Chapter

# Biological Degradation of Polymers in the Environment

*John A. Glaser*

## Abstract

Polymers present to modern society remarkable performance characteristics desired by a wide range of consumers but the fate of polymers in the environment has become a massive management problem. Polymer applications offer molecular structures attractive to product engineers desirous of prolonged lifetime properties. These characteristics also figure prominently in the environmental lifetimes of polymers or plastics. Recently, reports of microbial degradation of polymeric materials offer new emerging technological opportunities to modify the enormous pollution threat incurred through use of polymers/plastics. A significant literature exists from which developmental directions for possible biological technologies can be discerned. Each report of microbial mediated degradation of polymers must be characterized in detail to provide the database from which a new technology developed. Part of the development must address the kinetics of the degradation process and find new approaches to enhance the rate of degradation. The understanding of the interaction of biotic and abiotic degradation is implicit to the technology development effort.

**Keywords:** polymers, plastics, degradation, microbial degradation, biofilms, extent of degradation

## 1. Introduction

In 1869, the first synthetic polymer was invented in response to a commercial $10,000 prize to provide a suitable replacement to ivory. A continuous string of discoveries and inventions contributed new polymers to meet the various requirements of society. Polymers are constructed of long chains of atoms, organized in repeating components or units often exceeding those found in nature. Plastic can refer to matter that is pliable and easily shaped. Recent usage finds it to be a name for materials called polymers. High molecular weight organic polymers derived from various hydrocarbon and petroleum materials are now referred to as plastics [1].

Synthetic polymers are constructed of long chains of smaller molecules connected by strong chemical bonds and arranged in repeating units which provide desirable properties. The chain length of the polymers and patterns of polymeric assembly provide properties such as strength, flexibility, and a lightweight feature that identify them as plastics. The properties have demonstrated the general utility of polymers and their manipulation for construction of a multitude of widely useful items leading to a world saturation and recognition of their unattractive properties too. A major trend of ever increasing consumption of plastics has been seen in the

| Polymer | Abbreviation | Density (23/4°C) | Crystallinity (%) | Lifespan (year) |
|---|---|---|---|---|
| Polyethylene | PE | 0.91–0.925 | 50 | 10–600 |
| Polypropylene | PP | 0.94–0.97 | 50 | 10–600 |
| Polystyrene | PS | 0.902–0.909 | 0 | 50–80 |
| Polyethylene glycol terephthalate | PET | 1.03–1.09 | 0–50 | 450 |
| Polyvinyl chloride | PVC | 1.35–1.45 | 0 | 50–100+ |

**Table 1.**
*Selected features of major commercial thermoplastic polymers [7].*

areas of industrial and domestic applications. Much of this polymer production is composed of plastic materials that are generally non-biodegradable. This widespread use of plastics raises a significant threat to the environment due to the lack of proper waste management and a until recently cavalier community behavior to maintain proper control of this waste stream. Response to these conditions has elicited an effort to devise innovative strategies for plastic waste management, invention of biodegradable polymers, and education to promote proper disposal. Technologies available for current polymer degradation strategies are chemical, thermal, photo, and biological techniques [2–6]. The physical properties displayed in **Table 1** show little differences in density but remarkable differences in crystallinity and lifespan. Crystallinity has been shown to play a very directing role in certain biodegradation processes on select polymers.

Polymers are generally carbon-based commercialized polymeric materials that have been found to have desirable physical and chemical properties in a wide range of applications. A recent assessment attests to the broad range of commercial materials that entered to global economy since 1950 as plastics. The mass production of virgin polymers has been assessed to be 8300 million metric tons for the period of 1950 through 2015 [8]. Globally consumed at a pace of some 311 million tons per year with 90% having a petroleum origin, plastic materials have become a major worldwide solid waste problem. Plastic composition of solid waste has increased for less than 1% in 1960 to greater than 10% in 2005 which was attributed largely to packaging. Packaging plastics are recycled in remarkably low quantities. Should current production and waste management trends continue, landfill plastic waste and that in the natural environment could exceed 12,000 Mt of plastic waste by 2050 [9].

## 2. Polymer structures and features

A polymer is easily recognized as a valuable chemical made of many repeating units [10]. The basic repeating unit of a polymer is referred to as the "-mer" with "poly-mer" denoting a chemical composed of many repeating units. Polymers can be chemically synthesized in a variety of ways depending on the chemical characteristics of the monomers thus forming a desired product. Nature affords many examples of polymers which can be used directly or transformed to form materials required by society serving specific needs. The polymers of concern are generally composed of carbon and hydrogen with extension to oxygen, nitrogen and chlorine functionalities (see **Figure 1** for examples). Chemical resistance, thermal and electrical insulation, strong and light-weight, and myriad applications where no alternative exists are polymer characteristics that continue to make polymers attractive. Significant polymer application can be found in the automotive, building and construction, and packaging industries [12].

