

Polymer Degradation and the Environment

*P*olymers are susceptible to attack by a wide variety of naturally occurring and man-made agents. Some of these environmental agents and examples of polymers that are particularly susceptible to their action are listed in Table 6-1. In most cases, such environmental action is deleterious. For example, UV radiation and ozone can seriously degrade the unsaturated elastomers used in rubber tires. This degradation will limit the lifetime of the tire and could cause catastrophic failure. In practice, UV and ozone resistance is provided by adding various fillers and stabilizers to tire formulations (see Chapter 7).

In some cases, degradation may be a desirable goal. For example, it would be advantageous to be able to design plastic bottles and packaging film so that they rapidly degrade into environmentally safe by-products (e.g., carbon dioxide, water, and biomass) that will occupy less volume in a landfill. The challenge is to ensure that degradation does not occur during the normal shelf life of the plastic and that

cost and mechanical and other properties are not overly compromised to achieve biodegradability.

Table 6-1 Effects of Environmental Agents on Polymers

Agent	Susceptible Polymers	Examples
Biodegradation	Short-chain polymers, nitrogen-containing polymers, polyesters	Polyurethanes Polyether-polyurethane
Ionizing radiation	Aliphatic polymers having quaternary carbon atoms	Poly(methyl methacrylate) Polyisobutylene Polypropylene
Moisture	Heterochain polymers	Polyesters Polyamides Polyurethanes
Organic liquids and vapors	Amorphous polymers	Polystyrene Poly(methyl methacrylate)
Ozone	Unsaturated elastomers	Polyisoprene Polybutadiene
Sunlight	Photosensitive polymers	Polyacetals Polycarbonate

6.1 Polymer Degradation and Stability

Polymers can degrade by exposure to high temperature (thermal degradation), shear action (mechanodegradation), oxygen and ozone, electromagnetic (γ , UV) and ultrasonic radiation, moisture (hydrolysis), and chemical agents. Often, multiple exposures, such as a combination of moisture and heat or oxygen and light (photooxidation), can result in accelerated deterioration. Deterioration of plastics to normal environmental conditions is called *weathering*. Factors that contribute to weathering include radiation (UV, visible, and near-infrared), moisture, temperature cycling, and wind. Factors regulating the effects of temperature, oxygen, moisture, radiation, and chemical agents on the degradation of plastics are discussed in this section.

6.1.1 Thermal Degradation

In general, vinyl polymers are particularly susceptible to thermal degradation, which can occur either by chain scission involving the breakage of the backbone bonds to yield free-radical segments, or by non-chain scission, involving the elimi-

nation of a small molecule from a substituent group and subsequent double-bond formation. These two routes are illustrated for a vinyl polymer in Figure 6-1.

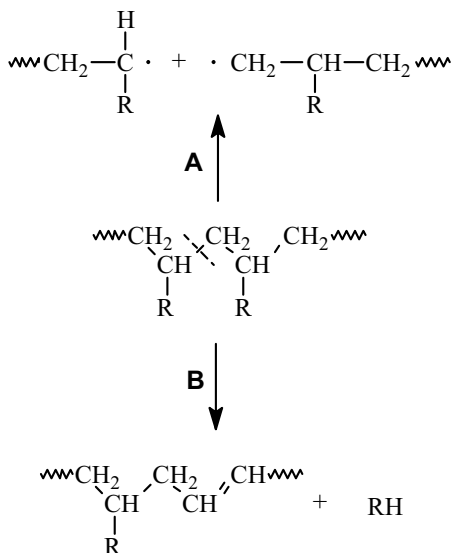
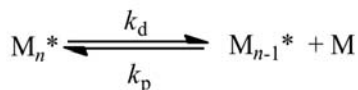


Figure 6-1 Illustration of thermal degradation of a vinyl polymer by (A) random chain scission and (B) non-chain scission mechanisms.

Chain Scission. Chain scission can occur by one of three mechanisms. These are (1) *random degradation*, where the chain is broken at random sites; (2) *depolymerization*, where monomer units are released at an active chain end; and (3) *weak-link degradation*, where the chain breaks at the lowest-energy bonds. In addition to thermal energy, degradation may be initiated by photochemical action, irradiation, or mechanical action.

Random homolytic cleavage of a polymer chain will result in a complex mixture of low-molecular-weight degradation products. Polyethylene and polypropylene degrade in this manner. In the case of 1,1-disubstituted vinyl polymers, the radical segments formed from the initial scission reaction will then depolymerize. This results in a gradual reduction in molecular weight and the production of monomer. Depolymerization may also be preceded by an initial scission at the chain end, as in the case of poly(methyl methacrylate).

