework for the use of recycled plastics in contact with food.

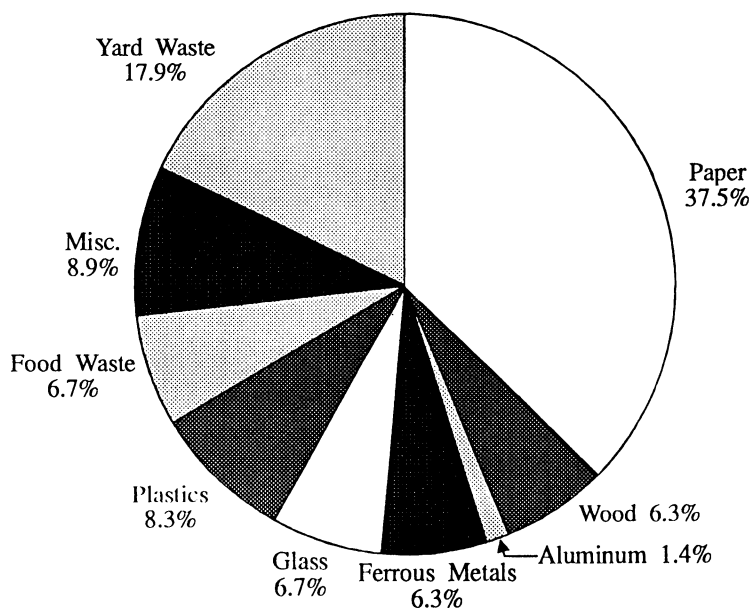


Figure 1. Composition of municipal solid waste (181 million tons, 1992).

## Regulatory Framework

FDA's primary responsibility under the Federal Food, Drug, and Cosmetic Act is to ensure that the products it regulates are wholesome, safe, and effective. Furthermore, the National Environmental Policy Act requires that FDA assess the impact of new food-packaging materials on the environment (4). Although FDA supports recycling and the broader societal goal of diverting material from the solid waste stream, it can only do so when it is in harmony with FDA's mission to protect the public health.

No federal regulations presently exist that explicitly address the use of post-consumer recycled plastics for food-contact applications. The regulations for indirect food additives in Title 21 of the United States *Code of Federal Regulations* (21 CFR), Part 175 (Adhesives and Components of Coatings), Part 177 (Polymers), Part 178 (Adjuvants, Production Aids, and Sanitizers), and the requirements specified in Section 174.5 relating to Good Manufacturing Practice are applicable, however. In particular, Section 174.5(a)(2) states, "Any substance used as a component of articles that contact food shall be of a purity suitable for its intended use." Thus, manufacturers of food-contact articles made from recycled plastic must ensure that the recycled material, like virgin material, is of suitable purity and meets all existing specifications for the virgin material. And it must be remembered that compliance with regulations extends to any adjuvants, such as antioxidants, colorants, or antistatic agents, that have been incorporated into polymer resins.

In addition to actively working over the past three years to improve the guidance to the industry for evaluating the technology for recycling plastics into food-contact articles (5,6), CFSAN personnel have also been considering whether there is a need to establish any new regulations that would explicitly apply to the use of recycled plastics for food-contact articles. In the interim, industry is urged to continue its consultations with the agency in order to satisfy FDA's concerns regarding the safe use of recycled plastics. FDA wishes to continue to be responsive to industry requests for guidance and opinions on specific applications of recycled plastics. Some of these applications and opinions will be discussed below. Because these opinions have been based on the "Points," it is appropriate now to consider that document at greater length.

## Points to Consider

The "Points" begins with a brief discussion of the basic types of plastic recycling including recycling of pre-consumer industrial scrap and salvage and some specific concerns relevant to each. Re-use of containers, which pertains to source reduction, is also discussed. This is followed by a description of an approach for estimating the maximum level of a chemical contaminant in the recycled material that would be acceptable and would not compromise the public health. Finally, an experimental protocol is *suggested* by which analytical chemistry data can be developed for evaluating the adequacy of a recycling process to remove chemical contaminants.

Post-consumer recycling processes can be classified as either physical or chemical reprocessing. *Physical* reprocessing involves grinding, melting, and reforming plastic packaging material. The basic polymer is not chemically altered. Before the polymer is melted and reformed, the ground, flaked, or pelletized resin is washed to remove contaminants. The wash step is a critical part of physical reprocessing, and many companies engaged in evaluating physical reprocessing methods regard their wash procedures and washing agents as proprietary information. Processors should avoid using substances that are not regulated for food contact, as these substances may become incorporated into the polymer resin and subsequently migrate into food at concentrations that may render the food adulterated. Different resins may also require different reforming conditions, such as different processing temperatures, the use of vacuum stripping, or other procedures that could influence contaminant levels and affect the polymer properties and functionality of the recycled material. Scientists at the Chicago-based National Center for Food Safety and Technology (NCFST), a consortium of government (FDA), industry, and academia dedicated to cooperative research in food safety and technology, have also been exploring various aspects of the cleanup of physically processed recycled plastics (7). Some of this work involving recycled PETE was presented at the August, 1994, National Meeting of the American Chemical Society (Kamolprasert, V., and Lawson, A., in press; Kamolprasert, V., et al., in press).

Recyclers must be able to demonstrate that potential contaminant levels in the reformed plastic can be sufficiently reduced to ensure that the resulting packaging will not adulterate food. Production of a resin with the desired qualities, however, may require the addition of antioxidants, processing aids, or other adjuvants to the recycled resin. The type and total amount of additives must be in compliance with existing regulations. Recycled resins that require new additives or amounts of additives in excess of what is currently regulated may require an amendment to the food additive regulations via the petition process.

Physical reprocessing presents some unique problems that may make it inappropriate for the production of food-contact articles, particularly if the recycler has little or no control over the quality of the feedstock entering the recycling facility. If effective source control can be established, however, the problem of commingling post-consumer plastic food-contact materials with other post-consumer plastics that may be made of unregulated resin or that may contain unregulated adjuvants can be minimized or eliminated. Source control is an important element of Good Manufacturing Practice. Additionally, the development of sorting procedures that result in the reprocessing of only a single characteristic container, e.g., a PETE soda bottle, adds additional assurance that the recycled article is suitable for food contact.

*Chemical* reprocessing may involve depolymerization of the used packaging material with subsequent regeneration and purification of resulting monomers or oligomers. These materials are then repolymerized and the regenerated polymer is formed into new packaging. Regenerated monomer, polymer, or both may be blended with virgin polymer. The regeneration process may involve a variety of

monomer/polymer purification steps, such as distillation, crystallization, and additional chemical reaction, in addition to washings. The primary goal of chemical reprocessing is the regeneration of purified starting materials. The use of additional adjuvants must be in compliance with regulations. Compared with physically reprocessed recycled plastics, it is considerably simpler to demonstrate that chemically reprocessed material is of suitable purity for its intended use. However, chemical reprocessing does not appear to be cost effective. Hence, there has been considerable industry interest of late in developing physical reprocessing technology that can provide the necessary assurance that the recycled material is indeed "of suitable purity."

The meaning of "suitable purity" has been linked in the "Points" to the establishment of an acceptable upper-limit of dietary exposure to chemical contaminants from recycled material. Therefore, the residual concentration of a contaminant in the plastic that corresponds to the dietary exposure limit needs to be determined. The "Points" discussed the potential risk to consumers from acute exposure and chronic (long-term) exposure to chemical contaminants migrating into food from recycled packaging. Because the concentrations of contaminants in recycled plastic are expected to be extremely low, acute exposures would be too low to manifest acute toxicological effects. The possibility was considered, however, that traces of carcinogenic substances (or any other substances that may constitute a chronic health hazard) could be carried through multiple recyclings to establish very low steady-state concentrations in the recycled material over the long term. Therefore, the possibility that a consumer could be exposed to low concentrations of a particular carcinogen over a long period of time had to be addressed.

Consideration was given to the question of carcinogenic risk in a probabilistic way rather than on a compound-by-compound basis. The principles used were those that formed the basis for FDA's 1993 proposal to establish a "Threshold of Regulation" (T/R) for substances purposely used in the manufacture of food-contact articles (8,9). The T/R proposal would sanction the use of food additives in packaging materials for which the probable exposure to a consumer is expected to be sufficiently low as to constitute negligible risk; such use would not require a food additive petition. The "Points" stated that "Preliminary thinking" in CFSAN suggested that exposure to a contaminant at 1 part per billion (ppb) in the daily diet, the same figure that was being considered for the T/R policy, could be considered a negligible risk. Subsequently, FDA proposed 0.5 ppb of the daily diet as the exposure level for negligible risk (8). This is the exposure that CFSAN's Office of Premarket Approval now also considers appropriate in assessing recycling applications. Illustrations of calculations and assumptions used to determine the maximum residual level of a contaminant in recycled plastic that would contribute no more than 1 ppb to the diet are given in the "Points." The calculations are easily adapted to an exposure of 0.5 ppb.

The ability of a particular recycling process to reduce contaminant levels in plastic containers or packaging to levels below those corresponding to a dietary exposure of 0.5 ppb should be demonstrated. A scheme for doing this involving

analytical studies with surrogate contaminants was elaborated in the "Points." In summary, consumer misuse could be simulated by exposing plastic packaging, either in container form or as flaked or ground resin, to selected surrogate contaminants. Following this exposure, the containers or resin would be subjected to the recycling process. Analysis of the resin for the surrogates would demonstrate the efficacy of the recycling process.

According to the "Points," the selection of surrogate contaminants should attempt to bracket a variety of chemical and physical properties. It is suggested that the surrogates be "common" materials accessible to the consumer and include a volatile nonpolar organic substance, a volatile polar organic substance, a nonvolatile nonpolar organic substance, and a nonvolatile polar substance. Other selection criteria are being evaluated by NCFST and by the plastics industry. To date, CFSAN's Office of Premarket Approval has reviewed data on surrogate contaminant analyses from several companies for evaluating the recycling of PETE. The surrogates that have been used are listed in Table I along with the results of the analyses. Some surrogates have proved difficult or unsuitable. For example, disodium monomethylarsonate (crabgrass killer) has been tested as a surrogate contaminant for PETE. Analysis for arsenic using atomic absorption spectroscopy is apparently confounded by the presence of antimony in PETE; antimony-containing catalysts are used in the manufacture of PETE. *Ortho*-cresol, which is known to significantly swell PETE and was suggested in the "Points," may actually dissolve PETE under the conditions of the study protocol; it is no longer recommended. Gasoline, motor oil, and kerosene would initially appear to be appropriate choices as surrogates. Analytical difficulties in achieving adequately low detection limits, however, preclude their further recommendation. The detection limits for the other surrogates listed in Table I were low enough for a reasonable assessment of the data.

The "Points" also considered the possibility that a proposed recycling process may fail the surrogate challenge, i.e., it would not reduce contaminant levels in the recycled polymer below the acceptable limit corresponding to a dietary exposure of 0.5 ppb. It is important to keep in mind, however, that an estimation of dietary exposure to a surrogate contaminant based only on the determination of its concentration in the recycled polymer assumes that all of the contaminant (100%) migrates from the package to the food. This is a highly conservative assumption. The relevant point with respect to food safety, therefore, is not how much contaminant is in the plastic packaging material, but rather how much migrates into food during the time of food contact. This can be assessed by performing migration studies of the type typically recommended to support a food additive petition for regulating a new packaging material or polymer adjuvant (10). (Copies are available from the Office of Premarket Approval, HFS-200, CFSAN, FDA, 200 C Street, SW, Washington, DC 20204.) In addition to migration studies, other factors that can be used to lower the exposure estimate include blending virgin with recycled resin, improving source controls, restricting uses for recycled material, or using a functional barrier for certain applications (see below).

Table I: Surrogate Contaminants for Evaluation of Recycled PETE

<i>Surrogate</i>	<i>Spiking Level</i>	<i>Pre-Process Level in Resin</i>	<i>Post-Process Level<sup>a</sup> in Resin [in Extract]</i>
gasoline <sup>b</sup>	neat <sup>c</sup>	670 ppm	< 5 ppm
cupric acetoarsenite	at use conc. <sup>c</sup>	not reported	< 25 ppb
chlordane	at use conc. <sup>c</sup>	not reported	< 0.5 ppm
lindane <sup>b</sup>	2% aqueous emulsion <sup>c,d</sup>	281 ppm	< 25 ppb [ $< 10$ ppb]
diazinon <sup>b</sup>	1% aqueous solution <sup>c,e</sup>	100 ppm	< 10 ppb
motor oil	neat <sup>c</sup>	24,600 ppm	< 25 ppm
toluene <sup>b</sup>	1635 ppm <sup>e,f</sup>	404 ppm	< 100 ppb [ $< 10$ ppb]
chloroform <sup>b</sup>	1256 ppm <sup>e,f</sup>	899 ppm	< 50 ppb [ $< 10$ ppb]
carbaryl	1000 ppm <sup>d</sup>	0.356 ppm	[ $< 20$ ppb]
malathion	1000 ppm <sup>d</sup>	247 ppm	[ $< 0.05$ ppb]
*chromium salt*	1000 ppm (as Cr) <sup>d</sup>	51.2 ppm (as Cr)	[ $< 5$ ppb (as Cr)]
lead oxide	1000 ppm (as Pb) <sup>d</sup>	152 ppm (as Pb)	[ $< 1$ ppb (as Pb)]
kerosene	1000 ppm <sup>d</sup>	< 2.5 ppm	[ $< 1.0$ ppm]
lead sulfate	293 ppm (as Pb) <sup>d</sup>	189 ppm (as Pb)	[ $< 10$ ppb (as Pb)]
cadmium acetate	268 ppm <sup>d</sup>	not reported	< 10 ppb (as Cd)

<sup>a</sup>Plastic samples were extracted with 8% ethanol for 10 days at 120°F. Levels reported in brackets are from 10-day extracts.

<sup>b</sup>Surrogate was used in more than one study. The highest reported levels are listed.

<sup>c</sup>Samples spiked by filling bottles with surrogate.

<sup>d</sup>Samples spiked by blending surrogates into pellets.

<sup>e</sup>Chemical reprocessing mixture spiked with surrogate.

<sup>f</sup>Samples spiked by soaking flaked plastic in surrogate.

The Plastics Recycling Task Force (PRTF), an *ad hoc* industry group formed under the joint auspices of the National Food Processors Association (NFPA) and the Society of the Plastics Industry (SPI), in March, 1992, submitted to CFSAN for comment a draft document entitled "Guidelines for the Safe Use of Recycled Plastics for Food Packaging Applications" (11). The PRTF also recommended the surrogate contaminant approach for challenging a recycling process. In addition, a plan was presented that would call for migration studies to be conducted to assess the amount of contaminant that would actually be expected to migrate into food should the analysis of residual contaminant in the polymer be above the acceptable limit based on 100% migration. The March 19, 1994, *Technical Highlights* newsletter published by NFPA announced completion of PRTF work on recycled HDPE for food packaging and claimed development of analytical methodology with a detection limit of at least 0.3 parts per million (ppm) for all surrogates, corresponding to a dietary exposure of 0.5 ppb.

### Migration Principles and Functional Barriers

The use of recycled material as a nonfood-contact layer of a multilayer food package would appear to be an excellent application for recycled plastics. Risk

from contaminant migration into food would be expected to be negligible provided that the recycled resin is separated from the food by an effective barrier constructed of regulated virgin resin or other appropriate material, e.g., aluminum foil. Chemists at CFSAN (6) have recently addressed the question of migration of contaminants from recycled plastics into food through theoretical calculations based on principles of diffusion in polymers (12). They have shown that it is possible to calculate for a given polymer the maximum acceptable concentration of a contaminant that would result in a dietary exposure considered to be of negligible risk. Furthermore, they have applied the diffusion model to a two-layer construction with recycled polymer as the nonfood-contact layer and have shown how to estimate the minimum thickness of a virgin food-contact layer that would serve as a functional barrier.

In the first instance, it was assumed that the food package consists of a monolayer of 100% recycled material in which any contaminant is homogeneously distributed (Figure 2a) and that the diffusion of the contaminant into the food obeys Fick's law. This means that the amount of migration into food can be expressed as

$$M_t = 2C_0(Dt/\pi)^{1/2} \quad (1)$$

where  $M_t$  is the amount of a substance migrating from a unit surface area of package ( $\mu\text{g}/\text{cm}^2$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ) - assumed to be concentration-independent,  $C_0$  is the concentration ( $\mu\text{g}/\text{cm}^3$ ) of the contaminant in the polymer at zero time, and  $t$  is time (s). The general assumptions behind equation 1 are 1) the concentration of migrant in the polymer does not significantly change during food-contact time and 2) the food is an infinite sink with no resistance to mass transfer (i.e., there will be no partitioning effects to inhibit migration from polymer to food). Begley and Hollifield (6) point out that equation 1 has been shown in numerous studies to be useful in predicting migration from food packaging to food.

The two-layer or laminate package was modeled by Begley and Hollifield in terms of the pseudo-membrane problem (12), which assumes a fixed concentration ( $C_0$ ) on one side of the membrane (i.e., at the virgin polymer/recycle layer interface) of thickness  $l$  and a zero concentration on the other side (in the food). See Figure 2b. The solution to the problem, which assumes the food to be an infinite sink for the migrant, is given by equation 2.

$$M_t = \left\{ \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \left[ \frac{(-1)^n}{n^2} \exp\left(\frac{-n^2\pi^2 Dt}{l^2}\right) \right] \right\} C_0 l \quad (2)$$



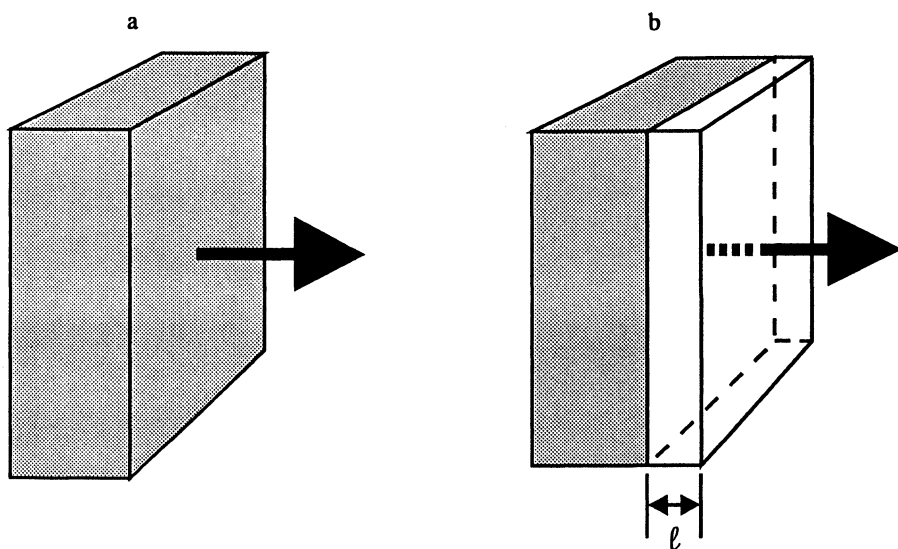


Figure 2. Migration of contaminants from recycled plastic into food for (a) monolayer and (b) multilayer packaging structures, where  $l$  is the thickness of a layer of virgin plastic.

Equation 2 is highly complex. To simplify matters, Begley and Hollifield defined a unitless variable,  $\tau$ , for the purpose of providing a general perspective on the diffusion rate for a contaminant through the virgin layer into the food:

$$\tau = Dt/l^2. \quad (3)$$

It can be seen from equation 2 that the larger  $\tau$  is, the faster will a contaminant cross the virgin layer into the food. Solving equation 2 for  $\tau \leq 0.1$  predicts that at most 1% of the initial contaminant concentration at the recycle/virgin interface will move across the virgin layer. For  $\tau = 0.6$ , diffusion will be rapid and approximately 45% of the migrant will migrate into the food. At values of  $\tau$  above 0.6, the magnitude of migration is predicted to approach that of the monolayer package. (For values of  $\tau$  greater than 0.6, the migration from a laminated package, calculated by using equation 2, may exceed the calculated migration from a monolayer package. At high values of  $\tau$ , the assumption that  $C_o$  is a constant is no longer valid.)

To evaluate contaminant migration from a food package by using the above models and thereby determine whether an initial contaminant level will be acceptable in terms of the 0.5-ppb exposure benchmark, the diffusion coefficient for the contaminant in the polymer must be known for the maximum temperature conditions to which the polymer will be subjected during food contact (e.g., refrigerated conditions, retort conditions). Combining diffusion coefficients with expected time of food contact for a given temperature and using FDA's basic assumption that 10 grams of food contacts 1 square inch of packaging surface (or 1.55 g/cm<sup>2</sup>), Begley and Hollifield calculated the extent of migration to food that could be expected for different initial contaminant levels in a set of four polymers. Their calculations for a 2-mil (0.051 mm) thick monolayer package for 30 days of food contact are presented graphically in Figure 3 for PETE, polystyrene (PS), poly(vinyl chloride) (PVC), and LDPE. (Migration predicted by using equation 1 is independent of monolayer thickness. However, dividing equation 1 on both sides by  $l$  gives

$$\frac{M_t}{l} = 2C_o \left( \frac{Dt}{l^2\pi} \right)^{1/2} \text{ or } 2C_o(\tau/\pi)^{1/2} \text{ and } M_t = 2lC_o(\tau/\pi)^{1/2}. \quad (4)$$

$M_t$  can then be plotted as a function of  $C_o$  for various values of  $\tau$  (i.e.,  $D$ ) where  $l$  and  $t$  are fixed.) With fixed  $t$  and  $l$ ,  $D$  was varied around  $1 \times 10^{-12}$  cm<sup>2</sup>/s to obtain the different lines for each value of  $\tau$ . For example, for  $D = 3.5 \times 10^{-12}$  cm<sup>2</sup>/s,  $\tau = 0.35$ . The horizontal lines represent those concentrations in the food corresponding to a dietary intake of 1 ppb. The different concentrations are a result of the differing proportions in which the polymers are used for food packaging (10). Thus, for  $\tau = 0.15$ , if the initial concentration of a contaminant in PETE were to exceed 13  $\mu\text{g}/\text{cm}^3$  (9  $\mu\text{g}/\text{g}$ ), the predicted dietary exposure

would exceed 1 ppb. Similarly, in order not to exceed an exposure of 0.5 ppb, the initial contaminant level should not exceed about  $7 \mu\text{g}/\text{cm}^3$ .

The graph in Figure 4 for the laminate structure was constructed by using the same values of  $\tau$ , i.e.,  $t$ ,  $D$ , and  $l$ , as were used for the monolayer. The ordinate represents the migration expected through the virgin layer into the food for a given concentration in the recycled layer.

For a 2-mil thick virgin PETE layer, the calculations indicate that the concentration of contaminant in the recycled layer could be as high as  $200 \mu\text{g}/\text{cm}^3$  ( $\tau = 0.15$ ) before migration would result in a dietary exposure of 1 ppb. This is 15 times the level of contamination calculated for the monolayer package,  $13 \mu\text{g}/\text{cm}^3$ . Such large differences should not lead to a conclusion that highly contaminated recycled resins are suitable for food packaging. The intentional use of highly contaminated materials would not be considered good manufacturing practice (GMP). The modeling, however, is clearly useful in providing guidance and insight for evaluating a particular recycling process. CFSAN's Chemistry Review Branch has already used this approach in evaluating the suitability of several recycled resins for food-packaging applications.

### FDA Opinions

The early requests for agency opinions on specific applications for post-consumer recycled polymers were the easiest to consider in a favorable light. The principal issue was and is the likelihood and magnitude of potential consumer exposure to contaminants. Those applications for which the food-/package-contact time is extremely short (e.g., some fast-food-service applications), the temperature of the food in contact with recycled material is room temperature or lower (e.g., produce trays in supermarkets), the ratio of a unit surface area of food-contact material to the mass of food contacting the area is extremely small (e.g., large shipping crates used for grapefruit), or the contact of packaging material with nonedible portions of foods (e.g., shells of eggs and skins of bananas) are not expected to result in exposures to contaminants that would compromise public health.

Among those submissions that CFSAN has favorably reviewed are four based on surrogate contaminant analyses for chemically reprocessed PETE soda bottles. One of the PETE submissions pertained to its use as a nonfood-contact layer in a laminate structure. In addition, a number of favorable opinions for physically reprocessed polymer have been given to date (Table II). Some were based solely on the considerations mentioned above relating to short contact times, low temperatures during food/package contact, etc. Others were based on theoretical calculations using equation 2 above, or on migration studies demonstrating an effective barrier under the proposed conditions of use. Migration data submitted for a multilayer package construction supported a conclusion that a 1-mil thick virgin food-contact layer of PETE would serve as a functional barrier to contaminants from a recycled PETE layer for up to 1 year with filling and storage

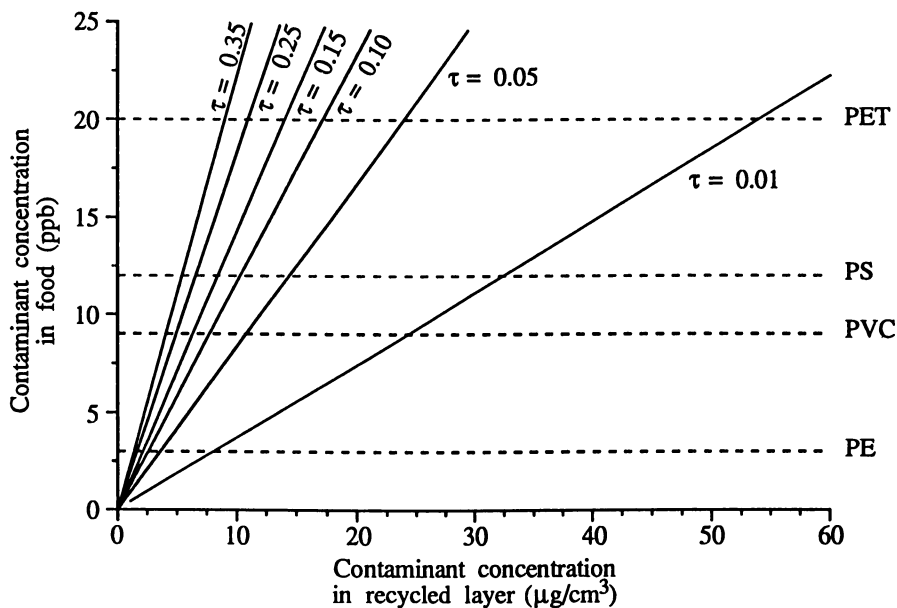


Figure 3. Migration from a monolayer package, predicted by using equation 1 (from Ref. 6, with permission).

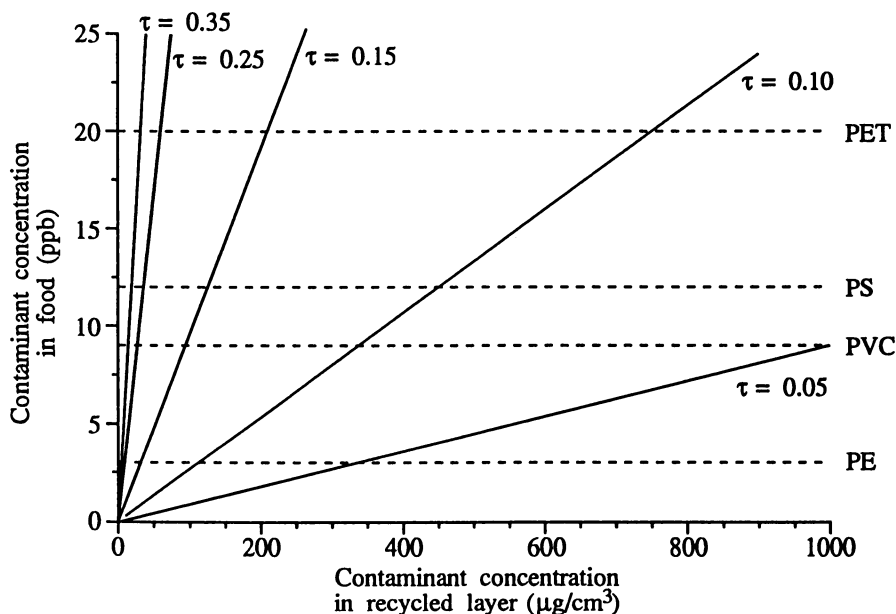


Figure 4. Migration from a two-layer package, predicted by using equation 2 (from Ref. 6, with permission).

Table II. Physically Reprocessed Plastics — Favorable Opinions

<i>Polymer<sup>a</sup></i>	<i>Application</i>
PETE	berry baskets
PETE	deli foods
PETE	deli and bakery foods
PETE	all bottles
PE and PP	shipping containers for meat, poultry, and seafood; harvesting crates
PE	grocery bags
PS	airline snack boxes
PS	retail meat and poultry trays
PS	produce trays
PS	egg cartons

<sup>a</sup>PETE = polyethylene terephthalate; PE = polyethylene; PP = polypropylene; PS = polystyrene.

temperatures not exceeding room temperature. Theoretical modeling has also shown that a 1-mil virgin PETE layer can be an effective barrier for up to 1 year even for products that are hot-filled or pasteurized above 66°C (150°F). Calculations for polystyrene for a 2-week food-contact time at room temperature also predict a 1-mil virgin layer to be a barrier. Currently, CFSAN has several additional requests for evaluation that are under review. It is expected that most of the submissions during the next few years will be concerned with physically reprocessed polymers because of the unfavorable economics for chemical reprocessing.

### Summary and Conclusions

FDA has a positive outlook on plastics recycling for many types of food-packaging and other food-contact applications. In attempting to be responsive to requests from the food and food-packaging industries for guidance in this area, CFSAN developed the "Points" and is now considering whether proposing any new regulations would be beneficial to the industry and to consumers. During the past 3 years, CFSAN personnel have met with industry representatives, including the PRTF, on a number of occasions to discuss approaches to encourage the proper use of post-consumer recycled plastic for food-contact applications.

The "Points" describes the rationale, based on the probabilistic approach that led to the agency's Threshold of Regulation proposal, for establishing an acceptable upper limit of potential dietary exposure to contaminants in recycled plastic. This is now set at 0.5 ppb of the daily diet. The "Points" also introduces the concept

of using surrogate contaminants for assessing the efficiency of a recycling process to remove contaminants and highlights good source control of materials and consumer education as major factors contributing to the successful use of recycled plastic for food-contact applications. CFSAN personnel have demonstrated the utility of calculations based on Fick's Law for evaluating contaminant migration from recycled polymers into food, and scientists at NCFST are making progress in their work on surrogate contaminant analysis and are assessing the effectiveness of various steps in a recycling process to remove contaminants while maintaining the functionality of the recycled material. An update of the "Points," which would include more discussion on functional barriers and would reflect the change from 1 ppb to 0.5 ppb of dietary exposure for a contaminant, is being contemplated.

The agency will continue to consider additional requests for food-contact uses of recycled polymers on a case-by-case basis. The industry must still meet its burden to ensure that recycled plastic is, as the CFR requires, "of a purity suitable for its intended use."

#### Literature Cited

1. Anon. *Consum. Rep.* **1994**, *59*, 91-101.
2. Lampo, R.; Finney, D. *ASTM Standardization News* **1993**, *22*, 36-45.
3. Anon. *Mod. Plast.* **1994**, *71*, 73ff.
4. Hoffmann, B.L.; Nowell, L.H. *Food Drug Cosmet. Law J.* **1990**, *45*, 615-621.
5. Thorsheim, H.R.; Armstrong, D.J. *CHEMTECH.* **1993**, *23(8)*, 55-58.
6. Begley, T.H.; Hollifield, H.C. *Food Technol.* **1993**, *47(11)*, 109-112.
7. Komolprasert, V.; Lawson, A. "Effect of Aqueous-Based Washing on Removal of Hydrocarbons from Recycled Polyethylene Terephthalate (PETE)," Proceedings of the Annual Meeting of the Society of Plastics Engineers, May 1-5, 1994; Society of Plastics Engineers: San Francisco, CA, **1994**; *3*, 2206-2209.
8. U.S. Food and Drug Administration. *Fed. Regist.* **October 12, 1993**, *58* (195), 52719-52729.
9. Rulis, A.M. In *Risk Assessment in Setting National Priorities*; Bonin, J.; Stevenson, D., Eds.; Plenum Publishing Corp.: New York, NY, **1989**, pp 271-278.
10. U.S. Food and Drug Administration. *Recommendations for Chemistry Data for Indirect Food Additive Petitions*; Office of Premarket Approval: Washington, DC, **1988**.
11. National Food Processors Association (NFPA) and Science in the Public Interest (SPI). Letters of March 17, **1992**, from the Law Offices of Keller and Heckman, Washington, DC, to Director, Division of Food and Color Additives, CFSAN, FDA; NFPA and SPI: Washington, DC, **1992**.
12. Crank, J., *The Mathematics of Diffusion*, 2nd Ed.; Oxford Press: London, **1975**.

RECEIVED July 24, 1995

## Chapter 31

# Recycling of Polymers for Food Use: A Current Perspective

George D. Sadler

**Illinois Institute of Technology, National Center for Food Safety and  
Technology, 6502 South Archer Road, Summit-Argo, IL 60501-1933**

Popular conviction holds that discarded food containers should be recycled into new food containers. However, special technical challenges accompany the recycling of polymers into containers for food-contact use.

The FDA, State and International regulators approve of the environmental objectives of recycling. However, they are concerned with the unknown impact contaminated polymers might have on consumers. Proving the safety of recycled polymers poses many technical problems. The contamination frequency of recycled materials is difficult to establish, the degree of interaction between post-consumer contaminants and plastics is not well documented and the rate of contaminant migration from second generation containers is only known for relatively few post-consumer contaminants. Commercial technologies exist which either answer these concerns or make them irrelevant. Unfortunately, the expense of these technologies often drives recycled resin costs near or even beyond the cost of virgin resins. There are many economical options for recycled resins besides food-use to food-use container applications. The ultimate fate of recycled polymers for food contact will depend on development of more economical recycling technologies, a better understanding of the behavior of contaminants in recycled materials, competitive pressures from rival technologies and the evolving regulatory climate for recycling.

A public skepticism of science began to emerge in America during the late 1960's. The technological zeal which had taken men to the moon was perceived to be arrogantly unconcerned with environmental quality here on earth. This criticism brought about serious self-analysis among many professionals in the fields of science and technology. The public also became more conscious of their own waste disposal habits and began to acknowledge some personal responsibility for the decline in environmental quality. Over the years, this increased awareness has fostered a growing sense of environmental stewardship and cooperation among consumers, scientists and American industry. Recycling in its present form reflects inputs from

0097-6156/95/0609-0380\$12.00/0  
© 1995 American Chemical Society

each of these groups. However, the public perception of recycling is often simplistic. Consumers tend to view environmental issues through examples which are close to their own experience. As a result, the public is sometimes impatient to see their idealized environmental vision achieved without understanding all the intricate arguments these ends would require. For example, consumers are interested in seeing recycled polymers (both natural, as in paper; and synthetic plastics) in food containers. History has taught them that aluminum and glass can be safely recycled into new containers. However, the recycling of plastics for food contact involves many complex issues which are not casually apparent to most consumers.

### **Recycling Problems Unique to Polymers Intended for Food Contact**

Regulators consider aluminum and glass to be recycle-safe since microbial and post-consumer organic contaminants are destroyed by the extreme processing conditions required to form new containers (1). Microorganisms are a potential problem in paper; however, microorganisms are destroyed by elevated temperatures required in plastics recycling. Fortunately, drying rollers destroy vegetative organisms in paper. The low water content of dried paper inhibits germination of surviving thermostable spores. Although off-odors may follow spore germination in water water damaged paperboard or paperboard stored under high humidity, as yet, no pathogenic outbreaks have ever been traced to contaminated paper products. This is probably due to FDA's restriction of recycled paperboard to dry foods, the use of coatings on the food-contact surface of recycled paperboard and the general absence of aerobic sporeforming pathogens associated with paper recycling processes.

Paper and plastics also differ from metal and glass in their ability to absorb detectable quantities of organic compounds. As discussed in their chapter, Kuznesof and Vanderveer indicated that carryover of non-approved adjuvants and post-consumer adulterants concerns the FDA. Regulators fear pesticides, lawn treatment wastes, automotive fluids, cleaning compounds and other domestic chemicals absorbed as a result of post-consumer storage abuses may survive recycling and ultimately emerge from food-contact articles made from tainted recycled materials. When first approached with industry interest in recycling post-consumer polymers for foods use, the FDA expressed a pessimism that such approval would ever be possible due to the complexity and lack of control inherent in the post-consumer recycling process. However, several forces softened this position. Significant breakthroughs were made in processing technology. The FDA extensively reviewed toxicology-based studies to understand what general contaminant level would be safe in the food supply (2). The NEPA (The National Environmental Protection) act dictated that all government agencies should endeavor to maximize recycling in an effort to preserve natural resources (3). Such factors provided the FDA with the scientific and doctrinal motivation to seriously address recycling.

### **FDA Guidelines for Reviewing Recycled Polymers for Food Use**

Developing a suitable FDA test protocol for assessing the safety of recycled polymers was not a straightforward task. Even if it were possible to develop an authoritative list of potential post-consumer contaminants, it would be a clearly



intractable undertaking to study the interaction of all these contaminants with a given recyclable polymer. In order to simplify the process, the FDA developed an informal guidance document entitled, "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations" (1). Informally, the guideline has become known as the "Points to Consider" document. The guideline separates post-consumer contaminants into 4 broad groups based on volatility and polarity. An organometallic compound was also selected to model heavy metal-containing contaminants. These 5 compounds serve as surrogates to model the behavior of the universe of post-consumer contaminants in plastics. Many of the surrogates which the FDA has allowed in submissions for letters of non-objection are reported in the chapter by Kuznesof and Vanderveer.

The FDA's review of toxicological data for hundreds of compounds indicated that non-carcinogenic compounds present below 1 ppb in the food supply would pose an insignificant threat to public health and; therefore, need not be regulated by the FDA. In 1994, the 1 ppb threshold was lowered to 1/2 ppb to provide additional assurance of safety. This critical cutoff has come to be known as the "Threshold of Regulation" (2). Therefore, the FDA would provide letters of non-objection for recycling processes if they could be shown to remove all surrogates to sub-threshold levels.

In the absence of extensive field data, the "Points to Consider" guideline assumes all recycled polymers are adulterated with post-consumer contaminants, and that all entrained contaminants migrate from second generation containers into the food. It is difficult to obtain comprehensive information on the frequency of post-consumer contamination of polymers. Statistical models would require large volumes of data from many vendors to assess geographical and seasonal influences on post-consumer contamination. As a result, 100% adulteration assumption proposed by the "Points to Consider" document is difficult to challenge on statistical grounds. However, since the issuance of the "Points to Consider" document, the FDA has become more familiar with the character of recycling streams. The agency now feels a 50% contamination assumption can be used and still provide sufficient conservatism to protect consumers.

The 100% migration assumption is less difficult to challenge. Extraction studies with food simulating solvents may be performed when the 100% migration assumption is believed to be extreme. Under certain circumstances, the FDA is willing to consider model migration data without the need to perform actual extractions. The chapter by Begley and Hollifield describes an approach for predicting the actual level of migration from packages into foods for monolayer and bilayer materials assuming the diffusion coefficient of the compound in the polymer is known.

### **Recycling Status of Principal Polymers Used in Food Containers.**

**Paper Recycling.** Paper does not currently have its own "Point to Consider"-type recycling guideline; however, paper-based studies will likely borrow many "Point to Consider" elements, possibly with additional recommendations to assure that pathogenic microorganisms do not survive recycling. Little is known about levels of

environmental contamination in recycled paper. However, the behavior of organic and inorganic compounds with paper can be inferred from paper chromatography. Metallic cations are strongly bound to cellulose. Paper tends to bind organic cations more strongly than organic anions; however, the character of the organic moiety often eclipses any ionic contribution. Compounds with limited water solubility have low mobility in paper chromatography when aqueous mobile phases are used. Therefore, recycled paper would likely bind heavy metal cations and retain non-polar, non-volatile compounds.

Title 21 CFR §176.180 has allowed recycled paperboard as packaging for dry foods under the assumption that dry foods do not provide a practical medium for migration. Title 21 CFR §176.260 permits recycled paperboard for fatty and aqueous foods provided no "poisonous or deleterious" substances are transferred from the package to the food. However, the absolute absence of "poisonous or deleterious" materials is difficult to prove.

**Plastic Recycling Overview.** In his chapter, Tacito has reviewed many of the important technological benchmarks in the history of plastics recycling since its inception with acrylonitrile in 1975. To date, most of the letters of non-objection for broad-use recycled resin has been for poly(ethylene terephthalate) (PET), the polymer in 2 liter soda bottles. PET's clear identification with soft drink bottles, its large commercial volume, and its high value have made it a logical target for recycling. High density polyethylene (HDPE) shares many of the advantages of PET. It is explicitly associated with plastic milk containers and laundry detergent bottles. It also claims commendable disposal volumes. However, its lower value and greater tendency for contaminant absorption makes it less attractive for recycling than PET.

Foamed polystyrene also shows promise for recycling. Its low density makes separation from other polymers straightforward. However, it is very susceptible to interaction with petroleum-based products and is; therefore, a good candidate for post-consumer contamination. The FDA has recently granted the first letter of non-objection for recycled foamed polystyrene. Polystyrene was collected from a school lunch environment with sufficient safeguards that FDA was convinced opportunities for post-consumer contamination were minimal.

Limited recycling options are forcing the container market away from multilayer containers made from heterogeneous materials. Polymers, such as poly vinyl chloride (PVC) are also being de-emphasized due to their incompatibility with PET recycling. De-emphasis of laminates and incompatible polymers is not a criticism of the commercial virtue of these technologies. In many cases, they provide the optimal solution to food packaging problems. The sacrifice of these technologies demonstrates the importance container manufacturers attach to consumer and legislative demands for recyclable containers.