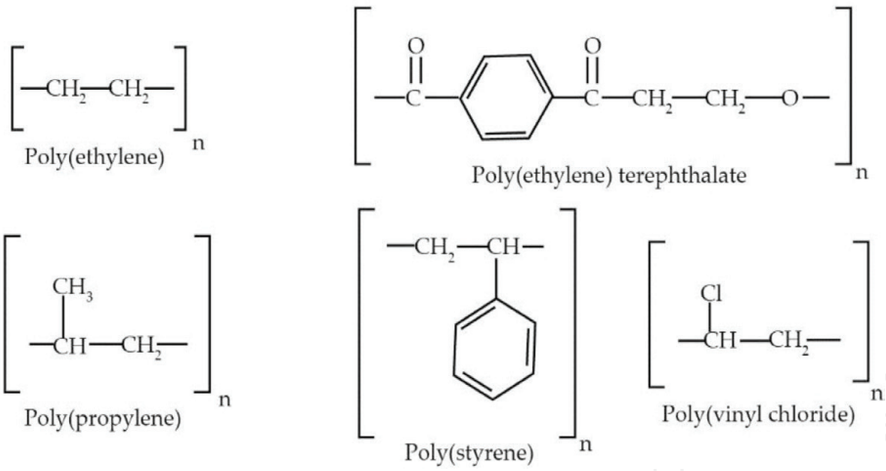


**Figure 1.**
*Structures of major commercial thermoplastic polymers [11].*

The environmental behavior of polymers can be only discerned through an understanding of the interaction between polymers and environment under ambient conditions. This interaction can be observed from surface properties changes that lead to new chemical functionality formation in the polymer matrix. New functional groups contribute to continued deterioration of the polymeric structure in conditions such as weathering. Discoloration and mechanical stiffness of the polymeric mass are often hallmarks of the degradative cycle in which heat, mechanical energy, radiation, and ozone are contributing factors [13].

Polyolefins (PO) are the front-runners of the global industrial polymer market where a broad range of commercial products contribute to our daily lives in the form o packaging, bottles, automobile parts and piping. The PO class family is comprised of saturated hydrocarbon polymers such as high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), propylene and higher terminal olefins or monomer combinations as copolymers. The sources of these polymers are low-cost petrochemicals and natural gas with monomers production dependent on cracking or refining of petroleum. This class of polymers has a unique advantage derived from their basic composition of carbon and hydrogen in contrast to other available polymers such as polyurethanes, poly(vinyl chloride) and polyamides [14].

The copolymers of ethylene and propylene are produced in quantities that exceed 40% of plastics produced per annum with no production leveling in sight. This continuous increase suggests that as material use broadens yearly, the amount of waste will also increase and present waste disposal problems. Polyolefin biological and chemical inertness continues to be recognized as an advantage. However, this remarkable stability found at many environmental conditions and the degradation resistance leads to environmental accumulation and an obvious increase to visible pollution and ancillary contributing problems. Desired environmental properties impact the polyolefin market on the production side as well as product recyclability [15].

## 3. Biological degradation

Biodegradation utilizes the functions of microbial species to convert organic substrates (polymers) to small molecular weight fragments that can be further degraded to carbon dioxide and water [16–21]. The physical and chemical properties of a polymer are important to biodegradation. Biodegradation efficiency

achieved by the microorganisms is directly related to the key properties such as molecular weight and crystallinity of the polymers. Enzymes engaged in polymer degradation initially are outside the cell and are referred to as exo-enzymes having a wide reactivity ranging from oxidative to hydrolytic functionality. Their action on the polymer can be generally described as depolymerization. The exo-enzymes generally degrade complex polymer structure to smaller, simple units that can take in the microbial cell to complete the process of degradation.

### 3.1 Requirements to assay polymer biodegradation

Polymer degradation proceeds to form new products during the degradation path leading to mineralization which results in the formation of process end-products such as, e.g., $CO_2$, $H_2O$ or $CH_4$ [22]. Oxygen is the required terminal electron acceptor for the aerobic degradation process. Aerobic conditions lead to the formation of $CO_2$ and $H_2O$ in addition to the cellular biomass of microorganisms during the degradation of the plastic forms. Where sulfidogenic conditions are found, polymer biodegradation leads to the formation of $CO_2$ and $H_2O$. Polymer degradation accomplished under anaerobic conditions produces organic acids, $H_2O$, $CO_2$, and $CH_4$. Contrasting aerobic degradation with anaerobic conditions, the aerobic process is found to be more efficient. When considering energy production the anaerobic process produces less energy due to the absence of $O_2$, serving the electron acceptor which is more efficient in comparison to $CO_2$ and $SO_4^{-2}$ [23].

