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OPPORTUNITIES FOR ENVIRONMENTALLY DEGRADABLE POLYMERS

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ABSTRACT

Environmentally degradable polymers, including polymers that are biodegradable, photodegradable, oxidatively degradable, and hydrolytically degradable, have attracted a great deal of attention over the last 20 years or so, particularly as part of plastics waste-management. Undelivered promises, unsatisfied expectations, and unproved claims of degradation have raised serious questions as to the future of this class of polymers. Consequently, we are now at the stage where environmentally degradable polymers need to be carefully evaluated in order to assess what value or benefit, if any, they offer to the polymer industry and the consumer. This assessment must include clear and universally accepted definitions for terms that describe the various environmental degradation pathways, the definition of an acceptable environmentally biodegradable polymer, and methodologies that are able to quantify the degree of degradation. When all these are achieved, it should be possible to recognize and take advantage of the opportunities that are available for environmentally degradable polymers, provided that other requirements such as cost and properties are acceptable. In this article, the key issues of terminology and test methodology are addressed, and, based on the results, some personal prognoses are made on the selective opportunities that may be available for environmentally acceptable degradable polymers.

INTRODUCTION

Synthetic polymers, natural polymers, and modified natural polymers are widely used throughout most of the world today and contribute enormously to the quality of life in the industrial world and are helping to raise living standards in the Third World. Because polymer properties are readily controlled by their chemical composition and manufacturing process, they are used as commodity plastics in such diverse applications as packaging, personal hygiene products, construction of automobiles, computers, houses, clothing, etc.; they are also used as specialty additives in many applications such as water-soluble polymers in detergents, paints, adhesives, concrete, etc., and in medical applications for drug delivery and as temporary and permanent prostheses such as sutures and bone replacements, respectively. Yet, in spite of all these enormous benefits, synthetic specialty polymers and plastics have, in the minds of many people in the general public, legislative bodies, and environmental groups, an overriding connotation of being harmful to the environment, regardless of all their other attributes. The word "environment" is used loosely here to include the human body and the natural environment, since many of the issues encountered by degradable polymers are common to both; this paper, however, is only concerned with the natural environment.

The concern for polymers in the environment is borne out of the association of synthetic plastics and polymers with a waste-management problem that has emerged in the last 20 years. The problem is to some extent real and to some extent a misguided perception, especially with the current commercial and widely used plastic products which were defined and developed for their durability and resistance properties, and, after disposal, they are visible in the environment as litter and they contribute to landfill overcapacity [1]. This problem was acknowledged several years ago by some segments of the polymer industry, and attempts were made to develop environmentally degradable polymers that on disposal, after use, would harmlessly degrade and return to nature. They were anticipated and promoted to be a total solution to the waste-management problem. Unfortunately, no acceptable test methods or definitions were available as guidelines at the time these polymers were introduced, and in many cases they were overpublicized as meeting an admirable objective. The result, when the deficiencies were exposed, was skepticism for the degradable polymer industry and a severe setback for the acceptance of environmentally degradable polymers. Since then, however, with dedicated hard work, industrial and academic scientists have diligently applied themselves to developing meaningful and realistic standard test methods and definitions such that the newer polymers in advanced development and now becoming commercially available should be acceptable in selective applications where environmental degradation is competitive with other recognized waste-management options such as incineration, recycle, and source reduction.

In this paper I will explore opportunities for this new generation of environmentally degradable polymers, the success of which I believe is critically dependent on the general acceptance of the definitions and test methods being developed, and the resolution of environmental safety issues and stigmas associated with the earlier polymers. With these established, only cost and performance, as with any other competitive polymer, will need to be addressed in order to gain market share in appropriate application areas.

ENVIRONMENTALLY ACCEPTABLE DEGRADABLE POLYMERS

Definitions and Test Methodology

Environmentally degradable polymers are generally divided into four different categories which describe their degradation pathways: biodegradation, hydrolytic degradation, photodegradation, and oxidative degradation. They have been defined in many publications and in many different ways. The definitions established by the American Society of Testing and Materials (ASTM) for plastics [2] are probably as close to universal acceptance as any, and these are included here in a more general sense addressing the more general and broader classification of polymers as a starting point.

A *degradable polymer* is designed to undergo a significant change in its chemical structure under specific environmental conditions, resulting in a loss of properties that may vary as measured by standard tests methods appropriate to the polymer and the application in a period of time that determines its classification.

A *biodegradable polymer* is a degradable polymer in which the degradation results from the action of naturally-occurring microorganisms such as bacteria, fungi, and algae.

A *hydrolytically degradable polymer* is a degradable polymer in which the degradation results from hydrolysis.