Future innovation will inevitably bring laminants and de-emphasized plastics back into the mainstream. Currently, cost effective separation of layers in multilayer constructions is being developed for some composites. In the chapter by Lemieux, a method for separating foil from paper/foil/polyethylene laminants was described. The procedure provided recovery of both aluminum and organic components. PVC

manufacturers are supporting PET/PVC separations research and establishing an information network to facilitate PVC recycling (4). The safety of polypropylene for food-contact use is also currently under study.

### **PET Recycling**

**Chemically Recycled PET for Food Contact**-- Currently, recycled PET deemed suitable for food-contact by the FDA come from fairly expensive recycling processes. As discussed in the chapter by Oblath and Nowak, and the chapter by Beyer, Myers, and Gage, early FDA letters of non-objection for recycled material were issued to virgin PET producers for such chemical processes as methanolysis and glycolysis. Chemical processes reduce PET to its monomers or low molecular weight oligomers. Contaminant removal is much easier from chain-fragmented structures than from the intact PET polymer. The FDA has adopted EPA recycling terminology (5). Under this nomenclature, the term tertiary recycling has been assigned to chemical recycling processes.

In their chapter, Pierce, King and Sadler show that thermal extraction can identify a complex array of chemical constituents in PET which often reveal detailed clues to the use, treatment and disposal history of the polymer. However, as yet, no consistent differences have been identified between tertiary recycled and virgin PET resins. Unfortunately, the cost of tertiary recycled resin often exceeds that of virgin material. The added cost is usually less than 1¢ per 2 liter beverage container. However, this additional cost is justifiable when recycle content is demanded by law or if environmentally sensitive consumers are willing to absorb the extra cost out of a conviction for recycling. Pepsi and Coke have both introduced soda bottles containing tertiary recycled PET. However, consumer buying practices appear to indicate that price is a more important issue than recycle content in their selection of carbonated beverages.

**Physically Recycled PET for Food Contact** --The future challenge of recycling will be to exploit progressively cheaper recycling streams. Of necessity, this means dealing with less controlled sources of recycled resin and employing less extreme recycling processes. Physical recycling is better suited to these objectives than chemical recycling. In physical recycling, the polymer is cleaned, remelted and formed into a new container. Depending on the polymer, additional steps such as crystallization and solid stating may be added to improve the performance of the finished resin. Under EPA/FDA nomenclature, post-consumer polymers which have been physically recycled are classified as secondary recycled materials. Secondary recycled polymers can be used in food containers, if recycling treatments adequately remove contaminants or if a functional barrier is used between contaminated resin and the food. A functional barrier may be a foil, a virgin layer of the polymer or a totally different barrier material. Its purpose is to limit migration from contaminated polymers to levels below the threshold of regulation.

Johnson Controls, Inc. (JCI) has recently received the first FDA letter of non-objection for bottle-grade PET suitable for monolayer containers at all use temperatures approved for virgin resin. JCI's proprietary process appears to combine

August 10, 2012 | <http://pubs.acs.org>  
Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch031

high temperature treatments, special cleaning steps and solid stating to optimize contaminant removal from the recycled polymer. The cost of JCI resin is projected to be similar to virgin material.

Many recyclers view JCI's contribution as both a technical and moral breakthrough for recycling, since it shows that secondary recycled resins can, by some process, be made suitable for food use. Based on the positive review of JCI's submission, several recyclers are either conducting or planing "Points to Consider"-based studies on their own secondary recycling processes. A growing availability of secondary recycle food grade PET is inevitable.

There is experimental evidence that food-contact PET resins may be obtained through recycling processes which do not vary dramatically from those in common use. In their chapter, Komolprasert and Lawson suggest that washing and drying removes 97-99% of most surrogates used in their "Points to Consider"-based recycling study. In themselves, these high levels of removal were not adequate to reduce contaminants below "Threshold of Regulation" values assuming 100% migration from the package into the foods they contain. However, migration studies indicate polymer-entrained surrogates generally do not migrate into foods at super-threshold amounts. Although rare exceptions can be found, these tend to be irrelevant to likely routes of post-consumer contamination and include such extreme cases as treatment of PET with neat solvents which swell the polymer.

Thermal extraction studies of Pierce, King and Sadler indicate efficient volatile stripping above 160°C. Essentially all beverage-related and post-consumer volatiles were removed after 3 minutes of thermal exposure. This temperature is similar to that used to dry PET and is much lower than solid stating temperatures. Imaginative engineering of thermal treatments should effectively strip volatile contaminants from recycled PET. Unfortunately, desiccant driers recirculate air. Although water is stripped from recirculated air with adsorbents, thermally liberated volatiles typically are not. Unless volatiles are removed, they will be redeposited as a surface coat over the polymer bed. Migration models suggests that restructuring drying and solid stating steps may be sufficient to produce resin suitable for food use even at extreme levels of contamination.

**Multilayer Technology**-In 1993, the FDA provided a letter of non-objection to Continental PET Technologies for the use of a trilayer PET container having secondary recycled material as a middle polymer layer. The internal food-contact layer serves as a functional barrier to contaminant migration from the bulk recycle layer in the center of the container wall.

Equipment costs for trilayer containers are greater than for prevailing monolayer technology. Monolayer equipment typically has double the cavity number of trilayer equipment. However, extensive tests with the trilayer container indicate that the recycled layer does not require solid stating to produce a suitable carbonated beverage container. Secondary recycled resin for monolayer applications require solid stating to bring intrinsic viscosity to a level suitable for containment of carbonation and optimal bottle forming properties (6). Solid stating is an expensive process requiring up to 30 hours of treatment at 220° C in a vacuum or vacuum/inert

gas environment. Therefore, the resin cost for secondary recycled PET for trilayer applications is potentially less expensive than resin for secondary or tertiary recycled monolayer bottles. Trilayer containers have the greatest potential in countries with high virgin PET costs and little current investment in monolayer equipment.

**Recycled Polymers and Food Quality.** Although an FDA non-objection letter may provide reassurance that a recycled polymer has been rigorously reviewed for food safety, it does not address quality issues. PET recyclers believe that post-consumer contamination with hazardous materials is a relatively rare event. However, bottles will inevitably be contaminated with flavor compounds, label adhesives and processing detergents. Comprehensive tests are currently underway to assure that quality-related migration defects such as flavor and odor transfer are not an issue with recycled PET resins which have passed FDA muster for food-contact. The trilayer container's virgin food-contact layer would favor low flavor and odor migration.

### Recycling of HDPE

Although most FDA letters of non-objections for the broad use of recycled polymers have been for PET, there has been considerable interest in recycling polyolefins. The FDA has approved polyolefins for grocery bags and shipping crates. However, the FDA has not approved polyolefins for direct food-contact applications. The National Food Processors Association (NFPA) has conducted a "Points to Consider"-based study with HDPE. The NFPA expanded the surrogate selection to encompass a broad range of solubility parameters. In their chapter, Allen and Blakistone indicated that surrogates with solubility parameters similar to those of HDPE were not removed below "Points to Consider" target values, assuming 100% migration into a food.

Unlike PET, HDPE recycling does not experience sustained periods with high processing temperatures. Therefore, thermally-driven contaminant removal is much lower than with PET. The possibility that moderate engineering modification might reduce contaminant concentration below "Threshold of Regulation" levels does not appear as likely with HDPE as it does with PET. However, the possibility that added processing steps at elevated temperatures might produce resin suitable for food contact should not be overlooked. In general, the migration rate of organic compounds in HDPE is much greater than with PET. Therefore, compounds in HDPE are potentially easier to remove. Also, the true frequency of contamination is still unknown. Allen and Blackistone indicate hydrocarbon "sniffers" rejected only 0.3 to 1% of PET bottles as contaminated. The majority of sniffer rejections come from containers with exotic beverages, not harmful post-consumer contaminants. Therefore, even the cited rejection frequency may be high. Once the true rate of contamination is known, HDPE recycling may appear more favorable. The solubility parameters for highly retained compounds are also much lower than the solubility parameter for water. This incompatibility suggests compounds which interact strongly with HDPE are not likely to be extracted by aqueous foods. Until migration

and exposure issues are fully understood and additional processing options are explored, it would be premature to dismiss HDPE recycling as inevitably impractical for food-contact articles.

### **Role of Local and International Law on Food-Contact Recycling**

The FDA is not the only regulatory agency which will influence the fate of plastics recycling for food applications. State legislation may have a more profound impact on the evolution of recycling for food use than the federal government. Unlike the federal government, several states have placed mandatory requirements on recycling (7). In California and Oregon, food containers will ultimately be required to achieve an imposed recycle content which will escalate over time. Virgin markets would be jeopardized if recycling benchmarks are not achieved.

Barring such legislation, recycling for food-contact use would not be necessary. There are many non-food end uses for recycled material. Currently, food-grade recycled polymers constitute only a small portion of the food-contact resin market and there are high demands on existing reserves of recycled materials.

The recycle content dilemma is characteristic of a broader problem confronting the packaging industry. Packages rarely have the flexibility to tailor their products to the regulatory peculiarities of a single region. Therefore, polymers must be processed to the standards of the most extreme state laws. As a result, state laws take on the weight of national legislation which may, as in mandatory recycling rates for food-contact containers, be antagonistic to the USFDA position which demands rigorous guarantees that polymers are safe for food use. State laws will become further empowered as efforts to decrease the size of the federal government continues.

International laws may also influence food-use polymer recycling . Conflicting safety validation philosophies exist among America's foreign trading partners. These conflicts pose potential trade burdens to American products packaged in recycled materials. Dialog with European regulators is underway and some progress has been made in harmonizing validation protocols across the Atlantic. As indicated in the chapter by Bayer, Myers and Gage, the European Union, like the United States, is struggling to understand all the safety ramifications of recycling. As a result, many recycling issues are still under debate. US trading partners in the Pacific have been more willing to embrace FDA policy and accept technologies which are FDA approved.

### **Non-Food-Use Polymer Applications: Their Impact on Resins for Food Use**

The ultimate destiny of food-use recycling will also be shaped by the public viewpoint on what constitutes acceptable disposal practices for discarded polymers. Incineration and landfilling have historically been denounced as unacceptable. However, there appears to be a slowly growing acceptance of incineration with energy recovery as a means of polymer disposal. Incineration can provide very

August 10, 2012 | <http://pubs.acs.org>  
Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch031

clean, high BTU fuel with limited need for sortation or treatment of the mixed polymer streams. It also appears that the much publicized crisis over disappearing landfill space was overly pessimistic (8). Low disposal costs may divert raw materials away from recycling end-uses and into landfills. Technologies which crack polymers back into oil are being explored. Although, currently the technology is prohibitively expensive, it has the appeal of providing carte blanc freedom to produce any petrochemically-based products from the recycle stream. All end-use options provide competitive pressures to food-use recycled polymers. Technologies which reduce the cost of high purity recycled resins help establish a secure future for food-application resins. Sortation technology including hydrocarbon sniffers and spectral scanners, will help produce recycled resins with the highest standards of performance quality and compatibility with foods.

The future for food-contact recycled polymers is bright. Advances will be episodic as technological innovation leap-frog over current barriers in regulations. Ultimately, the current crazy quilt of local recycling laws will evolve into a more uniform body of recycling policy. Although PET and HDPE are the clear favorites in the recycling game, it is too early to determine if there will be any lasting losers. It is certain the future pace and direction for food-contact recycling will depend upon competitive pressures within the resin markets, consumer interest in recycling, technological innovation and legislative attitudes.

### Literature Cited

1. FDA. Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations. Food and Drug Adman., Center for Food Safety and Applied Nutrition (HFS-245), Washington, DC 20204.
2. Machuga, E. J.; Pauli, G. H. and Rulis, A. M. *Food Control*. 1992. Vol 3, pp. 180-183.
3. National Environmental Policy Act. Section 101(b)(6).
4. Ryder, R.G. and Klöckner, R. *Plastics Recycling: Technology Charts the Course*. Progress in PET recycling. Plastics Recycling Conference Proceedings. A Technical Conference Sponsored by the Recycling Division and the Chicago Section of the Society of Plastics Engineers. November 3-4, 1994, Schaumburg, IL pp 87-99.
5. EPA. 1991. Environ. Protect. Agency, Fed. Reg. 56:49992.
6. Hayward, D.W. *Plastics Recycling: Technology Charts the Course*. Utilizing Post-consumer Recycled PETE in Your Process: An Evaluation of Flake Versus Pellets. Plastics Recycling Conference Proceedings. A Technical Conference Sponsored by the Recycling Division and the Chicago Section of the Society of Plastics Engineers. November 3-4, 1994, Schaumburg, IL pp. 111-120.
7. NFPA. *State Legislative Update*. National Food Processors Association, 1401 New York Ave, NW, Washington, DC 20005. 1993, vol 3, pp 1-6.
8. Waste of a Sort. Wall Street Journal. Tuesday, January 19, 1995.

RECEIVED August 2, 1995

## Chapter 33

# Protocol To Verify Contaminant Removal from Postconsumer Poly(ethylene terephthalate)

E. N. Nowak<sup>1</sup> and R. M. Oblath<sup>2</sup>

<sup>1</sup>Product Safety and Compliance, Polyester Business, and <sup>2</sup>Polyester  
Technical Center, Shell Chemical Company, 130 Johns Avenue,  
Akron, OH 44305

This paper discusses a test protocol used to verify that model contaminants were efficiently removed from intentionally contaminated PET by Shell's process for manufacturing REPETE polyester resin. The first step of the protocol consisted of developing a model for post-consumer contamination. The model included: identification of contamination routes, identification of potential contaminants, selection of model contaminants, and estimation of the level of contamination. An experimental protocol was then developed to simulate the model and data was developed to assess process efficiency.

In December, 1991, Goodyear's Polyester Division, now Shell Chemical's Polyester Business, obtained from FDA a "letter of no objection" to the use of REPETE polyester resin for manufacturing food packaging (*Rulis, Alan M., FDA, personal communication, December 6, 1991*). REPETE is a registered trademark for PET made from post-consumer recycled PET via Shell's tertiary recycle process. FDA's decision was based on their review of data generated at our facilities over a two year period through a protocol developed to validate the safety of our process for manufacturing REPETE from post-consumer recycle.

Shell's process takes advantage of the unique chemistry of PET. Before discussing our protocol, it will be useful to briefly review the chemistry and manufacturing process for PET made by the acid route (Figure 1). In a vessel heated to greater than 260°C and operated under positive pressure, the acid and glycol are reacted to form low molecular weight, low viscosity oligomers containing from two to ten repeat units. Water coproduced in the esterification is taken overhead.

The oligomers are then conveyed to a second vessel where, over several hours at greater than 270°C in the presence of catalysts, the molecular weight is increased by polycondensation. The reaction is driven by removal under high vacuum of ethylene glycol and small amounts of water.

0097-6156/95/0609-0404\$12.00/0  
© 1995 American Chemical Society



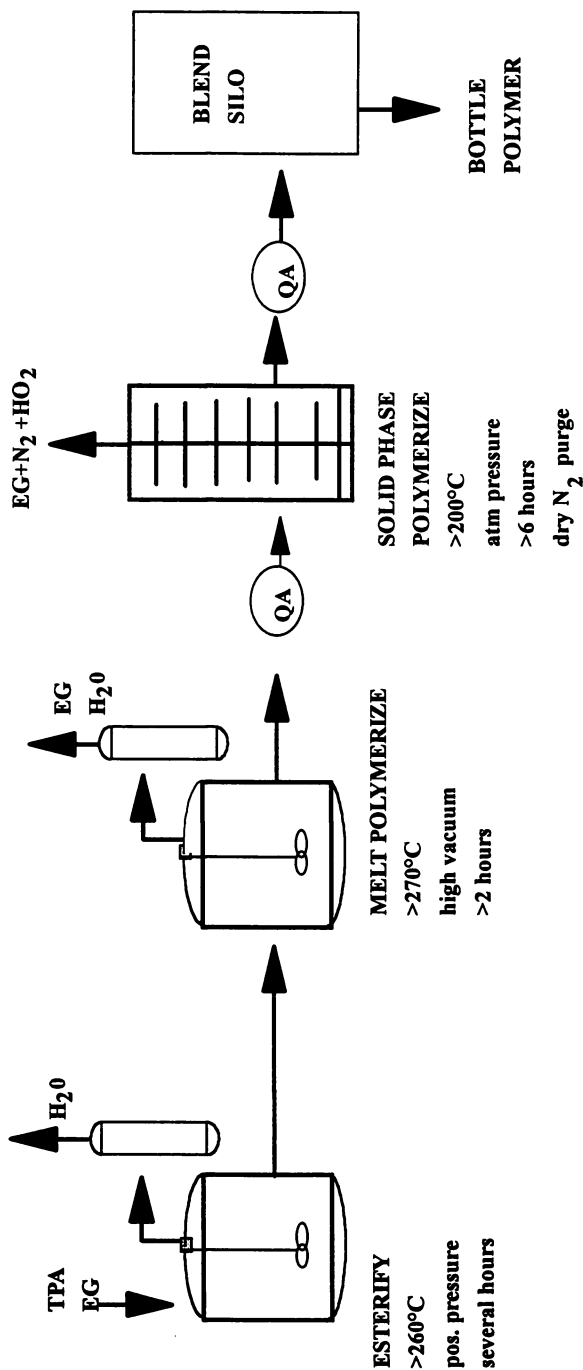


Figure 1. Shell's PET Polymerization Process (Reproduced with Permission from Reference 5).

The resulting polymer, containing from 100 to 120 repeat units, is discharged, cooled to ambient temperature and cut into pellets. The pellets are fed to a final polymerization vessel operated at temperatures below the melt point of the polymer. In this vessel, which may be operated either under vacuum or with a dry nitrogen purge, the molecular weight of the polymer is increased to the desired level over a six-hour period. The final polymer is then discharged to a certification vessel, subjected to quality assurance tests and then sent to inventory.

An inherent characteristic which makes PET uniquely suitable for closed-loop tertiary recycling is that the polycondensation (polymerization) reaction (Figure 2) is reversible. That is, if PET is heated in the presence of TPA and/or EG, the condensation reaction will reverse (depolymerize) with the monomers progressively cleaving the polymer chains, ultimately to low molecular weight oligomers containing from two to ten repeat units. This ability to depolymerize PET is the basis of Shell's process for manufacturing PET resins from post-consumer recycle.

Shell's process is shown, in part, in Figure 3. Although Figure 3 shows the fundamental depolymerization/repolymerization steps used in Shell's process, it should be noted that our process contains additional proprietary steps not shown in this schematic. The principal difference between the typical PET polymerization process depicted in Figure 1 and Shell's process for manufacturing REPETE polyester shown in Figure 3 is that our recycle process includes cleaned post-consumer flake as an additional raw material. During esterification, in the presence of TPA and EG, flake is depolymerized to low molecular weight oligomers. Any contaminants which may have absorbed into the polymer matrix due to consumer misuse are thereby released for facile removal during subsequent processing, including the proprietary elements of Shell's process. The mixture of oligomers is fed to the melt polymerization vessel where, under the conditions of high temperature and vacuum, REPETE resin is produced. The resulting purified melt polymer is finished through the normal processing steps.

When we began to design a protocol to evaluate tertiary recycle processes for producing PET suitable for food packaging, no guidelines were available to aid in protocol development. We believed that an appropriate protocol should be based on a holistic approach. That is, the recycle process was considered to begin when the container is delivered to the consumer and to include collection, sortation and flake cleaning as well as the subsequent tertiary processing. The first consideration, then, was to identify, by broad classification, the contaminants most likely to be found in the recycle loop. These contaminants, and the various steps in the recycle loop where they are removed from the stream, are shown in Figure 4.

Microbiological contamination is effectively removed by the hot caustic wash during flake cleaning. Any trace microbiological contamination is destroyed during subsequent processing in polymerization reactors which are operated at temperatures greater than those typically encountered in an autoclave.

Foreign materials, such as wood from pallets, aluminum from bottle caps, and glass are removed through the handling practices used in the collection, sorting and cleaning operations. Shell specifications for flake also limit these materials. Proprietary steps in Shell's process also effectively remove foreign materials.

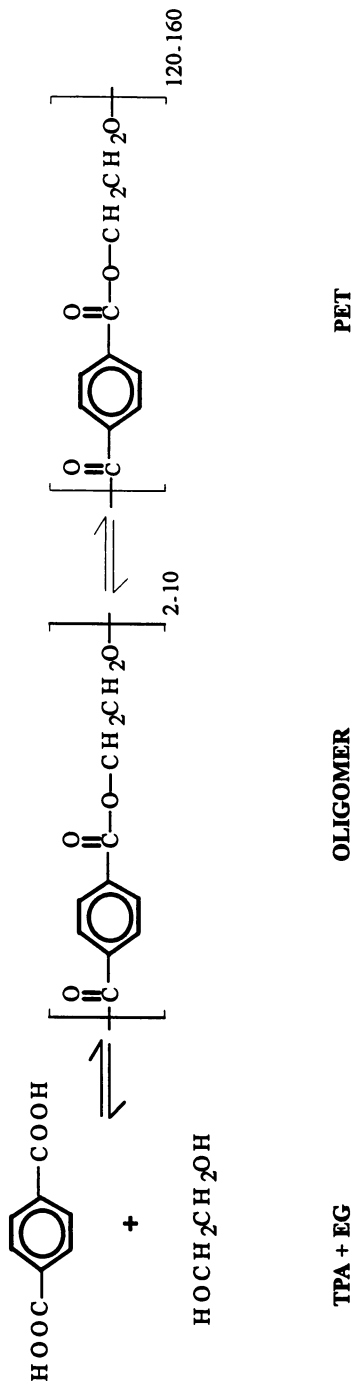


Figure 2. Reversible Polycondensation of TPA and EG to PET (Reproduced with Permission from Reference 5).

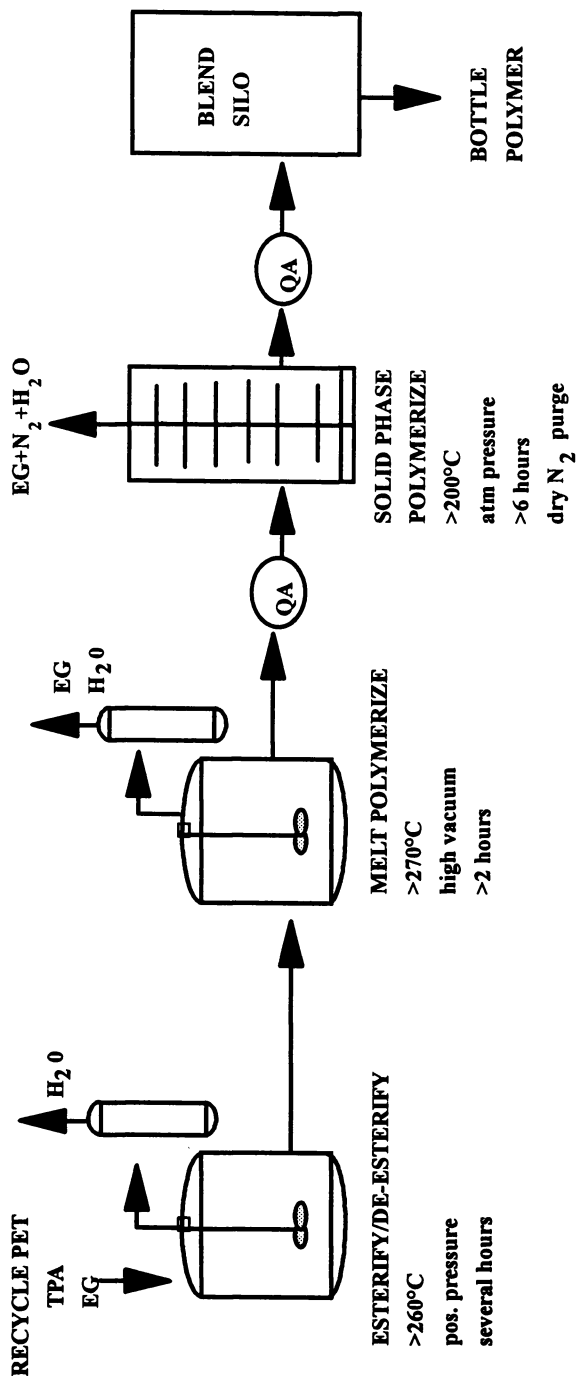


Figure 3. Shell's Tertiary Recycle Process (Reproduced with Permission from Reference 5).

<u>CONTAMINANT</u>	<u>REMOVAL STEP</u>
<b>Microbiological</b>	<b>Hot caustic wash, Shell process</b>
<b>Foreign material</b>	<b>Handling practices, Specifications, Shell process</b>
<b>Wood</b>	
<b>Aluminum</b>	
<b>Glass</b>	
<b>Mixed plastics</b>	<b>Sorting, handling, flotation, Specifications, Shell process</b>
<b>PP</b>	
<b>HDPE</b>	
<b>PVC</b>	
<b>Non-food residues</b>	<b>Sorting, washing, Shell process</b>
<b>Contaminants from consumer misuse</b>	<b>Shell process</b>
<b>Pesticides</b>	
<b>Petroleum products</b>	
<b>Metal Compounds</b>	

Figure 4. Removal of Potential Contaminants in Post-Consumer PET (Reproduced with Permission from Reference 5).

Mixed plastics, such as polypropylene from bottle caps, high density polyethylene from base cups and PVC from cap liners are removed by sorting, handling and flotation procedures. These materials are also limited by our specifications and are removed in the proprietary steps of our process.

Non-food residues, e.g., detergents, are removed by washing and in the depolymerization/repolymerization phase of our process.

Contaminants resulting from consumer misuse of containers present perhaps the greatest concern associated with use of post-consumer recycle in food packaging. Pesticides and heavy metal compounds, because of toxicological considerations, and petroleum products, because of broad accessibility to consumers, are of particular concern. These materials also present the greatest challenge to any recycle process. For these reasons it was felt necessary to clearly demonstrate, through validation studies, that our process has both the capacity and the efficiency to remove contaminants which may be present in the recycle stream as a result of consumer misuse.

In order to design an appropriate experimental program to validate a recycle process, it is necessary to first develop a model for post-consumer contamination. Development of a suitable model consists of four steps. First, the routes and scenarios

by which contamination is most likely to occur are identified. Second, the universe of potential compounds which may enter the recycle stream via those routes are identified. Third, model compounds representative of that universe are selected. Finally, the likely level of contaminants in the recycle stream is estimated. Based on this model, an experimental protocol can then be developed to simulate the model.

It is generally believed that by far the most likely scenario for contamination of the recycle stream is that involving secondary storage in beverage bottles. Both pesticides and petroleum products sold in bulk are likely to enter the stream via this route. In this scenario, a consumer would purchase a pesticide concentrate from a local garden supply store, make up a dilution for application to his garden and save the unused portion in a two liter PET bottle for application the following week. The implications of this scenario to further model development are that only pesticides sold as concentrates are included in the universe of possible contaminants and that time be allowed for contaminants to absorb into the matrix of the polymer.

Because of this "most likely" scenario, the universe of potential contaminants was limited to pesticides and petroleum products.

The universe of potential pesticide contaminants was developed for the model from several EPA documents, marketing research reports, and from information obtained from the National Pesticide Clearing House (*Hankes, Jill, Texas Tech, personal communication, 1990*) (1,2,3). From these documents, some 56 pesticides were identified. This list of 56 candidate compounds was narrowed to approximately 24 by applying the following selection criteria:

- Pesticides either banned by EPA or voluntarily withdrawn by the manufacturer were eliminated.
- Pesticides not generally available to the consumer (those regulated for use by professional applicators only) were eliminated.
- Pesticides sold as dusts or aerosols were eliminated. Only those sold as concentrates and requiring dilution for use were considered.
- Pesticides for which no sufficiently sensitive analytical methods existed (and were not likely to be developed) were eliminated.

This list of 24 compounds was loosely grouped by chemical class and further narrowed by considering:

- Toxicity. From among a group of similar compounds, the most toxic compound was selected.
- Stability. Likewise, the most stable among a group of structurally similar compounds was selected.
- Removal difficulty. The compound judged to be the most difficult to remove, based on boiling point, was selected from each group of structurally similar compounds.
- Breadth of usage. The compound which enjoyed the greatest usage, based on market volume and number of approved uses, was selected from its grouping.

This tentative final list was then reexamined to assure that any individual class of compounds was not unduly over-represented.

Through this selection process, the model compounds chosen from the identified universe of pesticides were those which met the usage criteria, were the most toxic

and most stable, were the most difficult to remove, and for which suitably sensitive analytical methods either existed or could be developed. While developing the model and test protocol, ongoing discussions were held with FDA (April 25, 1990; September 5, 1990; December 20, 1990), and it was concluded from those discussions that the Agency's general approach to validating a recycle process contained the following elements:

- 100% of the post-consumer flake should be contaminated with model contaminants.
- The contamination level should be 100 ppm.
- Model contaminants should represent:
  - Nonvolatile, nonpolar compounds; nonvolatile, polar compounds; volatile, nonpolar compounds; volatile, polar compounds; heavy metal compounds.
  - The detection limits should be 50-100 ppb.

Although FDA's general approach recommends the inclusion of a heavy metal surrogate, and, while this may be appropriate for other plastics, our model for post-consumer contamination indicated this was not the case for PET. Exclusion of a heavy metal surrogate from validation studies of recycle processes for PET is further supported by migration data. In migration studies conducted at 120°F for extended periods (30 days) with the very aggressive solvent, 95% ethanol, no migration of metallic PET catalysts (antimony and cobalt) was detected using a method having a lower detection limit of 3 ppb. In evaluations of cleaned PET flake supplied to our plant over a three-year period, no heavy metal contamination was detected by X-ray fluorescence having a detection limit of 2-15 ppb.

FDA's general approach to evaluation of recycling processes calls for measurement of residual contamination in the processed polymer using an analytical method having a lower detection limit of 50-100 ppb. To achieve a level of contamination in the incoming flake of 50 ppb would require a "spike" of contamination consisting of more than 1000 bottles, each contaminated with ca 200 ppm metal, a highly unlikely event.

Lastly, consumer accessibility to heavy metal containing products is extremely limited. Only two metal containing pesticides were registered for use in the US in 1987, and the registration was for use as a herbicide on cotton crops. Lead and mercury containing paints are being phased out and chromium based pigments are used only in industrial paints.

After consideration of all the above, including FDA's general approach, the following model compounds were selected for use in our validation studies: Lindane, representing a nonvolatile, nonpolar compound; Diazinon, representing a nonvolatile, polar compound; toluene, representing a volatile, nonpolar compound; chloroform, representing a volatile, polar compound; motor oil, representing a mixture of nonvolatile, nonpolar compounds; and gasoline, representing a mixture of volatile, nonpolar compounds. Having selected surrogates for the universe of materials which could enter the recycle stream through consumer misuse, the next step was to design experiments to simulate our model and evaluate the efficiency and capacity of our process to remove these surrogates. Two separate sets of experiments were conducted. In one set, Lindane, Diazinon, motor oil and gasoline were stored in PET bottles for two weeks at 40°C to allow ample time for absorption of the contaminants.

The bottles were then rinsed briefly with distilled water to remove gross surface contamination. The bottles were ground to flake and subjected to a washing sequence typical of that used in the industry. After washed flake was air dried at ambient temperature it was blended with uncontaminated flake at the 2-4% level. Blend levels were chosen to represent maximum levels of contamination estimated to be likely in post-consumer recycle using marketing data and other considerations which are beyond the scope of the present discussion. The blends were then subjected to our REPETE polyester process. Samples were analyzed for contaminants after the water rinse, after washing and after processing into REPETE polyester. Data are shown in Table I. Whereas washing in 2% caustic resulted in an approximate 50% reduction in contaminant level, the complete depolymerization/repolymerization process reduced the contaminant levels to below the detection limits shown in Table I.

Because of the multicomponent nature of motor oil and gasoline, analysis of these materials at extremely low levels presents a major challenge to analytical chemists. Although the analytical methods for motor oil and gasoline developed for these studies represented significant improvements in sensitivity over previously published methods, the limits of detection were not sufficiently low to provide adequate assurance of safety. The data for gasoline and motor oil however indicate the process has the capacity to remove fairly high levels of complex mixtures of volatile and nonvolatile compounds. According to the principles discussed in FDA's 'Guidelines'; toluene (nonpolar, volatile) and Lindane (nonpolar, nonvolatile) can be considered as surrogates for gasoline and motor oil, respectively (4). Based on this consideration, a separate series of experiments were conducted in which neat Lindane, Diazinon, toluene, and chloroform were individually and quantitatively added to separate samples of ground PET flake to produce 100 ppm in the flake. [Appropriate amounts of each contaminant were added directly to the flake at the time flake was introduced into the depolymerization vessel to assure that all the contaminant was introduced into the process.] The contaminated flake was then individually processed into REPETE polyester containing 50% recycle. Data from analysis of the resins after repolymerization, are shown in Table II. It should be noted that analyses were conducted after the melt polymerization step, not after the final solid-state polymerization step. In all cases, no residual contaminant was detected in the polymer after processing. The detection limits of the analytical methods used are also shown in Table II. It can be seen that the detection limits of the methods were as low as, and in some cases significantly lower than, those recommended by FDA.

Figure 5 describes the totality of our results, showing the range of volatilities on the Y axis and the reduction of contamination (on a log scale) along the X axis. Superimposed is the "de minimis" level of contamination which would result in a level of 0.5 ppb in the diet. This chart clearly shows both the capacity of our process to remove fairly high levels of contaminant (motor oil) and its efficiency in removing a broad range of compounds of varying volatility and polarity. These data clearly demonstrate the ability of this process to remove unrealistically high levels of model contaminants and its ability to produce for food packaging, suitably pure PET containing up to 50% post-consumer recycle.

During the course of these studies, data were developed to permit preliminary evaluation of four technologies of varying complexity: simple washing, with no further



**Table I. Concentrations of Contaminants in PET at Various Stages of Shell's Depolymerization/Repolymerization Process**

<b><u>Model Compound</u></b>	<b><u>After Storage</u></b>	<b><u>After Blending</u></b>	<b><u>After Wash</u></b>	<b><u>LOD</u></b>
<b>Lindane</b>	280 ppm	187 ppm	ND	25 ppb
<b>Diazinon</b>	40 ppm	23 ppm	ND	10 ppb
<b>Gasoline</b>	670 ppm	120 ppm	ND	5 ppb
<b>Motor Oil</b>	25,000 ppm	13,000 ppm	ND	25 ppb

Table II. Residual Contaminant Concentration in REPETE

<u>Model Compound</u>	<u>Contamination Level</u>	<u>After Repolymerize</u>	<u>LOD</u>
Lindane	100 ppm	ND	25 ppb
Diazinon	100 ppm	ND	10 ppb
Toluene	200 ppm	ND	100 ppb
Chloroform	200 ppm	ND	50 ppb

August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch033

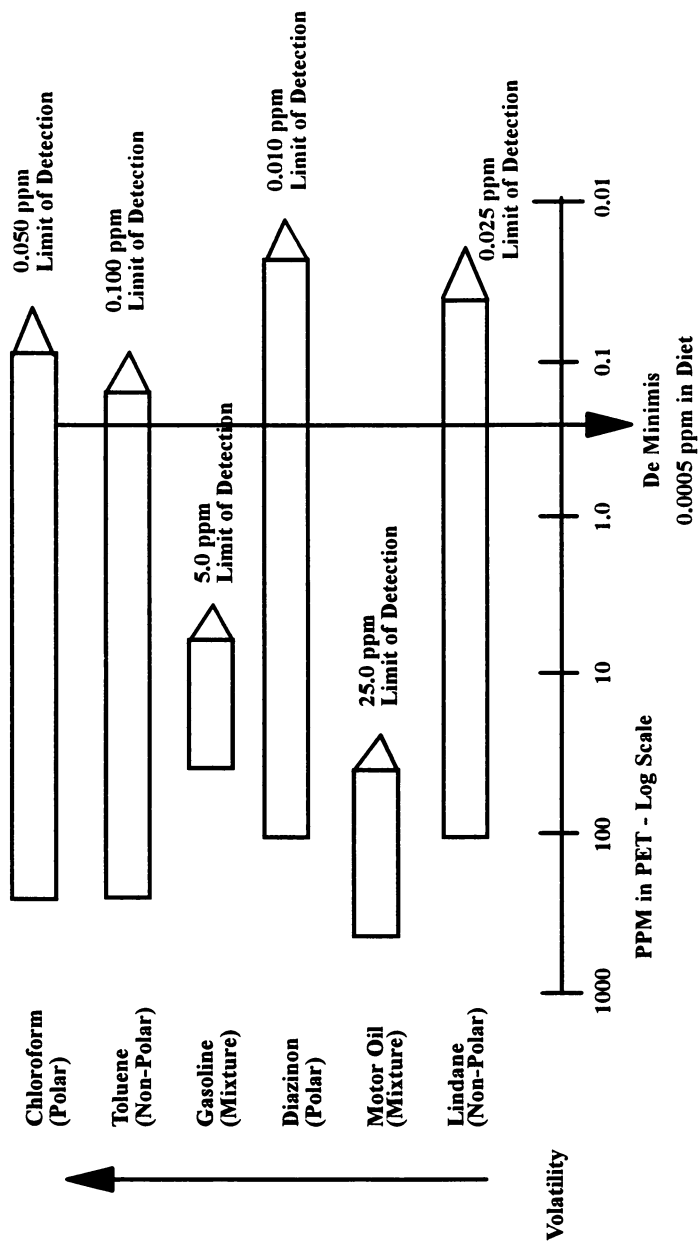


Figure 5. Summary of Efficiency and Capacity for Contaminant Removal (Reproduced with Permission from Reference 5).

**Table III. Concentrational Selected Contaminants in PET Following Processing Operations**

<u>COMPOUND</u>	<u>BEFORE WASH</u>	<u>AFTER WASH</u>	<u>AFTER BLENDING</u>	<u>AFTER REPELLETIZE</u>	<u>AFTER SOLID PHASE</u>
Motor Oil	24600	13300	333	270	45
Lindane	281	187	2	2	0.6

**All Values in ppm in PET**

SOURCE: From Proceedings of Recyclingplas VII Conference: Plastics Recycling as a Business Opportunity, Table II.

process; washing followed by melt extrusion into pellets; washing, pelletizing and solid state polymerizing; and, finally, washing followed by our depolymerization/repolymerization process. The results of these limited studies using motor oil and Lindane as examples are shown in Table III. In this case, bottles were exposed to the contaminants for two weeks at 40°C. The bottles were washed, ground, dried in air at ambient temperature and then blended with uncontaminated flake at a 2-4% level. The blended flake was then extruded and repelletized and, finally, solid stated. As can be seen from Table III, extrusion/pelletization was not effective in removing these contaminants. Although solid-stating did effect a fourfold reduction in these contaminants, the washing, pelletizing and solid-stating sequence used in this study was not adequate for producing resin of suitable purity for use in food packaging.

In summary, we have developed a model for post-consumer contamination and designed experiments to simulate the model. Through these experiments, data was developed which demonstrate the suitability of Shell's process for manufacturing for food packaging, polyester resin containing post-consumer recycle.

### Literature Cited

- (1) *Nonoccupational Pesticide Exposure Study (NOPES)*, EPA/600/3-90/003, 1990.
- (2) *National Household Pesticide Usage Study, 1976-1977*, EPA 540/9080-002, 1980.
- (3) Caldereni, Phil, *Pesticide Industry Overview*, CEH Marketing Research Report, Chemical Economics Handbook - SRI International, 1988.
- (4) *Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations*, Division of Food Chemistry and Technology, HFF-410, Center for Food Safety and Applied Nutrition, NS Food and Drug Administration, 1992.
- (5) Plastics Institute of America, Inc, Recyclingplas VII Conference, *Plastics Recycling as a Business Opportunity*, May 20-21, 1992.

RECEIVED April 14, 1995

## Chapter 34

# Assessing Reclamation Processes for Plastics Recycling

Bradford H. Allen<sup>1</sup> and Barbara A. Blakistone<sup>2,3</sup>

National Food Processors Association, <sup>1</sup>6363 Clark Avenue,  
Dublin, CA 94568, and <sup>2</sup>1401 New York Avenue, NW,  
Washington, DC 20005

A coalition between members of the National Food Processors Association and the Society of the Plastics Industry, Inc. has developed safety guidelines for considering the use of plastics in contact with food and a protocol useful in determining whether particular reclamation processes produce material safe for use in food contact applications. Based on the characteristics of volatility and solubility, the protocol recommends seven process monitoring surrogates (copper-2-ethylhexanoate, 2, 4-dichlorophenol, ethylene glycol, isopropanol, methyl salicylate, methyl stearate, and 2, 2, 4-trimethylpentane) which offer the greatest potential for extrapolation of the results to other potential contaminants of post-consumer recycle. The protocol has been proven with high density polyethylene using an incidental contamination rate of 1% in a laboratory scale model of a reclamation system. Results presented will verify utility of the analytical methodology, universal applicability of the surrogates to challenge plastics reclamation processes, and validity of the protocol for assessing the efficacy of such processes.

In 1991 the National Food Processors Association (NFPA) invited The Society of the Plastics Industry, Inc. to form a coalition that came to be known as the Plastics Recycling Task Force (PRTF). The objectives of the PRTF were to write guidelines for industry to consider when evaluating the safe use of recycled plastics and to prepare a protocol complete with test methods for assessing if possible or probable contaminants in post-consumer recycled (PCR) plastics could pass through a recycling process and remain a potential hazard to foods packaged in the recycled material. At the time the PRTF formed, little was known about PCR as a food packaging material. Environmentalists were urging its use with no special regard for the safety aspects of food packaging. That prompted NFPA to become pro-active in chemically evaluating high density polyethylene (HDPE) using surrogates of potential PCR contaminants.