The mechanism of *depolymerization* may be represented as



where k_d and k_p are the constants for depropagation and propagation, respectively, and M^* represents an active chain. At some temperature, called the *ceiling temperature*, T_c (see Section 2.2.1), the rates of propagation and depolymerization are equal and, therefore,

$$k_d [M_n^*] = k_p [M_{n-1}^*][M]. \quad (6.1)$$

If the molecular weight is high (i.e., $n \gg 1$), then M_{n-1} and M_n are indistinguishable and, therefore,

$$k_d = k_p [M]. \quad (6.2)$$

Expressing the rate constants in Arrhenius form then gives

$$A_d \exp\left(\frac{-E_d}{RT_c}\right) = A_p \exp\left(\frac{-E_p}{RT_c}\right)[M] \quad (6.3)$$

where A_d and A_p are called the collision frequency factors and E_d and E_p are the activation energies for depolymerization and polymerization, respectively. Rearrangement gives the following relationship for the ceiling temperature:

$$T_c = \left(\frac{E_p - E_d}{R \ln(A_p [M] / A_d)} \right). \quad (6.4)$$

The ceiling temperature varies widely with polymer structure, as illustrated by values given for several vinyl polymers in Table 6-2. For example, the ceiling temperature of polystyrene is 310°C but only 61°C for the 1,1-disubstituted vinyl polymer, poly(α -methylstyrene), which is much more sterically hindered at the radical site due to the presence of the methyl substituent at the α carbon site.

Whether or not a polymer will thermally depolymerize to yield monomer is only partly related to its ceiling temperature. Two other factors affecting depolymerization are the reactivity of the polymer-chain radicals in chain-transfer reaction and the activity of the available chain-transfer sites in the polymer. For example, polytetrafluoroethylene (PTFE) with a very high T_c (500°C) will produce almost a quantitative yield of monomer upon thermal degradation at temperatures *well below* T_c . The reason for this behavior is that the C–F bond of PTFE is very unreactive to a free-radical chain-transfer reaction and, as a result, the polymer provides no active chain-transfer sites to compete with the depolymerization process.

Table 6-2 Ceiling Temperatures of Some Common Vinyl Polymers

Polymer	Structure	T_c (°C)
Poly(α -methylstyrene)	$\left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\overset{\text{CH}_3}{\text{C}}} \right]$	61
Poly(methyl methacrylate)	$\left[\text{CH}_2 - \underset{\text{C}(=\text{O})\text{OCH}_3}{\overset{\text{CH}_3}{\text{C}}} \right]$	220
Polypropylene	$\left[\text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right]$	300
Polystyrene	$\left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]$	310
Polyethylene	$\left[\text{CH}_2 - \text{CH}_2 \right]$	400
Polytetrafluoroethylene	$\left[\underset{\text{F}}{\overset{\text{F}}{\text{C}}} - \underset{\text{F}}{\overset{\text{F}}{\text{C}}} \right]$	580

Non-chain Scission Reactions. One example of a common non-chain scission reaction is *dehydrohalogenation*, which results from the breakage of a carbon-halogen bond and the subsequent liberation of hydrogen halide. The most important example of a polymer that degrades by dehydrohalogenation is poly(vinyl chloride) (PVC). As illustrated in Figure 6-2, PVC undergoes dehydrochlorination at temperatures near and above its T_g (ca. 87°C) to yield hydrogen chloride and ultimately a *polyene* (i.e., conjugated double-bond) structure, which is accompanied by intense color formation. The presence of hydrogen chloride will accelerate the dehydrochlorination process, resulting in further property deterioration. PVC can be stabilized by adding compounds that interfere with the degradation process, neutralize hydrochloric acid as it is formed, trap free radicals, or react with double bonds to prevent subsequent chain scission. Commercial PVC resins usually contain organo-tin or similar thermal stabilizers (see Section 7.1.3). Another example of a commercial polymer that undergoes a non-chain scission reaction at high temperatures is

poly(vinyl alcohol) (PVA). Thermal degradation liberates acetic acid and results in polyene formation as in the case of PVC.

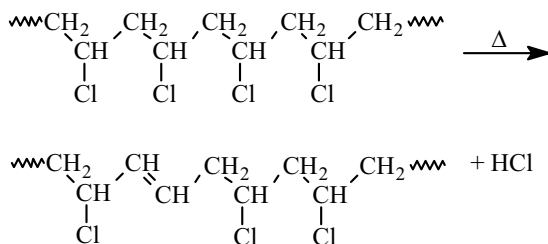


Figure 6-2 Partial dehydrochlorination of a repeating unit of PVC resulting in double-bond formation and the liberation of hydrogen chloride.

Polyacrylonitrile (PAN) is an interesting polymer with good gas-barrier properties suitable for packaging film (see Chapter 12). Although PAN can be solution-cast into film or solution-spun into textile (acrylic) fibers from organic solvents such as dimethylformamide (see Section 8.2.4), it cannot be melt-processed like other thermoplastics. This is because the nitrile ($-\text{C}\equiv\text{N}$) groups of PAN undergo a cyclization reaction at elevated temperatures to yield a ladder-type polymer, as shown in Figure 6-3. This thermally modified form is deeply colored and insoluble but is important as the starting material in the production of some carbon and graphite fibers (see Section 7.1.2). Acrylonitrile finds use in thermoplastic and elastomer applications only as a copolymer with other monomers such as styrene and butadiene (e.g., ABS, SAN, NBR).

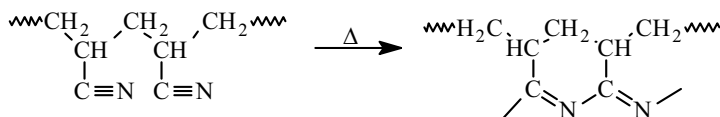
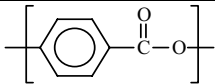
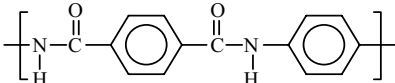
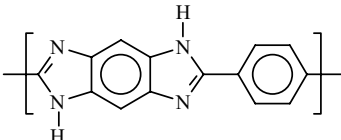
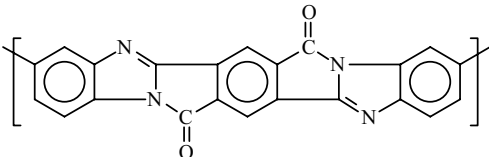
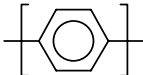


Figure 6-3 Cyclization of polyacrylonitrile at melt temperatures.