An *oxidative polymer* is a degradable polymer in which the degradation results from oxidation.

A *photodegradable polymer* is a degradable polymer in which the degradation results from the action of natural daylight.

Unfortunately, the key definition has not yet been addressed: How do we define an environmentally acceptable degradable polymer? This is the issue that must be resolved in order to get acceptance by the general public and other agencies such as regulatory, legislative, environmental groups, etc. The definitions for biodegradable, hydrolytically degradable, oxidatively degradable, and photodegradable polymers refer to a process of degradation, not to a final result. They are all part of a process which leads to establishing the fate and effects of the polymers in the environment, which is the *real issue* of environmental acceptance, regardless of the degradation mechanism. This is sometimes overlooked in the zeal to develop degradable polymers. In this sense, polymers are no different, and should not be treated differently, from any other chemical introduced into the environment. As stated, therefore, none of the accepted definitions for degradation pathways is really of any value beyond the scientist and certainly not to a legislator, an environmentalist, the public, or a developer of new polymers. To develop a definition of an environmentally acceptable degradable polymer, we have to look carefully at the different degradation pathways and determine what questions must be answered in order to ensure that the polymer and its degradation products are safe and pose no harm to the disposal environment.

Figure 1 is a schematic of the four degradation pathways mentioned and what further events beyond initial degradation may occur in the environment. All the degradation mechanisms initially produce fragments which may remain in the environment as recalcitrant pieces with unknown fate and effects or they may be completely biodegraded and ultimately mineralized. The key role of biodegradation is

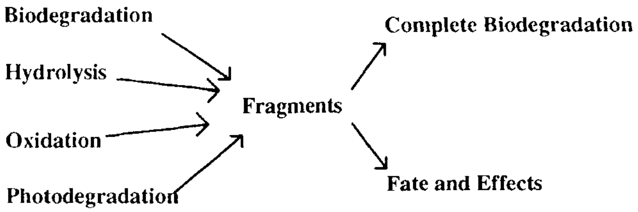

FIG. 1. Pathways for environmentally degradable polymers.

very apparent: it is the only degradation pathway that is able to completely remove a polymer or its degradation products from the environment. Therefore, polymers designed for any of the environmental degradations pathways should also take into consideration that their fragments must either completely biodegrade or be harmless in the environment.

The chemistry of the key degradation process, biodegradation, is represented below by Eqs. (1) and (2), where C represents either a polymer or a fragment from any of the degradation processes defined earlier. For simplicity here, the polymer or fragment is considered to be composed only of carbon, hydrogen, and oxygen; other elements may, of course, be incorporated in the polymer, and these would appear in an oxidized or reduced form after biodegradation depending on whether the conditions are aerobic or anaerobic, respectively.

Aerobic biodegradation:

$$C + O_2 \rightarrow CO_2/H_2O + \text{residue} + \text{biomass} + \text{salts} \qquad (1)$$

Anaerobic biodegradation:

$$C \rightarrow CO_2/CH_4/H_2O + \text{residue} + \text{biomass} + \text{salts} \qquad (2)$$

Complete biodegradation is when no residue remains, and mineralization is when the original substrate, C in this example, is completely converted into gaseous products and salts. Mineralization is really a very slow process because some of the polymer undergoing biodegradation initially produces biomass, and complete biodegradation and not mineralization is the measurable goal when assessing removal from the environment.

Test methods under development at ASTM [2] and in Japan and Europe for assessing the degree of biodegradation in many potential disposal environments are all based on the above chemical equations. The measurements that are required are the original carbon content of the polymer/fragments and its conversion into gaseous products, residue, and biomass. With these measurements the degree of biodegradation, i.e., the degree of removability of any environmentally degradable polymer from a given test environment, may be assessed. If there are fragments, i.e., incomplete biodegradation, these have to be identified and quantified for assessment of environmental fate and effects, which will be discussed in the next section. Major problems with the current laboratory testing methods make them unsuitable for evaluating polymers that are not rapidly, a few weeks at the most, biodegradable, so-called readily biodegradable. This is unfortunate and, as has been indicated by the author previously [3], requires the development of new test methods for polymers and fragments requiring extended time for biodegradation. These will be the subject of future activities within ASTM, and presumably elsewhere. Inevitably, by their nature, these tests will be expensive and probably will require radiolabeling of polymers with, for example, carbon-14. However, environmental safety demands this price, and the degradable polymer industry will not survive if it ignores these requirements.