<sup>3</sup>Corresponding author

0097-6156/95/0609-0418\$12.00/0  
© 1995 American Chemical Society

**Interim Guidelines for the Safe Use of Recycled Plastics in Food Packaging Applications (1).** This first guideline document released by the PRTF in January, 1993 provided producers and users of plastic packaging a framework within which they could begin to determine the safety and legality of using recycle for food packaging. The document thoroughly discussed the three key interrelated issues in considering PCR for a particular application:

- Source of the Recycle.** The ability to control the source of the feedstock used in a recycling process through the use of specifications or limitations on the character, origin, utilization, disposal, collection, sortation, storage, transportation, and handling of these materials so as to ensure the quality and compliance of the finished product;
- Efficacy of the Recycling Process.** The capability of the process, by which the feedstock is reclaimed, to remove or neutralize contaminants in the feedstock; and
- Conditions of Use.** The conditions under which the packaging is intended to be used, including food types, time and temperature conditions, and packaging structures.

**Federal Regulations.** PRTF was begun at a time when recycling was being aggressively promoted, but there was a paucity of scientific data on this subject. Further, no federal regulations governed recycled food packaging and still do not. The Federal Food, Drug, and Cosmetic Act (FFDCA) (approved June 25, 1936) and Food Additive Regulations (Sections 201 (s) and 409 of the FFDCA and 21 CFR Part 170, *et seq.*) are the regulations which apply to virgin materials and to recycled materials. Companies which wish to use recycled plastics to make new food packages must assure the safety of their materials within the context of the FFDCA and the Food Additive Regulations promulgated by the Food and Drug Administration (FDA). Although additional FDA regulations specifically permitting the use of recycled plastics are not necessary for such use to occur legally, companies must assure compliance with the existing statutory requirements and generic regulations and assure suitable purity of the package for use with food. Food packaging is federally controlled by issuing regulations permitting the use of stated substances which must meet technical specifications and limitations.

**Plastics Recycling Task Force.** The Technical Subcommittee began its work to formulate a protocol for evaluation of recycled materials within the context of the current regulations. The objectives of this committee were 1) to identify model compounds as surrogates for contaminants in post-consumer waste; 2) to develop and validate methodology to detect and quantify the surrogates in plastics; and 3) to test the analytical methodology on a laboratory-scale washing and extrusion operation.

## **Methods and Materials**

**Surrogate Selection.** The test plastic selected for evaluation was HDPE. Volatility and solubility parameter were the bases for selection of the PRTF surrogates because removal of a compound from plastics is most likely a function of the solubility

parameter characteristics of a compound, its concentration in the plastic, and its volatility. Volatility was also a parameter chosen by the FDA in surrogates they proposed in the federal document entitled, "Points To Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations." (2) The other FDA parameter was polarity which PRTF chose to express quantitatively by the Hildebrand expression, solubility parameter,  $\delta$  (3). The solubility parameter,  $\delta$ , was defined by Hildebrand as the square root of the cohesive energy density:  $\delta = (\Delta H_v/RT/V)^{1/2}$ . According to solubility parameter theory, the solubility of one chemical in another increases as the difference between their solubility parameters decreases (i.e. "like dissolves like"). Solubility parameter can be considered the "internal pressure" of the solvent. Although developed to predict mutual solubility of liquids, the theory has been applied with some success to predict solubility of liquids in polymers (3). Table I shows the surrogates selected covered a broad range of volatility and solubility parameters. The constants were taken from *References 4, 5, and 6* or calculated from other values in these texts by the PRTF.

**Table I. Vapor pressure and solubility parameter constants at 25°C for surrogates selected for the recycling study**

Surrogate	Vapor Pressure (Atm)	Solubility Parameter [ $\delta/(\text{cal}/\text{cm}^3)^{1/2}$ ]
copper-2-ethylhexanoate	NA	NA
2,4 dichlorophenol	$2 \times 10^{-4}$	10.5
ethylene glycol	$1 \times 10^{-4}$	16.3
isopropanol	0.06	11.6
methyl salicylate	$2 \times 10^{-4}$	10.6
methyl stearate	$< 7 \times 10^{-3}$	8.4
2,2,4-trimethylpentane	0.04	7.0
xylene ( <i>o</i> , <i>m</i> , and <i>p</i> )	$1 \times 10^{-2}$	8.9

In addition to selecting compounds on the basis of the above parameters and the need for extrapolation of test results to the broadest range of possible contaminants with reasonable scientific judgment, other criteria were considered such as the need for test compounds that can be easily detected and quantitated by analytical procedures and compounds that are relatively non-toxic to handle in the laboratory and in system testing.

The most likely contaminants in post-consumer waste are those that a consumer can purchase at retail. Table II compares the model compounds chosen by PRTF to categories of incidental contaminants that may be present in the home to contaminate plastics in the waste stream:



**Table II. Selected surrogates were chosen by the Plastics Recycling Task Force to represent categories of common household waste contaminants**

Surrogates	Contaminant Category
copper-2-ethylhexanoate	heavy metal bound into organic matrix; crabgrass killer
2,4-dichlorophenol	pesticides
ethylene glycol	antifreeze
isopropanol	paint strippers, household cleaners, wind- shield washer fluids
methyl salicylate	oil-based household cleaners
methyl stearate	fats and oils, motor oils, brake fluids, waterless hand cleaners
2,2,4-trimethylpentane	gasoline, paint thinners, charcoal lighter fluids
xylene*	aromatic fraction of gasoline, paint thin- ners, etc.

\*Xylene was not originally selected as a surrogate but became a surrogate because it was used to dissolve copper conjugate, dichlorophenol, and methyl stearate.

**Preparation of Flakes for Laboratory Reclamation Study.** HDPE flakes were supplied by Union Carbide (DMDC-6400) and were ground from virgin milk and water bottles. Seven (7) lots of 20 mil thick HDPE flake were soaked in each surrogate for 7 days at 23°C. Seven days represented the time frame in which at least 50% of the surrogate was absorbed (unpublished data) as summarized in Appendix I. Admittedly, more time is required to reach equilibrium, but the availability of Union Carbide's facility allowed for only one week of absorption. Flakes were analyzed following sorption but not prior to the reclamation step because interest was in proving the methodology, not in assessing the efficiency of the reclamation process for HDPE.

The polymer flakes were soaked in neat solutions except as follows:

- copper-2-ethylhexanoate      1% solution in xylene (w/w)
- 2, 4-dichlorophenol          10% solution in xylene (w/w)
- methyl stearate                10% solution in xylene (w/w)

Each individually soaked surrogate was blended at a level of 1% (w/w) with virgin HDPE flakes. This provided an effective contamination rate of 7%, which is believed to exaggerate the level of contaminated containers that can be expected to be found in the recycled waste stream. Evidence of excessive contamination rate came from company literature of Thermedics Detection, Inc. (Chelmsford, MA) which manufactures a sophisticated "sniffer" device to determine a broad range of contaminants in

post consumer bottles. Use of these devices in numerous plants around Europe has shown that, for returnable polyethylene terephthalate (PET) bottles, 3000 to 10,000 bottles per million (0.3 - 1.0%) are rejected by the devices indicating that the bottles may have been compromised by the consumer.

**Reclamation Process.** The laboratory scale reclamation system processed 50 g batches. Three runs were necessary to have sufficient flake for a single extrusion. Thus, 150 g comprised a single trial, and there were 7 trials. Exact wash conditions were proprietary to Union Carbide but included low and high temperature washings with and without surfactant. The processed flakes were melted and extruded through a devolatilizing extruder after washing.

**Determination of Extractable Levels.** Virgin pellets as well as flakes were analyzed for background presence of surrogates. Soaking flakes were removed at designated time intervals and were drained and blotted dry prior to analysis. Complete extraction procedures are in **Appendix II**. (Weighings were not done because of anticipated sorption of some surrogates at  $< 1 \mu\text{g}$ .) Copper-2-ethylhexanoate samples were ashed. The other HDPE samples were extracted to determine surrogate absorption concentrations using a Soxhlet extractor with aggressive solvents chosen for their miscibility with each surrogate. The solvents used for each surrogate are as follows:

<u>Surrogate</u>	<u>Solvent</u>
2,4-dichlorophenol	dichloromethane
ethylene glycol	acetone
isopropanol	acetone
methyl salicylate	dichloromethane
methyl stearate	dichloromethane
2,2,4-trimethylpentane	ethyl ether

**Analytical Methods.** Gas chromatography/mass spectroscopy (GC/MS) was used to detect the surrogates in the extracts except for copper. Copper conjugate was measured using atomic absorption spectroscopy (AA) after ashing the HDPE samples. Descriptive analytical procedures may be found in the **Appendix II**.

<u>Surrogate</u>	<u>Method</u>
copper conjugate	AA
2,4-dichlorophenol	GC/MS
ethylene glycol	GC/MS
isopropanol	GC/MS
methyl salicylate	GC/MS
methyl stearate	GC/MS
2,2,4-trimethylpentane	GC/MS
xylene	GC/MS

**Calculations.** Calculation examples are presented for surrogate absorption and analytical sensitivity.

**Surrogate Absorption.** The concentration of each surrogate in the solvent extracts was calculated from a standard curve of each surrogate. The amount absorbed in  $\mu\text{g}/\text{cm}^3$  was calculated by multiplying the concentration of surrogate in the extract by the volume of the extracting solution divided by the weight of the sample prior to soaking. The concentration per unit volume was calculated using the density factor of  $0.96 \text{ g}/\text{cm}^3$ .

The following is an example of the calculation:

$$\text{Amount absorbed } (\mu\text{g}/\text{cm}^3) = [(\text{Concentration in extract} \times \text{volume})/\text{wt}] \times 0.96 \text{ g}/\text{cm}^3$$

**Analytical Sensitivity.** The maximum level of surrogate contamination in food is 0.01 ppm because the FDA consumption factor for recycled HDPE is 5% and 5% times 0.01 ppm is the 0.5 ppb proposed FDA Threshold of Regulation value [58 Fed. Reg. 52719 (Oct. 12, 1993)] (to be codified at 21 CFR §170.39), the maximum estimated dietary intake amount allowed of a contaminant. If 10 g of food contact 1  $\text{in}^2$  of plastic and a 1  $\text{in}^2$ , 10 mil thick piece of HDPE weighs 0.154 g, then the sensitivity required to determine the concentration of surrogate in HDPE yielding 0.01 ppm in food is 0.65 ppm ( $0.01 \text{ ppm} \times 10 \text{ g}/\text{in}^2 \div 0.154 \text{ g}/\text{in}^2$ ). Analytical methods were sensitive to at least this amount.

## Results

Table III shows the remaining concentration of surrogates after washing, melting, and extruding into pellets. The initial concentration shown is 1/100 (1%) of the value obtained from extracting the flakes after soaking for seven days. Extraction was not performed on the flakes after batching.

A comparison of Trials 1 through 4 (set one of washing conditions) versus 5 through 7 (set two of washing conditions) in Table III shows little difference in the efficacy of the reclamation conditions to clean the surrogate-impregnated HDPE for most surrogates tested except copper conjugate. The latter was removed from HDPE following the reclamation process at the average rate of 4% under one set of reclamation conditions and 23% under the other. (Laboratory experiments [7] showed that efficiency of surrogate recovery from HDPE is nearly 100% for all surrogates except copper conjugate which was ashed.) Some surrogate concentrations were either totally removed or greatly reduced from HDPE under the trial conditions (Table III). These included ethylene glycol, which was completely removed, and isopropanol, methyl salicylate, and methyl stearate which were removed at a rate of 90% or greater during the process. Not as easily removed were dichlorophenol and xylene with percentages of extraction between 80 and 84%. The least removed were copper conjugate, removed between 4 and 23% depending upon reclamation condition, and trimethylpentane which was removed at slightly greater than 50%. To be in compliance with FDA Threshold of Regulation, the maximum remaining surrogate, assuming 100% migration of the surrogate into the food, cannot exceed 0.65 ppm. Six

**Table III. Summary of Protocol Confirmation Study showing surrogate extracted from pellets after reclamation washing Trials 1-7. Wash steps represented typical reclamation procedures. Trials 1-4 and 5-7 are replicates.**

Trial #	Surrogate							
	Copper Conju- gate	Dichloro- phenol	Ethylene Glycol	Isopropanol	Methyl Salicylate	Methyl Stea- rate	Trimethyl Pentane	Xylene
	Initial Concentration in ppm from 1 % soaked flake samples for each surrogate, 93 % unsoaked flakes							
	0.30	62	13	8	846	113	63	648
	Final Concentration After Reclamation							
1 <sup>a</sup>	0.21	9	ND <sup>d</sup>	0.2	82	8	36	132
2 <sup>a</sup>	0.39	10	2.1	0.3	74	8	30	119
3 <sup>a</sup>	0.23	10	ND	0.2	74	3	24	136
4 <sup>a</sup>	0.32	10	ND	0.2	72	3	32	118
5 <sup>aa</sup>	0.15	10	ND	0.2	72	2	18	126
6 <sup>aa</sup>	0.27	9	ND	0.3	73	1	34	114
7 <sup>aa</sup>	0.28	9	ND	0.2	75	2	38	106
8 <sup>b</sup>	0.09	ND	ND	ND	ND	ND	ND	ND
9 <sup>c</sup>	0.06	ND	ND	ND	ND	ND	ND	ND

Detection Limits in HDPE: copper-2-ethylhexanoate, 0.02 ppm; dichlorophenol, methyl salicylate, methyl stearate, and xylene, 0.40 ppm; ethylene glycol, 0.36 ppm; isopropanol, 0.32 ppm; and trimethylpentane, 0.24 ppm.

<sup>a</sup> and <sup>aa</sup> = Each are replicate trials.

<sup>b</sup> = Flakes from virgin HDPE bottles before spiking with surrogates

<sup>c</sup> = Virgin HDPE pellets

ND is "not detected."

(6) of the 8 surrogates exceeded this value. By this testing regimen, recycled HDPE cannot be safely used for food packaging. Validity of the analytical methods and the procedures for testing the HDPE has been proven by the laboratory reclamation study.

## Discussion

Chemicals having solubility parameters similar to HDPE were not removed during the recycling process modeled in this test to a sufficient degree as to demonstrate HDPE's suitability for direct contact food packaging. Trimethylpentane (iso-octane) is most similar to HDPE by comparison of the solubility parameter which is 7.0 for trimethylpentane and 7.8-8.3 for HDPE. Increasing percentages of removed surrogates in HDPE mirror the difference increase in solubility parameters of surrogate from that of HDPE as shown in Table I. In a large scale reclamation process test, the most important data to observe will be that of the surrogates methyl stearate, trimethylpentane, and xylene because their solubility parameters are most similar to HDPE.

Neither set of trial conditions cleaned the HDPE sufficiently in the laboratory reclamation system to consider recycled HDPE safe for use in food packaging. Because this work was intended to confirm the protocol, no other challenge conditions were considered. Logically, the lower the challenge concentration of surrogates in the HDPE initially, the lower the retained amounts in the recycle. But there may be an unacceptable level of contamination retained regardless of the initial concentration. A future question for exploration is the effect of challenge level on surrogate retained.

The results of the laboratory scale model reclamation process for HDPE, which was used to test the usefulness of the protocol, demonstrated the need for a case-by-case approach to the use of recycled plastics with food. This is because the model used was found to be inadequate in removing contaminant surrogates with solubility parameters similar to that of HDPE to the degree needed to demonstrate the capability of the process to produce resin suitably pure for direct contact food packaging. While the model recycling process did not remove sufficient contaminants, and there is no known published scientific data to show this can be done commercially for direct food contact situations, other processes may exist or be developed to meet removal requirements. Further experimentation is needed to remove surrogates to insignificant levels if excessive migration of unremoved residues to food will occur. Until such processes are validated as acceptable, use of recycled HDPE for food packaging must be reviewed on a case-by-case basis. The same is true, of course, with respect to any other recycled material where the same circumstances apply.

The analytical methodology and procedures used to assess the efficacy of recycling processes worked extremely well under test conditions. The method adequately demonstrated the levels of surrogate chemicals that remained in the laboratory-scale reclamation operation tested. The protocol is expected to work equally as well in evaluating a commercial HDPE operation. The PRTF work will be useful for companies in exploring the development of safe uses for recycled plastics in food packaging. For instance, the work has proven that the protocol for evaluating contamination removal from post-consumer HDPE is valid, the protocol is universally applicable, and the analytical methodology is appropriate. The formal protocol

followed during this laboratory scale trial and recommended for testing of commercial reclamation operations is outlined in Appendix III.

The PRTF project is a practical demonstration of the progressive steps industry is undertaking in solid waste management and in particular in facilitating recycling initiatives. The PRTF encourages plastics companies to make use of the Interim Guidelines and the Proposed Test Protocol to evaluate the suitability and safety of a specific reclamation process for the production of food grade HDPE.

## Appendix I

**Summary of Equilibration Study.** The Plastics Recycling Task Force (PRTF) is a coalition between the National Food Processors Association and the Society of the Plastics Industry which was encouraged by the Food and Drug Administration (FDA) in its development of methodologies sufficient to establish whether recycled plastics may be safely used in contact with food in compliance with the Federal Food, Drug, and Cosmetic Act. The PRTF accepted as its mandate: 1) the development of guidelines pertaining to the safe use of recycled plastics in food packaging and 2) the development of methodology that could be used to determine whether particular reclamation processes produce material suitable for use in food packaging applications. A subcommittee on methodology was established to carry out the PRTF mandate on methodology development. The subcommittee decided to proceed with a three phase approach using high density polyethylene (HDPE) as a case study:

*Phase One identified a set of surrogates representing, by virtue of their physical properties, substances reasonably expected to be found in the post-use waste stream that could contaminate food as a result of their presence in HDPE. Analytical methods appropriate to the individual surrogates in high density polyethylene (HDPE) are to be used to determine surrogate sorption as a function of time and the resulting equilibrium concentrations in HDPE.*

*Phase Two will measure the ability of the test protocol to quantitate the effectiveness of the reclaiming process in reducing the surrogate concentration to insignificant levels.*

*Phase Three will be done on a company-by-company basis depending on the reclamation process used and the intended use of the recycled plastic. If significant levels of the surrogates are found in the reclaimed HDPE and if significant levels still remain after fabrication of a test sample from the reclaimed polymer, extraction studies will be needed. Phase Three will involve determining migration characteristics of the surrogates in these test samples.*

Phase One work has been completed. The approach, consistent with FDA's suggestion, consisted of placing chemicals within a two dimensional matrix based on volatility and solubility. A number of surrogates were identified with the intent to

represent the universe of potential contaminants. By selecting compounds that covered a broad range of volatility and solubility parameters, the PRTF's intention was to achieve universal applicability for the methodology. The most likely contaminants in post-consumer waste are those compounds that a consumer can purchase at retail. A comparison of the chosen model compounds to substances that may be present in the home that could act to contaminate plastics in the waste stream is shown in Table II in the text.

Uptake of the surrogates was fairly rapid with 50% of the concentration of the chemicals in HDPE being absorbed in less than five days (Figures 1 and 2). Time required to equilibrate the surrogates was less than 20 days with the exceptions of ethylene glycol and the copper conjugate which required close to 50 days. A complete description of analytical methods developed as part of the study appears in **Appendix II**. The equilibrium uptake levels and the amount of time needed for equilibrium are reported in the following table:

Surrogate	Amount Absorbed		No. of days to equilibrium
	$\mu\text{g}/\text{cm}^3$	(ppm)	
xylene + ( <i>o</i> , <i>m</i> , and <i>p</i> )	105348	111000	2
methyl salicylate	96647	100674	2
methyl stearate	14911	15532	4
2,2,4-trimethylpentane	14688	15400	17
2,4-dichlorophenol	13015	13573	8
isopropanol	6202	6500	15
ethylene glycol*	1384	1393	49
copper-2-ethylhexanoate	29	30	42

+ Xylene was the solvent for copper-2-ethylhexanoate, dichlorophenol, and methyl stearate and therefore an incidental surrogate.

\*Ethylene glycol did not reach equilibrium. However data presented is beyond the inflection point of the graph (Figure 1).

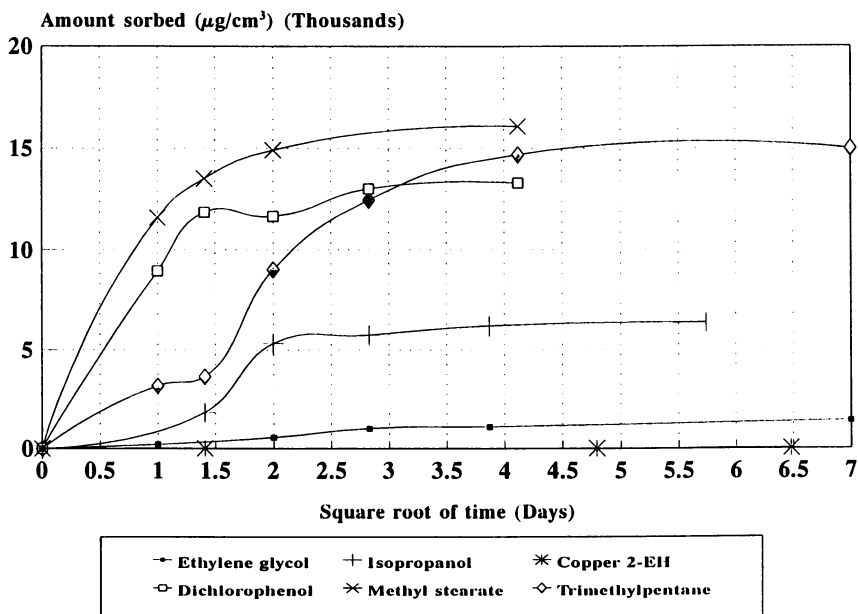


Figure 1. Surrogate sorption into high density polyethylene versus the square root of time.

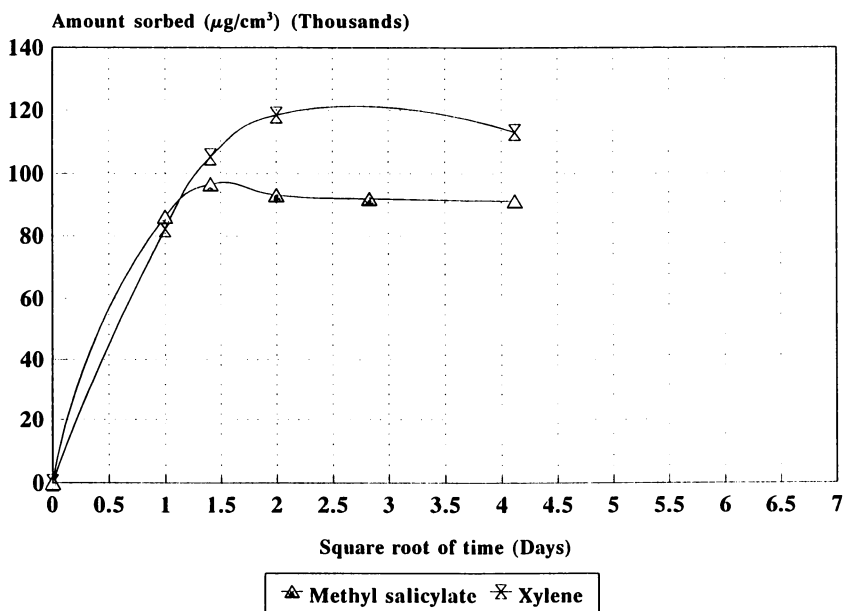


Figure 2. Surrogate sorption into high density polyethylene versus the square root of time.



## Appendix II

### Soxhlet Extraction Procedure

**Reagents.** Copper-2-ethylhexanoate (99%), 2,4-dichlorophenol (99%), methyl salicylate (99+%), ethylene glycol (99+%), trimethyl pentane (99+%), and methyl stearate (99%) were purchased from Aldrich Chemical Company. Acetone (OmniSolve) and isopropanol (OmniSolve) were purchased from E.M. Science. Dichloromethane (Ultra-analyzed), diethyl ether (Baker Analyzed) and xylene (Baker Analyzed) were purchased from J.T. Baker.

**Apparatus.** Soxhlet Extraction Apparatus - consisting of a 250 ml round bottom flask, a 40 mm x 205 mm extractor tube, and an Allihn condenser maintained at temperature of 0°C using a circulating cooler.

Extraction heater - 250 ml capacity heater block (Glas-Col Company)

Extraction thimbles - 33 mm x 94 mm cellulose extraction thimbles (Whatman)

Absorbent pads - Hazorb pillows, 1 liter capacity (Lab Safety Supply)

Balance - analytical balance, accurate to 0.001 g (Mettler)

Volumetric flasks - 250 ml to contain capacity (Kimax)

**Procedure.** Approximately 50 grams of flakes were weighed and placed in separate 400 ml beakers. Fill the beakers with the surrogate solutions so that the HDPE flakes are completely submerged. The beakers containing the flakes and surrogate solutions were kept at (23°C) for the duration of the storage study. After 7 days, the surrogate solutions were drained, the flakes removed and blotted between two absorbent pads to remove all excess surrogate solution. The flakes were then placed in metal containers, sealed, and shipped to Union Carbide (NJ) for processing. After reclamation and pelletizing, the resulting pellets were shipped to the NFPA Dublin, CA laboratory for determination of surrogate extractables. The pellets were weighed and placed in an extraction thimble which was then refluxed in the Soxhlet extractor for six hours using 180 ml of extracting solvent. At the completion of the extraction period the solvent in the flask was diluted in a volumetric flask to a volume of 250 ml. Aliquots for chromatographic analysis were removed and stored at 4°F until they were analyzed.

**Ashing Procedure.** The HDPE samples were analyzed for copper after ashing. The samples were ashed by placing the sample into a quartz beaker, adding 1 ml of an ashing aid, 7.5% magnesium oxide and 20% nitric acid. The treated samples were heated at 300°C for one hour, 400°C for two hours, and then 525°C for two additional hours. After cooling, the residue was dissolved in 1:1 nitric acid and transferred to plastic sample tubes.

**Analytical Methods.** Concentrations of the surrogates in the extraction solutions were determined by external calibration using a five point standard curve.

### **Xylene; Methyl Salicylate; Dichlorophenol; Methyl Stearate**

**Instrument:** Varian 3400 gas chromatograph with Finnigan INCOS 50 Mass Spectrometer.

**GC Column:** J & W DB5-MS 30 meter x .32 mm ID 0.5  $\mu\text{m}$  film thickness.

#### **Column temperature profile:**

initial temperature:	70°C
initial time:	2 minutes
program rate:	5°C/minute
temperature 1:	160°C
temperature 1 time:	0 minutes
program 2 rate:	50°C/minute
final temperature:	230°C
final time:	10 minutes

<b>Injector temperature:</b>	230°C
<b>Injection volume:</b>	1 $\mu\text{l}$ splitless mode
<b>Carrier gas:</b>	helium
<b>Linear velocity:</b>	40 cm/sec
<b>Detector:</b>	INCOS 50 mass spectrometer
	mass range/scan time: 50-300
	AMU/.8 second
	transfer line temperature: 280°C
	ion source temperature: 180°C

### **Trimethylpentane**

**Instrument:** Varian 3400 gas chromatograph with Finnigan INCOS 50 Mass Spectrometer.

**GC Column:** J & W DB5-MS 30 meter x .32 mm ID 0.5  $\mu\text{m}$  film thickness.

#### **Column temperature profile:**

initial temperature:	40°C
initial time:	2 minutes
program rate:	15°C/minute
final temperature:	160°C
final time:	0 minutes

**Injector temperature:** 230°C  
**Injection volume:** 1  $\mu$ l splitless mode  
**Carrier gas:** helium  
**Linear velocity:** 40 cm/sec  
**Detector:** INCOS 50 mass spectrometer  
mass range/scan time:40-300  
AMU/.8 second  
transfer line temperature: 280°C  
ion source temperature: 180°C

### Ethylene glycol

**Instrument:** Varian 3400 gas chromatograph with Finnigan INCOS 50 Mass Spectrometer.

**GC Column:** J & W DB5-MS 30 meter x .32 mm ID 0.5  $\mu$ m film thickness.

#### Column temperature profile:

initial temperature: 40°C  
initial time: 2 minutes  
program rate: 20°C/minute  
final temperature: 150°C  
final time: 0 minutes

**Injector temperature:** 230°C  
**Injection volume:** 1  $\mu$ l splitless mode  
**Carrier gas:** helium  
**Linear velocity:** 40 cm/sec  
**Detector:** INCOS 50 mass spectrometer  
mass range/scan time:30-80  
AMU/.325 second  
transfer line temperature: 280°C  
ion source temperature: 180°C

### Isopropanol

**Instrument:** Varian 3400 gas chromatograph with Finnigan INCOS 50 Mass Spectrometer.

**GC Column:** J & W DB-Wax 30 meter x .32 mm ID 0.5  $\mu$ m film thickness.

**Column temperature profile:**

initial temperature:	40°C
initial time:	2 minutes
program rate:	20°C/minute
final temperature:	150°C
final time:	0 minutes

<b>Injector temperature:</b>	230°C
<b>Injection volume:</b>	1 $\mu$ l splitless mode
<b>Carrier gas:</b>	helium

<b>Linear velocity:</b>	40 cm/sec
<b>Detector:</b>	INCOS 50 mass spectrometer mass range/scan time:30-80 AMU/.325 second
	transfer line temperature: 280°C
	ion source temperature: 180°C

**Copper**

<b>Instrument:</b>	PE 3030 Atomic Absorption Spectrophotometer using a multi-element hollow cathode lamp.
<b>Lamp energy:</b>	30 ma
<b>Wavelength:</b>	1324.5 nm
<b>Split:</b>	0.7 mm
<b>Flame:</b>	air-acetylene

**Appendix III**

**Protocol for Assessing Adequacy of a Plastics Reclamation Process.** Survey the entire reclamation system from the point where the post consumer recycle (PCR) material enters the system to the point where the marketable end product is produced. Determine the maximum capacity by weight of the largest surge point of the system. A batch of challenge material equal to twice the maximum surge capacity will need to be prepared as outlined in the following steps.

Determine if the incidental contamination of the PCR is known or can be measured. If it is, then prepare enough surrogate soaked flakes in Steps 4 through 6 below to mix with virgin flakes to obtain a surrogate contaminant level of each surrogate equivalent to the incidental contaminant level.

If the level of incidental contamination is unknown, use a one percent surrogate contamination level, i.e. mix 1% of each of the surrogate saturated flakes respectively (total of 7 surrogates) and 93% of virgin flakes. This will be equivalent to an incidental contamination of 1 contaminated bottle in 100 uncontaminated ones or the flakes from one contaminated bottle commingling with the flakes of 99 uncontaminated ones during reclamation.

Weigh out seven portions of virgin plastic flakes. The quantity necessary will be that determined in Steps 2 or 3 above plus enough flakes to carry out the necessary analytical determination prior to the system challenge steps. Place in appropriate containers, and cover the flakes with the following seven surrogate solutions respectively:

copper-2-ethylhexanoate	10% in isopropanol*
2, 4-dichlorophenol	10% in xylene
ethylene glycol	undiluted
isopropanol	undiluted
methyl salicylate	undiluted
methyl stearate	10% in xylene
2, 2, 4-trimethylpentane	undiluted

**\*Isopropanol was later determined to be a better solvent than xylene.**

Cover the containers and soak at approximately 23°C for a minimum of two weeks.

Drain the soaked flakes, and remove excess surrogate solution from the surface of the flakes. Store the saturated flakes tightly wrapped in aluminum foil or in a vapor tight container which will assure minimize loss of surrogate before use. Analyze concentrations of surrogates in flakes prior to reclamation trials.

Just prior to Step 8, remove 50 g samples for analysis to verify the level of surrogate absorbed into the flakes. See analytical procedures in Appendix II.

Blend the required amount of surrogate soaked flakes with virgin resin as determined in Steps 2 or 3 above. (For example, if using the 1% incidence contamination level, to prepare a 1000 lb batch, combine 10 lb of each of the seven prepared surrogate saturated flakes and 930 lbs of virgin flakes.) Mix thoroughly to assure homogeneity.

Determine the lag time of the reclamation process, i.e. the time interval between the point PCR flakes are added to the system and the time those respective flakes will be at the output point of the system.

Add the surrogate contaminated flakes mixture to the reclamation system at the point where PCR flakes would normally enter the system. Process the flakes by the normal reclamation procedure.

Collect samples (minimum of 50 g) from the output of the reclamation process at time intervals representing 10% of the surrogate batch size. For example, in a process which operates at 50 lb/min, a spiked batch of 1000 lb should be sampled at two minute intervals (every 100 lb). Begin sampling at several time intervals before the lag time determined in Step 9 and also at several intervals afterward to assure that the reclaimed surrogate flakes are being sampled. It is best to collect replicate samples and store the replicates wrapped tightly in aluminum foil or in sealed containers.

Analyze the output samples using the analytical procedures in Appendix II. To minimize the analytical work, it is best to analyze the sample collected at the middle of the sample collection procedure. If surrogates are found in that sample, the reclamation process is not effectively removing them, and no further analytical work need be done. If no surrogates are found in the middle sample, the remaining collected samples should be analyzed to assure the reclamation process consistently removes contaminants from the flakes.

### Literature Cited.

1. Interim Guidelines for the Safe Use of Recycled Plastics for Food Packaging Applications. The Society of the Plastics Industry, Inc. 1275 K Street, N.W., Washington, D.C. 20005, 1993. 202-371-5200.
2. Points To Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations. Division of Food Chemistry and Technology, HFS-216, Center for Food Science and Applied Nutrition, 200 C Street, Washington, D.C. 20204, 1992.
3. Bagley, E.B. In Theories of Solvency and Solution; Edited by Craver, J.K. and Tess, R.W. Applied Polymer Science; American Chemical Society: Washington, D.C., 1975; pp. 632-643.
4. Barton, A.F.M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters. CRC Press, Inc.: Boca Raton, FL, 1983.
5. Dean, John A. Lange's Handbook of Chemistry, 13th Edition. Section 10, Physical Properties. McGraw-Hill, Inc., New York, 1985.
6. Grulke, Eric A. Solubility Parameter Values. Polymer Handbook, Second Edition, ed. by Brandrup, J. and Immergut, E.H. Wiley Interscience, New York, 1975.
7. Allen, Bradford H. Unpublished data.

RECEIVED March 10, 1995

## Chapter 35

# Residual Contaminants in Recycled Poly(ethylene terephthalate)

## Effects of Washing and Drying

V. Komolprasert<sup>1,2</sup> and A. Lawson<sup>2</sup>

<sup>1</sup>Division of Food Processing and Packaging, U.S. Food and Drug Administration, and <sup>2</sup>National Center for Food Safety and Technology, 6502 South Archer Road, Summit-Argo, IL 60501

Because residual contaminants in recycled plastics intended for food packaging could be a risk to public health, the guidelines of the U.S. Food and Drug Administration suggest that the concentrations of any residual contaminants be determined after the recycling processes. This paper presents the results obtained from small-scale washing and drying experiments using polyethylene terephthalate (PETE) chips made from 2-L beverage bottles. The chips were individually contaminated with benzene, tetracosane, lindane, butyric acid, malathion and copper (II) 2-ethylhexanoate before they were washed and dried. The results show that washing significantly affected the removal of each contaminant from the PETE chips, but the effectiveness varied with the contaminant and washing conditions. Tetracosane was removed in the highest amount, followed by lindane, malathion, copper, butyric acid and benzene. After washing, the residues were present at 1 (tetracosane) to 90% (benzene) of their initial concentrations. Drying at 170°C also significantly affected the removal of the organic contaminants but not copper. After drying, the concentrations of the organic residues ranged from 0.1 (benzene) to 21% (copper) of initial concentrations.

To determine the efficacy of recycling process, the guidelines of the U.S. Food and Drug Administration (*1*) suggest that at least five different surrogates with various physical and chemical properties be used for testing the levels of potential contaminants that could conceivably be retained through recycling processes. In this study, benzene, tetracosane and lindane, butyric acid, malathion and copper (II) 2-ethylhexanoate were chosen to represent compounds that fall into the general categories of volatile, non-polar; non-volatile, non-polar; volatile, polar; non-volatile, polar; and organically bound heavy metal, respectively. These surrogates

0097-6156/95/0609-0435\$12.00/0  
© 1995 American Chemical Society

were intentionally added to polyethylene terephthalate (PETE) chips prior to the recycling processes. In secondary or physical recycling, water-based washing and thermal drying are common procedures for recycling PETE. Therefore, the residual concentration of these surrogates were determined after washing and drying. The objective of this study was to evaluate the efficacy of washing and drying on the removal of these surrogates from the spiked PETE chips.

## Materials and Methods

### Chemicals

Benzene - 99% purity, reagent grade (Fisher Scientific, Pittsburgh, PA)  
Copper (II) 2-ethylhexanoate - (Aldrich Chemical Company, Inc., Milwaukee, WI)  
Tetracosane - 99% purity (Sigma Chemical Co., St. Louis, MO)  
Lindane - 99% purity (Supelco Inc., Bellefonte, PA)  
Butyric acid - purified (J.T. Baker Inc., Phillipsburg, NJ)  
Malathion - 57% purity, commercial grade (Platte Chemical Co., Inc., Fremont, NE)  
Sodium hydroxide (NaOH) - reagent grade (Fisher Scientific)  
Methylene chloride (MC) - HPLC grade (Fisher Scientific)  
2-Propanol - reagent grade (Fisher Scientific)  
Hexane - HPLC grade (Fisher Scientific)  
Potassium acetate - 99.2% purity (Fisher Scientific)  
Copper reference solution - 1000 ppm (Fisher Scientific)  
Hexafluoroisopropanol (HFIP) - 100% purity (Eastman Kodak Company, Rochester, NY)  
Trifluoroacetic acid (TFA) - 97% purity (Fisher Scientific)  
n-Heptane - HPLC grade (Fisher Scientific)  
Triton X-100 - Union Carbide, Danbury, NJ

### Apparatus

Perkin Elmer 3100 atomic absorption spectrometer, Tekmar LSC 2000 concentrator and Varian 3400 gas chromatograph system with flame ionization detector, flame photometric detector and electron capture detector were used. The Varian system was controlled by a 486 computer using STAR workstation software.

**PETE Material.** Clean, blow-molded 2-L clear PETE bottles without caps and base cups were supplied by Eastman Chemical Co. (Kingsport, TN). They were pre-chipped by Eastman Chemical Co. (Kingsport, TN) before they were shipped to the test laboratory.

**Spiking Method.** Clean PETE chips were soaked separately in each surrogate at the concentrations shown in Table I. A 950-mL glass jar containing a mixture of 270 g of chips and 600 mL of surrogate contaminant solution was sealed and placed in an incubator maintained at 40°C for 2 weeks. The mixture was periodically stirred to ensure uniform soaking. The chips were removed from the



spiking solution and allowed to air-dry for 2-3 h in a hood before washing and drying.

Additional spiking experiments were conducted using 2-L PETE bottles which were filled with the surrogate solutions (Table II), capped and placed in the 40°C incubator. The bottles were cut in half and blotted twice with kimwipe and hexane prior to using.

**Table I. Concentrations of Surrogates Used for Spiking PETE Chips**

Surrogate	Category	Concentration (w/v)
Benzene	volatile, non-polar	99% purity
Butyric acid	volatile, polar	1% in hexane
Tetracosane	non-volatile, non-polar	1% in hexane
Malathion	non-volatile, polar	5% commercial in water
Copper (II) 2-ethylhexanoate	heavy metal	1% in 2-propanol

**Table II. Concentrations of Surrogates Used for Spiking 2-L PETE Bottles**

Surrogate	Category	Concentration (w/v)
Benzene	volatile, non-polar	10% in hexane
Butyric acid	volatile, polar	1% in hexane
Lindane	non-volatile, non-polar	0.1% in hexane
Tetracosane	non-volatile, non-polar	1% in hexane
Malathion	non-volatile, polar	5% commercial in water
Copper (II) 2-ethylhexanoate	heavy metal	1% in 2-propanol

**Small-scale Washing Experiments.** Small-scale washing experiments were performed using a 250-mL beaker containing 10 g of spiked PETE and 100 mL of washing solution consisting of 1% Triton X-100 surfactant dissolved in deionized water or aqueous 4% NaOH. The washing solution was preheated to 90°C on a hot plate before the spiked PETE chips were added. The mixture was stirred with a 3.4 mm ID three-blade-propeller agitator equipped with a laboratory mixer

(Lightnin Model DS 3014)(Mixing Equipment Co., Avon, NY) operated at 600 rpm for 20 min. These were optimum conditions as determined in previous experiments (2). The chips were removed from the washing solution and subsequently rinsed for 15 min with 200 mL of deionized water preheated to 80-90°C. The chips were then removed with a sieve and dried using a sieve shaker and an IR lamp.

**Small-scale Drying Experiments.** Drying experiments were performed with an electric laboratory muffle furnace (Eberbach Corp., Ann Arbor, MI). The washed, spiked PETE chips were contained in an aluminum foil dish (5 cm ID) and placed in the furnace, which was preheated and maintained at 160-170°C for 4 h. For test portions weighing more than 10 g, the chips were manually agitated periodically to ensure uniform heating. The chips were cooled to room temperature prior to quantitation.