Strategies for Thermally Stable Polymers. Many flame-retardant additives as well as comonomers designed to improve the fire resistance of certain polymers are thermally labile and, therefore, the thermal stability of the polymer can be reduced. For use at high temperatures for extended periods of time, the most successful polymers are those with highly aromatic structures, especially those with heterocyclic rings. Resonance stabilization (with energies up to 16.7 kJ mol^{-1}) results in high main-chain bond strength and consequently high thermal stability. Examples of high-temperature polymers and their decomposition temperatures are given in Table 6-3.

Table 6-3 Examples of Thermally Stable Polymers

Polymer	Structure	T_d (°C) ^a
Aromatic polyester		480
Polybenzamide		500
Polybenzimidazole		650
Polypyrrole		660
Poly(<i>p</i> -phenylene)		660

^a Temperature at onset of weight loss in an inert atmosphere as determined by thermal gravimetric analysis (TGA).

Polymers having high-temperature stability as well as other high-performance properties are examples of specialty polymers designed for limited use in aerospace, electronics, and other applications and are discussed in Section 10.2. Unfortunately, the same factors that contribute to high-temperature stability of these polymers also translate to high T_g , high melt viscosity, and insolubility in common organic solvents, which make these polymers difficult or impossible to process by usual methods, such as extrusion and injection molding. Successful commercialization, therefore, always requires some compromise between thermal properties and processability.

6.1.2 Oxidative and UV Stability

With the exception of fluoropolymers, most polymers are susceptible to oxidation, particularly at elevated temperature or during exposure to ultraviolet light. Oxidation usually leads to increasing brittleness and deterioration in strength. Generally, the mechanism of oxidative degradation is free radical and is initiated by the ther-

mal or photolytic cleavage of bonds. The free radicals then react with oxygen to yield peroxides and hydroperoxides.

In general, unsaturated polyolefins are particularly susceptible to attack by oxygen and by ozone. The combined effect of light and oxygen (photooxidation) and the action of ozone (ozonolysis) on the degradation of a common elastomer, polyisoprene, are illustrated in Figures 6-4A and 6-4B, respectively. In both cases, an intermediate cyclic ozonide structure is formed. Subsequent breakage of the labile O–O bonds leads to chain scission and lower-molecular-weight polymer chains with carbonyl end groups. In the case of ozonolysis (Figure 6-4B), subsequent hydrolysis leads to chain scission and liberation of hydrogen peroxide.

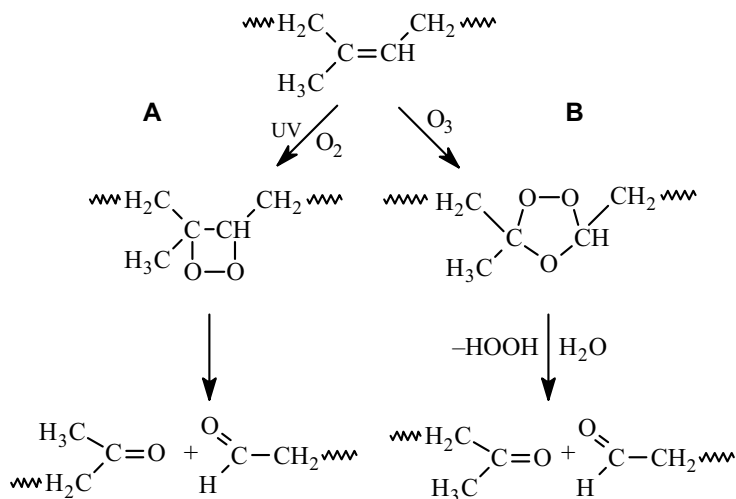


Figure 6-4 Degradation of polyisoprene by (A) photooxidation and (B) ozonolysis.

Oxidative degradation of saturated polymers can also occur through a complex series of reactions that involve the intermediate formation of peroxy radicals. Polystyrene is especially susceptible to photooxidative degradation. In this case, UV radiation is absorbed by the phenyl group, which can transfer the energy to nearby units along the polymer chain. Cleavage of the main chain can then occur with carbonyl-group formation. The result is yellowing and embrittlement of the plastic.

Commercial antioxidants include organic compounds like hindered phenols and aromatic amines, which act as free-radical scavengers, as well as agents that serve to suppress homolytic breakdown, such as organic phosphites. Effects of UV radiation may be reduced by incorporating additives, such as carbon black widely used in tire manufacture, that screen wavelengths in the UV range from 300 to 400 nm. Transparent thermoplastics like polycarbonate can be protected against yellowing and embrittlement from UV light by incorporating compounds, such as benzo-

phenone derivatives, that have a high extinction coefficient in the UV range and are able to convert absorbed radiation into heat without chemical change.