There are nonquantitative test practices, developed in ASTM [2], that measure the preliminary degradation of polymers in the mentioned pathways by observing polymer property decay; but since these only lead to fragmentation and not to removal from the environment, they will not be discussed here. Our interest is in what happens to the fragments, and as we have seen they must be tested for fate and effects unless they demonstratably completely biodegrade. The reader interested in test methodology for hydrolysis, oxidation, and photodegradation is referred to the appropriate references for further information.

In order to utilize the information on the biodegradation of polymers and fragments, the test environment must be representative of the disposal environment and the time frame of the disposal method. Since I have already indicated the problem with assessing long-term biodegradation, long-term biodegradable polymers must, at present, be treated as being incompletely biodegradable, and fate and effects in the environment must be established over the period of time in which they are predicted to biodegrade. Hence we must develop new test methods that are predictive of the degree of biodegradation of polymers that are slowly biodegraded so that fate and effects of the environment can be more easily evaluated and an environmental safety assessment (ESA) made. If this cannot be achieved, biodegradable polymers and fragments that degrade over several months and beyond will be difficult to accept for disposal in any environment.

Environmental Safety Assessment

Environmentally degradable polymers and ESAs are related by Eqs. (3) and (4). An ESA on a particular compound is, among other variables, a function of the environmental concentration of the xenobiotic, which in the case of environmentally degradable polymers is related to its concentration and its degradation products at any given time in the degradation cycle.

$$\text{ESA} = f[\text{environmental concentration}] \tag{3}$$

$$\text{ESA} = f[\text{polymer} + \text{degradation products}] \tag{4}$$

The implication, then, is that for any of the degradation pathways, the degradation products must be identified and quantified so that their fate and effects on the environment can be assessed. If the degradation products are completely biodegradable, are identified as naturally occurring or environmentally benign, the polymer is probably acceptable in the environment.

To reemphasize, if fragments remain in the environment after degradation, the polymer is slowly biodegradable, or if the polymer is recalcitrant, it will be necessary to establish the identity and concentrations for all the intermediates and residues so that their fate and effects can be established. This will be an assessment of the no effect concentration (NOEC) of the polymer and/or its degradation products as represented in Eq. (5) by testing or by reference if a particular compound is known. The NOEC is referenced against the most sensitive species that the compounds may be in contact within the environment. The NOEC must be higher than the predicted environmental concentration of the intermediate, and the test method used to establish (predict) the concentration of the compound in the environment is assigned an assessment factor (AF) of from 1 to 1000 depending on its reliability and reproducibility. Real world environmental testing is given a factor of 1, laboratory testing is generally in the range of 10 to 1000. Hence the need for reproducible and reliable test methods and confirmation in real world testing, so that the AF is as low as possible.

$$\text{NOEC/AF} > [\text{environmental concentration}] \qquad (5)$$

This requirement for ESAs and the limited testing acceptability of the current test methods beyond a few weeks strongly implies that there is a need to be able to design polymers for waste management that will completely biodegrade (regardless of initial degradation mechanism) within the time frame of the disposal method; for example, a few days in a wastewater treatment facility for water-soluble polymers and a few weeks for composting. In this way the degradation will be complete in the disposal environmental compartment and further testing in subsequent environments will not be necessary. This will save considerable effort that would be necessary for fate and effects testing and environmental safety assessments as well as their associated costs. The concept is captured in the hypothetical degradation profiles shown in Fig. 2. Here the time to completely biodegrade is shown for three different hypothetical polymers which require T1, T2, and T3 time units. The message is that this time to completely biodegrade should be as short as possible and no longer than the time available in the disposal environment. This rate of biodegradation is related to the polymer structure. Once this is understood, it should be possible to modify the rate to meet the desired goal of any particular controlled disposal method.

Considering all these discussed limitations, we are now able to define an environmentally acceptable degradable polymer as:

> a degradable polymer that introduces no harmful or toxic residues into the environment either during or after its degradation is complete

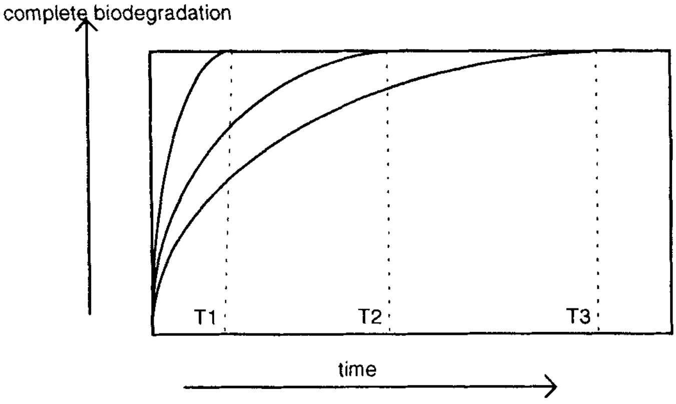

FIG. 2. Environmental safety assessment and time to biodegrade.