**Benzene Determination.** Concentrations of benzene in the spiked PETE chips were quantified using either dynamic or static headspace gas chromatography (HS/GC) with flame ionization detection (FID) as described by Komolprasert and co-workers (3, 4). In the dynamic headspace method, approximately 1 g of ground spiked PETE was loaded into a purge tube that was interfaced with the GC/FID system. In the static headspace method, 1 g of ground spiked PETE was loaded into a headspace vial, which was heated at 90°C to attain vapor equilibrium prior to GC/FID. The limits of detection (LOD) were 2 ppb for the dynamic HS/GC procedure and 100 ppb for the static HS/GC procedure. Recoveries ranged from 70 to 102% with repeatability of  $\pm 10\%$  for PETE chips contaminated with benzene at concentrations of 0.1 to 120 ppm.

**Tetracosane Determination.** Concentrations of tetracosane in spiked PETE were quantified using a procedure developed by Pierce and co-workers (Pierce and co-workers, Illinois Institute of Technology, unpublished data). Approximately 2 g of spiked PETE was dissolved in a mixture of 15 mL of TFA and 2 mL of deionized distilled water. Tetracosane was then extracted using 15 mL of n-heptane and quantified by GC/FID. The LOD was 50 ppb in a standard solution. Recoveries ranged from 94 to 104% with repeatability of  $\pm 10\%$  for PETE chips contaminated with tetracosane at concentrations of 1 to 500 ppm.

**Butyric acid Determination.** Concentrations of butyric acid in spiked PETE were quantified using a procedure developed by Komolprasert and co-workers (5). Approximately 2 g of spiked PETE was dissolved in a mixture of 5 mL of HFIP and 10 mL of MC. The solution was diluted with an additional 60 mL of MC before polymer precipitation using 100 mL of acetone. The mixture was vacuum-filtered and the filtrate was subsequently concentrated by rotary evaporation to a final volume of 2-3 mL. The concentrated solution was diluted to 10 mL with acetone. The solution was filtered and butyric acid was quantified by GC/FID.

The LOD was 50 ppb in a standard solution. Recoveries ranged from 85 to 95% with repeatability of  $\pm 5\%$  for PETE chips contaminated with butyric acid at concentrations of 1 to 500 ppm.

**Malathion Determination.** Concentrations of malathion in spiked PETE were quantified using the procedure developed by Komolprasert et al. (5). In the analysis, 2 g of spiked PETE was dissolved in a mixture of 5 mL of HFIP and 10 mL of MC. The solution was diluted with an additional 60 mL of MC before polymer precipitation using 100 mL of methanol instead of acetone as was used in the butyric acid determination. The mixture was vacuum-filtered and the filtrate was subsequently concentrated by rotary evaporation. The concentrate was dissolved in potassium acetate buffer solution (pH 5.3) and the mixture was filtered through C18 cartridge for cleanup using a C18 cartridge prior to determination of malathion by GC with flame photometric detection (FPD). The LOD was 50 ppb in a standard solution. Recoveries ranged from 72 to 93% with repeatability of  $\pm 8\%$  for PETE chips contaminated with malathion at concentrations of 1 to 500 ppm.

**Lindane Determination.** Concentrations of lindane in spiked PETE were quantified using the procedure used for malathion analysis with modifications. The modifications included the use of TFA instead of the HFIP, use of deionized distilled water instead of the buffer solution and determination of lindane by GC with electron capture detection (ECD) instead of the FPD. The LOD was 1 ppb in a standard solution. Recoveries of lindane are in a range of 70-80% with repeatability of  $\pm 5\%$  for PETE chips spiked with lindane at concentrations of 15 ppb and 5 ppm.

**Copper Determination.** Concentrations of copper in spiked PETE were quantified using AOAC method 969.32 (6) with slight modifications. Approximately 5 or 10 g of spiked PETE chips was ashed in an electric laboratory muffle furnace which was preheated to 300°C. The temperature of the furnace was raised to 400°C and then to 500°C. The ash was cooled, and copper was extracted and determined by atomic absorption spectrometry at 324.8 nm. The LOD was 100 ppb in a standard solution. Recoveries ranged from 95 to 105% with repeatability of  $\pm 20\%$  for PETE chips contaminated with copper at concentrations of 0.5 to 5 ppm.

### Results and Discussion

The average initial concentrations and the coefficients of variation (CV) of these surrogates in PETE chips from several spiking experiments were determined and are shown in Table III. The results suggest that the initial concentrations obtained in the various runs were quite variable. This variability could be due to the different amounts of the surrogate adsorbed on the surface of the chips. It may also depend on how much of the surrogate diffuses or is absorbed into the polymer matrix. The variation in absorption may be affected by irregular size, shape and

thickness of the chips. The variation in surface area may be a key parameter which dictates the amount of surrogate that diffuses into the PETE matrix.

**Table III. Initial Concentration of Surrogates in spiked PETE chips and in 2-L PETE Bottles**

Surrogate	Spiked chips (ppm)	2-L bottles (ppm)
Benzene	7383 ± 270 <sup>a</sup>	310 ± 5 <sup>b</sup>
Butyric acid	755 ± 21	69 ± 6
Tetracosane	1928 ± 299	51 ± 2
Lindane	N/A	0.275 ± 0.021
Malathion	5860 ± 2440	599 ± 524
Copper (II) - ethylhexanoate	636 ± 110	3.81 ± 0.05

<sup>a</sup>Obtained by using 99% purity benzene

<sup>b</sup>Obtained by using 10% benzene in hexane

N/A : Not available

Table III also shows that the initial concentrations of the surrogates in spiked bottle material are much lower than those in chips. This may result from the difference in surface area exposed to surrogates. These concentrations represent the actual amounts absorbed by the bottles and may simulate the incidental contamination that may occur in the commercial processes.

**Effects of Washing on Removal of Surrogate Contaminants from Spiked PETE Chips.** The percentages of benzene, tetracosane, butyric acid, malathion and copper remaining in the spiked PETE chips after the washing experiments are summarized in Table IV. The results suggest that washing has a significant effect on removal of each surrogate from spiked PETE chips. In the absence of NaOH, 86% of the benzene remained while only 9% of the tetracosane was left. Even in the presence of NaOH, 70% of the benzene residue still remained and 11% of the tetracosane was left. These results indicate that NaOH had a slight effect on the further reduction of benzene but no effect of on the further reduction of tetracosane. Washing appears to be more effective for removal of tetracosane than for removal of benzene.

The other surrogates were intermediate in the amount of residue that remained after washing. The addition of NaOH appeared to have a significant effect on further reduction of the amount of surrogate residue. Regardless of the washing conditions, the level of the tetracosane residue was the lowest, followed by the levels of malathion, copper, butyric acid and benzene.

**Table IV. Initial Concentration and Percent of Residual Benzene, Tetracosane, Butyric acid, Malathion, and Copper in Spiked PETE Chips Washed with and without added NaOH at 90°C for 20 min**

Surrogate	Av. initial concn. <sup>a</sup> (ppm) ± CV	% Residue after washing (± CV)	
		Without addition of NaOH	With addition of NaOH
Benzene	7383 ± 270	86 ± 6	70 ± 1
Tetracosane	1928 ± 299	9 ± 2	11 ± 4
Butyric acid	755 ± 21	44 ± 2	35 ± 4
Malathion	5860 ± 2440	31 ± 5	16 ± 1
Copper (II)	636 ± 110	50 ± 5	21 ± 2

<sup>a</sup> Determined from several experiments

**Effect of Drying on Removal of Surrogate Contaminants from Spiked PETE Chips.** The percentages of residual benzene, tetracosane, butyric acid, malathion and copper after small-scale drying experiments using the washed PETE chips were determined; the results are shown in Table V. The results indicate that drying for 4 h at 170 ± 5°C has a significant effect on removal of the organic contaminants,

**Table V. Initial Concentration and Percent of Residual Benzene, Tetracosane, Butyric acid, Malathion, and Copper in Spiked PETE Chips, Washed with and without added NaOH, and Dried at 160-170°C for 4 h**

Surrogate	Av. initial concn. <sup>a</sup> (ppm) ± CV	% Residual after drying (± CV)	
		Without addition of NaOH	With addition of NaOH
Benzene	7383 ± 270	2.0 ± 1.0	ND
Tetracosane	1928 ± 299	1.0 ± 0.5	ND
Butyric acid	755 ± 21	0.3 ± 0.1	0.3 ± 0.1
Malathion	5860 ± 2440	4.0 ± 1.0	1.0 ± 0.3
Copper (II)	636 ± 110	48.0 ± 5.0	22.0 ± 3.0

<sup>a</sup> Determined from several experiments

ND: Not determined

particularly benzene from the washed, spiked PETE chips. A combination of washing and drying removed 98% of the benzene from the spiked PETE. The drying was more effective than washing in removing benzene from PETE. Drying affected the volatile surrogates more than the non-volatile surrogates. The combination of washing and drying removed up to 99% of tetracosane, 99.7% of butyric acid and 99% of malathion (with NaOH) from the spiked PETE. Drying further reduced malathion from the washed chips by thermal decomposition. In contrast, drying has no effect on removal of copper from the washed, spiked PETE.

**Effects of Washing and Drying on Removal of Surrogate Contaminants from Spiked Bottle Material.** The percentages of benzene, tetracosane, butyric acid, malathion, lindane and copper remaining in the spiked PETE chips after the small-scale washing experiments are summarized in Table VI. The results suggest that washing has a significant effect on removal of each surrogate from the spiked PETE bottle material. The effects appear to depend on surrogate and its initial concentration; the higher the initial concentration, the lower the percent removed. After washing, residual concentrations were 74% malathion, 55% benzene and 41% butyric acid, respectively. The other surrogate residues were lower, 35% copper, 1.5% lindane and < 0.6% tetracosane.

**Table VI. Initial Concentration and Percent of Residual Benzene, Tetracosane, Lindane, Butyric acid, Malathion, and Copper in Spiked PETE Bottle Material, After Washing without added NaOH, and After Washing and Drying (160-170°C for 4 h)**

Surrogate	Initial concn. (ppm) $\pm$ CV	% Residual after ( $\pm$ CV)	
		Washing	Washing and drying
Benzene	310 $\pm$ 5	55 $\pm$ 2	2.0 $\pm$ 0.6
Tetracosane	51 $\pm$ 2	< 0.6	< 0.6
Lindane	0.275 $\pm$ 0.021	1.5 $\pm$ 0.1	< 0.1
Butyric acid	69 $\pm$ 6	41 $\pm$ 2	0.4 $\pm$ 0.1
Malathion	599 $\pm$ 524	74 $\pm$ 58	20 $\pm$ 16
Copper (II)	3.81 $\pm$ 0.05	30 $\pm$ 7	21 $\pm$ 2

The results may also be because tetracosane and lindane which are non-polar and non-volatile tend to diffuse so slowly that they were probably on the

surface. Therefore, they were removed more rapidly than the other surrogates. On the other hand, malathion which is polar and non-volatile, and benzene which is non-polar and volatile diffuse so rapidly that it was probably present in the matrix of polymer and therefore was not removed easily by washing.

The percentages of the surrogates in the spiked PETE after small-scale drying experiments are also shown in Table VI. The results indicate that drying further removed the surrogates to 21% or lower. Drying affected the volatile surrogates more than the non-volatile surrogates. Drying significantly reduced residual benzene and butyric acid from the washed PETE to <2% of the initial concentrations. Drying further reduced malathion from the washed chips by thermal decomposition. Drying had a small effect on further removal of copper from the washed chips. The combination of washing and drying removed 79% of copper, 80% of malathion, 98% of benzene, 99.6% of butyric acid, >99% of tetracosane and lindane.

### Conclusions

In this study, the uptake concentration of benzene, butyric acid, tetracosane, lindane, malathion and copper in 2-L PETE bottles was at least ten-fold lower than the initial concentrations observed by spiking the chips with the surrogate solutions.

The results in this study indicate that washing alone significantly removed 10-90% of the surrogates from the spiked PETE chips and removed 26-99% of the surrogates from the spiked PETE bottle material. The combination of washing and drying removed >99% of the organic surrogates from the spiked chips, regardless of how the spiked chips were prepared. Although the results in this study suggest that >99% of most organic contaminants can be removed by washing and drying, it is still not known whether the recommended levels of residual organic contaminants in the secondary recycled PETE can be attained. Future work will determine the effect of remelting on the removal of organic and inorganic surrogates as well as the potential migration of these surrogates into several food simulants.

### Acknowledgments

This research was supported by Cooperative Agreement FD-000431 from the U.S. Food and Drug Administration and by the National Center for Food Safety and Technology.

### Literature cited

- (1) "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations." Chemistry Review Branch, U.S. Food and Drug Administration, Indirect Additives Branch, HFS-247, 200 C Street, S.W., Washington, DC 20204, 1992.
- (2) Komolprasert, V. and Lawson, A. 1994. Effect of aqueous-based washing on removal of hydrocarbons from recycled polyethylene terephthalate (PETE). Proceedings of the annual SPE meeting, held on May 1-5, in San Francisco, CA.

- (3) Komolprasert, V.; Hargraves, W.A.; Armstrong, D. *Food Addit. Contam.*, **1994**, vol. 11, pp 605-614.
- (4) Komolprasert, V.; Hargraves, W.A.; Armstrong, D.J. and Sadler G. 1993. Determination of benzene in recycled polyethylene terephthalate (PETE) by dynamic and static headspace gas chromatography. Paper presented at the annual IFT meeting, held on July 11-14, in Chicago, IL.
- (5) Komolprasert, V., Lawson, A. and Hargraves, W.A. 1994. An analytical method for quantifying polar contaminants in recycled polyethylene terephthalate (PETE). Paper presented at the annual ACS meeting, held on August 21-25, in Washington, DC.
- (6) *Official Methods of Analysis of the Association of Analytical Chemists*; Williams, S., Ed.; Association of Official Analytical Chemists, Inc.: Arlington, VA, 1990; 15th Ed., pp 272-273.

RECEIVED March 8, 1994



## Chapter 36

# Food Packaging Made from Recycled Polymers

## Functional Barrier Considerations

Timothy H. Begley and Henry C. Hollifield

Division of Product Manufacture and Use, U.S. Food and Drug Administration, Washington, DC 20204

Over the past few years the curbside collection of post-consumer recyclable products has created a supply of raw materials that can easily be recycled into new products or packaging materials. Recycled materials used for food packaging require some special considerations to ensure that nonregulated chemicals or contaminants either are not present in the material or do not migrate into the food. Because all chemicals diffuse through polymers, a potential for food contamination exists if unregulated chemicals or contaminants are present in the recycled material. The potential for recycled polymers to contaminate food may be reduced by using alternative package designs. This paper will discuss diffusion considerations for recycled polymers and the functional barrier characteristics of polymers (i.e., polyethylene terephthalate (PET)) as they apply to food packages made from recycled polymer resins. The functional barrier concept is discussed relative to the Food and Drug Administration's proposed Threshold of Regulation Policy. Diffusion coefficients for a nonvolatile plasticizer in PET at temperatures above 100°C were measured and used to evaluate the barrier properties of PET dual ovenable trays potentially made from recycled polymer.

### Overview

It is well established that polymers absorb chemicals from their surroundings as well as give off chemicals to their surroundings. In the case of food packaging, flavor

This chapter not subject to U.S. copyright  
Published 1995 American Chemical Society

components generally diffuse into the package material, and polymer oligomers and additives diffuse out of the package and migrate into the food. From a regulatory food safety standpoint, it is this general type of behavior, absorption/desorption by plastics, that makes polymers difficult to recycle directly into new food packaging.

The ability to demonstrate that recycled polymers and virgin food-packaging polymers are of comparable purity and to satisfy quality assurance requirements (1) is a difficult analytical chemistry problem. There is no reasonable way to assay a product when you don't know which contaminants you are looking for, and the history of the product is unknown and constantly changing. This quality control problem can be simplified somewhat by using only post-consumer collected food packaging to make new food packaging. This does not eliminate the potential problem of consumer abuse before recycling, or the recycling of nonfood containers that are similar in appearance into food packaging. Once a package/polymer has left the manufacturing/converting facility, it is very difficult to know if the package has been contaminated with nonfood-related chemicals. Following post-consumer collection, the plastic that is to be converted into new food packaging can be subjected to additional reprocessing steps to reduce or remove contaminants. Some of these more rigorous reprocessing steps are expensive. Therefore, it seems appropriate to consider alternative approaches to ensure the safe use of recycled polymers in food applications.

Instead of rigorously attempting to reduce contaminant levels in recycled polymers to those found in virgin materials, an alternative approach may be to use diffusion theory to estimate the amount of contamination likely to migrate into food. The maximum allowable migration may be defined by the Threshold of Regulation Policy proposed by the Food and Drug Administration (FDA) in October 1993 (2). This threshold policy proposes a maximum safe dietary exposure of 0.5 ppb to a noncarcinogenic chemical compound. This same 0.5 ppb dietary exposure threshold may be used to determine maximum permissible exposure to a contaminant migrating from a package construction into food. Therefore, for our discussions in this paper, a package construction will be considered an insignificant contaminant source if the migration of chemical/contaminant from a package construction to food results in a dietary exposure of 0.5 ppb or less.

The determination of the threshold values is described by FDA in its "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations" document (3), in which a 1 ppb dietary exposure was used to determine threshold values. Since this document was published, FDA has decided that a 0.5 ppb dietary exposure would be more appropriate. By using the method described in the "Points to Consider" document and a 0.5 ppb dietary exposure, threshold values were calculated and are listed

Table I. Threshold Values for Maximum Residual Contamination and Migration Amounts Which Result in a 0.5 ppb (ng/g) Dietary Exposure to a Contaminant

Polymer	Residual Contamination (ppb) <sup>a</sup>	Migration Amount (ppb) <sup>b</sup>
Polyethylene terephthalate (PET)	215	10
Polystyrene (PS)	180	6
Polyvinyl chloride (PVC)	90	5
High-density polyethylene (HDPE)	123	4
Polypropylene (PP)	778	25
Low-density polyethylene (LDPE)	92	3

<sup>a</sup> It is assumed that the base package thickness is 20 mil (0.0508 cm) and that 100% of the chemical migrates into the food.

<sup>b</sup> The maximum tolerable migration from the polymer into food that results in a 0.5 ppb dietary exposure.

in Table I. The two columns of numbers in Table I refer to thresholds for the maximum residual contamination in the package, assuming complete migration to the food, and the maximum amount of migration that could occur from a package into a food and still yield a dietary exposure of  $\leq 0.5$  ppb. For example, in a polymer like high-density polyethylene (HDPE), the maximum concentration of contaminant in the polymer, assuming 100% migration, would be 123 ppb. This amount will restrict dietary exposure to  $\leq 0.5$  ppb. The amount of tolerable migration from HDPE to food, based on the threshold policy, is 4 ppb. That is, if an HDPE package construction restricts the amount of migration to 4 ppb or less, irrespective of the total amount of contaminant in the polymer, use of the package could be considered to constitute a minimal health risk, and the package construction, an insignificant contaminant source.

As alluded to above, when the threshold policy is applied to packages made from recycled polymers, there are two approaches that can be followed. One is to assume 100% migration of a residual contaminant, that is, all of the contaminant in the polymer will migrate to the food. The other is to assume that only a fraction of the residual contamination will migrate to the food, that is, diffusion in the polymer controls the amount of contamination going to the food. In the second case, the maximum amount of contamination allowed in the polymer could be much higher than the amount that corresponds to the 100% migration assumption in Table I. This approach does not imply that contaminated resin should be used for food packaging. Using

diffusion properties in polymers as an alternative way to evaluate migration, especially from recycled polymers, has been suggested elsewhere (4,5). In this second approach, the case limited by migration, the diffusion properties within the polymer must be characterized. These properties can be evaluated by studying diffusion at various temperatures for test molecules that are likely to survive reprocessing of the recycled polymers. Additionally, the likely concentration of the test molecules after reprocessing must be known. Once the diffusion properties of the polymer are known, one can estimate the likelihood of a contaminant entering the food in amounts above the threshold level.

The amount of contamination that may enter the food can be estimated by using those mathematical relationships that describe diffusion in polymers. There are numerous literature citations showing that diffusion of chemicals in food-packaging polymers obeys Fick's Law. For example, Till et al. (6) showed that the solution to Fick's Law expressed in equation 1 can give reasonable estimates of the amount of migration to food.

$$M_t = 2C_0 \sqrt{\frac{Dt}{\pi}} \quad (1)$$

Equation 1 states that the amount of migration to food ( $M_t$ ) is directly related to the amount of contaminant in the polymer ( $C_0$ , mass/cm<sup>3</sup>) and related to the square root of the diffusion coefficient ( $D$ , cm<sup>2</sup>/s) and the time ( $t$ , seconds). By using equation 1 and FDA's assumption that uses 1.55 g/cm<sup>2</sup> of food contact for each cm<sup>2</sup> of packaging to convert food-package surface area to food mass, the amount of migration over the shelf life of the package can be calculated. This calculation assumes that the concentration and the diffusion coefficient are known. If the general diffusion characteristics of the polymer at the temperature conditions of use are known, then an estimate of the amount of migration can be calculated from equation 1 once the amount of expected residual contamination after reprocessing is known.

An alternative approach to putting potentially contaminated recycled polymer in direct contact with food is to put a thin layer of virgin polymer over the recycled layer. As a first approximation, any apparent advantage of using a virgin layer can be estimated by using the solution to Fick's Law for the case of diffusion through a film where the initial concentration in the film is zero and the concentration on the outside of one side of the film is constant. This case is described mathematically in equation 2 (7), where  $l$  is the film thickness,  $C_0$  is the surface concentration, and  $D$  and  $t$  are the same as described for equation 1.

$$M_t = \left[ \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{-1^n}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{l^2}\right) \right] C_0 l \quad (2)$$

To compare equations 1 and 2, we assume the following: the level of contamination in the recycled package material was 100 ppm, the food was stored for 30 days in the package, and the diffusion coefficient for the contaminant in the polymer was  $4 \times 10^{-13}$  cm<sup>2</sup>/s. Using these values in equation 1, we calculate that 101 ppb of the contaminant would be in the food. This value is well above all threshold values listed in Table I. For the case in which a virgin layer 1 mil (0.00254 cm) thick is used, we calculate from equation 2 that only 8 ppb of the contaminant would be in the food after 30 days. Obviously, the presence of the virgin layer has a significant advantage in reducing the possible exposure to a contaminant. This effect has been demonstrated experimentally by Franz et al. (8) for recycled polypropylene (PP) covered with a virgin layer. They concluded that a virgin layer of PP acted as a barrier to the migration of components from recycled PP under the intended conditions of use.

In order to apply diffusion principles to the evaluation of recycled polymers for food packaging, diffusion coefficient information must be known. There is a large amount of diffusion data for some polymers used in food packaging (e.g., polyolefins) but little information for others. Polyethylene terephthalate (PET) is one of the major food-packaging polymers for which very little information exists on the diffusion of large molecules in the polymer (i.e., those molecules that are likely to survive a recycling process). This is especially true for diffusion in PET above room temperature. PET is also a unique food-packaging polymer in that it is used over the largest temperature range (0°C to approximately 175°C). Additionally, in the United States, PET represents one of the largest fractions of collected post-consumer plastics (9). This supply of post-consumer PET and some state regulations requiring the use of post-consumer plastics in packaging have prompted numerous requests to FDA for the use of post-consumer PET for food packaging. Because of the lack of information on diffusion characteristics in PET, this polymer was chosen for diffusion coefficient measurements in order to assess the potential of recycled PET as a food-packaging polymer. The particular temperature range studied was above 100°C, because these temperatures correspond to cooking temperatures used in the microwave and convection ovens. Because diffusion will be the greatest for food applications at these temperatures, the magnitude of this diffusion needs to be known for safety evaluations.

Diffusion coefficients in PET were measured by using the lag-time technique. In a typical lag-time experiment, the amount of chemical penetrating through a polymer is plotted versus time. For a polymer/penetrant system that obeys Fick's Law, this type of plot is illustrated in Figure 1. The lag time is determined by extrapolating the steady-state portion of the curve to a time when the concentration is zero. The diffusion coefficient can be calculated from the lag time by using the following relationship (10).

$$\text{Lagtime} = \frac{l^2}{6D} \quad (3)$$

### Experimental

The PET used in these experiments was biaxially oriented, 12.7  $\mu\text{m}$  (0.5 mil) thick, crystallized (CPET), and cut from a dual ovenable tray, 200-250  $\mu\text{m}$  (20-25 mil) thick. The CPET contained a nucleating agent.

The test molecule used to evaluate the diffusion through PET at temperatures above 100°C was diethylene glycol dibenzoate (DEGDB). Tests were carried out by making a layered structure consisting of DEGDB-spiked paperboard covered by PET in contact with a food oil. The layered configuration was held together by a compression migration cell originally designed at Dow Chemical Co. and similar to the cell used by Figge and Koch (11). The cell was purchased from Kayeness, Inc., 115 Thousand Oaks Blvd., Suite 101, P.O. Box 709, Morgantown, PA 19543. The configuration is illustrated in Figure 2. The paperboard used was uncoated, solid, bleached sulfate board, 450  $\mu\text{m}$  (18 mil) thick. The paperboard was spiked with DEGDB in a petri dish with 2 mL of a 2 mg/mL solution of DEGDB. The solvent was methylene chloride. After spiking, the solvent in the petri dish was allowed to evaporate. The test cell was assembled, filled with 51 g of oil (Miglyol 812), and sealed. These conditions produced a mass of oil-to-polymer surface area ratio of 1.1 g/cm<sup>2</sup>. Test cells were placed in an oven and, after specific time intervals, they were removed, and the oil was analyzed for the total amount of DEGDB that had penetrated the PET film and entered the oil. Duplicate measurements were made at each temperature. This procedure permitted lag-time measurements to be made for the evaluation of effective diffusion coefficients.

The procedure for quantitating DEGDB in the oil involved removing 1 g of oil from the test cell, diluting the oil with 50 mL of hexane, pouring the hexane solution through an aminopropyl solid-phase extraction tube, followed by elution with 5 mL of 90% acetonitrile/10% water solution. The DEGDB was quantitated by high-performance liquid chromatography with a method similar to that described by Begley and Hollifield (12).

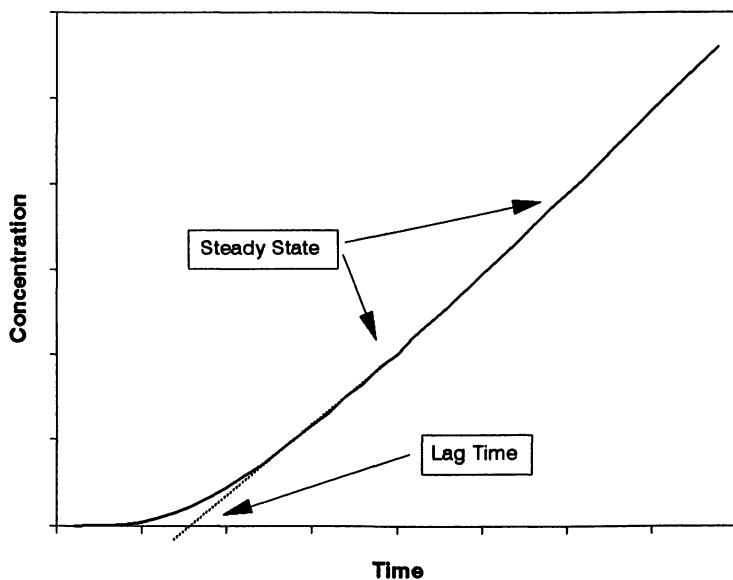


Figure 1. Plot of ideal concentration versus time for diffusion through a film. Lag-time measurements are made by extrapolating the steady-state portion of the curve to zero concentration.

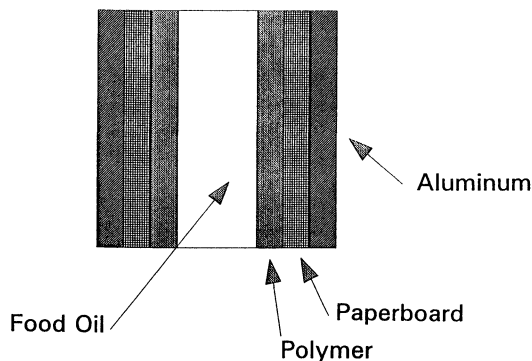


Figure 2. Configuration of the migration cell, showing the layers of materials.

August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch036

## Results

The results of a typical lag-time experiment, using the procedure described above at 110°C, are shown in Figure 3. This figure suggests that migration from the PET/DEGDB-paperboard configuration exhibits Fickian type behavior. From the lag time of 0.6 h, the effective diffusion coefficient for DEGDB in PET at 110°C, calculated with equation 3, is  $1.2 \times 10^{-10}$  cm<sup>2</sup>/s. Similar experiments were conducted at 100 and 120°C.

To determine how the effective diffusion coefficients of DEGDB behave as a function of temperature, an Arrhenius-type plot was constructed and is shown in Figure 4. When these data are extrapolated from 85 to 150°C, the effective diffusion coefficients for DEGDB in PET range from  $2 \times 10^{-12}$  to  $9 \times 10^{-9}$  cm<sup>2</sup>/s. Additional experiments at 150°C were performed to further evaluate diffusion at this temperature. Because diffusion is so rapid at 150°C, the 0.5 mil PET film was not thick enough for this experimental configuration. A thicker CPET film cut from the bottom of a dual ovenable tray was used to test the diffusion at 150°C. This film, 20-25 mil thick, was highly crystallized and contained a polyolefin nucleating agent. When this film was used, the amount of migration to the oil was about 5 times less than that predicted by equation 2 with a diffusion coefficient of  $9 \times 10^{-9}$  cm<sup>2</sup>/s. This migration actually corresponds to a 25% change in diffusion or  $D = 7 \times 10^{-9}$  cm<sup>2</sup>/s. This variability in diffusion coefficients is reasonable because the morphology of the CPET film is much different from that of the biaxially oriented film. Differences in morphology are known to affect diffusion.

One of the shortcomings of using equation 2 to estimate migration of a contaminant into food from a laminate package structure is overestimation, which generally occurs when the value for  $Dt/l^2$  exceeds 1.5. This situation is depicted in Figure 5, where the amounts of migration predicted by using equations 1 and 2 are plotted versus time. This figure shows that after about 1 h, equation 2 predicts more migration from a layered package than would be expected from a monolayer package (equation 1); this is physically unreasonable. Migration cannot be greater from a package with a virgin layer than from a package without the layer. This overestimation results because equation 2 assumes that the concentration on one side of the layer is always constant and is free to move directly into the film (i.e., a pure liquid always in contact with one side of the film). But in actuality, in a layered package, the total concentration that enters the film is governed by equation 1. A more realistic approach to evaluating the amount of potential migration through a layered package is to consider the package as an infinitely thick, single layer, where the contamination is initially confined within a limited space. Migration can be estimated by evaluating the concentration-distance function given



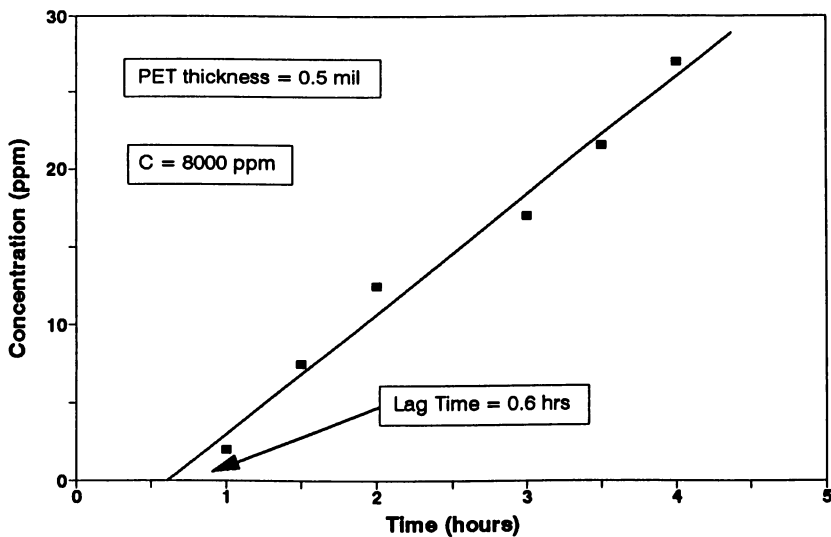


Figure 3. Plot of concentration versus time for the diffusion of DEGDB through a 0.5 mil PET film at 110°C.

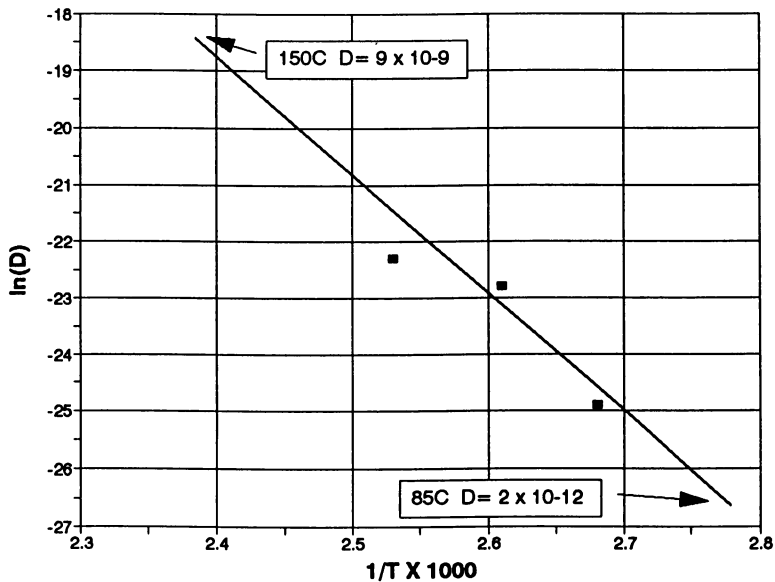


Figure 4. Arrhenius plot for the diffusion of DEGDB through PET.

August 10, 2012 | http://pubs.acs.org  
Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch036

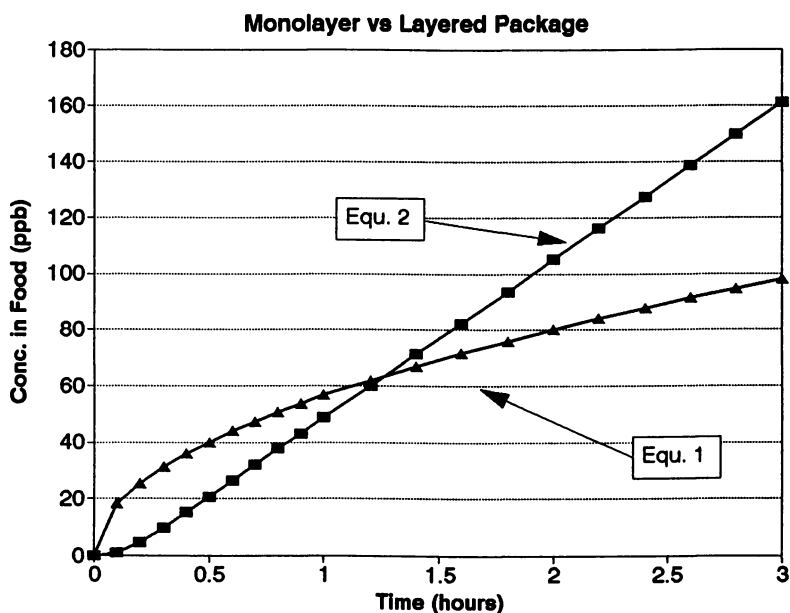


Figure 5. Plots of calculated concentration versus time, illustrating the relative differences in using equations 1 and 2 to estimate the amount of expected migration.  $D = 9 \times 10^{-9} \text{ cm}^2/\text{s}$ ,  $l = 2 \text{ mil}$ , and  $C_0 = 10 \text{ ppm}$ .

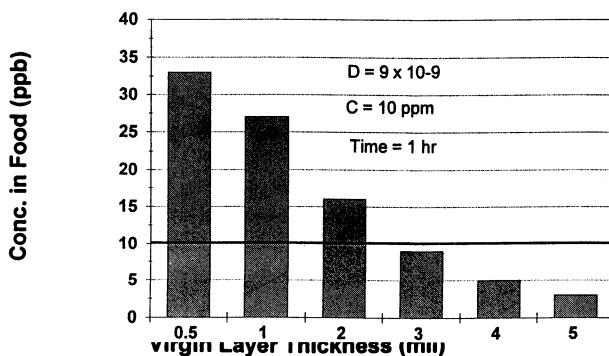
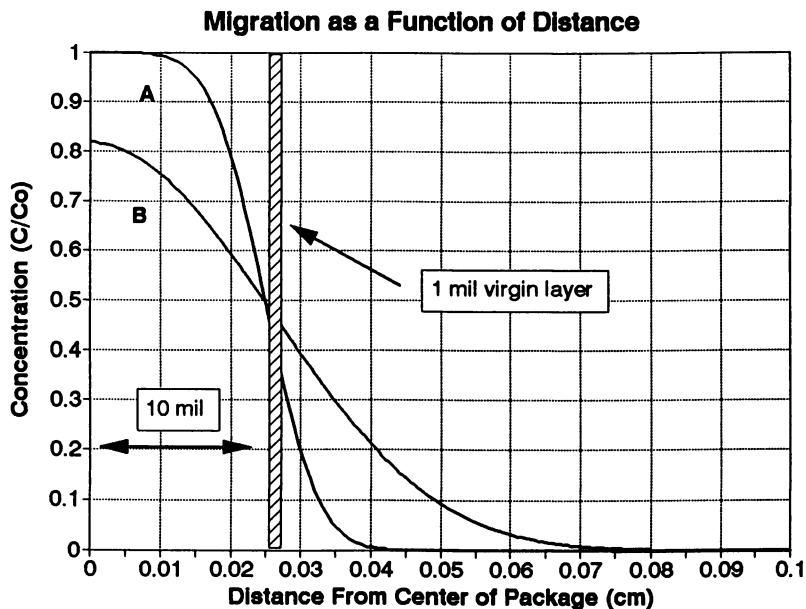
below in equation 4 (7) at a time equivalent to the package lifetime.

$$C = \frac{1}{2} C_0 \left[ \operatorname{erf} \left( \frac{h-x}{2\sqrt{Dt}} \right) + \operatorname{erf} \left( \frac{h+x}{2\sqrt{Dt}} \right) \right] \quad (4)$$

In equation 4,  $h$  is the thickness of the package material (i.e., 20 mil or 0.051 cm), and  $x$  is the distance from the center of the package material. An illustration of equation 4 with the perspective of a layered package is given in Figure 6. This figure illustrates the concentration profiles for two migrants, A and B, having diffusion coefficients equal to  $5 \times 10^{-8}$  and  $5 \times 10^{-9}$  cm<sup>2</sup>/s, respectively, and using a time of 1 h and a base package thickness of 20 mil. The bar in this figure represents a 1 mil virgin layer and is positioned on the graph to indicate how the concentration distance profiles cross a package with a virgin layer. This figure clearly illustrates that contaminants with these diffusion coefficients would diffuse past the 1 mil virgin layer in 1 h and would be expected to enter the food. The actual amount of migration to food is also dependent on the mass transfer characteristics at the food/package interface. For safety evaluations, it is assumed that all migrants at the food/package interface enter the food.

Migration from the layered package is evaluated by integrating the area under the curve at distances beyond the 1 mil virgin layer. For example in Figure 6, the quantitative migration beyond the 1 mil layer would be 5 and 25% of the total amount in the package for contaminants with diffusion coefficients of  $5 \times 10^{-9}$  and  $5 \times 10^{-8}$  cm<sup>2</sup>/s, respectively.

By using the data obtained from the DEGDB experiments, general package specifications can be calculated. For example, what would the maximum concentration of a contaminant be for a given thickness or how thick a layer would be needed for a PET tray used for heating food at 150°C (302°F) to prevent migration from exceeding FDA's Threshold of Regulation value (Table I)? Some data submitted to FDA (FDA, Center for Food Safety and Applied Nutrition, Office of Premarket Approval, Food Master File #553, Washington, DC 20204) suggest that the concentration of a nonvolatile contaminant remaining in a PET resin after rigorous secondary recycling\reprocessing may be as high as 10 ppm, whereas concentrations of volatile contaminants have been found to be less than 0.1 ppm. If it is assumed that a tray made of recycled PET has 10 ppm of a contaminant, equation 4 can be used to calculate the approximate amount that might be expected to migrate into food for different thicknesses of a virgin layer. Figure 7 illustrates the results of this type of analysis in which the thickness of the recycled layer in a package is 20 mil



and the cooking time is 1 h. This figure indicates that a thickness of 3 mil should keep the contamination below the 10 ppb migration threshold for PET; therefore, the 3 mil virgin layer would be considered a functional barrier under these conditions of use.

In summary, the data and calculations suggest that coupling the Threshold of Regulation concept with diffusion calculations permits the evaluation of recycled polymers for food packaging. When this approach is used, the amount of contamination in the polymer may be greater than the 100% migration threshold value because diffusion properties in polymers place physical limits on the amount of contamination that can enter the food. Additionally, application of a virgin layer provides another effective approach for reducing the amount of contamination that can enter the food.

#### Literature Cited

1. *Code of Federal Regulations*; U.S. Government Printing Office: Washington, DC, 1994; Section 21, Part 174.5.
2. *Fed. Regist.*, 1993 (October 12), 58, 52719-52729.
3. FDA, "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations." Food and Drug Administration, Center for Food Safety and Applied Nutrition (HFS-245): Washington, DC 20204, 1992.
4. Begley, T.H.; Hollifield, H.C. *Food Technol.* 1993, 47(11), 109-112.
5. Baner, L.A.; Franz, R.; Piringner, O. *Dtsch. Lebensm. Rundsch.* 1994, 90(5), 137-143.
6. Till, D.E.; Ehntholt, D.J.; Reid, R.C.; Schwartz, P.S.; Sidman, K.R.; Schwope, A.D.; Whelan, R.H., *I&EC Prod. Res. Dev.* 1982, 21, 106-113.
7. Crank, J. *The Mathematics of Diffusion*, 2nd Ed.; Oxford University Press: Oxford, 1975.
8. Franz, R.; Huber, M.; Piringner, O.G. *Food Addit. Contam.* 1994, 11, 479-496.
9. Beck, R.W. 1993 *National Post-Consumer Plastics Recycling Rate Study*; American Plastics Council: Washington, DC, May, 1994.
10. Daynes, H.A. *Proc. R. Soc. (London)* 1920, 97, 628.
11. Figge, K.; Koch, J. *Food Cosmet. Toxicol.* 1973, 11, 975-988.
12. Begley, T.H.; Hollifield, H.C. *J. Food Prot.* 1990, 53, 1062-1066.