6.1.3 Chemical and Hydrolytic Stability

Solvent Crazing and Cracking. Virtually all thermoplastics in contact with organic liquids and vapors will fail at lower levels of stress or strain even if the interacting chemical is not ordinarily considered to be a solvent for the polymer. The effect of these chemicals is believed to be due to localized plasticization that allows the development of crazes or cracks (see Section 4.4.1) at reduced stress.

As discussed in Chapter 4, crazes consist mostly of voids that can absorb low-molecular-weight stress-cracking or stress-crazing agents. Plasticization reduces the effective T_g in the region of the craze and, therefore, increases the localized mobility of polymer chains and promotes craze and crack development. It is, therefore, not unexpected that the critical strain, ϵ_c , for solvent craze initiation is often closely related to the solubility parameter (see Section 3.2.6) of the agent in relation to that of the polymer. Minimum critical strains will be observed for solvents with solubility parameters close to that of the polymer. Under these circumstances, cracks will rapidly develop. The time for initiation of a craze depends on the rate of absorption, with the longest times to reach critical stress or strain observed for fluids of the highest viscosity. Crazes developing in the presence of a solvent grow more rapidly and to larger size than those grown in a solvent-free environment.

The relationship between solubility parameter and ϵ_c is illustrated for two engineering thermoplastics in Figure 6-5. The two polymers are (bisphenol-A) polysulfone and poly(2,6-dimethyl-1,4-phenylene oxide), whose solubility parameters were reported in this study [1] to be 10.7 and 8.6 (cal/cm³)^{1/2}, respectively. As shown, the minimum in ϵ_c is observed in the case of organic liquids whose solubility parameters approximate those of the two polymers (i.e., cracking agents); however, significant reduction in ϵ_c is observed for organic liquids whose solubility parameters fall on either side of the minima. Hansen solubility parameters (see Section 3.2.6) arranged in a 3-D plot of δ_d , δ_p , and δ_h can also be used to correlate environmental stress cracking. In addition to solubility, the diffusivity of the cracking/crazing agent can be an important factor in determining the rate of uptake [2]. Diffusivity, in turn, strongly depends on the size and shape of the sorbed molecule as discussed in Section 12.1.2.

Hydrolysis. Many polymers are susceptible to degradation due to the effect of water, particularly under acidic conditions. These include some naturally occurring polymers, such as polysaccharides and proteins, as well as some synthetic polymers, principally condensation polymers such as polyesters and polyamides. In general, vinyl polymers are not susceptible to hydrolysis. Factors that influence the susceptibility of a given polymer to hydrolysis include water permeability and solubility and

are determined by the chemical structure of the polymer and its physical state (e.g., crystallinity, glass-transition temperature, etc.). Autocatalysis of hydrolysis is possible if acidic or basic groups are produced by the polymer breakdown as in the case of polyesters. The hydrolysis of a polyester results in the formation of chain segments terminated by hydroxyl and carboxylic groups as follows:

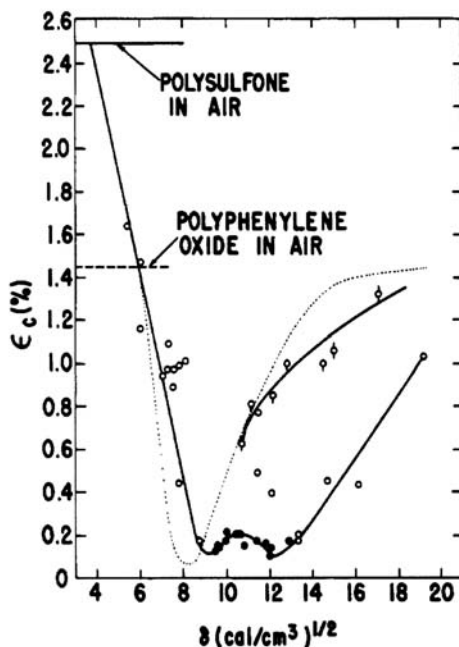
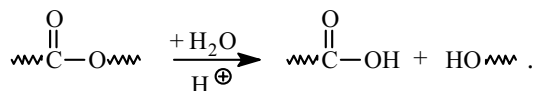
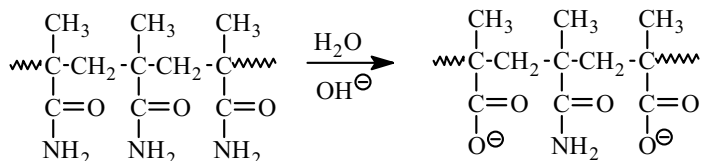


Figure 6-5 Plot of critical strain, ϵ_c , for crazing and cracking of polysulfone and poly(2,6-dimethyl-1,4-phenylene oxide) as a function of the solubility parameter, δ , of the cracking/crazing agent. Open circles represent crazing agents, while filled circles represent cracking agents. Open circles with single tabs are monohydric alcohols; those with double tabs are dihydric alcohols. Solid curves represent a fit of polysulfone data. The dotted curve fits data for poly(2,6-dimethyl-1,4-phenylene oxide) [3]. Reprinted with permission from R. P. Kambour, E. E. Romagosa, and C. L. Gruner, *Swelling, Crazing, and Cracking of an Aromatic Sulfone in Organic Media*. *Macromolecules*, 1972. **5**: p. 335. Copyright 1972 American Chemical Society.

