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Polymer Recycling: Thermodynamics and Economics

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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.

Introduction

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 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_2. 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

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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 lanfills 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 or 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 "Hupercar",* 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, ΔS 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 ΔH_{mix} which is greater that the $T\Delta S_{mix}$ term arising because of its dissolution. The positive ΔH_{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, ΔS_{mix} *is less positive* so that this driving force *is less* and solubility *is more dependent upon* ΔH_{mix}. If the positive ΔH_{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, ΔH_{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 ΔH_{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, ΔH_{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-ε-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 LSCT depends upon molecular weight, becoming lower with higher molecular weight as ΔS_{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 ΔH_{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 ΔH_{mix} becomes greater, and consequently, adhesion becomes less. Thus PS and PMMA adhere weakly whereas poly-ε-caprolactone and polycarbonate have a smaller ΔH_{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 require 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 affects 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-e-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_2 and H_2O. (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_2,, and NO_2 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..

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