RECEIVED June 6, 1995

## Chapter 37

# Analysis of Contaminants in Recycled Poly(ethylene terephthalate) by Thermal-Extraction Gas Chromatography–Mass Spectroscopy

D. E. Pierce<sup>1,3</sup>, D. B. King<sup>2</sup>, and George D. Sadler<sup>1</sup>

<sup>1</sup>Illinois Institute of Technology, National Center for Food Safety and Technology, 6502 South Archer Road, Summit-Argo, IL 60501–1933

<sup>2</sup>Ruska Instrument Corporation, 3601 Dunvale Road, Houston, TX 77063

Thermal extraction-GC/MS has provided a means of determining the identity and origin of contaminants associated with food grade virgin and commercially recycled poly(ethylene terephthalate) PET. In order to address the problem of recycling PET for food use, a study was begun that examined a number of sources of recycled material. The effects of various stages of reprocessing and remanufacture were also examined and the material compared to virgin resin. In addition to determining purity, thermal extraction analysis could be used to model reprocessing steps involving heat (crystallization, drying, extrusion, etc.). Possible avenues for standardizing thermal extraction analysis as a simple and rapid screening method for recycled PET for food use will also be considered.

The public increasingly feels that recycling demonstrates stewardship to the environment and represents a vital step in the preservation of dwindling natural resources. Federal, state, and community recycling laws have resulted from this popular conviction (1). Public understanding of recycling has largely been shaped by successful recycling programs with aluminum and glass. Extreme processing temperatures applied in recycling these materials assure that organic contaminants will not survive recycling steps to subsequently taint foods held in second generation containers.

The FDA has expressed concern that compounds acquired from one recycling iteration might survive to contaminate foods held in containers made from these polymers (2). Even if the safety of recycled materials can be shown, many food companies are reluctant to embrace the use of recycled resins until they are certain that recycling-induced flavor and odor properties are not imparted to their products.

<sup>3</sup>Current address: Physical Science Directorate, U.S. Army Research Laboratory, Fort Monmoth, NJ 07703–5601

Thermal extraction GC/MS offers a powerful tool for identifying minute concentrations of contaminants in recycled polymers. It may, therefore, hold potential as an endpoint test for the quality and safety of recycled resins. The approach has been successfully used to identify trace volatiles in polymers, composites, elastomers, fibers, and adhesives. Although several thermal extraction strategies exist, they all rely on heat to remove volatile and semi-volatile compounds from test samples. Volatiles may be cryofocused, absorbed on resins, or introduced directly onto a GC column for separations. Separated peaks are identified by GC-MS. Contaminants can usually be detected in the low ppb range with relatively small sample sizes. The method is often more aggressive in removing contaminants than solvent extraction and does not result in solvent disposal problems.

In addition to routine quality analysis, thermal extraction could help identify the general types and frequencies of contaminants in post-consumer resins. In the absence of controverting data, FDA calculations for estimated daily intake (EDI)(3) conservatively assume all containers are contaminated with hazardous materials. (2) Routine thermal extraction could help map the true occurrence of contamination and identify markers to differentiate virgin, chemically recycled, and physically recycled materials. The method might provide guidance for selection of surrogates in FDA's guidelines for testing plastics for food contact use.

PET (polyethylene terephthalate) is an excellent candidate for recycling. It is readily identified with 2L soda bottles, is present in large volumes in recycle streams, has a reasonably high resale value, and has many end uses. Its high melting point and thermal stability also make it an excellent candidate for aggressive thermal extraction. The purpose of this paper was to examine thermal extractables from virgin, chemically recycled, and physically recycled resins provided by major commercial vendors, and from the data compile an emerging sketch (with reflection on relevance) of specific volatile constituents in recycled PET.

## Experimental Approach

**Sample Separation.** Clear PET samples were acquired from various commercial sources of virgin and recycled materials. Recycled resins were from 2° (physically recycled) and 3° (chemically recycled) resins. Virgin material was received either as blown bottles which were subsequently shredded into flake or in the form of pellets. Tertiary recycled/virgin blends were received in pellet form while secondary recycled material was received as washed flake or washed flake that had been further processed into pellet form. A total of 18 samples were examined. All samples were ground in a high speed stainless steel grinder which used a 1 mm stainless steel screen to classify the particles. Particles passing through the screen were used for thermal extraction analysis. In order to minimize the heating effects of the grinding process, samples were ground with solid CO<sub>2</sub> added to the grinder. The dry ice was produced from research grade CO<sub>2</sub> gas just prior to the grinding. After a sample was removed, remaining particles were brushed/vacuumed from the grinder surfaces. Then, a green colored virgin PET was subjected to the same cryogenic grinding procedure and subsequent cleanup steps as the clear samples. The

result of this step was to reduce cross contamination between analyzed samples to an insignificant level. If green residues were observed in clear samples, the grinder was recleaned and the clear sample was reground.

**Thermal Extraction.** The thermal extraction-GC-MS (TE-GC-MS) procedure involved a controlled heating of .1-.3g PET samples in a stream of flowing helium followed by analysis of the thermally extracted volatiles. The extraction cell was made of fused quartz and for the purposes of contaminant bakeoff could be heated to as high as 750°C with temperature ramp rates as high as 150°C/min. For PET analysis, samples were subjected to one of two procedures labelled A and B. In procedure A, the thermal extraction cell was first maintained at 50°C, then ramped to 160°C in 9 minutes, and finally held at 160°C for 3 minutes. In procedure B, the sample was held at 160°C for 15 minutes. With increasing temperature, compounds liberated from the sample were swept by the helium through a fused silica transfer line heated to 350°C to the capillary chromatographic column where they were trapped at the head of the column by cryogenic focussing ( $\leq -120^\circ\text{C}$ ).

During the thermal extraction process, the chromatographic column was held at 35°C. The column was 30m x 0.32mm ID with a 0.25 micron thick DB-5 phase. After the extraction period, the trapped volatiles were transferred to the column by heating the cryofocused region to 310°C at a ramp rate of about 60°C/sec. In procedure A, the column temperature was programmed to ramp from 40°C to 160°C at 5°C/min followed by a ramp to 285°C at 10°C/min and 1.5 min hold time. For procedure B, the ramp was from 35°C to 55°C at 10°C/min followed by a ramp to 310°C at 15°C/min and then a hold period of 10 min. The detector was a quadrupole mass spectrometer scanning the range 29-400 amu at a rate of 1.5 sec/scan.

## Results

**Extractable Compounds.** The chromatogram shown in Figure 1, is the summation of the total ion current from TE-GC-MS analysis of eight representy samples of secondary recycled PET washed flake obtained from locations in six states. It should be immediately apparent from the sheer number of peaks in the chromatogram that recycled material is a complex chemical system. Determining the identity and the effects of temperature on this considerable number of compounds presented a challenge to which the thermal extraction technique was well suited.

All compounds were identified by comparing experimental mass spectra with spectra catalogued in the NBS library of compounds. In most cases, positive identification was possible; however, in a few cases ambiguity resulted from the similarities in mass spectra of closely related compounds. For certain compounds, it was necessary to examine mass spectral fragmentation patterns and only a portion of the compound's chemical structure could be determined (e.g. phthalic acid, terephthalic acid, and isophthalic acid diesters). Compounds identified were loosely classified into categories associated with their chemical nature or presumed origins:



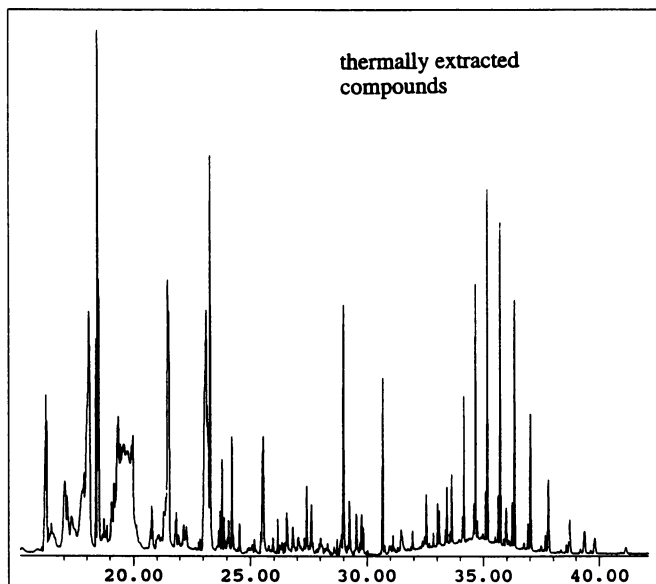


Figure 1. Sum of total ion current from thermal extraction of eight representative virgin and recycled resins.

- I. Small and Ethylene Glycol Related
- II. Flavor Compounds
- III. Benzoic Acid Related
- IV. Benzene Dicarboxylic Acid Related
- V. Aliphatic Hydrocarbons and Acids
- VI. Unexpected Contaminants
- VII. Miscellaneous Compounds

**Small and Ethylene Glycol Related Molecules (Class I):** Compounds identified in this category were polar oxygenated species with retention times between 16 minutes and approximately 21 minutes as shown in Figures 2, #1-#10. Ethylene glycol (#6) was a major component in the chromatograms of all virgin, tertiary recycled/virgin blends, and secondary recycled samples. Compounds #3,#7-#10 are clearly related to ethylene glycol being condensation products of ethylene glycol with itself and with methanol, formic acid, acetaldehyde, and acetic acid. Compounds #1,#2,#4, and #5 are examples of small molecules which may be byproducts of the manufacture of some PET resins. Compounds in this category were found in various concentrations and combinations in both virgin and recycled samples.

**Flavor Compounds (Class II).** In this category there were numerous compounds (#11-#18) thermally extracted from 2°-recycled material with retention times of 21-24 minutes. None of these compounds were found in virgin or 3°-recycled/virgin blends. The most predominant species in this category was d-limonene (#11), a volatile common to citrus peel oil. The family consists of eight closely related terpenes which are well known flavor constituents. Each compound has ten carbons and a six membered ring. Other similar compounds which appeared at minimum detection levels were not positively identified.

**Benzoic Acid Related Compounds (Class III).** Another class of compounds were those related to benzoic acid. These include benzoic acid (#20), benzoic acid esters (#21,#22,#23), and benzaldehyde (#19) with retention times of 23.15, 26.5, 23.3, 25.5 and 20.8 minutes, respectively. The presence of benzoic acid is not surprising; its salts are widely used as preservatives in beverage products. Benzoic acid esters and benzaldehyde can be understood as flavoring agents, the most common being methyl salicylate (#22), the principal component in root beer flavor. The origin of n-propyl benzoic acid as a beverage constituent, however, is doubtful since it was also found in samples of virgin and 3°-recycled/virgin blends.

**Benzene Dicarboxylic Acid Related Compounds (Class IV).** Terephthalic acid (i.e. 1,4-benzene dicarboxylic acid) is a main structural component of PET. As a result, it is not surprising that various terephthalic acid related compounds were thermally extracted and detected from both virgin and recycled material. The various mono ( $R_1=H$ ) and diesters ( $R_1, R_2 =$  hydrocarbon chain) are represented in #24. These were identified by comparison to catalogued mass spectra or strongly indicated by the presence of characteristic mass spectral fragmentation species. Some virgin material showed diesters

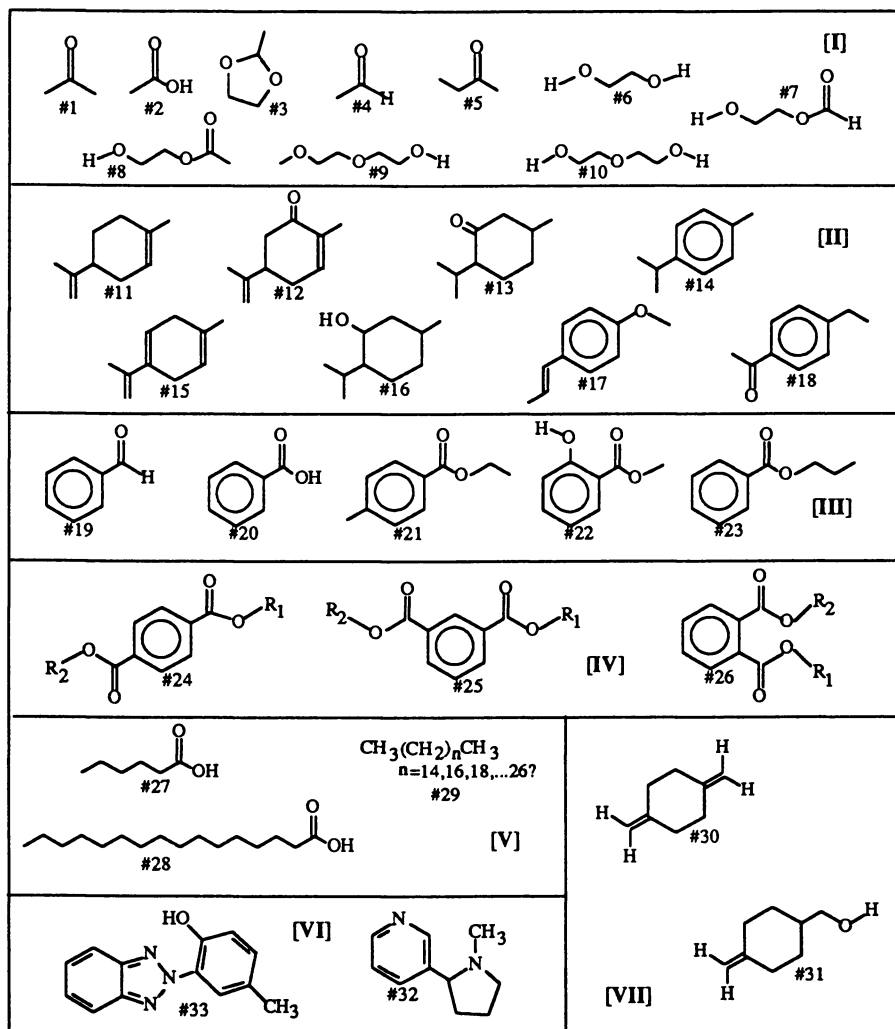


Figure 2. Compounds associated with thermally extracted PETE

of this type, while others, even from the same manufacturer, did not. On the other hand, all secondary recycled material showed a variety of this type of compound. For example, the prominent peak in the chromatogram in Figure 1 at 29.0 minutes has a mass spectrum very similar to terephthalic acid, methyl vinyl diester or terephthalic acid, dimethyl diester. The presence of terephthalic acid esters, which is particularly extensive in the recycled material, may be related to the hydrolysis of PET. Methyl and other esters may be present at the terminus of PET polymer chains.

In addition to terephthalic acid derivatives, phthalic acid and isophthalic acid derivatives (#26 and #25 respectively) were found. In some virgin samples for example, isophthalic acid, decyl methyl ester (at 31.5 min.) and phthalic acid, di-n-octyl ester (at 33.4 min.) or closely related compounds were found. Compound #25 is a known chain modifier used in at least one process for PET manufacture. Compound #26 is possibly a polymer adjuvants used in the manufacture of PET. These two compounds were found in secondary recycled material (at 31.5 and 33.4 minutes) along with a number of other phthalic and isophthalic acid related compounds. Compounds having high molecular weight mass spectral fragments in addition to the characteristic diester fragments were found at 36.0 minutes and 39.4 minutes. With the exception of the compounds found at 31.5, 33.4, 36.0 and 39.4 minutes, all other diesters appeared between 26 and 30 minutes in the 2° recycled material.

**Aliphatic Hydrocarbons and Acids (Class V).** In all samples of washed flake, a plume of 12 aliphatic hydrocarbons was detected with retention times from 33 to 41 minutes. These compounds appear to be the members of a homologous series of long chain hydrocarbons. These are evidently waxy components, possibly the result of residues left from external package components such as base cup and label adhesives. One sample of washed flake was subjected to 3 minutes of thermal extraction at 160°C and the hydrocarbon plume of compounds dominated the chromatogram shown in Figure 3a. This same sample was reheated immediately after the first chromatographic analysis ceased. After the second heating to 160°C for 3 minutes the hydrocarbon plume was again seen with a decrease in intensity and a shift of the plume peak distribution to longer retention times. The repeated extraction of these hydrocarbons from secondary recycled flake indicated a reservoir of hydrocarbons whereas the shift in the hydrocarbons peak distribution indicated that more volatile compounds are preferentially removed.

The straight chain organic acids, hexanoic acid, hexadecanoic acid, and octadecanoic acid were found in secondary recycled flake with retention times of 21.1, 29.75, and 31.1 minutes in Figure 1, respectively. These compounds do not appear as homologous series of acid that might be expected from a natural source of fatty acid material. Instead, these compounds seem likely to be release agents and detergent residues left from the cleaning solution. A few other complex organic molecules were detected but not clearly identified which may also be residual from the wash solution.

**Unexpected Contaminants (Class VI).** Two examples of compounds in this category were drometrizole (Tinuvin) and nicotine. Drometrizole is a UV-absorber and is used to stabilize plastics and other organic materials from discoloration and deterioration. Though this compound was not found in any of the virgin PET samples examined, it was found

in nearly all recycled flake at a retention time of 30.64 minutes. With some flake samples the drometrizole peak was a dominant peak. Possible sources for this compound are base cup polymers and adhesives, label components and adhesives. However, drometrizole is usually not added to food incorporated into food grade PET resins. The size of the drometrizole peak was highly variable. In the cleanest recycled flake material, no drometrizole was detected.

Nicotine was also observed in recycled flake from a single recycler. This facility was located within a densely populated metropolitan area and the chromatogram of the sample is shown in Figure 3a. The nicotine peak at 28.1 minutes is comparable in size to some of the beverage related compounds (e.g. 1/2 the size of limonene). The variable presence and quantity of drometrizole and nicotine present examples of unexpected "spiking" of contaminants in recycled PET.

**Miscellaneous Compounds (Class VII):** Other kinds of compounds could be seen that appear to be incorporated during the production of PET. Compounds (#30 and #31) were found at low levels in samples of both virgin and 3<sup>0</sup>-virgin blends. These may have originated as 1,4-cyclohexane dimethanol where dehydration has occurred at one or both of the hydroxyl groups producing methylene groups on the cyclohexane ring.

### Effects of Recycling Steps

**Moderately High Temperature ( $\leq 160^{\circ}\text{C}$ ).** The dramatic effect of heat on the contaminant content and distribution in recycled flake can be seen in Figure 3. The sample was heated to  $160^{\circ}\text{C}$  for three minutes and the species analyzed and then heated a second time and analyzed. The extraction temperature of  $160^{\circ}\text{C}$  is typical of the temperature at which PET is dried in recycling process and serves as a simple model for understanding some of the effects of the drying step in the recycling process. Based on the thermal extraction results, it is clear that the drying process can be effective in removing residual compounds.

**High Temperature ( $260\text{-}280^{\circ}\text{C}$ ).** High temperatures are used at various stages in the manufacture of PET and in the extrusion process where temperatures near the melting point (i.e.  $260\text{-}280^{\circ}\text{C}$ ) of the polymer are necessary. To examine the effects of extrusion on the contaminants, samples of extruded washed flake material were studied by thermal extraction. Figures 4a and 4b show washed flake obtained from the same source before and after extrusion. A definite decrease in the quantity of compounds extracted was seen particularly for the flavor and benzoic acid related compounds such as d-limonene and methyl salicylate at 23.3 and 23.7 minutes respectively. On the other hand, a number of compounds appeared less affected by the heating process; in fact, one compound at 27.1 minutes was increased. The mass spectrum of this compound suggested dibutyl phthalate. The peak representing hexadecanoic acid was only slightly affected. Finally, the hydrocarbon plume at long retention times showed some decrease at the onset of the plume, a shift in the peak distribution, and even an increase in the trailing compounds.

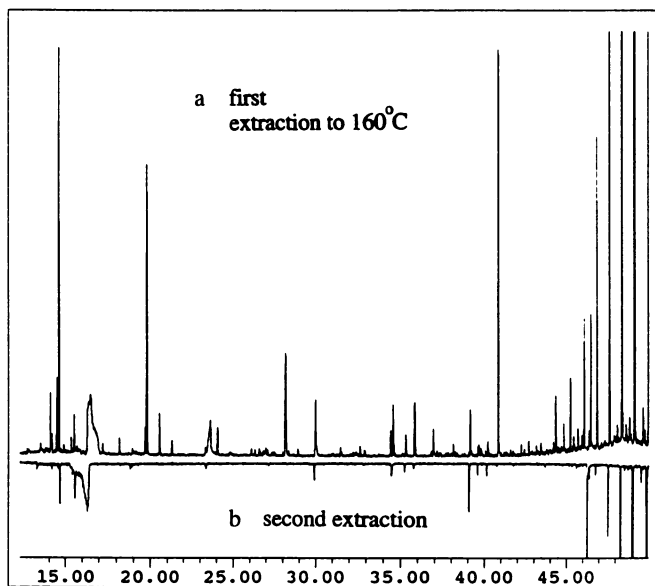


Figure 3. Total ion current chromatograms of 2° recycled PETE from first (a) and second (b) thermal extractions.

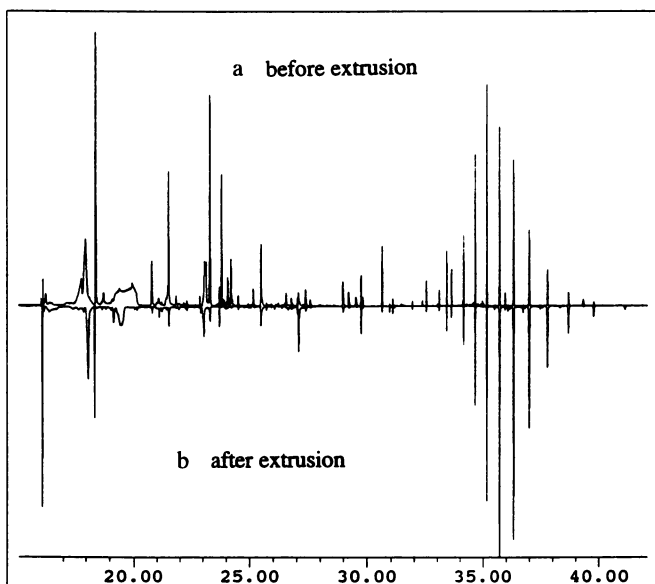


Figure 4. Total ion current chromatograms of 2° recycled PETE before (a) and (b) after extrusion.

**Selective Recycling Stream.** The effect of using a select stream of recycled PET can be seen in Figure 5. Both samples shown in this figure were from the same recycler located in a "bottle state" where beverage bottles are redeemable for refund by the consumer. First, the effect of the "bottle states" policy on the quality of source material can be seen by comparing Figure 5a with Figure 1. Source material obtained through curbside collection may contain as much as 10% non-beverage standard PET. A somewhat different assemblage of contaminants can be expected for curbside than for a pure beverage bottle stream; but the similarities are certainly more obvious than the differences.

A striking difference can be seen, however, when the select stream is made highly selective. An example would be the current state-of-the-art beverage bottle package that uses an integral molded base rather than a base cup and advanced labelling technology minimizing adhesives. Figure 5b is representative of the advantages of exceptional recycling efforts involving public policy and industrial innovation. By far, the most persistent and dominant contaminants in ordinary recycled flake, including extruded material was the high molecular weight hydrocarbons. This problem appears to be considerably lessened, if not totally removed, in the case of the superior source material from the most selective recycling stream.

As a final comparison, thermal extraction results from samples of both virgin and the "most selective" washed flake are compared in Figure 6. With the exception of a handful of molecules from categories I, II, III, IV, and V, the chromatograms were roughly comparable. An even more favorable comparison can be made when the effects of heating in both the drying (approx. 160°C) and extrusion (260-280°C) are taken into account. In this case, most of the compounds in categories I through V will be reduced and under ideal condition even totally be removed.

## Discussion

The thermal extraction information provides a basis for understanding some of the complex issues involved in the recycling of PET. For the sake of simplification, a schematic presentation of the secondary recycling process is given in Figure 7. A division of the steps can be made based upon the temperature at which the step in the process takes place. Steps expected to thermally activate the PET are shown in the shaded box. Low temperature steps are curbside collection and redemption, flake production, and washing and can be discussed individually.

**Curbside Collection.** At present, this is the most common source of recycled material. This material is generally hand sorted to separate PET bottles from other recyclables. Along with hand sortation comes human error, so, it must be expected that undesirable components can be incorporated from other polymers, misused containers, food stuffs, domestic chemicals, etc. Additionally, contamination is expected from the original stored contents. Many of these type of compounds originating from beverage and condiment contents were detected by thermal extraction. Furthermore, a wide range of contaminants assumed to have originated from non-food contact packaging materials were seen. The

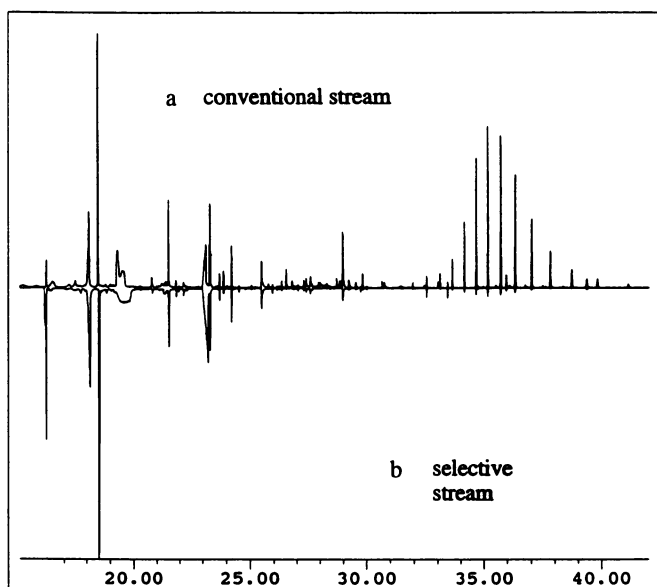


Figure 5. Total ion current chromatogram of conventional (a) and select stream (b) recycled PETE from one bottle- state recycler.

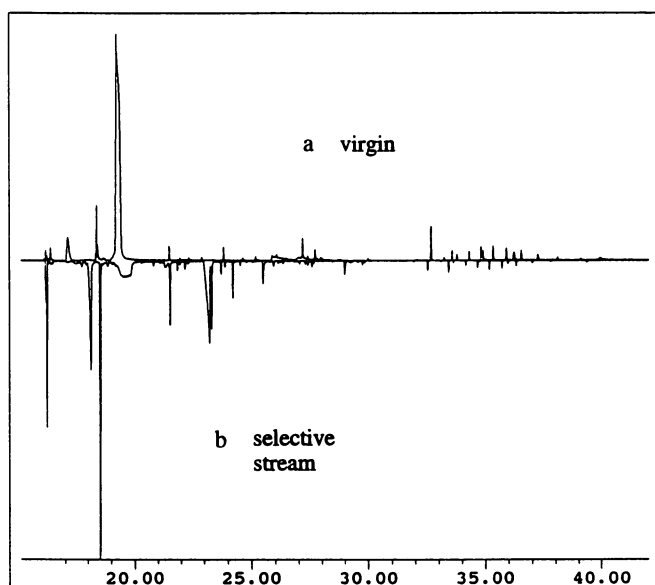


Figure 6. Comparison of virgin (a) and most selective (b) 2° recycled PETE.



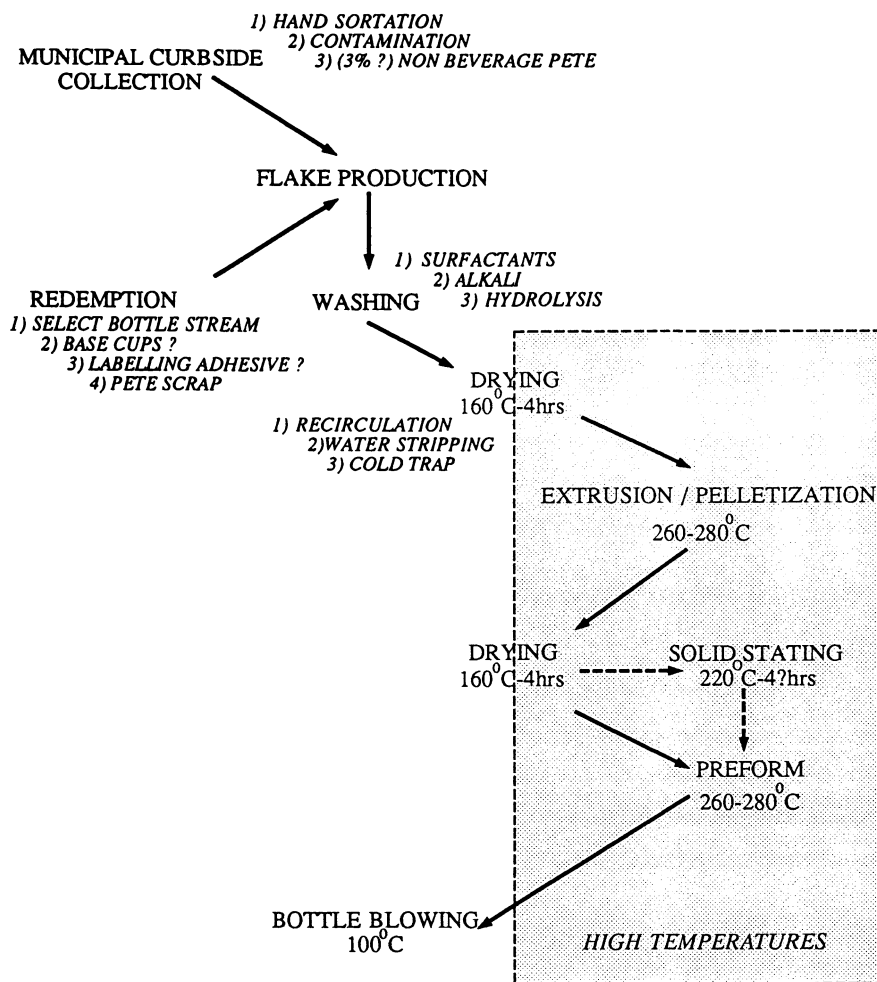


Figure 7. Typical steps involved in processing recycled PETE (thermal steps shown inside the shaded envelope).

substantial hydrocarbon plume seen with all but the most selective stream can be explained as a wax or paraffin component in base cup and label adhesive or possibly oligomers of HDPE base cups. In addition, a number of the phthalic acid esters that appeared in secondary recycled material can be possibly explained as plasticisers used in the fabrication of the common beverage bottle base cup adhesives.

**Redemption.** Bottle redemption policy in certain states resulted in a much cleaner source material. The source could be divided into "select" stream and "highly select" stream. The "select" refers to high quality beverage bottles returned at a point of purchase by the consumer. "Highly select" refers to specialized beverage bottles, designed for ease of recycling, and collected as a uniform sub-stream. Thermal extraction showed that the "select stream" was in many respects similar to the municipal stream. Differences in the number of flavor and other compounds existed, making the "select" stream a somewhat superior source material. The waxy hydrocarbons were especially persistent, being found in both curbside collected and redeemed, washed flake and extruded pellets. From the standpoint of food safety, the waxy material may not constitute a serious threat. From the point of view of polymer engineering for food containers, the incorporation of unwanted compounds can compromise processibility.

The "highly select" stream represents another significant improvement in source material. From the comparison showed in Figure 5, by selecting a sub-stream with an optimized package design (e.g. integral molded base cup), recycling problems can be avoided.

**Flake Production.** Flake production is essentially mechanical; although, some elevated temperature may occur, causing slight chemical effects. During the shredding process, cross-contamination potentially occurs and unwanted materials may become irretrievably incorporated.

**Washing.** Washing introduces a major chemical effect on the recycling process. Recycling facilities may use widely different washing formulations and techniques. Surfactant and detergent composition, wash temperature, washing stages, alkali content, etc. have a pronounced effect; however, it was not possible to assess these parameters in the present study. In a number of samples, it appeared that hydrolysis products of the PET resin were present. These will certainly be greatly affected by the washing step particularly the alkali content of the solutions. With the development of an accepted analysis method (such as thermal extraction or others) for comparing various washing parameters, it should be possible to tailor the washing process to the source material.

**Drying.** Typically, washed flake is then dried at an elevated temperature (approx 160°C for 4 hours) to remove moisture. Thermal extraction at 160°C for 3 minutes of ground samples (see Figure 3), were effective in removing a considerable number of contaminants present in washed flake. The efficiency of this, depends largely on the volatility of the compound and the solubility of the compound in the polymer. Several considerations can be taken into account to maximize the beneficial effect of the drying step for cleaning recycled flake. Recirculation of the drying air is essential; otherwise,

volatile contaminants can only redistribute, essentially smearing the contamination over the entire batch.

It is essential to trap water, as well as volatile organic contaminants liberated in this step. Water can be removed with a desiccant and organics can be removed by cold trapping. Recyclers using cold trapping find a substantial quantity of resinous material. Thermal extraction analysis, performed on ground (<1 mm) particles in flowing helium, represents an ideal case of extractibility that could be approached in the drying step maximizing air flow and trapping.

**High Temperature.** High temperature treatments exist in the extrusion /pelletization, solid stating, and preform step in the recycling process. When flake samples were examined before and after extrusion (see Figure 4), it was found that some benefit was seen in reducing the more volatile compounds but little effect was seen on the waxy hydrocarbons. The extrusion process is short lived involving only minutes. In addition, volatile compounds may not have a chance to escape the extruder because of a closed geometry.

### Conclusions

Thermal extraction of a limited cross-section of virgin and recycled resin provided interesting insights into the history and behavior of commercial PET. Virgin and 3° recycled material exhibited no uniform differences which would betray their separate origins. However, much information could be gained from extraction profiles of 2° recycled PET. Discrimination of curb-side, bottle state and highly select PET streams appeared possible. Unexpected contaminants were sufficiently contrasted against the ambient chemical background to serve as a suitable means for identifying dangerous contaminants in the recycling resins. The data suggested that high temperature treatments could be optimized to enhance contaminant removal. PET degradation pathways were proposed. These might ultimately provide clues to less abusive recycling strategies. The ratio shifts in hydrocarbon data may provide a useful index to the thermal history of recycled PET. Over a period of time, routine thermal extraction could provide a picture of actual incidence of contamination of post-consumer resins.

### Literature Cited

1. National Environmental Policy Act. Section 101(b)(6).
2. FDA. Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations. Food and Drug Administration. Center for Food Safety and Applied Nutrition (HFS-245), Washington DC 20204. 1991.
3. FDA. Recommendations for Chemistry Data for Indirect Food Additive Petitions. Food and Drug Administration, Center for Food Safety and Applied Nutrition (HFS-245), Washington, DC. 1988.

RECEIVED May 26, 1995

## Chapter 38

# Chemically Induced Delamination for Recycling of Coated Aluminum Scrap: Exploratory Phase

Even J. Lemieux

Kingston Research and Development Centre, Alcan International  
Limited, 945 Princess Street, Kingston, Ontario K7L 5L9, Canada

We applied metal corrosion principles in a multi-material recycling perspective and found that soaking laminates in carboxylic acid solutions can efficiently separate plastic, paper, paint or lacquer coatings from metallic surfaces. Carboxylic acids diffuse through organic coatings within a few minutes. Self-delamination is induced through interfacial corrosion of the metal substrate. Delaminated coatings are not degraded by this acid treatment. Delamination maps have been generated for a broad range of laminated structures. The effects of physico-chemical structure, acid concentration and solution temperature on delamination performance are discussed. We also propose a route for the sequential delamination of commingled coated scrap in order to recover value-added organic coatings.

With the advent of the "Green Dot" legislation in Germany (1), a significant amount of plain, lacquered and laminated aluminum foils are now being collected for recycling. Although thermal decoating, such as by a rotary kiln, can efficiently process thick gauge coated scrap (2), handling of high organic content/thin gauge laminated foils would necessitate significant equipment upgrade so as not to compromise aluminum recovery through excessive oxidation. Moreover, burning off the organic fraction of aluminum laminates may not be a viable recycling option. A technique to recover coatings without degrading the aluminum foil is highly desirable.

Corrosion of aluminum alloys by organic acids is well documented (3). For instance, McKee and Binger (4) studied the effect of carboxylic acid chain length, acid concentration and solution temperature on metal digestion. They found that, under similar acid concentration and solution temperature, a short-chain carboxylic acid such as formic acid caused faster metal digestion than longer chain acids such as acetic and propionic acids. Moreover, adsorption and decomposition of acetic

0097-6156/95/0609-0472\$12.00/0  
© 1995 American Chemical Society

acid on clean Al(III) crystals form an acetate reaction product at a fairly low temperature which thermally decomposes to produce hydrogen gas (5).

Delamination of organic coatings from a metal substrate has also been the object of extensive corrosion work (6-11) aimed at predicting the service lives of paints, measuring the permeation of corrosive chemicals through protective coatings and understanding reactivity at the coating/metal interface. Still, these studies focused on the long term corrosion of metallic surfaces while being limited to delamination rates of only a few  $\text{mm}^2$  per hour.

We applied these metal corrosion principles in a multi-material recycling perspective and found that soaking laminates in carboxylic acid solutions can efficiently separate plastic, paper, paint or lacquer coatings from metallic surfaces within a few minutes. The present work examines the effect of carboxylic acid chain length, polarity, solution concentration and temperature on chemically-induced delamination of different categories of coated scrap.

### Experimental

Scrap from commercially available coated products were used in this study. Selection of the products tested relied on design considerations as well as on the multiplicity of field applications: packaging for board stock and collapsible tube, printing for litho stock, construction for architectural sheet and electrical/electronics for cable wrap and shielding foil. These coated products are currently being recycled through thermal decoating i.e. by burning off the organic fraction and recovering the metal fraction.

A structural breakdown of each product is provided in Table I. Organic coatings were of three types: plastic laminates, paper laminates and paint/lacquer coatings. Aluminum thicknesses varied from  $9\ \mu\text{m}$  to  $515\ \mu\text{m}$ . Recoverable coating thicknesses varied from  $5\ \mu\text{m}$  to  $515\ \mu\text{m}$ . We did not attempt to recover extremely thin (less than  $4\ \mu\text{m}$ ) tie layers such as adhesive and primer.

Delaminating solutions contained either formic, acetic, propionic or lactic acids. Volume concentrations varied from 5% to 50%. Because of its low cost, environmental friendliness and industrial availability, most of our tests were performed with acetic acid at various concentration levels, solution temperatures and contact times.

Coupons of at least  $25\ \text{cm}^2$  were cut from each coated scrap source. The influence of temperature on self-delamination was evaluated by soaking each coupon in a preheated delaminating solution for a given contact time. Coupons were then removed from the solution, rinsed in distilled water and dried. A few tests were done where coupons were soaked into baths of the same acid concentration but operating at different temperatures. We recorded the residence time in each bath and tabulated contact time as being the sum of all residence times. Treated coupons were classified into three categories:

- no separation: coatings remain strongly adhered to the metal surface with no evidence of interfacial weakening.

- peelability: interfacial weakening is sufficiently pronounced to cause some loss of adhesion of the organic coatings which either delaminate during rinsing of the coupons or are peeled off through mechanical means.
- self-delamination: there is a total loss of adhesion of the organic coatings which debond from the metal surface while the scrap is in contact with the delaminating solution.

In some cases, we generated delamination maps which identify the transition zone between peelability and self-delamination by measuring contact times, at 100°C, in solutions of variable concentrations.

## Results

**Acetic Acid Concentration and Temperature.** A faster delamination of organic coatings was observed as we increased the concentration of acetic acid and/or the temperature of the delaminating solutions. The concentration and temperature required to achieve self-delamination within a reasonable contact time varied with the physico-chemical structure of the coatings being exposed to the delaminating solutions.

**Plastic Laminates.** As shown by Table II, self-delamination of the ethylene-acrylic acid (EAA) copolymer film from cable wrap occurred within 20 minutes in a boiling solution of 25% acetic acid. Self-delamination can be achieved at a lower concentration level (15%) but the required contact time is in the order of 30 minutes. A decrease in solution temperature caused the coating to peel off. Peelability is also observed if the contact time is too short. In a 5% acetic acid solution, a prolonged contact time of 50 minutes at 100°C did not lead to the self-delamination or to the peelability of the EAA film. Excessive dilution of the acetic acid prevented any separation of the plastic film from the metal surface within a reasonable time frame.

Table II also indicates that a brief residence time of 1 minute at 100°C followed by a slow cooling of the delaminating solution caused self-delamination of the polymeric film. We simulated a faster cooling rate of the delaminating solution by using two reactor vessels, one held at 100°C and the other held at 25°C. Samples were first soaked in the reactor vessel held at 100°C for a specific residence time and then transferred into the second reactor vessel held at 25°C to monitor their delamination behaviour. In order to achieve self-delamination within 20 minutes, the residence time at 100°C needed to be in the order of 10 minutes: we then observed self-delamination after a residence time of only 8 minutes in the solution held at 25°C. However, if residence time at 100°C is reduced to only 5 minutes followed by a 30 minute exposure to the solution held at 25°C, the EAA polymeric film could only be peeled off. Similarly, a residence time of 10 minutes in a 15% acetic acid solution held at 100°C followed by a 40 minute exposure to the solution held at 25°C was insufficient to cause self-delamination.