Poly(vinyl esters) and poly(vinyl amides) are hydrolyzed to poly(vinyl carboxylic acids) under basic conditions. In these cases, hydrolysis will be less than complete because the presence of the negatively charged groups of the poly(carboxylic acid) retards the approach of the reagent (OH^-) to the adjacent ester or amide groups as illustrated for polymethacrylamide.



6.1.4 Effects of Radiation

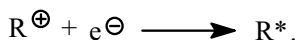
Many polymers are susceptible to degradation and crosslinking upon exposure to high-energy ionizing radiation (radiolysis) such as γ -radiation, electron beams, and X-rays. Sometimes, these effects can be used to an advantage. For example, integrated circuits can be prepared by microetching a polymeric coating of a silicon chip by electron-beam irradiation. The exposed silicon can then be doped. Radiation, particularly γ - and electron-beam radiation, can also be used to prepare graft copolymers. Radiation can also be used to polymerize a monomer in the solid state and to modify surfaces for adhesive bonding. In other cases, such as the use of plastics in space vehicles, nuclear power plants, and γ -sterilized medical disposables, polymers and composites selected for these applications must have good resistance to radiation. For example, it has been estimated that the total dosage of radiation for an object spending 30 years in space orbit is on the order of 10 Mrad. Sterilization of medical disposables (e.g., syringes, surgical gowns, and labware) by γ -irradiation has become increasingly important due to the limitations of other methods, such as the inefficiency of steam sterilization and the suspected carcinogenesis of ethylene oxide used in "cold" sterilization.

Some polymers such as polystyrene and polysulfone are very radiation resistant, but others such as polypropylene will readily degrade upon irradiation. In general, polymers with aromatic rings such as polystyrene, aromatic polyamides, and polysulfones are extremely radiation resistant, as are thermosets such as epoxies, phenolics, and urethanes. Fibers that have good radiation resistance include poly(ethylene terephthalate) and aromatic polyamides. Among elastomers, polyurethanes have particularly good radiation resistance.

The primary event in radiation damage is the ejection of a high-energy electron:



This primary electron can then ionize additional molecules with the release of additional electrons in a chain reaction. An electronically excited state will result when a positively charged molecule is recombined with an available electron:



An excited state will also result when the energy transfer associated with interaction of the radiation with the material is insufficient to cause ionization. Excited states in polymers can decay by chemical reactions involving heterolytic bond cleavage producing ionic species or by homolytic bond cleavage of the main chain or substituent groups resulting in the formation of radical species. Radical lifetimes can be hours and even weeks at room temperature. This provides ample opportunity for the radicals to initiate crosslinking or to react with oxygen in the atmosphere. Whether only chain scission or crosslinking will occur depends upon the chemical structure of the polymer chain. In general, polymers having quaternary carbon atoms, such as polyisobutylene or poly(methyl methacrylate), undergo chain scission in an inert atmosphere, while crosslinking is more probable for polymers without quaternary carbon atoms, such as polyethylene and polystyrene. In the presence of oxygen, which can react with the free radicals that are generated upon irradiation, chain scission becomes the predominant mechanism. Antioxidants, which act as radical scavengers, are effective stabilizers for radiation-oxidative degradation.

6.1.5 Mechanodegradation

Polymer degradation can also result from the application of stress such as high shear deformation of polymer solutions and melts. In the case of solids, stress-induced degradation may result from comminution (grinding, milling, or crushing), machining, stretching, fatigue, tearing, abrasion, or wear. Mechanodegradation is particularly severe for high-molecular-weight polymers that exist in a highly entangled state. The result of stress-induced degradation is the generation of macroradicals originating from random chain rupture. In a process called *mastication*, natural rubber is softened by passing between spiked rollers, which also serve to disperse filler and other additives such as accelerators, vulcanizers, and antioxidants.

6.2 Management of Plastics in the Environment

At present, plastics account for roughly a quarter of all solid waste by volume in U.S. landfills versus about 40% for paper. At the present rate, U.S. landfill capacity could be exhausted in a decade or two. To reduce the volume of plastic waste that

goes to landfills, there are three alternatives: recycling, incineration, and biodegradation.

6.2.1 Recycling

Recycling of commercial plastics is an important contemporary issue from several aspects, such as the need to reduce the volume of plastic waste that is sent to landfills and the need to conserve non-renewable petroleum resources. Plastics, as well as paper and cardboard, represent a major portion of most trash. Many commodity plastics are now being recycled in the United States and Europe. These include poly(ethylene terephthalate) (PET) used in beverage containers, as well as polyolefins (i.e., polyethylene and polypropylene), polystyrene, and poly(vinyl chloride) (PVC) used in packaging.

There are two contemporary approaches to recycling. The obvious route is simply the reprocessing of waste plastics, which may take other forms and find different applications. For example, PET waste has been used in the manufacture of insulation boards in competition to the use of expanded polystyrene. In this process, waste PET containers are washed, shredded, ground into 5-mm particles, and dried to remove water that would initiate hydrolysis during processing. The particles are then mixed with a nucleating agent and an additive to increase melt viscosity (to facilitate the foaming process) and processed in a standard foam slab extruder unit, where an expansion gas is injected into the molten recycled PET just before it emerges from the extruder. Insulation boards prepared from waste PET have some advantages over expanded polystyrene, including lower smoke emission during burning. In addition, the high T_m (260°C) of PET makes it suitable for use as a hot-melt adhesive in the preparation of laminates.