As solid materials, plastics encounter the effects of biodegradation at the exposed surface. In the unweathered polymeric structure, the surface is affected by biodegradation whereas the inner part is generally unavailable to the effects of biodegradation. Weathering may mechanically affect the structural integrity of the plastic to permit intrusion of bacteria or fungal hyphae to initiate biodegradation at inner loci of the plastic. The rate of biodegradation is functionally dependent on the surface area of the plastic. As the microbial-colonized surface area increases, a faster biodegradation rate will be observed assuming all other environmental conditions to be equal [24].

Microorganisms can break organic chemicals into simpler chemical forms through biochemical transformation. Polymer biodegradation is a process in which any change in the polymer structure occurs as a result of polymer properties alteration resulting from the transformative action of microbial enzymes, molecular weight reduction, and changes to mechanical strength and surface properties attributable to microbial action. The biodegradation reaction for a carbon-based polymer under aerobic conditions can be formulated as follows:

$$C_{Polymer} + O_2 + Biomass \longrightarrow CO_2 + H_2O + C_{biomass} \quad (1)$$

Assimilation of the carbon comprising the polymer ($C_{polymer}$) by microorganisms results in conversion to $CO_2$ and $H_2O$ with production of more microbial biomass ($C_{biomass}$). In turn, $C_{biomass}$ is mineralized across time by the microbial community or held in reserve as storage polymers [25].

The following set of equations is a more complete description of the aerobic plastic biodegradation process:

$$C_{Polymer} + O_2 \longrightarrow Oligomers + CO_2 + H_2O + C_{biomass} \quad (2)$$
$$Oligomers \longrightarrow C_{biomass} + H_2O + CO_2$$

where $C_{polymer}$ and newly formed oligomers are converted into $C_{biomass}$ but $C_{biomass}$ converts to $CO_2$ under a different kinetics scheme. The conversion to $CO_2$ is referred to as microbial mineralization. Each oligomeric fragment is expected to proceed through of sequential steps in which the chemical and physical properties are altered leading to the desired benign result. A technology for monitoring aerobic biodegradation has been developed and optimized for small organic pollutants using oxygen respirometry where the pollutant degrades at a sufficiently rapid rate for respirometry to provide expected rates of biodegradation. When polymers are considered, a variety of analytical approaches relating to physical and chemical changes are employed such as differential scanning calorimetry, scanning electron microscopy, thermal gravimetric analysis, Fourier transform infrared spectrometry, gas chromatograph-mass spectrometry, and atomic force microscopy [26].

Since most polymer disposal occurs in our oxygen atmosphere, it is important to recognize that aerobic biodegradation will be our focus but environmental anaerobic conditions do exist that may be useful to polymer degradation. The distinction between aerobic and anaerobic degradation is quite important since it has been observed that anaerobic conditions support slower biodegradation kinetics. Anaerobic biodegradation can occur in the environment in a variety of situations. Burial of polymeric materials initiates a complex series of chemical and biological reactions. Oxygen entrained in the buried materials is initially depleted by aerobic bacteria. The following oxygen depleted conditions provide conditions for the initiation of anaerobic biodegradation. The buried strata are generally covered by 3-m-thick layers which prevent oxygen replenishment. The alternate electron acceptors such as nitrate, sulfate, or methanogenic conditions enable the initiation of anaerobic biodegradation. Any introduction of oxygen will halt an established anaerobic degradation process.

### 3.2 Formulation of newer biodegradation schema

This formulation for the aerobic biodegradation of polymers can be improved due to the complexity of the processes involved in polymer biodegradation [27]. Biodegradation, defined as a decomposition of substances by the action of microorganisms, leading to mineralization and the formation of new biomass is not conveniently summarized. A new analysis is necessary to assist the formulation of comparative protocols to estimate biodegradability. In this context, polymer biodegradation is defined as a complex process composed of the stages of biodeterioration, biofragmentation, and assimilation [28].

The biological activity inferred in the term biodegradation is predominantly composed of, biological effects but within nature biotic and abiotic features act synergistically in the organic matter degradation process. Degradation modifying mechanical, physical and chemical properties of a material is generally referred to as deterioration. Abiotic and biotic effects combine to exert changes to these properties. This biological action occurs from the growth of microorganisms on the polymer surface or inside polymer material. Mechanical, chemical, and enzymatic means are exerted by microorganisms, thereby modifying the gross polymer material properties. Environmental conditions such as atmospheric pollutants, humidity, and weather strongly contribute to the overall process. The adsorbed pollutants can assist the material colonization by microbial species. A diverse collection of bacteria, protozoa, algae, and fungi are expected participants involved in biodeterioration. The development of different biota can increase biodeterioration by facilitating the production of simple molecules.