The most expedient way of ensuring this acceptability is for the polymer or fragments from degradation to be demonstrated to be completely biodegradable in the environment in the shortest possible time. Failing to achieve complete biodegradation means identification of residues and fate and effects evaluations which puts a considerable burden of proof on the developer and involves a risk assessment which must meet the scrutiny of many watch committees, including environmentalists, the public, and legislators. Table 1 lists some interesting facts on the public's perception of risk [4] that are worth considering when faced with persuasion of acceptability rather than complete biodegradation. Note that the public will have increased concerns depending on the risk origin, natural or synthetic; trust in authority is lacking; controlled is better than uncontrolled; media attention. They, the public and others opposed to environmentally degradable polymers, are not readily persuaded that a risk is acceptable, and the development of completely removable polymers may be the most prudent course to take with environmentally degradable polymers. This may make the goal much more difficult to achieve, but it will make the opportunities more permanent.

POTENTIAL USES FOR ENVIRONMENTALLY ACCEPTABLE DEGRADABLE POLYMERS

Given the foregoing discussion, we are now in a position to selectively choose potential uses for environmentally acceptable degradable polymers.

It is worth spending a short time to review the history of the use of these polymers in the environment. The early history in this is devoted almost entirely to plastics [5] in waste management. No one, until recently, seemed to recognize that it was a problem shared by all polymers. The first degradable polymers developed were promoted as the panacea for the plastics waste-management problem, promising a rapid and complete solution. Even though the polymers developed as solutions were elegant and very innovative, the environment degradation chemistry at best was only promising, and the polymers that were developed were largely untested in

TABLE 1. Important Factors in the Public's Perception of Risk

	Associated characteristics	
Factors	Increased concern	Decreased concern
Origin	Synthetic	Natural
Familiarity	Unfamiliar	Familiar
Volition	Involuntary	Voluntary
Controllability	Uncontrolled	Controlled
Media attention	Much exposure	Little exposure
History	Yes	No
Trust in authority	Lack of	Trust

the environment with any stringent test methodologies since they were not available. With few exceptions the polymers did not meet the requirements of acceptable environmental degradation, and the whole approach had to be reconsidered.

Currently, the horizon has broadened and environmentally degradable polymers are the focus rather than just plastics, recognizing that all polymers represent potential waste-management problems in the environment. Polymer waste-management is now more distinguished by polymer form, plastics are solids and for the most part readily recoverable after use (litter notwithstanding), and water-soluble polymers are very difficult, if not impossible, to recover after use. The difficulties and misrepresentations of the past have been acknowledged, and definitions and test methods are extant or in development to help in the acceptance process and to avoid unsubstantiated claims; there are no longer claims to a waste-management panacea for these polymers, competition with other options for polymer waste-management is accepted; and selective applications are being sought where the advantages of environmentally degradable polymers make them competitive.

Considering polymer waste-management options as shown schematically in Fig. 3, it is quite apparent that for both types of polymer, plastics and water-solubles, all environmental degradation options are applicable. Plastics, due to their form, are far more readily recoverable and amenable to recycle, either as is or after conversion into monomer or by pyrolysis to new feedstocks for polymers; for incineration as fuel; for disposal by burial; and for composting, which is environmental degradation involving primarily biodegradation, with some contribution by oxidative degradation and hydrolytic degradation. The plastics not recovered are generally considered litter, which may cause land or water pollution with undetermined degradation characteristics and fate and effects in the environment.

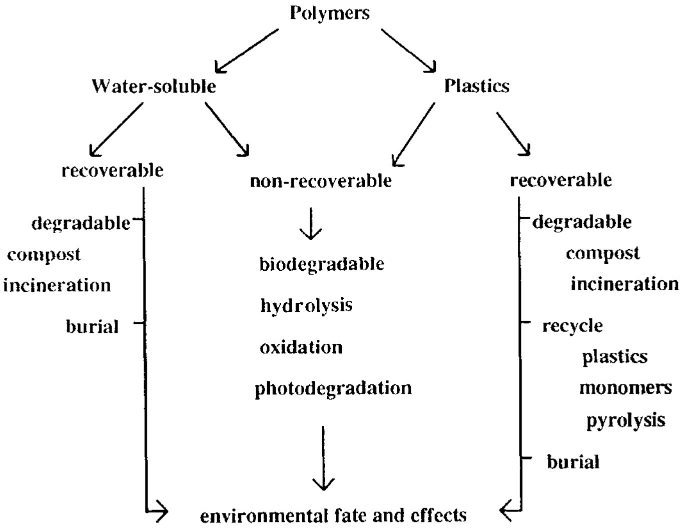

FIG. 3. Polymer waste-management options.