The other method of recycling, which may have more potential, is called *tertiary recycling*.^{*} In this approach, chemical or thermal treatment is used to transform waste plastics into monomers that can then be used in the polymerization of virgin resin. Condensation polymers such as polyesters, nylons, and polyurethanes can be depolymerized by chemical processes such as glycolysis, methanolysis, and hydrolysis. Addition polymers, such as polyolefins, acrylics, and fluoroplastics, require thermal or catalytic cracking. In the United States, tertiary recycling has focused primarily on PET. Waste polyester resin collected from bottles, fibers, and film is heated with methanol and a catalyst under pressure to cause the depolymerization of PET into ethylene glycol and dimethyl terephthalate (DMT). DMT can be used as a replacement for *p*-xylene in the synthesis of PET (for details of the com-

^{*} “Primary” recycling refers to regrind, while “secondary” recycling is the process of physical or thermal reprocessing into a secondary product.

mercial production of PET, see Chapter 9). In Europe, attention has been directed toward an acid-catalyzed process that can convert nylon-6 recovered from worn carpets into caprolactam at temperatures ranging from 536° to 752°F.

The recycling of tires is another major issue for which good solutions are critically needed. In the United States alone, over 234 million tires are discarded annually. The majority of this volume is eventually sent to landfills, but as the number of available landfill sites decreases, alternative solutions must be sought. One approach is to extend the service life of tires (i.e., source reduction). Recycling of tires includes use of retreads and grinding into crumb for use in pads, mats, carpet backing, moisture barriers, rubber-modified asphalt, and sport tracks. Whole scraped tires can be used in a variety of non-transportation applications, such as erosion control, playgrounds, and artificial reefs. Also, there has been interest in processes that can utilize the significant energy content of scrap tires (up to 15,000 Btu per lb) to generate electricity and produce synthesis gas (H_2 and CO) for ammonia and methanol production. In such operations, the tires are first mixed with waste oil, such as used motor oil, at 700°F in a liquefaction reactor. A rotating screw is used to remove steel belts from the melt. During liquefaction, high-molecular-weight chains, as well as disulfide bridges formed during the vulcanization process, are broken and a liquid hydrocarbon mixture is produced. The liquid mixture is mixed with oxygen (gasification reactor) at 2500°F and 500 to 900 psia to produce synthesis gas and leave an inert slag.

Although the volume of plastics that are recycled is rapidly increasing, it is still small in comparison to that of aluminum and paper. Part of the reason for this low recycling rate is that the total cost of producing recycled plastics, including collecting and recycling, is typically 20% higher than for the virgin resins. In addition, thermosets that account for a significant fraction of the total volume of plastics cannot be recycled; however, it has been possible in some cases to granulate glass-reinforced thermosets into 2- or 3-cm particles for use as fillers in other fiber-reinforced composites.

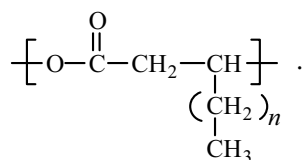
6.2.2 Incineration

Many plastics can be burned as cleanly as natural gas. Emissions include carbon dioxide, nitrogen oxides, and water vapor. As a pound of plastic produces 16,000 Btu when burned (more than twice the energy in a pound of coal), incineration can be used to generate energy, but not without serious attention to health issues. For example, some significant amounts of toxic compounds such as cadmium and other heavy metals will remain in the incinerator ash or can produce toxic emissions during combustion. Another problem is that the incineration of PVC, a significant component of many plastic wastes, may produce carcinogenic dioxins unless burned at very high temperatures.

6.2.3 Biodegradation

Biodegradable Polymers. Virtually no plastic is totally biodegradable. In fact, most polymers, including polyamides, polyfluorocarbons, polyethylene, polypropylene, and polycarbonate, are highly resistant to microbial attack. Among synthetic polymers, polyurethanes, especially polyether-polyurethanes, are susceptible to biological degradation. In general, naturally occurring polymers are more biodegradable than synthetic polymers. More specifically, polymers containing an ester functionality, particularly aliphatic polyesters, may be biodegradable. It is believed that biodegradation of these polymers proceeds by attack of the ester groups by nonspecific esterases produced by ground microflora combined with hydrolytic attack. Products of the degradation can be quickly metabolized by microorganisms. Complete biodegradation, or mineralization, occurs when all the polymer has been converted into gaseous products and/or biomass. Aerobic (in the presence of oxygen) and anaerobic (in the absence of oxygen) degradations yield similar degradation products; however, methane is produced in addition to water and carbon dioxide during anaerobic degradation.

One commercially important group of biodegradable polymers is the naturally occurring polyesters [4], the poly(β -hydroxyalkanoates), whose general structure is



Due to their biodegradability, polyhydroxyalkanoates have commercial potential as biomaterials as well as disposable plastic packaging materials. Originally identified in 1925, poly(β -hydroxybutyrate) (PHB), $n = 0$, is synthesized by the bacterium *Alcaligenes eutrophus*, which uses globules of PHB as an energy-storage medium analogous to fat in animals or starch in plants. The polymer is accumulated in discrete membrane-bound granules in the cytoplasm of the bacterium. PHB is a brittle polymer that is 100% isotactic and, therefore, highly crystalline (65% to 85%). The T_g of PHB is only 5° to 10°C while the crystalline-melting temperature is 175°C, which is close to its thermal decomposition temperature of 200°C. Poly(β -hydroxyalkanoates) with longer n -alkyl groups, such as poly(β -hydroxy-valerate) (PHV), $n = 1$, can be produced by *A. eutrophus* as well as another bacterium, *Pseudomonas oleovorans*, depending upon the type of carbon substrates available during the fermentation process.