**Table I. Selected Coated Scrap**

Type	Product	Structure
Plastic Laminates	Cable Wrap	50 $\mu\text{m}$ EAA/80 $\mu\text{m}$ Al
	Shielding Foil	13 $\mu\text{m}$ polyester/9 $\mu\text{m}$ Al
Paper Laminates	Litho Stock	60 $\mu\text{m}$ paper/1-4 $\mu\text{m}$ adhesive/ 15 $\mu\text{m}$ Al/1-4 $\mu\text{m}$ vinyl lacquer
	Board Stock	420 $\mu\text{m}$ paper/1-4 $\mu\text{m}$ adhesive/ 10 $\mu\text{m}$ Al/1-4 $\mu\text{m}$ lacquer
Paint or Lacquer Coatings	Collapsible Tube	13 $\mu\text{m}$ polyester enamel/120 $\mu\text{m}$ Al/ 5 $\mu\text{m}$ epoxy phenolic liner
	Architectural Sheet	21 $\mu\text{m}$ PVDF/1-4 $\mu\text{m}$ primer/ 515 $\mu\text{m}$ Al/1-4 $\mu\text{m}$ primer

**Table II. Delamination Behaviour of Cable Wrap Soaked in Acetic Acid Solutions**

Acid Concentration (% v/v)	Solution Temperature, T ( $^{\circ}\text{C}$ )	Residence Time at T (min)	Contact Time (min)	Observations
25	100	10	10	Peelability
25	100	20	20	Self-delamination
25	100	1	20	Self-delamination
25	100	10	18	Self-delamination
25	25	8		
25	100	5	35	Peelability
25	25	30		
25	70	30	30	Peelability
15	100	10	50	Peelability
15	25	40		
15	100	30	30	Self-delamination
15	80	50	50	Peelability
5	100	50	50	No separation

We also ran a limited number of tests on a shielding foil. Even though the polyester film on a shielding foil is considerably thinner than the EAA film applied on cable wrap, peelability of the polyester film was only possible after more than 50 minutes of contact time in a boiling 25% acetic acid solution. One would need to increase the acetic acid concentration in order to accelerate delamination.

**Paper Laminates.** Figure 1 compares delamination maps generated for litho stock (60  $\mu\text{m}$  paper) and board stock (420  $\mu\text{m}$  paper) laminates soaked in acetic acid solutions at 100°C. At such a solution temperature, litho stock self-delaminated after a contact time of about 15 minutes in 15% acetic acid while board stock required to be soaked in 25% acetic acid in order to self-delaminate as quickly as the litho stock. Attempts to induce self-delamination in board stock within five minutes by increasing the acetic acid concentration to 35% only led to the paper coating peeling off.

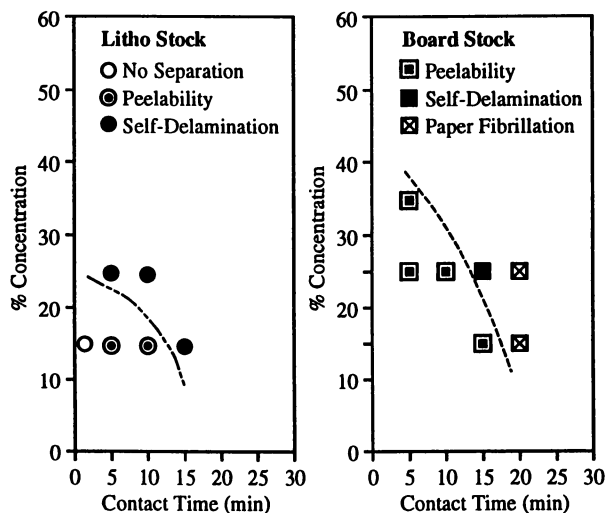
Increasing contact time caused paper fibrillation in board stock exposed to acetic acid solutions for more than 20 minutes. This can be desirable if a fiber suspension is required by the paper recycling industry. Fibers could be cleaned more readily than a mass of compacted paper sheets. The economics of handling paper fiber suspensions comparatively to delaminated paper sheets would need to be addressed in order to decide if controlled fibrillation is a desirable route to integrate within a self-delamination recycling operation.

**Paint or Lacquer Coatings.** A delamination map generated for fluoropolymer-coated (PVDF) architectural sheets and collapsible tubes soaked in acetic acid solutions heated to 100°C is shown in Figure 2. Each scrap source displayed a concave transition line between the peelability and self-delamination zones. A minimum acetic acid concentration was found to exist below which no delamination is possible within a reasonable time. In a boiling 25% acetic acid solution, it took at least 60 minutes before separating the PVDF coating from its aluminum sheet. At such a concentration level the metal was still coated with the primer. Increasing the concentration of the acetic acid solution to 50% significantly decreased the contact time required to self-delaminate the PVDF coating.

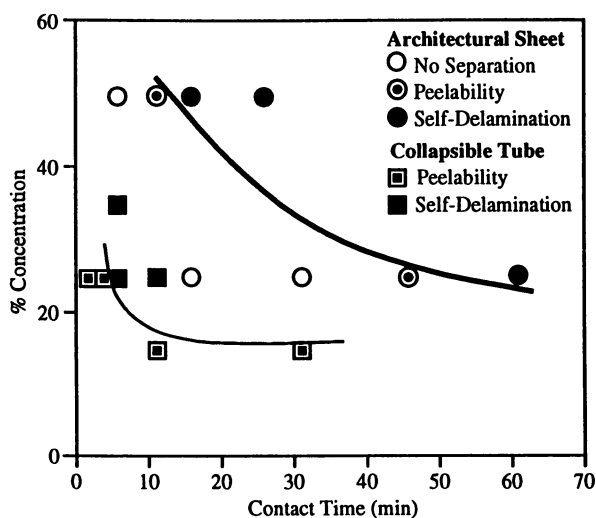
A contact time of 30 minutes in 5% acetic acid at 100°C caused the polyester enamel on collapsible tubes to peel off while the epoxy phenolic liner still adhered to the aluminum surface. Similar results were obtained with a higher acetic acid concentration (25%) at a lower temperature (70°C). Both coatings could be peeled off after 30 minutes in 15% acetic acid at 100°C. Peelability of both coatings was also observed in 25% acetic acid at 100°C with a contact time of only 1 minute. A contact time of at least 5 minutes in a 25% acetic acid solution was required in order to self-delaminate both coatings at 100°C. Under such conditions, the polyester enamel delaminated first and was quickly followed by the epoxy phenolic inner liner.

**Carboxylic Acid Chain Length and Polarity.** The effects of acid concentration, bath temperature, carboxylic acid chain length and polarity on the contact time





**Figure 1.** Influence of Acetic Acid Concentration on the Contact Time Required to Self-Delaminate, at 100°C, Paper Laminates Such as Litho Stock and Board Stock.



**Figure 2.** Influence of Acetic Acid Concentration on the Contact Time Required to Self-Delaminate, at 100°C, Architectural Sheet and Collapsible Tube.

required to achieve self-delamination of various organic coatings found on collapsible tubes, cable wrap and shielding foil are summarized in Table III. For the purpose of this comparison, we limited the concentration range to 5-25%, the bath temperature to 80-100°C and the contact time to a maximum of 50 minutes. If self-delamination was not observed within 50 minutes, a peelability test was performed: coatings could then be easily peeled off (P) or not separated (NS) at all. Results from Table III are reviewed both in terms of shorter carboxylic acid chain length (formic acid versus other acids) and of more polar acid chains (lactic acid versus propionic acid).

**Formic Acid Versus Other Acids.** Overall, formic acid performed much better than acetic, propionic or lactic acids under comparable soaking conditions. As noticed with the acetic acid system investigated earlier, an increase in the formic acid concentration reduced the contact time required for self-delamination of all coated scrap investigated. Among the four carboxylic acids compared, propionic acid displayed the weakest response: none of the conditions used in Table III were appropriate to achieve self-delamination in propionic acid within 50 minutes.

Self-delamination of the polyester enamel on collapsible tubes took less than 3 minutes at 100°C even in a 5% formic acid solution. Self-delamination of the epoxy phenolic inner liner required slightly longer contact times. Contact times in acetic, propionic or lactic acids were at least three times longer than in formic acid. In fact, by increasing the carboxylic acid chain length the necessary contact times to achieve self-delamination were even longer. Both the polyester enamel and the epoxy phenolic inner liner could not be separated from the aluminum surface after 50 minutes of soaking in a 5% propionic acid solution at 100°C whereas self-delamination in a 5% formic acid solution at 100°C was observed within only 8 minutes.

Self-delamination of the EAA film on cable wrap took less than 5 minutes at 100°C if at least 15% formic acid solutions were used. Similar soakings in acetic acid required at least 18 minutes for a complete separation to be observed. A decrease in solution temperature caused peelability of the EAA film whenever the cable wrap coupons were soaked in acetic, propionic or lactic acids. However, we could still observe self-delamination in a 15% formic acid solution heated to 80°C.

None of the carboxylic acids explored could achieve self-delamination of the EAA film on cable wrap if the acid concentration was too low. At a 5% concentration the EAA film could be peeled off in formic or lactic acids but could not be separated in the presence of acetic or propionic acids.

Self-delamination of the polyester film on shielding foil could only be achieved in the presence of formic acid. In contact with acetic, propionic or lactic acids, the film was peeled off. The contact times required to self-delaminate the polyester film in 15-25% formic acid solutions heated to 100°C were about 3 times longer than the contact times required to self-delaminate the EAA film on cable wrap under similar conditions. As with all other systems investigated, operating at a lower solution temperature considerably slowed down the reaction to a point where peelability was observed in a 15% formic acid solution heated to 80°C.

**Table III. Experimental Conditions Required to Self-Delaminate Organic Coatings from Scrap Soaked in Carboxylic Acid Solutions**

Coating/ Product	Acid Conc. (% v/v)	Bath Temp. (°C)	Contact Time (minutes) in Carboxylic Acid Solutions of:			
			Formic Acid	Acetic Acid	Propionic Acid	Lactic Acid
Polyester	25	100	1.0	3.0	P	4.3
Enamel/ Collapsible Tube	15	100	2.5	15.2	P	8.5
	15	90	2.5	28.0	P	22.0
	15	80	10.8	P	P	P
	5	100	3.0	10.0	NS	26.0
	25	100	1.5	5.0	P	11.0
Epoxy Phenolic Inner Liner/ Collapsible Tube	15	100	2.5	P	P	21.0
	15	90	7.0	P	P	P
	15	80	19.0	P	P	NS
	5	100	7.5	P	NS	P
	25	100	2.0	18.0	P	24.0
EAA Film/ Cable Wrap	15	100	3.0	30.0	P	P
	15	90	3.3	P	P	P
	15	80	6.7	P	P	P
	5	100	P	NS	NS	P
	25	100	6.0	P	P	P
Polyester Film/ Shielding Foil	15	100	9.0	P	P	P
	15	90	19.0	P	P	P
	15	80	P	P	P	P
	5	100	P	P	P	P

P = peelability within 50 minutes; NS = no separation within 50 minutes

**Lactic Acid Versus Propionic Acid.** None of the experimental conditions applied in Table III led to the self-delamination of organic coatings from aluminum surfaces in the presence of propionic acid. Peelability could be observed in most cases except for highly diluted solutions (5% propionic acid) where the polyester film on shielding foil was the only coating that could be peeled off.

In contrast, exposure of the same coated scrap to lactic acid solutions caused self-delamination in a few cases where acid concentration and solution temperature were sufficiently high. Decreasing either the acid concentration or the solution temperature led to peelability. In one case, 15% lactic acid at 80°C, the epoxy phenolic inner liner could not be separated from the aluminum surface of the collapsible tube.

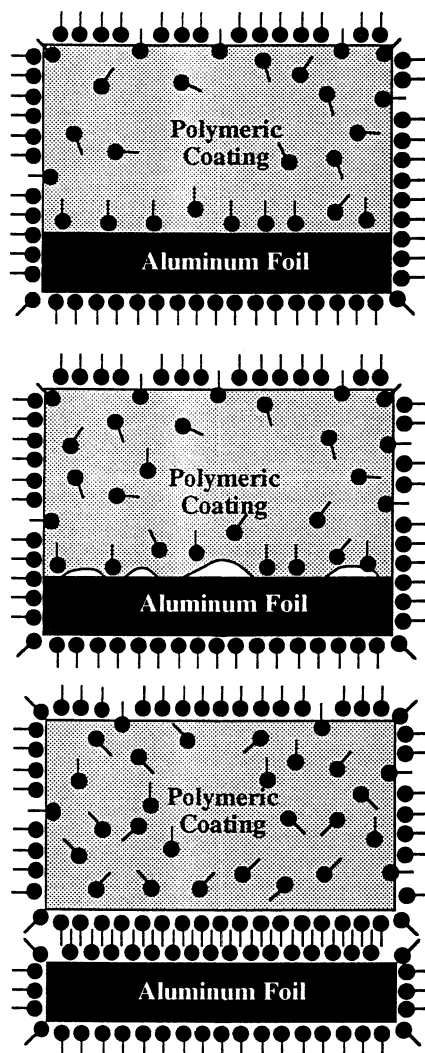
Using 25% lactic acid solutions heated to 100°C, both the polyester enamel and the epoxy phenolic liner self-delaminated within 11 minutes whereas prolonged soaking in propionic acid solutions under similar conditions did not provoke any delamination of the coatings. The main structural difference between propionic ( $\text{CH}_3\text{CH}_2\text{COOH}$ ) and lactic ( $\text{CH}_3\text{CHOHCOOH}$ ) acids is the presence of an hydroxyl group along the lactic acid chain which renders the molecule more polar. Increasing the polarity of the carboxylic acid chain favors delamination.

## Discussion

**Delamination Mechanism.** A relationship exists between the carboxylic acid chain length, the corrosion rate of the acid solution towards the metal surface, and the self-delamination of organic coatings from the metal surface. Figure 3 schematically illustrates the delamination mechanism which can be divided into three steps: accessibility of the acid solution to the metallic surface, reactivity of the acid at the coating/metal interface and self-delamination of the polymeric coating.

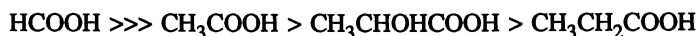
Accessibility of the acid solution to the metal surface requires proper diffusion of the carboxylic acid through the organic coating. Diffusion rate is controlled by the solution temperature, its concentration, the thickness of the organic coating, the presence or absence of inorganic fillers and the intrinsic barrier properties of the coating formulation. The chemical structure of the coating controls the rate at which a carboxylic acid solution will diffuse through it. Under similar conditions of temperature, concentration and coating thickness, a highly porous and permeable paper coating will self-delaminate faster than a more water-resistant and less porous polypropylene coating. Factors such as polymer morphology, crystallinity, and polymer orientation also affect small molecules diffusion (12).

The diffusion rate also depends upon the size and shape of the diffusing molecules (13-15). For example, diffusion coefficients for a series of long-chain n-alkanes (from  $\text{C}_{12}$  to  $\text{C}_{32}$ ) in various polyolefins were found to decrease as a function of the chain length of the diffusing molecules (14). Moreover, non-polar substances have the tendency of diffusing more slowly through polymeric membranes than polar substances (15). Lactic acid being more polar than propionic



**Figure 3.** Schematic View of the Delamination Mechanism: Diffusion of the Carboxylic Acid Solution Through the Coating (top), Reactivity of the Acid at the Coating/Metal Interface (middle) and Self-Delamination of the Coating (bottom).

acid, our classification of delaminating solutions based on their ability to diffuse through organic coatings is:



Reactivity of the acid at the coating/metal interface is a function of the corrosiveness of the carboxylic acid selected to perform self-delamination. Both the diffusion and the corrosion rates of a carboxylic acid solution are inversely proportional to the carboxylic acid chain length; the shorter the acid chain length, the greater will be its diffusion through an organic coating and its corrosion rate towards aluminum. Increasing the carboxylic acid chain length slows down the aluminum corrosion rate and its consequent microscopic surface corrosion. This in turn extends the time required for separation of an organic coating from the aluminum surface. Under our experimental conditions, none of the delaminated coatings were degraded by the carboxylic acid solutions.

More fundamental research would be required to determine if the carboxylic acid concentration at the interface between the organic coatings and the metal surfaces remains equal to the initial concentration of the delaminating solution. There is a possibility that some organic coatings behave like membranes which would prevent migration of the acid molecules through the coatings, affect the acid concentration at the interface and modify the consequent self-delamination rate.

Maximization of the self-delamination of polymeric coatings is achieved by operating at a high bath temperature, typically 100°C. A decrease in bath temperature of only 10°C can easily double the contact time required for self-delamination. This strong temperature dependence is in accordance with previously reported aluminum corrosion rates in carboxylic acids (2). The impact of bath temperature on delamination is also governed by the chemical nature of the organic coatings.

Based on Figures 1 and 2, a minimum acid concentration is needed for carboxylic acids to self-delaminate plastic, paint or lacquer coatings within a reasonable contact time while self-delamination of paper laminates is more time-dependent than concentration-dependent.

**Formic Acid Versus Acetic Acid.** Of all the carboxylic acids investigated in this study, formic acid provided the fastest delamination response, followed by acetic acid and lactic acid. From an economics viewpoint, lactic acid costs three to four times more than acetic or formic acids. From an occupational health and safety viewpoint, acetic acid is considered to be less toxic than formic acid. However, all carboxylic acids investigated can be properly handled using standard chemical engineering plant practices. All these elements need to be properly balanced in order to decide if a delamination plant ought to be operating with formic acid only, acetic acid only or a combination of several carboxylic acids.

Figure 4 compares the contact time required to self-delaminate cable wrap coupons at 100°C in the presence of various concentrations of formic or acetic acids. Self-delamination of cable wrap is considerably faster in the presence of

formic acid than in acetic acid. An increase in coating thickness and/or barrier properties will be shifting the self-delamination zones to higher acid concentrations and/or longer contact times. Given the faster response achieved by a formic acid delaminating solution, it would be advisable for one of the reactor vessels in a potential delamination plant to contain formic acid as a mean of handling more complex and/or less permeable forms of coated scrap.

Nevertheless, a broad range of coated scrap sources which would otherwise be troublesome to recycle via thermal decoating were shown to be easily processable by chemically-induced delamination. Our successful separation and recovery of plastic, paper, paint or lacquer coatings proves that the chemically-induced delamination route can adapt itself to specific scrap streams from the foil converting industry. Painted architectural sheets also exhibit controllable delaminating characteristics. Most coatings self-delaminate within 5-15 minutes in acetic acid solutions if the bath temperature and the acid concentration are properly balanced. This provides an environmentally-friendly solution to the recycling of flexible packaging and other forms of coated scrap. Local converting plants generating plastic-coated scrap can also gain faster delamination rates by using diluted formic acid delaminating solutions.

**Delamination Process - Technical Hurdles.** In order for carboxylic acid delaminating solutions to become a key part of the aluminum laminates recycling industry, certain issues must be further explored.

**Size Reduction.** Shredded laminated scrap has the tendency of packing itself together. This is detrimental to the accessibility of the carboxylic acid delaminating solutions. Other means of size reducing scrap so that materials can be treated more readily either by an organic solvent or by a carboxylic acid delaminating solution include a plastic granulator which is designed to minimize the amount of folding and compacting of size-reduced materials.

**Organics Isolation After Processing.** Isolation of delaminated paper fibers can be achieved through drainage and filtration of the delaminating solutions. However, plastic components will remain in suspension as flaky solids mixed with loosened aluminum foil.

There is a need to define a straightforward approach to segregate these delaminated materials. This may require the use of a density gradient column to separate polyolefins from polyester films and aluminum foil.

The geometry of the reactor vessel containing the delaminating solution can be adapted so as to facilitate the recovery of delaminated coatings through a sink-float operation. Indeed, less dense materials such as polyolefin films will float to the surface of a carboxylic acid delaminating solution while the aluminum fraction will sink. The polyolefin films can then be scooped out of the vessel, rinsed, dried and shipped to the plastic recycling plant while the aluminum fraction, recovered through drainage of the reactor vessel, can be shipped to the aluminum recycling plant.

Pilot-scale/industrial electrostatic separators configured for polyester/aluminum separation are commercially available. They are commonly used to separate, among other things, aluminum caps from granulated polyethylene terephthalate (PET) soft drink bottles.

**Organics Chemical Resistance.** Since our main objective is to demonstrate that the aluminum foil in laminates can be recycled as well as their organic components, conditions must be selected to cause self-delamination of organic coatings without leading to a chemical attack of the recovered materials. Acetic acid is milder than formic acid although prolonged soaking in a concentrated solution of the former may affect properties of recovered polymers as much as a brief soaking in a dilute solution of the latter.

Self-delamination is believed to be the beginning of a slow chemical degradation of the organic coatings, some being more sensitive than others. Delimitation of a maximum contact time as well as a maximum acid concentration for a targeted product delamination map would ensure the integrity of all recovered organic materials.

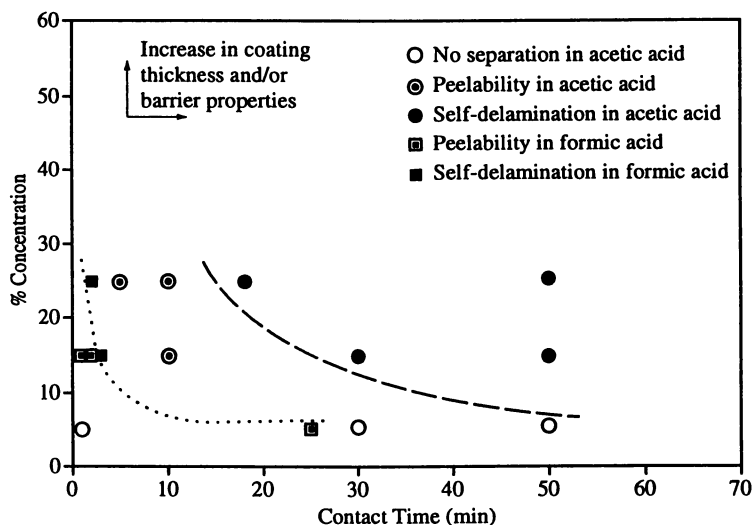
**Delaminating Solution Reusability.** Because of the corrosive nature of the carboxylic acids towards aluminum, some of the aluminum is being digested by the acid. We monitored the presence of aluminum ions in the carboxylic acid solutions and detected concentrations that are sufficiently low to minimize any concerns regarding the reusability of the delaminating media. If need be, reconditioning of the solutions can easily be achieved through distillation and ion-exchange resin chromatography.

**Commingled Laminates - Sequential Delamination.** Trends defined through our examination of individual delamination maps are summarized in Figure 5 which provides a general view of the transition lines beyond which delamination of certain categories of coated scrap is feasible in acetic acid solutions heated to 100°C. As mentioned earlier, there are two categories of transition lines: the time-dependent lines which refer to paper laminates and the concentration-dependent lines which refer to other forms of laminates such as collapsible tube, cable wrap and architectural sheet.

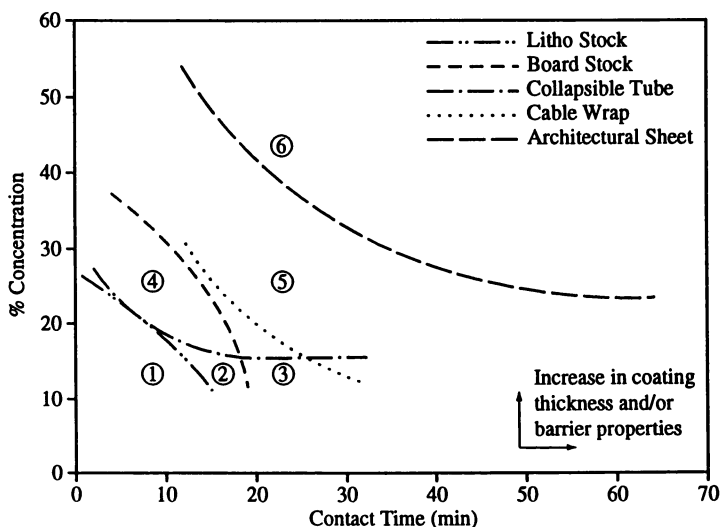
We have identified six self-delaminating zones where transition lines can be selectively or, if need be, sequentially crossed in order to separate certain coatings from a mixture of various laminates:

- zone # 1 → cigarette foil
- zone # 2 → litho stock and other forms of thin gauge paper laminates
- zone # 3 → board stock and other forms of thick gauge paper laminates
- zone # 4 → collapsible tubes
- zone # 5 → cable wrap and other forms of plastic laminates
- zone # 6 → architectural sheets





**Figure 4.** Influence of Formic Acid and Acetic Acid Concentrations on the Contact Time Required to Self-Delaminate, at 100°C, Plastic Laminates Such as Cable Wrap.



**Figure 5.** General View of the Acetic Acid Concentration/ Contact Time Transition Lines Beyond Which Sequential Delamination of Designated Sources of Coated Scrap is Achieved at 100°C (Numbered Self-Delamination Zones Are Described in the Text).

Zones #1-3 designate different grades of paper laminates, the thickness of the paper layer increasing as we move from zone #1 to zone #3. Paper laminates can be processed using a relatively low concentration of acetic acid (15%) and rather short contact times. Zones #4 and 5 address less permeable coatings such as enamels and plastic laminates whereas zone #6 targets weather-resistant coatings such as the ones found on architectural sheets.

All transition zones will be shifting to longer contact times and/or greater acetic acid concentrations if thicker coatings must be dealt with or if more resistant coatings, such as polyester films, are encountered in a given group category. In either case, a second treatment in a formic acid bath could potentially recover these less permeable coatings.

If all self-delamination zones are crossed sequentially, the coated scrap remaining in the processing chamber ought to consist of architectural sheets (zone #6). Operating within zone #6 is self-inclusive: any materials processable within zones #1-5 can readily be delaminated within zone #6. This means that a processing plant could very well recover a mixture of organic coatings rather than singulated coatings, if the recycling market favors such an approach.

## Conclusions

Carboxylic acid solutions can delaminate, i.e. separate, organic coatings from a metal substrate such as thin gauge foil packaging scrap. Our delamination mechanism suggests that the acids diffuse through organic coatings and induce self-delamination of the coatings through interfacial corrosion of the metallic substrate. This in turn decreases the adhesion strength between the organic layer and the metal. Delaminated coatings do not show evidence of chemical degradation and can be recovered for recycling.

A shorter carboxylic acid chain length increases the ability of the acid to induce self-delamination of organic coatings. Formic acid delaminates coatings faster than any other carboxylic acid investigated so far. Lactic acid performs better than propionic acid which means that polarity of the chain also affects coatings delamination.

Delamination maps generated for a broad range of coated scrap soaked in various concentrations of carboxylic acids show that highly polar or porous coatings such as cellulose delaminate faster than water barrier coatings such as polyolefins. The overall delamination rate is decreased by an increase in the thickness or in the barrier properties of the organic coatings.

Self-delamination is not only controlled by contact time, temperature, concentration and chemical structure of the carboxylic acid solutions but also by the physico-chemical structure of the organic coatings. Means of inducing selective delamination within a foil packaging scrap mix suggest that there is potential for a commercial process based on this approach having the advantages of:

- applicability to a broad range of coated scrap products,
- no need for costly pollution control units since none of the coatings are burned off,
- efficient recovery of the organic as well as the aluminum components.

### Acknowledgments

The author is grateful to Alcan International Limited for permission to publish this work and to A. Rosenfeld and J.G. McCubbin for helpful suggestions in the course of this investigation. The technical support of V. Hron and D. Pattemore was also greatly appreciated.

### Literature Cited

1. Wirtz, A.H. *The Canmaker and Canner* **1991**, 4, 55.
2. Fitzpatrick, N.P.; McCubbin, J.G.; Evans, J.F. In *Light Metals 1986*; Miller, R.E., Ed.; The Metallurgical Society, Inc.: Warrendale, PA, 1986; 793.
3. Elder, G.B. In *Metals Handbook: Corrosion*, 9th ed.; Korb, L.J.; Olson, D.L., Eds.; ASM International: Metals Park, OH, 1987, Vol. 13; 1157.
4. McKee, A.B.; Binger, W.W. *Corrosion* **1957**, 13, 786t.
5. Chen, J.G.; Crowell, J.E.; Yates Jr., J.T. *Surface Sci.* **1986**, 172, 733.
6. Funke, W.; Haagen, H. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, 17, 50.
7. Leidheiser, H. Jr.; Wang, W.; Igetoft, L. *Prog. Org. Coat.* **1983**, 11, 19.
8. Funke, W.; Leidheiser, H. Jr.; Dickie, R.A.; Dinger, H.; Fischer, W.; Haagen, H.; Herrmann, K.; Moslé, H.G.; Oechsner, W.P.; Ruf, J.; Scantlebury, J.S., Svoboda, M.; Sykes, J.M. *J. Coatings Technol.* **1986**, 58, 79.
9. Leidheiser, H. Jr.; Deck, P.D. *Science* **1988**, 241, 1176.
10. Martin J.W.; Embree, E.; Tsao, W. *J. Coatings Technol.* **1990**, 62, 25.
11. Nguyen, T.; Bentz, D.; Byrd, E. *J. Coatings Technol.* **1994**, 66, 39.
12. Schlotter, N.E.; Furlan, P.Y. *Polymer* **1992**, 33, 3323.
13. Mason, R.C.; DeLassus, P.T.; Strandburg, G.; Howell, B.A. *Tappi J.* **1992**, 75, 163.
14. Koszinowski, J. *J. Appl. Polym. Sci.* **1986**, 32, 4765.
15. Guo, C.J.; De Kee, D.; Harrison, B. *Chem. Eng. Sci.* **1992**, 47, 1525.

RECEIVED May 26, 1995

## Chapter 39

# Polymer Recycling Technology for Food-Use Technical Requirements To Meet Safety and Quality Assurance

L. D. Tacito

Plastics Forming Systems, Inc., 850 East Industrial Park Drive,  
Manchester, NH 03109

The ability to produce recycle polymers for Food-Use is very confusing to the average package designer/manufacturer. The primary issue after price is quality. This has been addressed primarily from the food safety perspective and not from the quality as it relates to flavor and taste. It is generally accepted, that if quality requirements are satisfied, then the material safety data will also meet the requirements. This paper is directed toward the technology required to produce recycled polymers that met the safety and quality assurance needed to satisfy the consumer product companies. We will be discussing the specific areas of:

- 1) Supply feedstock continuity and handling
- 2) Process Instrumentation and Control Strategy
- 3) Migration testing for Indirect Food Additives

The basic premise of the technology is to provide Good Manufacturing Practices (GMP) with the ability to have systems in place controlling the critical parameters. These will be addressed in the following area:

- 1) Statistical Automatic Sampling
- 2) Detection, Measurement and Control of Process and Quality
- 3) Recycling Process Control (SPC/ISO 9000)
- 4) Food Container Manufacturing

Various known contaminants required by both Government and Industry testing, need to be correlated to "Real World Data" for both safety and quality of the food products.

0097-6156/95/0609-0488\$12.00/0  
© 1995 American Chemical Society

We will present the technology currently produced by the recycling industry in Automatic Sortation, Cleaning Processes, Quality Assurance from Lot to Lot.

### **Environmental Roots**

The environmental issues were the initial starting point of interest in recovering the polymers used in producing food and beverage packaging. The litter issue created the first in a series of legislative actions that gave birth to deposit bills or bottle bills. This was the controlled means of guaranteeing the consumer a path to recover the waste that ended up by the side of the road. Along with the plastic bottles were aluminum cans, glass bottles and the cardboard boxes and plastic bags to collect these returned containers. As time progressed, the interest expanded into the landfill issues of running out of space and creating leach fields of toxic chemical wastes. The outgrowth was more legislation that focused on the domestic and industrial waste. The target of 25% reduction by 1995 was established by the EPA and shortly thereafter industry and government were in the Trash Business.

### **Commercial Interests**

The industry with the greatest interest was the consumer driven entities such as beverage and food manufacturers and the retail distribution outlets. Also, the collection and trash haulers became interested in the commercial aspects of landfill costs rising to higher and higher levels. As with all secondary materials recovered from the scrap piles, entrepreneurs and large companies alike looked long and hard at the profitability of such an investment. Commodity material values are established in the marketplace and will fluctuate with supply and demand. Plastic waste is in its infancy and will grow as the supply, technology and markets develop.

### **PET and HDPE**

However, the primary polymer materials being recovered are PET (#1) and HDPE (#2). Soda bottles and milk bottles were the first to be identified by the consumer, collectors and recyclers. Many programs are underway to increase the types of materials being collected but this is an oscillating process of environmental and commercial reality. PET bottle recycling is a maturing business opportunity because the primary resin producers and packaging converters are finding both the consumer demand and the recovery system are very profitable. HDPE is growing also for the same reason, but is not as rapid in its secondary applications for food use due to source control and migration issues. The other polymer materials are finding it difficult to compete with PET and HDPE and are needing a strategy to maintain and grow their applications in the largest markets such as packaging and durable goods. Plastics recycling other than PET and HDPE are competing with other materials perceived to be more recyclable as well. The key to the future markets will be to reduce the cost while creating less waste.

## RECYCLE PET PACKAGING

### History of Commercial Processing

Having been involved in the R & D of the polymer and processes, we were very involved in the strategy dating back to the mid-seventies where all of the technology and market development began. The first major effort to establish a process to produce a combined food and beverage package was Monsanto's CycleSafe Bottle. In 1975 this package was commercialized in New England, Midwest and Mid-Atlantic States until the FDA ruling on the migration of acrylonitrile stopped the production of the package. Research was being conducted to produce new bottles from the recovered polymer but was never implemented because of the shut down of the production operations.

Soon after, the birth of the PET bottle was launched. By 1980, this new rigid packaging material was being produced nationally and the soft drink industry has never been the same. Simultaneously, the deposit legislation caused the industry to collect the used beverage containers (UBC) and the existing PET polyester material market had a new raw material source.

<u>COMMERCIAL PROCESSORS</u>		<u>POLYMERS USED FOR FOOD AND BEVERAGE</u>
MONSANTO - CYCLE SAFE	1975	ACRYLONITRILE
CCC / OI	1978	PET / SOFT DRINK
CPT / JCI / CONSTAR	1985	PET/ HOT-FILL
ACI AUSTRALIA	1992	PET SOFT DRINK PCR*
CPT	1994	PET BARRIER / PCR*/HOT FILL

\* PCR - Post Consumer Recycled with FDA Approval  
PFS involved in the R & D and Commercialization

Continental Can Company (CCC) and Owens-Illinois (OI) were the two primary producers but found the maturity of the business and the subsequent profit margin were not acceptable and sold their operations. Hoover and Sewell Packaging who are Johnson Controls and Constar respectively became the two non-

captive suppliers in the US. Coke (CCE) and Pepsi (PPB) formed their self-manufacturing companies who today are Southeastern/ Western Container and Brunswick Container respectively. Continental Can sold their PET business to ACI Australia and are now Continental PET Technologies (CPT). The foundation of this industry was developed by these companies and the future growth of many new players worldwide is creating an industry comparable to metal and glass packaging. In the early nineties, the demand for Recycle Content gave birth to technologies to produce secondary polymers for packaging. The PET fiber business was the only large market for the material.

TABLE II

**MECHANICAL RECYCLING TECHNOLOGY DEVELOPMENT**

<u>COMPANY</u>	<u>YEAR</u>	<u>RECYCLE MARKET</u>
WELLMAN	1975	FIBER
ST. JUDE	1980	STRAPPING/SHEET
DAY PRODUCTS	1989	NON FOOD PACKAGING
ACI AUSTRALIA	1992	BEVERAGE *

\* PCR FDA Applications

Wellman, DuPont and St. Jude Polymers were the only three (3) producers who were buying the materials from the deposit state collection systems. Soon after the market started to grow. By the mid to late 1980's a number of PET recyclers started to emerge. But it was not until early 1990 the market needed FDA approved packages made from recycled material. The resin producers were the first (See Table III) to produce a polymer from repolymerized feed stocks. The market for non-food packaging applications was developing through producers such as Day Products (currently owned by Wellman).

The next year technical breakthrough was produced by ACI Australia when they produced an FDA approved beverage bottle using the CPT technology of multilayer bottles. This functional barrier approach was considered the option to the higher priced repolymerized resin but could only be produced under license to CPT. CPT also produced multilayer packages without recycle content in the US for products such as juice, ketchup, etc. With the recent approval of direct food contact of source controlled materials, JCI has introduced another possibility to produce Food Grade Recycled PET. It is somewhat uncertain as to the effect of source control and process efficacy on the acceptance by all consumer product companies. Technology will continue to advance as mentioned later in this paper.

**TABLE III****POLYMER RECYCLE METHODS OF PET**

<u>MANUFACTURER</u>	<u>METHOD</u>	<u>PROCESS</u>	<u>FORM</u>
HOECHST/SHELL	CHEMICAL DECOMPOSITION	METHANOLYSIS/ GLYCOLYSIS	RESIN
ACI/CPT	FUNCTIONAL BARRIER	COINJECTION MULTILAYER	BOTTLES CANS
JCI	BOTTLE TO BOTTLE BLENDS	"SUPERCLEAN" RECYCLING	RESIN

**TABLE IV**

<u>GLOBAL PET PACKAGING</u>	<u>GROWTH</u> <u>(000'S TONS/YR)</u>	
	<u>1995</u>	<u>2000</u>
NORTH AND SOUTH AMERICA	1,000	1,500
EUROPE	700	1,200
ASIA	<u>600</u>	<u>500</u>
	2,200	4,200
RECYCLE CONTENT POTENTIAL - 25%	550	1,050



### **Future Recycled PET Packaging**

Most of the existing recyclers in the US are preparing for global expansion. The ability to recycle other polymers with PET will become increasingly important especially if curbside collection systems expect to grow the fastest. Polymer recycling will need continued R & D for the higher quality applications such as food use.

The tremendous growth in PET packaging will be exciting to all of the world markets (See Table IV). By the year 2000, the market will have doubled in size from 1995 estimates. This means the growth of resin and recycled resin will be approximately 4,000,000 tons or 8 billion pounds per year. If 25% of this packaging is recovered, a potential of 2 billion pounds per year of Recycled Polymer could be used in secondary markets.

### **FOOD PACKAGING AND QUALITY REQUIREMENTS**

The federal regulations define the food product type and the conditions of use the polymer must be able to certify compliance. The typical migration data generated was produced by contaminating the recycled material and subsequently by processing into an article. The article is tested with the specific solvents simulating types of foods and beverages. From the quality assurance systems, the raw material certification and cleaning process control parameters can be set-up to certify the finished product is safe for food use.

The consumer product company sets the package specifications and direct the supplier to meet performance and taste requirements. The alternative choices for recycled PET are developing from:

- 1) Repolymerized Materials
- 2) Functional Barrier Layers
- 3) Direct Contact/Superclean Materials

The depolymerization and multilayer functional barriers are well proven and accepted methods by both the government and industry. The direct food contact is still not completely accepted due to the inability to guarantee the source control and process control to be completely "air tight".

### **Source Control**

The typical plastic recycling facility has multiple sources of supply from loose bottles to baled bottles to ground flake. The materials have incoming inspection to test for various quality standards. Supply systems are monitored and analyzed. Failure to meet specifications will cause the supplier to be rated accordingly and possibly disqualified.

The materials are manually and automatically sorted to separate the specific polymers from the non-polymer contaminants. The material is constantly monitored for levels of contaminants and non-compliance to specifications. The granulated material is stored in lots for feeding and cleaning process. The dirty flake data base allows the raw material to be certified prior to processing. The process and quality information is necessary to define the individual unit operations for the recycle process (See Figure 1).

Another element of the PET source control is the deposit collection system versus the curbside collection system. The specific handling techniques of bottle deposit system inherently produces a less contaminated material with overall better quality. The curbside bottles produce a wider range of Non-PET contaminants which must be sorted in the process. Technology continues to progress in both the sensing/detection and separation technologies for removing these various polymer and non-polymer contaminants. A number of technologies are available for detection of compounds which the FDA consider part of the source control strategy. In order to produce a feedstock from recycled containers the non-compliant polymers and additives need to be quantified and controlled using Good Manufacturing Practices (GMP). Studies confirming the incidences of contamination will help to support the acceptance of recycled containers “actually received” in the system. The statistics from these real world surveys will reinforce the requirements for purity to produce containers for Food-Use.

### Process Efficacy

This is the capability of the process to prepare these materials for the condition under which the packaging is intended for use. The FDA breaks down some of these conditions to the types of food and beverage, the time and temperature of service and the packaging structures. The Points to Consider and Guidelines for the Safe Use of Recycled Plastics are two good sources to better understand these basic principles other than the Federal Regulations themselves.

Process and Quality management technology helps insure food grade requirements and it achieves and maintains quality specifications. Quality assurance systems for food and beverage applications of post consumer polymers are essential. The chain of manufacturers needs to be coupled to the source. In other words, the 1) Food and Beverage Manufacturers need to certify the quality of the package manufacturer, the 2) Package Manufacturer needs to certify the raw material manufacturer and the 3) Raw Material Manufacturer needs to certify the source of the feedstocks. With the strong implementation of a Quality Assurance Database, corrective action and employee training reduces the risk to an acceptable level for the Consumer Product Companies and Government Regulations.

The Polymer Recycling industry continues to mature with some of the processing technologies used to achieve and maintain the purity levels being:

- 1) Automatic Sortation and Granulation with sophisticated detection systems
- 2) Cleaning Processes with SPC/ISO 9000 at critical points in the process.