Water-soluble polymers are generally released into the environment through some type of industrial or municipal wastewater treatment plant. Recovery is only possible by precipitation or by adsorption on the biomass and solids in a treatment facility. Precipitation and recovery is expensive and not likely to be widely practiced, but adsorption on biomass/solids is an option for recovering the polymer for other disposal options such as incineration, burial, environmental degradation in compost, or land application as fertilizer. If not recovered, water-soluble polymers have the option of degrading in the wastewater treatment plant or, if they pass through, the environment beyond. Nondegradables will remain in the environment with unknown fates and effects.

The areas immediately obvious as selective opportunities for environmentally degradable polymers are recoverable plastics and all water-soluble polymers. Plastic litter is a social problem which may be avoided by means other than degradation, however, the plastics that are generally recoverable form a large part of the problem. If these are replaced by environmentally acceptable degradable plastics, the litter problem should be reduced. It should be noted that plastics may utilize all the discussed degradation pathways whereas water-soluble polymers will not usually be susceptible to photodegradation.

In order to realize these opportunities, plastics and water-soluble polymers will have to have properties comparable to the products that they replace, will have to meet the stringent requirements for environmental acceptable degradable polymers, and will have to have some acceptable cost level. This cost factor is currently a major issue since there is no readily apparent agreed upon value for acceptable environmental degradability, and there is every expectation that these specialty polymers, being more chemically sophisticated, will be more expensive than their durable counterparts. Someone has to decide that value; the free market is unlikely to do so. If conscience will not, then legislation will be needed.

One of the major opportunities clearly flagged is that all water-soluble polymers should be biodegradable. Assuming that they all enter the environment through the wastewater treatment facility, the residence time in this compartment is a good target, though difficult, for the complete biodegradation of water-soluble polymers. The residence time will depend on the nature of the polymer. With adsorption on biomass, the polymer has typically 5 to 14 days for degradation to occur, which is the biomass retention time, whereas without adsorption the hydraulic residence time is 3 to 6 hours. Adsorption without complete degradation will allow the opportunity for continued degradation in subsequent environments as mentioned above, such as composting. Specific examples of opportunities are flushable polymers and other personal hygiene products, diapers, superabsorbents, detergent polymers, etc.

Plastics face significant competition from alternative technologies for waste management. The opportunities here are, therefore, more selective. They must be sought in areas where the value added is worth the change to a degradable plastic. Opportunities include packaging for fast-food and other one-way uses where sorting for recycle or incineration is not competitive with composting; agricultural film where labor costs for recycle are high; fishing gear when fish and marine mammal life may be preserved; and personal hygiene products. Litter problems would also benefit from additional plastics that photodegrade and then rapidly biodegrade [6] rather than just photodegrade as with the present plastics.

The significance of all these opportunities is that they must meet the goals of environmentally acceptable degradable polymers discussed here. To do this, there is a need to control the disposal method, the time and mechanism of degradation, and to be cost competitive with the nondegradable polymers currently in use for the targeted applications. This is a significant task. It can be accomplished, but it will take time to satisfy all the requirements for environmentally degradable polymers.

CONCLUSIONS

Environmentally acceptable degradable polymers have been defined as polymers that degrade in the environment by several mechanisms to produce no harmful or toxic residues; it is preferable that the different degradation pathways, biodegradation, hydrolytic degradation, oxidative degradation, and photodegradation, culminate in complete biodegradation so that no residue remains in the environment. This very stringent definition represents a difficult goal for polymer synthesis and is likely to result in degradable polymers having a higher cost than the products they must replace. Nevertheless, a clean, safe environment is the intent, and cost must be calculated by nonclassical methods. Somehow we have to factor in the cost of preserving the environment, something we have only recently begun to consider with commercial products. An example would be the introduction of catalytic converters on automobiles to improve air quality—at significant cost but with consumer support.

If we abide by the definitions discussed here, there are numerous opportunities for acceptable environmentally degradable polymers. These are primarily in the areas where polymers are difficult to recover. Water-soluble polymers are not recoverable economically and are, consequently, a big opportunity. With plastics, niche markets are more likely to be the major opportunities, and these are tied to plastic uses where the products are not readily amenable to alternative waste-management options. Opportunities include fast-food and one-way packaging, and personal hygiene products which are compostable without separation; agricultural films which are mulchable and require no collection; and fishing gear which may break free in the ocean and rivers to cause danger to fish and mammalian life.

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