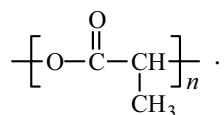
As shown by data given in Table 6-4, the principal difference in mechanical properties between PHB and the commodity thermoplastic, polypropylene, is the low extension-to-break of PHB. The toughness of PHB can be improved and its T_m

lowered with respect to its low thermal decomposition temperature by copolymerization with hydroxyvalerate. This copolymer is produced by *A. eutrophus* when grown in the presence of glucose and either propionic acid or valeric acid. Recently commercialized on a small scale, HB–HV copolymers are totally degradable to carbon dioxide and water by soil organisms in landfills or when composted with sewage. This plastic is expensive and may not be suitable for all applications, such as those that require long shelf life and for food-packaging applications where the propensity of PHB for bacterial growth is an obvious problem. One commercial use for PHB has been in the manufacture of shampoo bottles. HB–HV copolymers are suitable as matrices for controlled release of drugs due to their favorable biocompatibility and biodegradation properties. The relatively high cost of these biodegradable polymers may be reduced in the future by larger-scale production and advances in biotechnology. For example, the gene that synthesizes PHB has been recently identified, and it should, therefore, be possible to produce these polyesters in higher-productivity bacteria such as *E. coli* or even crop plants such as potatoes or turnips, which would then make PHB instead of starch.

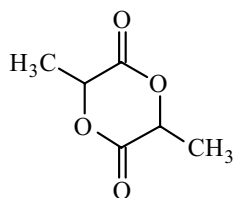
Table 6-4 Typical Properties of Polyhydroxybutyrate (PHB) Compared to Polypropylene (PP)

Property	PHB	PP
T_g (°C)	15	-10
T_m (°C)	175	176
Crystallinity (%)	80	70
Density (g cm ⁻³)	1.25	0.905
Flexural modulus (GPa)	4.0	1.7
Tensile strength (MPa)	40	38
Extension-to-break (%)	6	400
UV resistance	good	poor
Solvent resistance	poor	good

Another important biodegradable polyester is poly(lactic acid) (PLA):

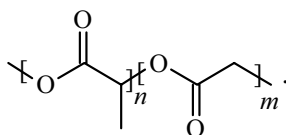


PLA can be polymerized from lactic acid or produced from corn- or rice-derived dextrose or from bacterially fermented starch obtained from food wastes such as potato peelings. The lactic acid is converted into lactide, a ring compound

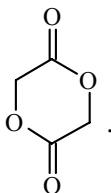


that is opened and polymerized to make PLA. Markets for PLA include fiber (apparel and carpeting) and packaging. PLA has good processability (e.g., can be thermoformed), high tensile strength and other desirable textile fiber properties, high odor barrier (important for food packaging), and resistance to grease, fats, and oils. PLA also has attractive deadfold characteristics suitable for confectionary wrapping. An advantage of PLA is that it degrades to lactic acid that can be metabolized in the body. For this reason, PLA finds important commercial use in a number of biomedical applications such as sutures, drug-delivery systems, and wound clips. It may also have some agricultural applications, such as timed-release coatings for fertilizers and pesticides and mulch films for moisture and heat retention and to reduce the weed population between rows of crops. In addition to the fact that PLA is derived from renewable agricultural resources, PLA can be composted and is, therefore, environmentally benign.

An important biodegradable copolymer is poly(lactide-*co*-glycolide) (PLGA):

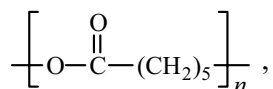


PLGA can be obtained from the copolymerization of lactide and glycolide:

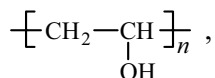


At compositions from about 25% to 75% GA, PLGA is amorphous and suitable for use in drug-delivery systems (see Section 12.2.1). PLGA has been considered as a substrate for incorporating hydroxyapatite (calcium phosphate hydroxide), the natural mineralization agent in bone, to develop artificial bone.

Other synthetic polymers that can be biodegraded (often with the help of specific microorganisms or addition of agents to promote chemical degradation) include polycaprolactone (PCL), a polyester,



poly(vinyl alcohol),



and cellulose and cellulose derivatives (see Section 8.2.2).

Biodegradation can also be used to dispose of unwanted monomers. For example, styrene is consumed by *P. aeruginosa* at the rate of 300 mg styrene/g bacteria/h [5]. Products of the biodegradation are biomass (the bacterial cellular matter formed during colony growth), carbon dioxide, and water.

Starch Additives. Another approach to biodegradability is to blend or graft a commercial thermoplastic with a naturally degradable material such as starch [6]. For example, starch can be blended with polyethylene during the blow molding of film for plastic bags. The expectation is that the starch will be eaten by soil microorganisms in a landfill and, therefore, the plastic matrix will be broken down into smaller particles. Starch obtained from corn is a glucose-based biopolymer consisting of linear amylose and highly branched, high-molecular-weight amylopectin (see Section 8.1.3). Advantages of starch are that it is inexpensive and totally biodegradable. Cornstarch granules retain about 6% to 20% moisture but are thermally stable up to 250°C in air. Extruded starch has a tensile strength of 20 to 30 MPa at 10% to 15% elongation. Acrylic and vinyl monomers, such as acrylic acid and styrene, can be grafted onto starch by ceric ion, Ce(IV), initiation.