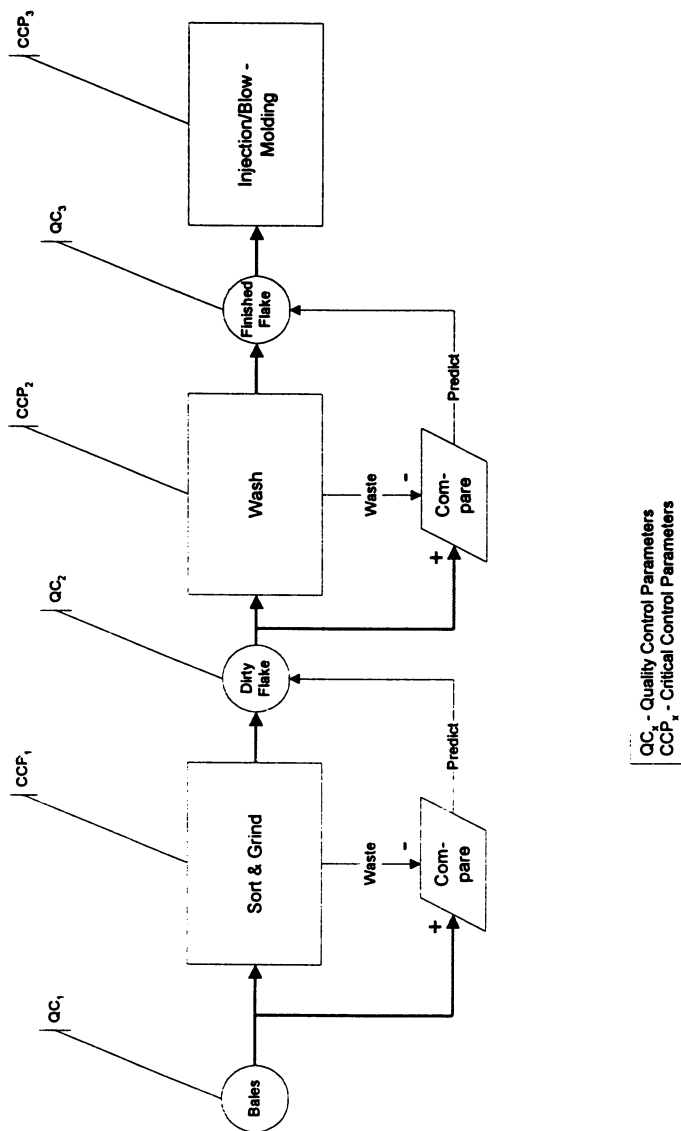


Figure 1. Process and quality information flowsheet: recycle process.

August 10, 2012 | <http://pubs.acs.org>  
 Publication Date: May 5, 1995 | doi: 10.1021/bk-1995-0609.ch039

- 3) Automatic sampling techniques to improve the SQC of the unit operations.
- 4) Additional Process Controls on the package manufacturing to insure safety and quality.

These advanced instrumentation's and control strategies for both standard processing as well as proprietary processing are key to the overall acceptance of recycled polymers. Much like the HACCP concepts for food safety on the product, these same basic techniques will also apply to the packaging manufacturers. Whether it is virgin or recycled materials, the process capability will depend on well engineered, well controlled processing facilities. The ability to apply these techniques to the recycle facility will be discussed in more detail. In summary, the processing efficacy will depend on:

- 1) On-Line Process Monitoring
- 2) Closed Loop Process Controls
- 3) Material Quality Certification

### Migration Testing

The detailed analytical science of migration testing will be covered by other authors in this publication. The objective in this section will be to explain how an engineer interprets this theory and data, then, applies it to commercialization of the recycling technology. The most well known article published is Begley and Hollifield which states, "when recycled polymers are used in packaging, the possibility that toxic contaminates may migrate into the food must be determined". This led to the

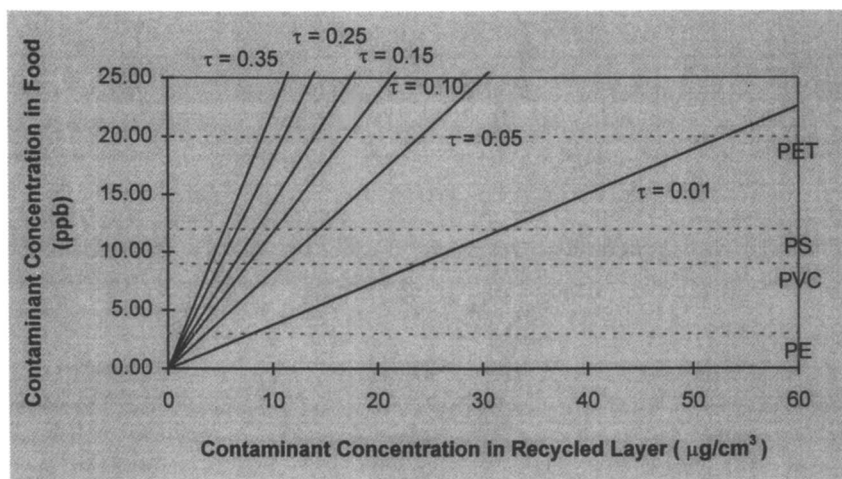


Figure 2. Predicted migration from a single layer package.

prediction model which compares monolayer to multilayer theory. Continental PET Technologies designed a packaging system to meet these predictions then tested it. It was also coupled to the "Points to Consider" when the Dietary Exposure Concentrations of specific volatile and solid surrogate contaminates was estimated in the recycled materials. These levels were purposely placed in both the monolayer and the multilayer to determine migration. The functional barrier proved to work very well and is commercially acceptable to both the FDA and consumer product companies. There appears to be data and psychological barriers to direct contact with the product. Recycled material is sandwiched between two virgin layers to ensure and maintain the function barrier layer. The predicted migration values for the single layer and two layer structures are proving to be a good estimate of the acceptable levels of contaminates in the recycled layer.

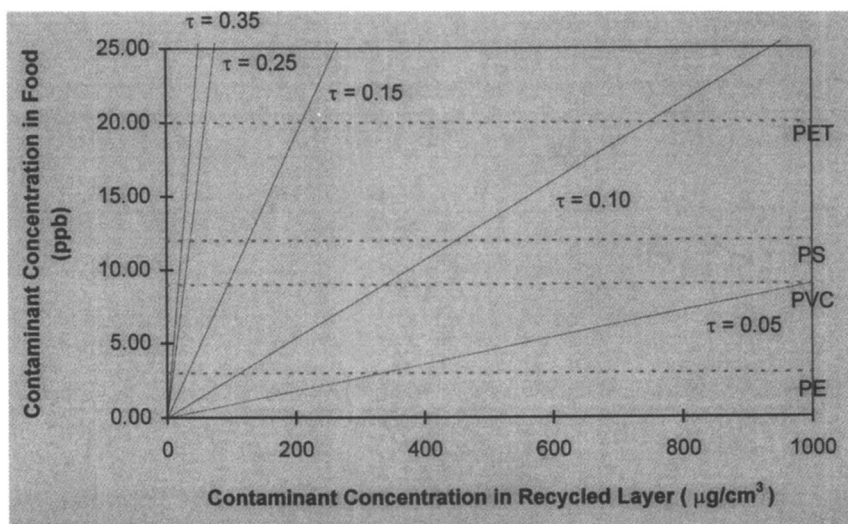


Figure 3. Predicted migration from a two layer package.

As you can see from these figures, there is an order of magnitude for the contaminate level in the food versus the concentration in the recycled polymer.

More recently, the approach to reduce the amount of specific surrogate through thermal processing has resulted in the JCI Non-Objection letter. Again, this will be a new approach to reducing the level of contaminates versus assuming the contamination making it through either the repolymerized or functional barrier layer processes. In the direct food contact by JCI, the responsibility is on the material producer and the package producer, as well as the consumer product company to ensure and maintain the maximum dietary concentration level. The current incidences of contamination reported will also help to define the statistical risk involved with direct food contact. As previously mention, the process

efficiency to detect and control these incidences will be even more important to the polymer recycling technology.

## **POLYMER RECYCLING TECHNOLOGY**

### **Separation Technology**

This specific area has been growing the fastest. Both whole bottle sortation and granulated flake separation techniques have advanced to a significant level where curbside sources of material are now acceptable for recycling into food use. Continuing evaluation and R & D will improve the equipment technology as well as the process capability to produce more purified streams of material. These unit operations are not restricted to either the dry process or to the wet process, therefore, a wide range of options can be engineered into the process. The least cost and highest quality material options are open to the collection system, cleaning system or packaging manufacturing system as long as the process efficacy can be ensured and maintained. The ability to have Processing and Quality Systems in place and controlling is the next generation of technology to produce high quality material for food-use applications.

### **Cleaning Process Technology**

Once the material has been tested and prepared for the washing operation, the process allows for the material to separate specific contaminants in the solid form and also penetrate, remove and rinse clean of dissolved solids and suspended solids. Depending on the specific end use, the unit operations can have multiple prewash, wash, separation, rinse and drying steps. The feedstock will determine the necessary process design required to meet the end-use. Food use is the most stringent! The cleaning process requires preparation of the cleaning solutions and the continuous monitoring and adjustment of the chemistry. This has to be accomplished while removing the contamination from the cleaning solutions and recovering the water and chemicals. This balance of wash chemistry needs to consider contents of the post consumer containers as well as the components of the container (such as labels, adhesives, inks, other polymer materials)

The basic principles of separation employ known and modified technologies from the refining processes associated with paper, glass, metal, and polymer industries. The systems integration of these technologies has been an evolution and the ultimate challenge has been the various raw materials and developing markets. The process development has proven to be exciting and rewarding. This aspect has turned the trash business into a high-tech business.

The emerging technologies fall into a couple of areas. The first is the dry purification of bottles and clean flake. The ability to detect and separate these contaminants we are now capable of operating at 95% efficiency. The second area is the cleaning processes based on statistical process controls (SPC) and ISO-9000

criteria to monitor on-line/off-line data and implementation of closed-loop controls. Computer Integrated Manufacturing (CIM) allows for a tremendous capability for all aspects of the recycling and container manufacturing facilities. This method of process and quality management technology is designed not only to feedback information and control but also to achieve and maintain Process and Quality specifications and certification of Lot to Lot through GMP.

Process and quality management technology is the application of these principles to the specific data. The (WAN) Wide Area Network and (LAN) Local Area Network now allow plant wide and enterprise wide networking to ensure the information is secured and maintained for specific users. Specific applications of the technology to the Packaging Industry are:

- 1) Incoming Raw Material Inspection and Certification
- 2) Process and Quality Monitoring of both on-line data and off-line data into a single sophisticated data base.
- 3) Integrated Database serves countless reporting functions
- 4) Computer System provides product quality and Lot to Lot certification.
- 5) Provides Plant Wide applications for:
  - a) Supervisory Control
  - b) QC Lab
  - c) Engineering/Development
  - d) Management

The key to Good Manufacturing Practice (GMP) is good people and good data. The ability to measure and control the process will grow into a multitude of Packaging, Food and Beverage Applications.

## CONCLUSIONS

The basic conclusion we have reached is recycled polymers will be driven by cost reduction in the raw material. This is a well developed business in the paper, metal and glass industries. The margin between primary and secondary materials may grow or shrink but it will always maintain a minimum value for collection and a maximum value below virgin. The supply is currently limiting the market growth but as with the commodities, it will cycle as the material value changes. Research and Development will continue to change the technology but economies of scale and vertical integration will determine the few players for each market. Packaging dominates the recycled material business because necessity caused the recovery process to be integrated into the metal, paper and glass packaging business.

We see the market developing in a similar manner with regional growth coming when economics drive the value and subsequently the investment. Environmental issues will remain cyclical and important to the manufacturers, distributors, consumers and the raw material suppliers.

**LITERATURE CITED**

- 1) USFDA, "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations".
- 2) Begley, T. H., Hollifield, HC, "Recycled Polymers in Food Packaging: Migration Considerations".
- 3) Plastics Recycling Task Force, National Food Processors Association, The Society of the Plastics Industry, Inc. "Guidelines for the Safe Use of Recycled Plastics for Food Packaging Applications".
- 4) Thorsheim, H. R., Ph.D., "Recycled Plastic in Food Contact Applications: The View from the Food and Drug Administration".
- 5) Sadler, G.D., IIT/NCFST, "Recycled PET for Food Contact: Current Status of Research Required for Regulatory Review".
- 6) Komolprasert, V., Lawson, A., USFDA/NCFST, "Residual Contaminants in Recycled PET-Effects of Washing and Drying".
- 7) Code of Federal Regulations, Indirect Food Additives: 21CFR175.300

RECEIVED September 22, 1995



## Chapter 40

# Polymer Recycling Research in the New Decade

G. Tesoro and Y. Wu

Department of Chemistry, Polytechnic University, 6 Metrotech Center,  
Brooklyn, NY 11201

For about 10-15 years, research and development efforts have addressed the need for commercially viable technologies for the conversion of post use polymeric materials to new products of value. In industry, organizations, government laboratories, and universities around the world, approaches that would combine unique technical features with economic feasibility have been investigated with varying degrees of success. The major focus has been on thermo-plastics' remelting and reprocessing, and on regrinding of cured thermosets for blending with virgin resin in controlled amounts. The challenges of chemical processing or modification for recovered polymers and of experimental polymers designed for recycling have been defined more slowly. They are now active areas of research that will provide the basis for recycling technologies in the future. This paper will discuss some of the problems and progress associated with the time scale of these creative new approaches, including, for example, pyrolysis, depolymerization of polyurethanes and novel experimental thermosets.

The need for new solutions for problems of solid waste disposal has been apparent since the late nineteen seventies and early nineteen eighties, with the ever-increasing pace of plastics volumes produced, utilized for new applications and discarded. The issues of environmental contamination and of energy conservation are now driving forces for the development of new generations of recoverable polymers and of creative new technologies for utilization of polymeric materials post use.

In 1980, the Department of Energy (DOE) established the Energy Conservation and Utilization Technologies (ECUT) program [1], with the mission to conduct generic, long-term high-risk applied research and exploratory development in areas pertaining to energy conservation. In the ECUT materials

0097-6156/95/0609-0502\$12.00/0  
© 1995 American Chemical Society

program, research on polymer recycling and recovery was an important element. For synthetic polymers, the initial focus was on technology for producing commercially viable commodities from automobile shredder residue [2]. Longer range efforts were contemplated on developing novel separation techniques, on recovery of value from specific polymer classes and on fundamental investigations of approaches to utilization and reuse of advanced polymeric materials and composites. The DOE/ECUT policy and program have been perhaps the most important factors in determining the progress of the nineteen eighties in polymer recycling research and development. The evaluation of current status and future needs can be attempted only in the context of accomplishments directly or indirectly related to this element of the DOE program. In this paper we will attempt to summarize the highlights of these accomplishments, concepts that have emerged as a basis for the research programs of the future, and problems that are now better understood regarding the time scale for technology transfer, and for commercial initiatives as well as the role of economics in every development.

The subjects of natural polymers, biodegradable polymers, renewable resources and rubber require consideration of factors that do not necessarily apply to recycling of synthetic polymers and are beyond the scope of the discussion which follows.

### Highlights of the Eighties

The conceptual approaches -- or strategies -- in the ECUT long-range research plan for utilization of polymer waste based on processes other than incineration or landfill were outlined in general terms in 1986 [3], as follows:

1. **Direct Reuse:** Processing by essentially known technologies for recovery of materials to be used either alone or in mixtures with virgin product. This approach has been valid primarily for thermoplastic uncontaminated materials. It has dominated engineering developments for recovery of PET and HDPE from beverage bottles and milk bottles.

2. **Reuse after Separation and/or Modification:** Processing of waste consisting of complex mixtures or contaminated materials that must be fractionated and/or modified for conversion to viable commercial products. Such industrial processes as reclaiming rubber from used automobile tires for blending with new rubber, and grinding of cured thermoset resins to be used as fillers, are examples of this approach.

3. **Isolation of Well-Characterized Molecular Species from Recovered Polymers (Recovery of Value-Chemical Recycling):** The complexity of this approach is evident from consideration of the numerous structures and properties in waste polymers, and of the changing character of products as newly developed materials reach the market place.

This classification is approximately equivalent to the terminology of "secondary recycling" for approaches 1 and 2, and "tertiary recycling" for those defined as type 3 [4]. It can also serve to identify relatively short range

engineering projects and long range research efforts aimed at creative new chemistries. The issues of energy conservation [5], of economic feasibility [6], of the challenge of markets [7] for recovered materials [7] are additional problems. These have been discussed in general terms, and also studied for numerous recycling processes and products that have been developed or proposed. However, the critical needs for continuing research and increased commitment to long range efforts, as well as for interdisciplinary activities in the industrial complex, have been only partially met as we begin the second decade of this effort. The research objectives identified about ten years ago [3] contemplated a new generation of recoverable polymers designed for recycling, the application of new, sophisticated techniques for reactions (e.g., fast pyrolysis) yielding well characterized chemical compounds, and optimization of chemical recycling processes providing recovery of value by classical reaction paths (e.g., hydrolysis, alcoholysis, glycolysis). Significant progress has been made towards each of these goals. Specific projects and objectives have been based initially on investigations of recovery of products from uncontaminated polymers available in significant volume in the waste stream. In addition, continuing research and development programs, with the active participation of industry, have provided a new basis for the (current and future) implementation of viable recycling processes for producing chemical compounds and materials of value.

A summary of major research efforts that have provided new insight into the opportunities and problems of future research is shown in Table I. A brief review of status is discussed below.

**Polyester (PET).** Recycling of polyethylene terephthalate (PET) from bottles has been a true success story. Over a period of 8-10 years, direct reuse of PET (and of HDPE base polymer) coupled with quality improvement technologies has evolved from early experimental programs on melting/reprocessing to the development and marketing of fiber grade PET in significant volume [8] and to the economically feasible recovery of monomers by methanolysis and glycolysis reactions [9]. The Chicago Board of Trades decision to launch electronic trading in recycled PET in 1994 reflects the growing role of market forces and the economic viability of those PET recycling processes that have reached commercial status. It is easy to understand the rapid growth of PET recovery from bottles, and of developments ranging from direct reuse to more demanding technologies for recovery of monomers or conversion to fibers. The availability of uncontaminated polymer and the relatively simple chemistry of polyethylene terephthalate have been important factors in this growth: the volume of reclaimed PET reportedly reached 400 million pounds in 1993. (N.Y. Times, Feb. 20, 1994, p. 9). It is evident that there are favorable in the recovery of value from PET beverage bottles that have benefitted both technology and economics.

**Polyurethanes (Foams).** In contrast to PET, the chemistry of polyurethanes is far more varied and complex. Progress on recycling has occurred on several fronts, including the use of regrind as filler in hot cure -- molded foam -- and recycling of glycolized RIM materials (12).



development of continuous processes covered in detail by a final report issued in August, 1981 [14]. Commercial processes recently announced by Bayer, ICI, and Dow Chemical [15] have a scientific foundation in the research of the late seventies on hydrolysis in Germany [14] and on glycolysis in the U. S. [16]. Also, and in-depth investigation was reported by the scientific research staff of the Ford Motor Co. [17] on the reaction of polyether-based PU foam with dry atmospheric pressure steam (190-230°C) to yield high quality polyol, isomeric toluene diamines and CO<sub>2</sub> as primary products. This was proposed as one approach to waste PU foam recovery at the time. In subsequent work on glycolysis of PU foam the Ford investigators [18, 19] examined the problems associated with "simple" glycolysis and the potential of a new Ford process termed "hydroglycolysis". Estimates of operating cost and process profitability (based on 1981 prices) showed at the time that economic incentive was "doubtful".

The results of this extensive research on chemical processes for monomer recovery [10-19] are seemingly used commercially to a very limited extent, and development decisions on polyurethane recycling have apparently been governed by economic considerations. Thus, the history of research on PU recovery where new techniques can yield well characterized monomers and chemical compounds highlights a dilemma of this day, namely, the difficulty in the translation of successful, creative laboratory results to viable commercial processes with realistic economics.

**Thermosets (Epoxy, Polyimide).** The problem of recovery of thermosets has been an even greater challenge. The conventional wisdom of grinding cured resin and using it as filler has been recognized as an interim approach to utilization of cured resins. In spite of the relatively low volume of thermoset resins as compared to thermoplastics [20], recycling of thermosets was viewed as a major challenge when the long range plans of the ECUT materials program were formulated in the mid-eighties. Exploratory research on recovery of thermosets was initiated for epoxy resins [21], well characterized chemically and important technologically, particularly for advanced composites. The results of this research propose experimental polymers where the molecular structure is designed for recovery, and the properties are comparable to those of commercial resins currently employed. An overview of the chemistry and of a preliminary evaluation of economic feasibility [22] suggest that the approach is viable for epoxy resins. In subsequent research, it has been successfully applied to new, recoverable thermoset polyimide copolymers [23] where labile bonds are introduced for the purpose of solubilizing and reprocessing resins. To the best of our knowledge, the results published on these developments and covered by patents in 1989-1993 have not been explored in industry to date.

There are significant opportunities for future development of the experimental polymers and for chemical modifications designed to impart special properties. The need for interactive research with industry for the optimization of these (and other) laboratory results is an objective for the next decade.

**Cured Unsaturated Polyesters.** The recovery and isolation of well characterized chemical compounds of potential value from thermosets has also been explored for cured unsaturated polyesters, employing a different approach [24]. In this case, laboratory results of neutral hydrolysis have shown that current interest and possible regulations for recovery of SMC from automotive applications [25] may stimulate further work in industry in the future, perhaps aimed at studies of process optimization, and of development of unsaturated polyesters of improved properties from recovered oligomers. At this time, however, industrial work reported on recovery of cured unsaturated polyester has been focused primarily on defining the amounts of SMC regrind which can be incorporated in virgin material without impairing its properties [26].

**Polystyrene.** Recycling of polystyrene by chemical processing has not been a primary objective for research, partly because specific functional groups can be introduced by employing comonomers in synthesis, and partly because the economics of chemical recovery and modification processes could not compete with current commercial production by regrind/reuse, for example of "Retain" resins (Dow Plastics-55% post consumer recycle content) or "Dylite" (Arco Chemical-25% recycle).

The National Polystyrene Recycling Company (NPRC) is a multimillion dollars organization including several major polystyrene producers which was started in 1989 with the goal of facilitating industry efforts to recycle 25% of the PS produced in the U.S. for food service and packaging applications each year [27]. The growth of this industry endeavor is certain as an increasing number of PS recycling facilities is implemented by NPRC.

**Pyrolysis.** For several years, the feasibility of recycling comingled post-use polymers by pyrolysis has been a controversial subject. However, several processes have been investigated in industry [28], and recycling technologies based on fluidized bed pyrolysis have been studied extensively at the University of Hamburg [29][a][b]. Research has focused on the suitability of plastic wastes, used tires, and oil residues as sources of well characterized purified olefins and other hydrocarbons. Pilot plants with capacity of 10-40 kg/hr of plastic and up to 120 kg/hr of used tires have been installed [29] and a semi-industrial plant using the Hamburg process has been built in Germany by the Asea Brown Boveri Company. According to a recent report, the American Plastics Council (a Washington, D.C., trade group) is promoting pyrolysis as a viable form of chemical recycling.

**Fast Pyrolysis.** In a long range program at NREL, the objective of research on fluidized-bed high temperature pyrolysis has been to translate an understanding of pyrolytic events at the molecular level to the design of processes requiring minimum mechanical separation and purification of products. Mixed plastic waste streams including nylon 6 carpet, polyurethane, and PET-containing wastes have been selected for study [30(a)]. Recovery of pure monomer (caprolactam) from nylon 6 (caprolactam) has been attained. Molecular Beam Mass

Spectrometry (MBMS) experiments have been employed in this research to evaluate the possibility of recovering specific monomers and compounds of interest from individual waste streams. Reportedly, polyurethane will be investigated in the future.

Recently issued patents describe a process for fractionating organic and aqueous condensates made by fast pyrolysis of biomass material [30(b)] and "a method for controlling the pyrolysis of a complex waste stream of plastics and for converting the stream into useful high value monomers" [30(c)].

**General Concepts.** The technological advances in recycling of PET, Polyurethanes and Polystyrene are evident from this brief discussion of accomplishments. It is also clear that chemical research results for recovery of polyurethanes, thermosets, and for fast pyrolysis of comingled polymers have not been implemented commercially at this time, perhaps for reasons of economic feasibility, and partly because major developmental efforts requiring industry participation have not been available to date. It is with these considerations in mind that we can attempt to formulate research needs for the next decade.

**Future Research and Development Needs.** Future needs for effective research can be defined on several levels, depending on the complexity of chemical problems, and on economic feasibility of potential solutions.

It is desirable to realize the benefits of research results now available, by process optimization, by chemical modification of existing systems as recovered, and by continuing efforts, with appreciation of industrial interests.

The time scale for implementing results of new laboratory research must be recognized. Changes in the composition and properties of materials require consideration, and interdisciplinary programs should be pursued. A prime example of this need is research for the recovery of polymer blends that are becoming increasingly important in the marketplace.

Long range programs are essential for implementing new concepts, and for creating markets for new experimental materials designed with recycling in mind. An increasing commitment to long range projects on the part of the industrial complex is needed, devoting talent and funds to new initiatives as well as to the utilization of available knowledge, to scale-up experimentation, and to optimization for technology developed in the laboratory. This may necessitate cooperative programs of industrial groups with research in universities, whenever knowledge of industrial products and processes can be coupled with the results of preceding or concurrent scientific investigations, and where constraints imposed by policy and patent problems can be dealt with. In addition, a broad research program sponsored by government for the exploration of a new generation of polymers designed for recycling and earmarked for specific applications would be desirable. This would be a major undertaking, comparable in some aspects to the polymer element of the ECUT material program as proposed in the early 1980's [1]. The underlying principles for such a program require fundamental knowledge of the relationships of properties with molecular structure, and also with effects of molecular assembly, intermolecular forces,

morphology in the solid state, and interactions in multicomponent systems [31]. Thus, an inter-disciplinary effort is essential. New polymer systems that satisfy performance properties in established applications -- and yet can be recovered and recycled economically, must be designed with these considerations in mind. This is a formidable challenge.

On the basis of knowledge and experience gained during a decade of progress, it is evident that a long time is required for the development and scale up of creative new concepts potentially applicable to the design of recyclable polymeric materials. For example, the principle of reversible crosslinks explored for thermosets [21, 22] and the results of research on thermally controlled covalent bond formation [32] have demonstrated the time and effort required for implementing promising approaches in the search for systems that can be practical for industrial use. Briefly stated, chemical research needs for the next decade may be summarized as follows:

- Optimization of approaches developed in the 1980's;
- Research on recycling of newly available commercial materials (e.g., polymer blends);
- Long range interactive programs of industry with universities;
- Early assessment of economic feasibility;
- Government sponsorship and leadership for projects designed to develop recyclable polymers for the future

#### References

- (1) J. A. Carpenter, Jr. et al., Long Range Program Plan for FY 1987-1994; ECUT Materials Program (ORNL), pp x-xx  
*See also ORNL reports of the ECUT Materials program under Contract No. DE-AC05-84OR21400*
- (2) Plastics Institute of America (PIA), Secondary Reclamation of Plastic Waste - Phase I and Phase II, Technomic Publishing, Lancaster, PA, (1987)
- (3) Reference 1 - Pages [2.2] - 2, 8, 9, 17
- (4) J. Leidner, Plastic Waste, M. Dekker, NY, pp 64-65 (1981)
- (5) T. R. Curlee, Materials and Society, 12 (1), 1-45 (1988)
- (6) T. R. Curlee, The Economic Feasibility of Plastics Recycling, Praeger NY (1986)
- (7) M. Alexander, Society of Women Engineers (SWE) *The Challenge of Markets*, pp 7-11, Nov/Dec (1993)
- (8) a, V. Comello, R & D Magazine, October 25, 20-22, (1993)  
b, R. Leaversuch, Modern Plastics, October, 79-80, (1993) and July, 48-50 (1994)  
c, S. Disenhouse, The New York Times, February 20, (1994) p 9
- (9) R. Leaversuch, Modern Plastics, July, 40-43 (1991)
- (10) a, USP 4,196,148 (1980) to Ford Motor Co.  
b, USP 4,316,992 (1982) to Ford Motor Co.  
c, USP 4,328,368 (1992) to General Motors  
d, USP 5,089,571 (1992) to Dow Chemical Co.
- (11) Materials World (6B), September, 485, (1993)



- (12) Modern Plastics, November, 71-73, (1993)  
(From a paper presented at the Polyurethane World Congress, Vancouver, B.C., October 10-13, (1993)
- (13) E. Grigat, *Kunststoffe*, **68** (5), 281-284, (1978)
- (14) G. Niederlmann, G. Hetzel, H. Petersen, Report No. BMFT-FB-T-83-199 (1981), (NTIS, PC-A09/MFAOI)
- (15) a, Modern Plastics, January, 47, (1991)  
b, Modern Plastics, February, 20, (1991)  
c, *Plastics and Rubber International*, June/July, 13, (1992)
- (16) H. Ulrich et al. *Polym. Eng. Sci.* **18** (11), 844-848 (1978)
- (17) J. L. Gerlock et al. *J. Polym. Sci. (chem.)*, **18**, 541-557 (1980)
- (18) J. L. Gerlock, J. Braslaw, M. Zimbo, *Industrial Engineering Chemistry - Process Res. Dev.*, **23**, (3), 545-552, July, (1984)
- (19) J. Braslaw, J. Gerlock, *Industrial Engineering Chemistry - Process Res. Dev.*, **23**, (3), 552-557, July, (1984)
- (20) T. R. Curlee - Preliminary Report to DOE by ORNL, Contract No. DE-AC05-84OR21400, April, (1989)
- (21) G. C. Tesoro and V. Sastri, *J. Appl. Polym. Sci.* **39**, 1425-1437; 1439-1457, (1990)
- (22) G. C. Tesoro, H. Chum and A. Power, Proceedings of the 47th Annual Conference of the Composites Institute, Sc. 4C, 1-8 February, (1992)
- (23) Y. Wu, G. C. Tesoro and I. Engelberg, in *Emerging Technologies in Plastics Recycling*, ACS Symposium #513, (G. Andrews and M. Subramanian, Editors), 186-196, (1992)
- (24) G. C. Tesoro and Y. Wu, *Advances in Polymer Technologies*, **12**, (2), 185-196 (1993)
- (25) Modern Plastics, April, 69-73 (1993)
- (26) Proceedings, 49th Annual Conference Composites Institute, session 15, February, (1994)
- (27) G. A. Mackey, R. C. Westphal, R. Coughanouz, in *Plastics Recycling* (R. J. Ehrig, Editor) 109-129 (1992)
- (28) Modern Plastics, January, 93, (1994)
- (29) a, W. Kaminski, in *Emerging Technologies in Polymer Recycling*, ACS symposium #513 (G. Andrews and M. Subramanian, Editors), 60-72 (1992)  
b, W. Kaminski and H. Rössler, *Chemtech*, February, 108-113, (1992)
- (30) a, Report to DOE, Office of Industrial Technologies by NREL, Industrial Technologies Division, First Quarter, 14-16, (1994)  
b, H.L. Chum et al. USP 5,223,601 (1993) to Midwest Research Institute  
c, R.J. Evans et al. USP 5, 321, 174 (1994) to Midwest Research Institute
- (31) H.R. Allcock, *Science*, **225**, 1106-1112, (1992)
- (32) L. P. Engle and K. B. Wagener, *Rev. Macromol. Chem. Phys.*, **C33** (3), 239-257, (1993)

RECEIVED May 2, 1995

## Author Index

- Allen, Bradford H., 418  
Atkins, W. Keith, 104  
Baldwin, Sheryl D., 274  
Bayer, F. L., 152  
Beck, Michael R., 254  
Begley, Timothy H., 445  
Bhakkad, V. V., 113  
Blakistone, Barbara A., 418  
Borchardt, John K., 323,342  
Burnett, Robert H., 97  
Cawker, Gordon, 296  
Cornell, David D., 72  
Eastman, Andrew L., 237  
Ellis, Jeffrey R., 62  
Friberg, Tom, 296  
Gage, M. J., 152  
Gatenholm, P., 367  
Golovoy, A., 47  
Hall, F. Keith, 286  
Hedenberg, P., 367  
Hollifield, Henry C., 445  
Huston, Jan, 296  
Jabarin, S. A., 113  
Janda, Bruce W., 306  
King, D. B., 458  
Klason, C., 367  
Klingensmith, William, 254  
Komolprasert, V., 435  
Koppang, R. R., 183  
Kryder, G. D., 183  
Kuznesof, P. M., 389  
Labana, S. S., 47  
Lawson, A., 435  
Lemieux, Even J., 472  
Mackey, George, 161  
Meszaros, Mark W., 170  
Myers, D. V., 152  
Nowak, E. N., 404  
Oblath, R. M., 404  
Payne, Marc T., 221  
Pearson, S. J., 183  
Pearson, Wayne E., 11  
Pett, R. A., 47  
Pierce, D. E., 458  
Prioleau, Robert M., 80  
Rader, Charles P., 2,196  
Rask, James H., 342  
Rowell, Roger M., 357  
Saba, Raymond G., 11  
Sadler, George D., 380,458  
Seeker, W. R., 183  
Serumgard, John R., 237  
Shiu, Frank J. Y., 139  
Smith, Fernley G., 202  
Stein, Richard S., 27  
Stockel, Richard F., 2  
Tacito, L. D., 488  
Tesoro, G., 502  
Thomson, David A., 89  
Tzeng, Donald D., 139  
VanDerveer, M. C., 389  
Warner, Walter C., 245  
Wu, Y., 502  
Yang, Iris C. Y., 139  
Yen, T. F., 139

## Affiliation Index

- Advanced Elastomer Systems, L.P.,  
2,196,221  
Akron Consulting Company, 254  
Alcan International Limited, 472  
Amoco Chemical Company, 170  
Canadian Polystyrene Recycling  
Association, 89  
Chalmers University of Technology, 367  
Coca-Cola Company, 152  
Dow Chemical Company, 161

- ETA, Inc., 202  
 Eastman Chemical Company, 72  
 Energy and Environmental Research Corporation, 183  
 Exxon Chemical Company, 80  
 Ford Motor Company, 47  
 Forest Service, U.S. Department of Agriculture, 357  
 Goodyear Tire & Rubber Company, 237  
 Illinois Institute of Technology, 380,458  
 International Paper, 286  
 J. R. Ellis, 62  
 James River Corporation, 306  
 National Center for Food Safety and Technology, 380,435,458  
 National Food Processors Association, 418  
 Packaging Research Foundation, 11  
 Philip Morris Research Center, 274  
 Plastics Forming Systems, Inc., 488  
 Polymer Valley Chemicals, Inc., 254  
 Polytechnic University, 502  
 Rubber World, 245  
 Ruska Instrument Corporation, 458  
 Rutgers, The State University of New Jersey, 11  
 Scrap Tire Management Council, 237  
 Shell Chemical Company, 323,342,404  
 Tosoh USA, Inc., 2  
 U.S. Food and Drug Administration, 389,435,445  
 Union Carbide Corporation, 104  
 United Technologies Chemical Systems, 139  
 University of Massachusetts, 27  
 University of Southern California, 139  
 University of Toledo, 113  
 Vinyl Institute, 97  
 Weyerhaeuser Company, 296

## Subject Index

### A

- Acetic acid concentration, role in chemically induced delamination for recycling of coated aluminum scrap, 474–476  
 Admer compatibilizer(s), bonding, 133–134  
 Admer compatibilizer role  
 mechanical properties of poly(ethylene terephthalate)–high-density polyethylene blends, 122,124–126f  
 thermal properties of poly(ethylene terephthalate)–high-density polyethylene blends, 128–131  
 Advanced recycling technology  
 advantages, 170  
 chemical vs. thermal, 162,163f  
 Conrad recycling unit, 171–182  
 developments, 170–171  
 economics, 168–169  
 markets, 162,164,165t  
 Advanced recycling technology—  
*Continued*  
 processes  
 degradative extrusion, 166,167t,  
 fluidized bed, 166,167f  
 gasifiers, 166,168t  
 hydrogenation, 166,168t  
 kilns and retorts, 164,166,167t  
 Advanced thermal recycling of mixed plastic waste, sprouted bed reactor, 183–192  
 Advanced waste recycling, potential products, 191  
 Agro-based fiber use for composites, recycled, *See* Recycled agro-based fiber use for composites  
 Air emissions, use of scrap tires as fuel, 242  
 Aliphatic hydrocarbons and acids, analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 464  
 Alternatives, polymer recycling, 9

- ETA, Inc., 202  
 Eastman Chemical Company, 72  
 Energy and Environmental Research Corporation, 183  
 Exxon Chemical Company, 80  
 Ford Motor Company, 47  
 Forest Service, U.S. Department of Agriculture, 357  
 Goodyear Tire & Rubber Company, 237  
 Illinois Institute of Technology, 380,458  
 International Paper, 286  
 J. R. Ellis, 62  
 James River Corporation, 306  
 National Center for Food Safety and Technology, 380,435,458  
 National Food Processors Association, 418  
 Packaging Research Foundation, 11  
 Philip Morris Research Center, 274  
 Plastics Forming Systems, Inc., 488  
 Polymer Valley Chemicals, Inc., 254  
 Polytechnic University, 502  
 Rubber World, 245  
 Ruska Instrument Corporation, 458  
 Rutgers, The State University of New Jersey, 11  
 Scrap Tire Management Council, 237  
 Shell Chemical Company, 323,342,404  
 Tosoh USA, Inc., 2  
 U.S. Food and Drug Administration, 389,435,445  
 Union Carbide Corporation, 104  
 United Technologies Chemical Systems, 139  
 University of Massachusetts, 27  
 University of Southern California, 139  
 University of Toledo, 113  
 Vinyl Institute, 97  
 Weyerhaeuser Company, 296

## Subject Index

### A

- Acetic acid concentration, role in chemically induced delamination for recycling of coated aluminum scrap, 474–476  
 Admer compatibilizer(s), bonding, 133–134  
 Admer compatibilizer role  
 mechanical properties of poly(ethylene terephthalate)–high-density polyethylene blends, 122,124–126f  
 thermal properties of poly(ethylene terephthalate)–high-density polyethylene blends, 128–131  
 Advanced recycling technology  
 advantages, 170  
 chemical vs. thermal, 162,163f  
 Conrad recycling unit, 171–182  
 developments, 170–171  
 economics, 168–169  
 markets, 162,164,165t  
 Advanced recycling technology—  
*Continued*  
 processes  
 degradative extrusion, 166,167t,  
 fluidized bed, 166,167f  
 gasifiers, 166,168t  
 hydrogenation, 166,168t  
 kilns and retorts, 164,166,167t  
 Advanced thermal recycling of mixed plastic waste, sprouted bed reactor, 183–192  
 Advanced waste recycling, potential products, 191  
 Agro-based fiber use for composites, recycled, *See* Recycled agro-based fiber use for composites  
 Air emissions, use of scrap tires as fuel, 242  
 Aliphatic hydrocarbons and acids, analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 464  
 Alternatives, polymer recycling, 9

- Aluminum alloys, corrosion by organic acids, 472–473
- Aluminum foils, delamination, 472
- Aluminum scrap, coated, recycling using chemically induced delamination, 474–486
- American Plastics Council, description, 60–61
- Asphalt rubber
- continuous blending process, 205,207
  - current status, 207–208
  - dry process, 205
  - polymer-modified process, 205
  - wet process, 205,206*f*
- Assessment, reclamation processes for plastics recycling, 418–434
- Automotive applications of ground rubber
- Ford Motor Company Guidelines, 209
  - General Motors Corporation Material Selections Guideline, 210–212*f*
- Automotive industry, rubber recycling, 197
- Automotive recycling
- contribution to solid waste, 50–52
  - elastomer recycling technologies, 52–56
  - infrastructure, 48–50
  - plastics recycling technologies, 56–58
  - trends, 58–61
- Automotive shredder(s)
- description, 49
  - profit opportunity as motive, 49–50
  - residue average composition, 49
- Automotive shredder residue
- amount, 51
  - composition, 49
  - incineration, 51–52
  - volume, 183
- Average dispersed phase particle size, calculation, 134
- B**
- Batteries, example of reclaimed/recycled automotive components, 48
- Benzene, washing and drying effect in removal from recycled poly(ethylene terephthalate), 435–443
- Benzene dicarboxylic acid related compounds, analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 462,464
- Benzoic acid related compounds, analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 462
- Biodegradation, description, 39
- Black filler for rubber from tire pyrolysis char, requirements, 254–271
- Bleaching, description, 335–336
- Business, plastics recycling, 72–73
- Butyric acid, washing and drying effect in removal from recycled poly(ethylene terephthalate), 435–443
- C**
- Carbon black
- applications, 254,255*t*
  - ash content, 257–258,260
  - DBP absorption, 257,259–260
  - history, 257,261–262
  - iodine adsorption, 257,259,262
  - manufacturing processes
    - channel process, 261–262
    - oil furnace process, 261,263
    - pyrolysis black process, 261,263,265
    - thermal process, 261,263  - market, 264–266
  - pour density, 257,259–260
  - properties, 257
  - reinforcing agent for rubber, 254
  - sales, 254,256
  - types and grades, 254–256
  - volume, 254
- Carbon sequestration, role in forest productivity, 292
- Carboxylic acid chain length and polarity, role in chemically induced delamination for recycling of coated aluminum scrap, 476
- Catalysis, devulcanization of thermoset rubber, 248
- Catalytic converters, example of reclaimed/recycled automotive components, 48–49