One problem with this approach is that starch-filled plastics are weak and, therefore, more petroleum-based material may be required to provide adequate strength for such consumer products as grocery bags. Since disposable diapers and trash bags made from blended plastic may contain as little as 5% starch, the net result could be to introduce more plastic into the environment.

Biodegradation as a Practical Issue. Although biodegradation may have significant potential to alleviate some of the problems associated with plastic waste disposal, there remains some controversy as to whether any significant biodegradation will actually occur in modern, well-designed landfills. In order to store potentially hazardous materials, landfills are built to be free of moisture and airtight. Such anaerobic conditions, which serve to guard against the release of hazardous chemicals from landfills, also retard biodegradation. Another problem concerns the compatibility of the two major approaches to plastic waste management—biodegradation and recycling—since biodegradable polymers are not suitable candidates in the recycling of commingled plastics.

SUGGESTED READING

- Albertsson, A.-C., ed., *Degradable Aliphatic Polyesters*. Advances in Polymer Science, 2002. **157**: p. 1.
- Andrady, A. L., *Assessment of Environmental Biodegradation of Synthetic Polymers*. Journal of Macromolecular Science—Reviews in Macromolecular Chemistry and Physics, 1994. **C34**(1): p. 25.
- Garlotta, D., *A Literature Review of Poly(lactic acid)*. Journal of Polymers and the Environment, 2002. **9**: p. 63–84.
- Lenz, R. W., *Biodegradable Polymers*. Advances in Polymer Science, 1993. **107**: p. 1.
- Maharama, T., Y. S. Negi, and B. Mohanty, *Review Article: Recycling of Polystyrene*. Polymer—Plastics Technology and Engineering, 2007. **46**: p. 729.
- Nayak, P. L., *Biodegradable Polymers: Opportunities and Challenges*. Journal of Macromolecular Science—Reviews in Macromolecular Chemistry and Physics, 1999. **C39**(3): p. 481.
- Nelson, G. L., ed., *Fire and Polymers II: Materials and Tests for Hazard Prevention*. 1995, ACS Symposium Series, vol. 599: Washington, DC: American Chemical Society.
- Nguyen, T. Q., *Kinetics of Mechanochemical Degradation by Gel Permeation Chromatography*. Polymer Degradation and Stability, 1994. **46**: p. 99.
- Nir, M. M., J. Miltz, and A. Ram, *Update on Plastics and the Environment: Progress and Trends*. Plastics Engineering, March 1993, p. 73.
- Rader, C. P., S. D. Baldwin, D. D. Cornell, G.D. Sadler, and R. F. Stockel, eds., *Plastics, Rubber, and Paper Recycling*. 1995, ACS Symposium Series, vol. 609: Washington, DC: American Chemical Society.
- Rånby, B., *Basic Reactions in the Photodegradation of Some Important Polymers*. Journal of Macromolecular Science—Pure and Applied Chemistry, 1993. **A30**(9&10): p. 583.
- Sharma, R. R., and A. R. Ray, *Polyhydroxybutyrate, Its Copolymers and Blends*. Journal of Macromolecular Science—Reviews in Macromolecular Chemistry and Physics, 1995. **C35**(2): p. 327.
- Stein, R. S., *Polymer Recycling: Thermodynamics and Economics*. Macromolecular Symposium, 1998. **135**: p. 295.
- Swanson, C. L., R. L. Shogren, G. F. Fanta, and S. H. Imam, *Starch—Plastic Materials—Preparation, Physical Properties, and Biodegradability (A Review of Recent USDA Research)*. Journal of Environmental Polymer Degradation, 1993. **1**(2): p. 155.

REFERENCES

1. Kambour, R. P., E. E. Romagosa, and C. L. Gruner, *Swelling, Crazing, and Cracking of an Aromatic Copolyether-Sulfone in Organic Media*. Macromolecules, 1972. **5**: p. 335–340.

2. Hansen, C. M., and L. Just, *Prediction of Environmental Stress Cracking in Plastics with Hansen Solubility Parameters*. Industrial and Engineering Chemistry and Research, 2001. **40**: p. 21–25.
3. Bernier, G. A., and R. P. Kambour, *The Role of Organic Agents in the Stress Cracking and Cracking of Poly(2,6-dimethyl-1,4-phenylene oxide)*. Macromolecules, 1968. **1**: p. 393–400.
4. Lenz, R. W., Y. B. Kim, and R. C. Fuller, *Polyesters Produced by Microorganisms*. Journal of Bioactive and Compatible Polymers, 1991. **6**: p. 382–392.
5. Aalam, S., A. Paus, and J.-M. Lebeault, *High Efficiency Styrene Biodegradation in a Biphasic Organic/Water Continuous Reactor*. Applied Microbiology and Biotechnology, 1993. **39**: p. 696–699.
6. Inoue, Y., and N. Yoshie, *Structure and Physical Properties of Bacterially Synthesized Polyesters*. Progress in Polymer Science, 1992. **17**: p. 571–619.