- Cellulose  
 applications, 274–275  
 occurrence, 274  
 recycling, 4
- Cellulose and paper recycling  
 critical properties, 277  
 current view, 280,283–284  
 infrastructure and sustainability, 277–278  
 infrastructure for recycling, 278–282  
 long view, 284  
 sustainable recycle, 275–277
- Cellulose fiber–plastic mixture,  
 advantages, 367–368
- Cellulosic reinforcement, mixed plastic  
 recycling, 367–376
- Cement kilns, use of tires, 241–242
- Channel process, manufacture of carbon  
 black, 261–262
- Chemical degradation, description, 39
- Chemical methods, devulcanization of  
 thermoset rubber, 245–251
- Chemical modification, economics, 65
- Chemical probes for rubber devulcanization  
 development, 246–247  
 dithiothreitol, 247  
 lithium aluminum hydride, 247  
 methyl iodide, 247–248  
 phenyl lithium, 247  
 sodium di-*n*-butyl phosphite, 247  
 thiol–amine reagent, 247  
 triphenyl phosphine, 247
- Chemical recycling, description,  
 93,162,163*f*
- Chemical reprocessing, description,  
 393–394
- Chemically induced delamination for  
 recycling of coated aluminum scrap  
 carboxylic acid chain length and  
 polarity, 476  
 delamination mechanism, 480–482  
 effect of acetic acid concentration,  
 474–476  
 experimental description, 473–475  
 formic acid vs. acetic acid, 482–483,485*f*  
 sequential delamination for commingled  
 laminates, 484–486
- Chemically induced delamination for  
 recycling of coated aluminum scrap  
 effect of acetic acid concentration—  
*Continued*  
 technical concerns  
 delaminating solution reusability, 484  
 organics chemical resistance, 484  
 organics isolation after processing,  
 483–484  
 size reduction, 483  
 temperature effect, 474–476
- Chemically purified monomers and  
 polymers, markets, 14
- Chemistry  
 olefinic thermoplastic vulcanizates,  
 228–230  
 unit operations in paper deinking mills,  
 323–339
- Chemithermomechanical pulp fibers, role in  
 recycled plastics properties, 367–376
- Clean processes, development, 27–28
- Cleaning process technology, polymer  
 recycling for food use, 498–499
- Clear-cutting, use by forest products  
 industry, 294
- Coated aluminum scrap, recycling using  
 chemically induced delamination,  
 474–486
- Cohesion parameter, determination, 142
- Collection, economics, 16–17
- Color matching, polyethylene recycling,  
 107–108
- Color measurement, polyethylene recycling,  
 106–107
- Commingled laminates, sequential  
 delamination, 484–486
- Commingled plastics  
 applications, 30  
 definition, 30  
 markets, 14
- Composites  
 recycled agro-based fiber use, 357–365  
 recycling, 37
- Composting, paper waste management, 291
- Computer-integrated manufacturing,  
 description, 499

- Conrad recycling unit, use in plastics recycling, 171–182
- Consumer  
interest in recycling, 66  
separation of polymers for recycling, 34–36
- Contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS  
aliphatic hydrocarbons and acids, 464  
benzene dicarboxylic acid related compounds, 462,464  
benzoic acid related compounds, 464  
curbside collection, 467,470  
drometrizole, 464–465  
drying, 470–471  
effect of high-temperature, 465–466,471  
effect of moderately high temperature, 465  
effect of select stream, 467,468*f*  
ethylene glycol related molecules, 462,463*f*  
extractable compounds, 460–462  
flake production, 470  
flavor compounds, 462  
miscellaneous compounds, 465  
nicotine, 464–466*f*  
redemption, 470  
sample separation procedure, 459–460  
secondary recycling process, 467,469*f*  
thermal extraction procedure, 460  
washing, 470
- Contaminant removal verification from postconsumer poly(ethylene terephthalate)  
capacity, 412,415*f*  
development, 406  
efficiency, 412,415,417  
model compound selection  
exclusion of heavy metal surrogates, 411  
pesticide contaminants, 410–411  
petroleum contaminants, 410  
model development, 409–410  
removal steps, 406,409*f*  
simulation experiments  
contaminant levels, 412,413*t*  
procedure, 411–412  
residual contaminant levels, 412,414*t*
- Controlled lifetimes, advantages, 40–41
- Copper 2-ethylhexanoate, reclamation process assessment, 418–434
- Copper(II) 2-ethylhexanoate, washing and drying effect in removal from recycled poly(ethylene terephthalate), 435–443
- Cost–benefit analysis, paper recycling, 294–295
- Curbside collection, poly(ethylene terephthalate), 467,470
- Cured unsaturated polyester recycling, future research, 505*t*,507
- D
- Degradation  
alternative to recycling, 39–42  
economics, 65
- Degradative extrusion, description, 166,167*t*
- Deinking, office paper, *See* Office–paper deinking
- Deinking agents  
interactions with toner inks, 342–355  
Office–paper deinking, 343,345
- Deinking process  
comparison to K–1 recycler project, 321  
deinking, 321  
fiber cleaning and bleaching, 320–321  
fiber sources, 320  
products, 321
- Delamination for recycling of coated aluminum scrap, chemically induced, *See* Chemically induced delamination for recycling of coated aluminum scrap
- Density method, olefinic thermoplastic vulcanizate recovery, 235
- Designing for recycling, economic driving forces of recycling, 20–21
- Detergent, polyethylene recycling, 107
- Devulcanization  
definition, 246  
thermoset rubber  
catalysis, 248  
chemical probes, 246–248  
comparison of probes and reclaiming, 250–251  
future work, 251

Devulcanization—*Continued*thermoset rubber—*Continued*

- grafting reactions, 248
- microbial action, 249–250
- microwaves, 249
- previous studies, 245–246
- solution by *o*-dichlorobenzene, 248–249
- steam autoclave, 250
- ultrasonics, 249

Diameter of circular particle of  
equivalent area, calculation, 115*o*-Dichlorobenzene, solution for  
devulcanization of thermoset rubber,  
248–249Dichlorophenol, reclamation process  
assessment, 418–434Diffusion coefficients, use for food  
packaging made from recycled polymers,  
445–457

## Dilation of brittle solid, calculation, 141

Direct reuse, polymer recycling  
research, 503

## Dispersion, description, 334–335

## Disposable diapers, disposal problems, 42

## Disposal

- materials, concerns, 47
- solid wastes
- methods, 2
- policy formulation, 44–45
- problem, 2
- solutions, 43–44

Dithiothreitol, chemical probe for rubber  
devulcanization, 247

## Downcycling, description, 303

Drometrizole, analysis in recycled  
poly(ethylene terephthalate) by  
thermal extraction–GC/MS, 464–465

## Drying role

- contaminant analysis in recycled  
poly(ethylene terephthalate) by  
thermal extraction–GC/MS, 470–471
- residual contaminants in  
recycled poly(ethylene  
terephthalate), 435–443

Durable goods, source of recyclable  
materials, 222

## E

## Economic(s)

- plastics recycling, 78
- polymer recycling, 6–7, 37–44, 62–69
- recycling technology
- collection, 16–17
- example, 15
- reclamation, 18–19
- sorting, 17–18

- thermal depolymerization of  
thermoplastic mixtures, 172, 181
- waste disposal methods, 63

## Economic driving forces of recycling

- designing for recycling, 20–21
- energy savings, 22
- higher alternative disposal fees, 20
- higher priced oil, 20
- legislation, 21
- technology to reduce cost, 21

## Eddy current separation, olefinic

- thermoplastic vulcanizate recovery, 235

Efficacy of recycling process, use of  
surrogates, 43Elastomer recycling technologies in  
automotive industry

- automotive use of elastomers, 52
- challenges, 55
- factors affecting elastomer choice, 52–53
- future, 56
- recycling, 54–55
- tire recycling, 53–54

## Electric generation boilers, use of tires, 242

Electrostatic ink composition, office  
paper deinking, 342–344*t,f*Electrostatic separation, olefinic  
thermoplastic vulcanizate recovery, 235Endangered species preservation, role of  
forests products industry, 293Energy Conservation and Utilization  
Technologies program, objectives,  
502–503

## Energy from waste, description, 93

Energy savings, economic driving force of  
recycling, 22

## Entropy, definition, 32



- Environment  
role  
paper recycling, 286–295  
thermodynamics, 33–34  
stewardship and cooperation among consumers, scientists, and American industry, 380–381
- Environmental scanning electron microscopy, Office-paper deinking, 342–355
- Ethylene glycol, reclamation process assessment, 418–434
- Ethylene glycol related molecules, analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 462,463*f*
- European regulatory criteria, poly(ethylene terephthalate) recycling for food use, 158–159
- Expandable polystyrene, synthesis, 89–90
- Extractable compounds, role in contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 460–462
- Extrusion, description, 87
- F
- Fast pyrolysis, use in polymer recycling, 505*t*,507–508
- Feasibility of recovery process for spent polyurethane-based propellants approach, 140  
enhancement, 147,148*f*  
flow chart, 149–150  
optimized process, 147,149  
propellant composition, 140–141  
solvent swelling, 141–144  
ultrasound irradiation, 144–147
- Feedstock quality, polyethylene recycling, 110–111
- First law of thermodynamics, description, 30–31
- Flake production, role in contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 470
- Flavor compounds, analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 462
- Flotation  
flotation deinking surfactants, 329–331  
laboratory flotation deinking, 332  
process, 328–330*f*
- Fluidized bed, description, 166,167*f*
- Food and Drug Administration guidelines, polymer recycling for food use, 157–158,381–382
- Food packaging, absorption/desorption by plastics, 445–446
- Food packaging and quality requirements migration testing, 496–497  
process efficiency, 494,496  
source control, 493–495*f*
- Food packaging made from recycled polymers  
calculated concentration–distance profiles, 455,456*f*  
calculated concentration vs. time, 452,454–455  
calculation of threshold values, 446–447  
concentration vs. time for diffusion, 452,453*f*  
diffusion coefficient measurement, 449–451*f*  
diffusion coefficients vs. temperature, 452,453*f*  
diffusion theory for estimation of contamination, 446  
experimental description, 450–451  
migration of chemicals, 447–448  
migration through layered package vs. virgin layer thickness, 455–457  
problems with determination of purity, 446  
use of virgin layer over recycled layer, 448–449
- Food use  
plastics recycling, 389–402  
poly(ethylene terephthalate) recycling, 152–160  
polymer recycling, 380–388  
polymer recycling technology, 488–499
- Footwear applications of ground rubber, example, 211–213

Forest productivity, influencing factors, 291–293  
 Formic acid, role in chemically induced delamination for recycling of coated aluminum scrap, 482–483,485f  
 Fractionation, description, 336–337  
 Fracture of brittle solid, calculation, 141–142  
 Free energy, definition, 32  
 Functional barrier, use for food packaging made from recycled polymers, 445–457

## G

Gasifiers, description, 166,168t  
 General Motors Corporation Material Selection Guideline recycling options for thermoset rubber, 210  
 use of recycled materials, 210–211,212f  
 Generic resins, recycling, 73–74  
 Glass, recycling problems, 29  
 Governments, commitment to recycling, 66  
 Grafting reactions, devulcanization of thermoset rubber, 248  
 Ground rubber applications, 203–205  
 market, 203  
 processing technologies, 202

## H

High-density cleaning and screening, description, 326  
 High-density polyethylene, recycling programs, 489  
 High-density polyethylene–poly(ethylene terephthalate) blends, *See* Poly(ethylene terephthalate)–high-density polyethylene blends  
 High-density polyethylene postconsumer resins, color matching, 107–108  
 High-density polyethylene recycling, food use, 386–387  
 Higher alternative disposal feed, economic driving forces of recycling, 20

Higher priced oil, economic driving force of recycling, 20  
 Highway construction, use of scrap tires, 243  
 Highway construction industry, rubber recycling, 197  
 Homopolymer general purpose polystyrene, synthesis, 90  
 Hunter unit, color measurement, 106–107  
 Hupercar, advantage, 31  
 Hydrogenation, description, 166,168t

## I

Impact resistance, role in mechanical properties of poly(ethylene terephthalate)–high-density polyethylene blends, 122,124–125f  
 Impact-resistant polystyrene, synthesis, 90  
 Incineration alternative to recycling, 9,42–43  
 automotive shredder residue, 51–52  
 Interfaces, thermodynamics, 33  
 Intermodal Surface Transportation Efficiency Act of 1991, use of scrap tires, 243  
 International law, role in polymer recycling for food use, 387  
 Isopropyl alcohol, reclamation process assessment, 418–434

## K

K–1 recycler project comparison to deinking process, 321  
 contaminant analysis, 317  
 continued advances, 320  
 description, 309–310  
 fiber preparation and cleaning, 311–321  
 fiber sources, 310–311  
 forming system, 317–319  
 paperboard process, 319  
 product applications, 319–320  
 stock preparation, 314–316  
 Kilns, description, 164,166,167t  
 Kneading, description, 334–335

## L

- Lacquer coatings, chemically induced delamination for recycling of coated aluminum scrap, 476,477f
- Laminates, recycling, 37–38
- Landfill(s), number, 50
- Landfilling
  - alternative to recycling, 9
  - paper waste management, 288
- Lindane, effect of washing and drying in removal from recycled poly(ethylene terephthalate), 435–443
- Linear expansion tests, description, 362
- Lithium aluminum hydride, chemical probe for rubber devulcanization, 247
- Local law, role in polymer recycling for food use, 387
- Logistics, polymer recycling, 7–8
- Low-density polyethylene rich feed, thermal depolymerization of thermoplastic mixtures, 175,176t

## M

- Malathion, washing and drying effect in removal from recycled poly(ethylene terephthalate), 435–443
- Maleic acid anhydride grafted styrene–ethylene/butylene–styrene block copolymer, recycling using cellulosic reinforcement, 367–376
- Manufacturing processes, carbon black, 261–263
- Market
  - carbon black, 264–266
  - ground rubber, 203
  - plastics recycling, 162,164,165t
  - polypropylene, 81–83
  - rubber recycling, 217–220
  - scrap tires, 238–239
  - vinyl, 97–98
- Market for recycled paper
  - alternate uses, 304t,305
  - fiber flows, 303
  - Market for recycled paper—*Continued*
    - government influences, 303,305
    - influencing cultures, 299
    - recycled paper properties, 303
    - reuse considerations, 299,303
    - utilization of recovered paper, 299,300–302f
- Markets for recycled plastics
  - chemically purified monomers and polymers, 14
  - commingled polymers, 14
  - mechanically separated polymers, 1–15
- Materials for recycling, availability, 65
- Materials recovery facility
  - advantages, 23
  - future facility
    - applications, 24–25
    - criteria, 23
    - design, 23–24
    - technology requirements, 25
  - products, 25
- Mechanical cleaning
  - cleaners, 332–334
  - process, 76–77,334
- Mechanical properties, poly(ethylene terephthalate)–high-density polyethylene blends, 122–127
- Mechanical recycling, description, 93
- Mechanical recycling business, discussion, 75–76
- Mechanically separated polymers, markets, 14–15
- Melt filtration, description, 87–88
- Metal-containing contaminants, incineration, 43
- Methyl iodide, chemical probe for rubber devulcanization, 247–248
- Methyl salicylate, reclamation process assessment, 418–434
- Methyl stearate, reclamation process assessment, 418–434
- Microwaves, devulcanization of thermoset rubber, 249
- Mixed plastics
  - recycling, 74
  - recycling technologies, 58

- Mixed plastics recycling using cellulosic reinforcement  
dynamic mechanical properties, 376  
effect of adhesion, 371–374f  
experimental description, 368–369  
fractured surfaces, 373,375  
mechanical properties, 369–370
- Mixed plastics waste, spouted bed reactor  
for advanced thermal recycling, 183–192
- Mixed polymers, markets, 15
- Mixing, thermodynamics, 32–33
- Morphology, poly(ethylene terephthalate)–high-density polyethylene blends, 117,119–124
- Municipal and industrial waste generation  
disposal methods, 183–184  
volume, 183
- Municipal solid waste  
advantages of recycling, 357  
amount generated, 50  
components, 357  
composition, 3,390,391f  
disposal methods, 2,12  
interest in recycling, 389  
materials recovered, 286  
need for reduction in quantity, 357  
plastics composition, 50–51  
recycling, 51,287  
role in environment, 287
- N**
- Natural fibers, comparison to synthetic fibers, 41–42
- New tires, use of scrap tires, 243–244
- Newspapers, growth in recycling, 13
- Nicotine, analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 464–466f
- Nonionic surfactants, role in recovery process for spent polyurethane-based propellants, 147,148f
- O**
- Office-paper deinking  
deinking agents for toner inks, 343,345
- Office-paper deinking—*Continued*  
electrostatic ink decomposition, 342–344t,f  
environmental scanning electron microscopy, 345–347f  
experimental procedure, 346  
microscopic analysis  
flexographic printing on newsprint, 346,347f  
photocopier printing using toner ink, 346,348,349f  
residual polyester resin toner ink with surfactant, 348,350f  
styrene–acrylate toner ink particles with surfactants, 348,350f  
without surfactant, 348,349f  
toner ink particle softening below glass transition temperature, 351,353f  
toner ink particle surface features, 348,351,352f  
presence of iron mineral particles in toner inks  
energy-dispersive X-ray spectroscopic analysis, 351,353f  
toner ink particle agglomeration and dispersion, 351,354–355
- Oil furnace process, manufacture of carbon black, 261,263
- Olefinic thermoplastic vulcanizates  
advantages compared to thermoset rubbers, 226–227  
applications, 223  
chemistry, 228–230  
description, 225–226  
disadvantages compared to thermoset rubbers, 227–228  
markets, 224  
performance properties, 224
- Olefinic thermoplastic vulcanizate recycling  
case study, 230–235  
methods, 225,235  
substitution areas, 226
- Organic coatings, delamination from metal substrate, 473
- Oxidants, role in recovery process for spent polyurethane-based propellants, 147,148f

## P

- Paint coatings, chemically induced  
  delamination for recycling of coated  
    aluminum scrap, 476,477f
- Paper, volume as packaging material, 306
- Paper deinking, office, *See* Office-paper  
  deinking
- Paper deinking mill unit operations  
  bleaching, 335–336  
  dispersion, 334–335  
  factors affecting sequence of unit  
    operations, 323–324  
  flotation, 328–332  
  fractionation, 336–337  
  high-density cleaning and  
    screening, 326  
  kneading, 334–335  
  mechanical cleaning, 332–334  
  pulping, 324–326  
  refining, 336–337  
  rejects and sludge handling, 338–339  
  technical challenges, 339  
  washing, 326–328  
  water clarification, 337–338
- Paper laminates, chemically induced  
  delamination for recycling of coated  
    aluminum scrap, 476,477f
- Paper recycling  
  benefits, 309  
  challenges and opportunities, 305  
  conceptual model  
    market demand, 299–305  
    production capacity, 296  
    raw material supply, 296–299  
  consumer response, 306–307  
  cost–benefit analysis, 294–295  
  deinking process, 320–321  
  effect of fiber contamination, 308  
  effect on fiber property, 307–308  
  food use, 382–383  
  forest productivity  
    amount, 291  
    carbon sequestration, 292  
    reforestation, 291  
    silviculture, 292,293f
- Paper recycling—*Continued*  
  forest products industry  
    clear-cutting, 294  
    endangered species preservation, 293  
    process modifications, 294  
    regulation vs. market forces, 287  
  K–1 recycler project, 309–320  
  recycled product quality, 308–309  
  waste management options  
    composting, 291  
    landfilling, 288  
    recycling, 289  
    source reduction, 290  
    waste to energy, 289–290  
  *See also* Cellulose and paper recycling
- Papermaking, development, 275
- Particle size distributions, poly(ethylene  
  terephthalate)–high-density polyethylene  
  blends, 117,120,122–124,134–137
- Petroleum, reduction of use, 27
- Phenyl lithium, chemical probe for rubber  
  devulcanization, 247
- Photodegradation, description, 39
- Physical reprocessing, description, 393
- Plastic beverage containers, growth in  
  recycling, 13
- Plastic laminates, chemically induced  
  delamination for recycling of coated  
    aluminum scrap, 474–476
- Plastic packaging  
  environmental legislation, 152–153  
  recycling rate, 152
- Plastics  
  importance of recycling, 221–222  
  recycled, *See* Recycled plastics  
  solid waste  
    amount, 50–51  
    lack of degradation, 50
- Plastics industry, role in recycling, 68–69
- Plastics processors, role in recycling, 68–69
- Plastics reclamation process, protocol for  
  adequacy assessment, 432–434
- Plastics recycling  
  applications, 367  
  business, 72–73  
  consumer cooperation, 63

- Plastics recycling—*Continued*  
 economic driving forces, 20–22  
 economic realities, 19  
 economics, 15–19,78  
 emerging technologies, 22–25  
 environmental effect on growth, 367  
 food use, 383–384  
 history, 12  
 importance, 11  
 incentives and disincentives, 62–63  
 markets, 162,164,165<sup>t</sup>  
 mechanical processing technology, 76–77  
 mechanical recycling business, 75–76  
 reclamation process assessment, 418–434  
 problem of heterogeneous composition, 368  
 technologies, 73–75  
 thermal depolymerization of thermoplastic mixtures, 170–182  
 thermal processing technology, 77–78  
 volume and composition, 389–390  
*See also* Polymer recycling
- Plastics Recycling Task Force  
 Interim Guidelines for the Safe Use of Recycled Plastics in Food Packaging Applications, 419  
 objectives, 418–419
- Plastics recycling technologies in automotive industry  
 reprocessing  
 mixed plastics, 58  
 thermoplastic waste, 57  
 thermosets, 57–58  
 separation techniques, 56–57
- Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations  
 description, 392–402  
 objective, 390
- Policy, recycled plastics for food-use applications, 389–402
- Poly-ε-caprolactone, degradation, 41
- Polyester recycling, future research, 504,505<sup>t</sup>
- Polyethylene, degradation, 40
- Polyethylene recycling  
 applications, 111  
 automation, 105–106  
 color matching, 107–108  
 color measurement, 106–107  
 compounding and extrusion stages, 105  
 detergent, 107  
 feedstock quality, 110–111  
 Food and Drug Administration Letter of No Objection, 109–110  
 future trends, 111–112  
 objective, 105  
 PRISMA postconsumer resins, 108–109  
 PRISMA resin color-sorting system, 105  
 supply requirements, 104–105
- Poly(ethylene terephthalate)  
 candidate for recycling, 459  
 environmental legislation, 152–153  
 need for waste management through recycling, 152  
 polymerization process, 404–406  
 postconsumer, contaminant removal verification, 409–417  
 recycled, residual contaminants, 435–443  
 recycling programs, 489  
 reversible polycondensation, 406,407<sup>f</sup>  
 sales, 152  
 tertiary recycle process, 406,408<sup>f</sup>
- Poly(ethylene terephthalate)–high-density polyethylene blends  
 commercial applications, 113  
 experimental description, 114–116  
 mechanical properties, 122–127  
 morphology, 117,119–124  
 previous studies, 113–114  
 rheological properties, 116–118<sup>f</sup>  
 spectroscopic analysis, 133–134  
 thermal properties, 127–133,136
- Poly(ethylene terephthalate) recycling  
 chemical recycling, 384  
 food use  
 approaches, 153  
 development, 153  
 European regulatory criteria, 158–159  
 Food and Drug Administration regulatory guidelines, 157–158

- Poly(ethylene terephthalate) recycling—  
*Continued*  
food use—*Continued*  
future directions, 159–160  
manufacturing process, 154  
secondary recycling, 154–156  
tertiary recycling, 155–157  
multilayer technology, 385–386  
physical recycling, 384–385  
thermal extraction–GC/MS recycling,  
458–471
- Poly(ethylene terephthalate)-rich feed,  
thermal depolymerization of  
thermoplastic mixtures, 175–176
- Poly(lactic acid), degradation, 41
- Polymer(s)  
absorption/desorption of chemicals from  
surroundings, 445–446  
advantages, 11  
applications, 12  
environmental impact, 27–28
- Polymer recycling  
alternatives  
degradation, 39–42  
incineration, 42–43  
amount recycled, 30  
automotive industry, 4  
benefits, 3  
composites, 37  
conditions for success, 5  
considerations, 30  
containers and packaging, 4  
depolymerization, 5  
disadvantages, 37  
economics, 6–7  
food use  
Food and Drug Administration  
guidelines, 381–382  
future, 388  
high-density polyethylene recycling,  
386–387  
impact of non-food-use applications on  
resins for food use, 387–388  
paper recycling, 382–383  
plastic recycling, 383–384  
poly(ethylene terephthalate) recycling,  
384–386
- Polymer recycling—*Continued*  
food use—*Continued*  
problems, 381  
quality, 386  
role of local and international law, 387  
inherent problems, 3  
laminates, 37–38  
logistics, 7–8  
postconsumer, *See* Postconsumer polymer  
recycling  
programs, 3  
recycling programs, 3  
separated vs. mixed polymers, 34  
separation by consumers, 34–36  
separation devices, 36  
technology, 8–9  
tertiary recycling, 38–39  
thermodynamics, 30–34  
thermosets, 37  
use of toughened polyolefins, 4
- Polymer recycling research  
1980s approaches  
direct reuse, 503  
reuse after separation and  
modification, 503  
value-chemical recycling, 503–504  
cured unsaturated polyesters, 505*t*, 507  
fast pyrolysis, 505*t*, 507–508  
future research and development needs,  
508–509  
polyester, 504, 505*t*  
polystyrene, 505*t*, 507  
polyurethanes, 504–506  
pyrolysis, 505*t*, 507  
thermosets, 505*t*, 506
- Polymer recycling technology for food use  
cleaning process technology, 498–499  
commercial interests, 489  
criteria, 488  
environmental roots, 489  
experimental materials, 489  
food packaging and quality requirements,  
493–497  
future recycled poly(ethylene  
terephthalate) packaging, 492*t*, 493  
history, 490–492  
separation technology, 498

- Polyolefins  
  degradation, 40  
  toughened, recycling, 4
- Polypropylene  
  recovery from battery cases, 80–81  
  recycle volume, 80
- Polypropylene feed, thermal depolymerization of thermoplastic mixtures, 177–178
- Polypropylene recycling  
  applications for reclaimed  
    polypropylene, 88  
  growth, 81  
  markets, 81–83  
  properties of reclaimed polypropylene, 88  
  reclaiming capacity, 83–85  
  recovery from battery cases, 80–81  
  trends in technology, 86–88
- Polystyrene  
  additives, 90  
  capacity, 91–92  
  consumption patterns, 92  
  copolymers, 90  
  products from fabrication techniques, 90,91*t*  
  recycling, 89–96  
  synthesis, 89–90
- Polystyrene feed, thermal depolymerization of thermoplastic mixtures, 178–179
- Polystyrene recycling  
  applications, 89  
  challenges, 94–95  
  development, 93  
  durable and semidurable products, 95–96  
  future, 96  
  future research, 505*t*,507  
  techniques, 93
- Polyurethane-based propellants, spent, feasibility of recovery process, 139–150
- Polyurethane degradation under ultrasonication, mechanism, 145
- Polyurethane recycling, future research, 504–506
- Poly(vinyl chloride)  
  degradation, 41  
  importance of recycling, 222
- Poly(vinyl chloride) recycling, *See* Vinyl recycling
- Postconsumer poly(ethylene terephthalate), contaminant removal verification, 409–417
- Postconsumer polymer recycling  
  items, 13–14  
  objective, 12–13  
  overview, 64–66  
  problems, 14
- Postconsumer recycling, economics, 66–69
- Polymer waste, reduction, 28–29
- Primary recycling, definition, 161
- PRISMA resins  
  color-sorting system, 105  
  description, 108–109
- Processing variables, role in morphology and properties of poly(ethylene terephthalate)–high-density polyethylene blends, 113–137
- Propellants, spent polyurethane based, feasibility of recovery process, 139–150
- Public, *See* Consumer
- Pulp and paper mills, use of tires, 242
- Pulping, description, 324–326
- Pyrolysis, use in polymer recycling, 505*t*,507
- Pyrolysis carbon  
  manufacture of carbon black, 261,263,265  
  market, 264–266  
  requirements for market acceptance, 268–271  
  technical requirements, 264,267,269
- Pyrolytic cracking, economics, 65
- Q
- Quaternary recycling, definition, 161
- R
- Raw material(s), regeneration, 75
- Raw material supply for paper recycling  
  collection and processing, 298–299  
  government influences, 299  
  recovered paper specifications, 296–298  
  sources of recovered paper, 298  
  types of collection, 298



- Reclaimed polypropylene  
  applications, 88  
  properties, 88
- Reclaiming capacity, polypropylene, 83–85
- Reclamation, economics, 18–19
- Reclamation processes for plastics  
  recycling  
  efficacy, 425  
  experimental procedure,  
    421–423, 427–432  
  federal regulations, 419  
  high-density polyethylene removal, 425  
  Interim Guidelines for the Safe Use of  
    Recycled Plastics in Food Packaging  
    Applications, 419  
  Plastics Recycling Task Force, 419  
  surrogate concentration after  
    reclamation, 423–425  
  surrogate selection, 419–421  
  validity, 425–426
- Recovery, scrap tires, 241
- Recovery process for spent  
  polyurethane-based propellants,  
  feasibility, 139–150
- Recycled agro-based fiber use for  
  composites  
  advantages, 357  
  challenges in recycling, 358–360  
  collection of recycled resources,  
    364–365  
  future work, 365  
  processing of fiber into boards  
  materials, 359, 361  
  resin application and board  
  fabrication procedures, 361  
  static bending, 363  
  tensile strength, 362, 363  
  testing of board properties  
  linear expansion tests, 365,  
  relative humidity tests, 362  
  static bending, 361  
  tensile strength, 361  
  water tests, 361  
  thickness swelling in water, 362, 363
- Recycled materials, quality concerns, 458
- Recycled packaging, importance, 389
- Recycled plastics  
  food-use applications  
  concerns, 390  
  demonstration of reduction of  
    contaminant levels below dietary  
    exposure, 394–395  
  determination of maximum residual level  
    of contaminant, 394  
  Food and Drug Administration opinions,  
    400, 402  
  functional barriers of migration, 396–401  
  migration principles, 396–401  
  migration studies, 395–396  
  regulatory framework, 392  
  surrogate contaminant selection, 395, 396  
  types of recycling, 393–394  
  markets, 14–15
- Recycled poly(ethylene terephthalate)  
  residual contaminants, 435–443  
  thermal extraction–GC/MS, contaminant  
  analysis, 458–471
- Recycled polymers, use for food packaging,  
  445–457
- Recycling  
  automotive, *See* Automotive recycling  
  cellulose and paper, *See* Cellulose and  
  paper recycling  
  coated aluminum scrap, chemically  
  induced delamination, 472–486  
  concerns, 47  
  economics, 62–63  
  high-density polyethylene, food use,  
    386–387  
  importance for plastics, 221–222  
  investment, 222  
  olefinic thermoplastic vulcanizates, *See*  
  Olefinic thermoplastic vulcanizate  
  recycling  
  paper, *See* Paper recycling  
  planning required, 67  
  political correctness, 286  
  polyethylene, *See* Polyethylene  
  recycling  
  poly(ethylene terephthalate), *See*  
  Poly(ethylene terephthalate) recycling  
  polymers, *See* Polymer recycling

**Recycling—Continued**

- polypropylene, *See* Polypropylene recycling
- postconsumer polymer, *See* Postconsumer polymer recycling
- public concept, 458
- rubber, *See* Rubber recycling
- scrap tires, 241
- sourcing problems, 65
- vinyl, *See* Vinyl recycling

Recycling technology, advanced, *See*  
Advanced recycling technology

Redemption, role in contaminant analysis  
in recycled poly(ethylene terephthalate)  
by thermal extraction–GC/MS, 470

**Reduction**

- polymer waste
  - importance, 28
  - packaging, 28
  - recycling, 29
  - replacement by other materials, 28–29
- scrap tires, 240

Refining, description, 336–337

Reforestation, role in forest productivity,  
291–292

**Regulation**

- recycled plastics for food-use  
applications, 389–402
- scrap tires, 239–240

Reinforcing agents for rubber,  
examples, 254

Rejects and sludge handling, description,  
338–339

Relative humidity tests, description, 362

**REPETE**

- description, 404
- tertiary recycle process, 406,408f

Research, polymer recycling in the 1990s,  
502–509

Residual contaminants in recycled  
poly(ethylene terephthalate)  
apparatus, 436  
effect of drying on surrogate removal,  
441–443  
experimental description, 436–439  
future work, 443

Residual contaminants in recycled  
poly(ethylene terephthalate)—*Continued*  
initial concentrations of surrogates,  
439–440

washing effect on surrogate removal,  
440–443

Resin companies, role in recycling, 69  
Retorts, description, 164,166,167t

Rheological properties, poly(ethylene  
terephthalate)–high-density  
polyethylene blends, 116–118f

Rubber, black filler from tile pyrolysis  
char, 254–271

Rubber industry, challenge of rubber goods  
disposal, 245

**Rubber recycling**

- applications, 199
- asphalt rubber, 205
- automotive applications, 209–212
- automotive industry, 197
- footwear applications, 211–213
- future, 200
- highway construction industry, 197
- history, 196
- impact of olefinic thermoplastic  
vulcanizates, 221–235
- logistics, 198–199
- market, 217–220
- new technologies, 217
- technology, 198–199
- tires, 213–217

**S**

Salvage dealers, vehicle dismantling, 48

Science, recycled plastics for food-use  
applications, 389–402

**Scrap tire(s)**

- disposal, 241
- markets, 238–239
- reduction, 240
- regulation, 239–240
- reuse, 240–241
- tire-derived fuel, 241–244
- volumes, 237–238

- Scrap tire recycling  
  economic incentives, 203  
  markets, 240–244  
  regulation, 239–240
- Scrap vehicle recycling  
  history, 47–48  
  vehicle dismantling, 48  
  vehicle shredding, 49–50
- Second law of thermodynamics  
  entropy, 32  
  free energy, 32
- Secondary recycling  
  definition, 161  
  description, 34  
  poly(ethylene terephthalate) for food use, 154–156
- Secondary recycling process, role in contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 467,469f
- Select stream, role in contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 467,468f
- Self-delamination, use for recycling of coated aluminum scrap, 472–480
- Separated plastics, economic values, 30
- Separated polymers, problem with mixing, 34
- Separation devices, polymer recycling, 36
- Separation of polymers by consumers, recycling, 34–36
- Separation technology, polymer recycling for food use, 498
- Shear sensitivity, poly(ethylene terephthalate)–high-density polyethylene blends, 116–118
- Silviculture, role in forest productivity, 292,293f
- Size reduction  
  description, 86–87  
  tires, processors, 203
- Small entrepreneurial companies, success at recycling, 64
- Sodium di-*n*-butyl phosphite, chemical probe for rubber devulcanization, 247
- Solid composite propellants  
  disposal problems, 139  
  recovery methods, 139–150
- Solid waste(s)  
  disposal, 2,502  
  need for reduction in quantity, 357
- Solvent swelling, spent polyurethane-based propellants, 141–144
- Sorting, economics, 17–18
- Source reduction, paper waste management, 290
- Soxhlet extraction, procedure, 429–432
- Spent polyurethane-based propellants, feasibility of recovery process, 139–150
- Spouted bed fluidization regimen, description, 184–186
- Spouted bed reactor for advanced thermal recycling of mixed plastic waste  
  applicability to wastes, 186  
  auger feeder, 189  
  automobile residues shredder analysis, 188–189  
  extrusion feeding, 188  
  fines recycle, 188  
  heat recovery, 188  
  hot cyclone, 188  
  importance, 184  
  potential products, 191  
  process development unit, 186–187  
  product gas analysis, 190–191  
  reactor, 188  
  sprouting action, 189  
  technological features, 191–192  
  technology, 184–186  
  temperatures of operation, 189–190
- Static bending, description, 361
- Steam autoclave, devulcanization of thermoset rubber, 250
- Suitable purity, description, 394
- Sustainable development, definition, 11
- Synthetic fibers, degradation, 42
- T
- Technology  
  plastics recycling, 73–75  
  polymer recycling, 8–9

Technology—*Continued*

- polystyrene recycling, 93
- rubber recycling, 198–199,217
- trends for polypropylene recycling, 86–88

## Temperature role

- chemically induced delamination for recycling of coated aluminum scrap, 474–476

- contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 465–466

## Tensile strength, description, 361

## Tertiary recycling

- advantages, 38–39
- chemical vs. thermal, 162,163f
- definition, 161
- economics, 38
- poly(ethylene terephthalate) for food use, 154–157

*See also* Chemical recycling

## Tetracosane, effect of washing and drying in removal from recycled poly(ethylene terephthalate), 435–443

## Thermal depolymerization of thermoplastic mixtures

- advantages of Conrad unit, 172–173
- base feed, 173–175
- chlorine capture studies, 179–180
- economics, 172,181
- experimental procedure, 181–182
- feed preparation, 172
- low-density polyethylene feed, 175,176t
- parametric study, 173
- poly(ethylene terephthalate)-rich feed, 175–176
- polypropylene feed, 177–178
- polystyrene feed, 175,178–179
- postconsumer plastics as feedstock, 180–181
- process, 171–172
- project description, 171

## Thermal extraction–GC/MS

- advantages for contaminant analysis in recycled materials, 459
- contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction–GC/MS, 458–471

Thermal extraction–GC/MS—*Continued*  
identification of types and frequencies of contaminants in postconsumer resins, 459

## Thermal process, manufacture of carbon black, 261,263

## Thermal processing technology, discussion, 77–78

## Thermal recycling

- description, 93,162,163f
- mixed plastic waste, advanced, spouted bed reactor, 183–192

## Thermodynamics

- environmental implications, 33–34
- interfaces, 33
- mixing, description, 32–33
- polymer recycling, 30–34
- recycling
  - first law, 30–31
  - mixing, 32–33
  - second law, 32

## Thermoplastic elastomers

- future, 200
- growth rate, 223
- recycling challenges, 223
- recycling technology and logistics, 198–199
- use in tire manufacture, 196

## Thermoplastic mixtures, thermal depolymerization, 170–182

## Thermoplastic polyolefins, applications, 224

Thermoplastic vulcanizates, olefinic, *See* Olefinic thermoplastic vulcanizates

## Thermoplastic waste, recycling technologies, 57

## Thermoplastics, definition, 12

## Thermoset rubbers

- advantages and disadvantages compared to olefinic thermoplastic vulcanizates, 226–228
- chemical methods of devulcanization, 245–251
- recycling problem, 222–223
- recycling technology and logistics, 198–199
- use in tire manufacture, 196

- Thermosets**  
 applications, 37  
 definition, 37  
 future research, 505*t*,506  
 recycling, 37  
 recycling technologies, 57–58
- Thiol–amine reagent, chemical probe for rubber devulcanization, 247**
- Tile pyrolysis char, black filler for rubber, 254–271**
- Tire(s), uses for discarded tires, 237**
- Tire applications of ground rubber construction elements of passenger tire, 213,214*t***  
 cost savings per unit, 213,216*t*,217  
 ground rubber usage, 213,214*t*  
 passenger tire usage, 213,214*t*  
 potential cost savings at 5 and 10%, 213,216*t*  
 raw material savings, 213,216*f*
- Tire-derived fuel, use of scrap tires, 241–244**
- Tire recycling, elastomer technologies, 53–54**
- Toner inks**  
 interactions with deinking agents, 342–355  
 recycling problems, 342
- Toughened polyolefins, recycling, 4**
- Transportation, role in economics for recycling, 65–66,68**
- Trends**  
 vehicle recycling  
   automotive plastic materials, 59  
   design for disassembly, 58–59  
   managing substances of concern, 59–60  
   recycling alliances and partnerships, 60–61  
 vinyl recycling, 101
- 2,2,4-Trimethylpentane, reclamation process assessment, 418–434**
- Triphenyl phosphine, chemical probe for rubber devulcanization, 247**
- Twin screw processing speed role**  
 mechanical properties of  
   poly(ethylene terephthalate)–high-density polyethylene blends, 122,126–127
- Twin screw processing speed role—*Continued***  
 thermal properties of poly(ethylene terephthalate)–high-density polyethylene blends, 128,131–134
- U**
- Ultrasonics, devulcanization of thermoset rubber, 249**
- Ultrasound irradiation, spent polyurethane-based propellants, 144–147**
- Union Carbide, perspective and experiences in polyethylene recycling, 104–112**
- V**
- Value-chemical recycling, polymer recycling research, 503–504**
- Vehicle Recycling Partnership, description, 60**
- Verification, contaminant removal from postconsumer poly(ethylene terephthalate), 409–417**
- Vinyl**  
 market, 97–98  
 presence in waste stream, 98–99
- Vinyl Environmental Resource Center, functions, 100–101**
- Vinyl recycling**  
 advances, 99–100  
 future, 103  
 growth incentives, 101–102  
 hidden market, 102  
 trends, 101
- Vinyl Environmental Resource Center, 100–101**
- Vulcanizates, olefinic thermoplastic, *See* Olefinic thermoplastic vulcanizates**
- W**
- Washing**  
 description, 326–327  
 pulp washing, 327–328

Washing—*Continued*

- role
  - contaminant analysis in recycled poly(ethylene terephthalate) by thermal extraction—GC/MS, 470
  - residual contaminants in recycled poly(ethylene terephthalate), 435–443
  - wash deinking surfactants, 327
- Waste, polymer, reduction, 28–29
- Waste disposal methods, economics, 63
- Waste stream, presence of vinyl, 98–99
- Waste to energy, paper waste management, 289–290
- Water clarification, description, 337–338
- Water tests, description, 361
- Weight saving, motivation for conventional materials replacement with plastic, 31

*Production: Meg Marshall*  
*Indexing: Deborah H. Steiner*  
*Acquisition: Anne Wilson*  
*Cover design: Cornithia Allen Harris*

*Printed and bound by Maple Press, York, PA*