Fragmentation is a material breaking phenomenon required to meet the constraints for the subsequent event called assimilation. Polymeric material has a high

molecular weight which is restricted by its size in its transit across the cell wall or cytoplasmic membrane. Reduction of polymeric molecule size is indispensable to this process. Changes to molecular size can occur through the involvement of abiotic and biotic processes which are expected to reduce molecular weight and size. The utility of enzymes derived from the microbial biomass could provide the required molecular weight reductions. Mixtures of oligomers and/or monomers are the expected products of the biological fragmentation.

Assimilation describes the integration of atoms from fragments of polymeric materials inside microbial cells. The microorganisms benefit from the input of energy, electrons and elements (i.e., carbon, nitrogen, oxygen, phosphorus, sulfur and so forth) required for the cell growth. Assimilated substrates are expected to be derived from biodeterioration and biofragmentation effects. Non-assimilated materials, impermeable to cellular membranes, are subject to biotransformation reactions yielding products that may be assimilated. Molecules transported across the cell membrane can be oxidized through catabolic pathways for energy storage and structural cell elements. Assimilation supports microbial growth and reproduction as nutrient substrates (e.g., polymeric materials) are consumed from the environment.

### 3.3 Factors affecting biodegradability

The polymer substrate properties are highly important to any colonization of the surface by either bacteria or fungi [29]. The topology of the surface may also be important to the colonization process. The polymer properties of molecular weight, shape, size and additives are each unique features which can limit biodegradability. The molecular weight of a polymer can be very limiting since the microbial colonization depends on surface features that enable the microorganisms to establish a locus from which to expand growth. Polymer crystallinity can play a strong role since it has been observed that microbial attachment to the polymer surface occurs and utilizes polymer material in amorphous sections of the polymer surface. Polymer additives are generally low molecular weight organic chemicals that can provide a starting point for microbial colonization due to their ease of biodegradation (**Figure 2**).

Weather is responsible for the deterioration of most exposed materials. Abiotic contributors to these conditions are moisture in its variety of forms, non-ionizing radiation, and atmospheric temperature. When combined with wind effects, pollution, and atmospheric gases, the overall process of deterioration can be quite formable. The ultraviolet (UV) component of the solar spectrum contributes ionizing radiation which plays a significant role in initiating weathering effects. Visible and near-infrared radiation can also contribute to the weathering process. Other factors

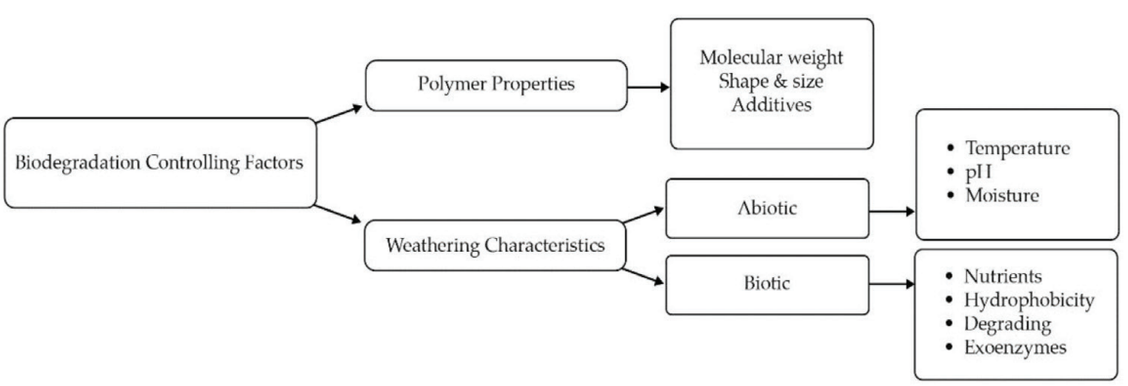


**Figure 2.**
*Factors controlling polymer biodegradation [30].*

couple with solar radiation synergistically to significantly influence the weathering processes. The quality and quantity of solar radiation, geographic location changes, time of day and year, and climatological conditions contribute to the overall effects. Effects of ozone and atmospheric pollutants are also important since each can interact with atmospheric radiation to result in mechanical stress such as stiffening and cracking. Moisture when combined with temperature effects can assist microbial colonization. The biotic contributors can strongly assist the colonization by providing the necessary nutrients for microbial growth. Hydrophilic surfaces may provide a more suitable place for colonization to ensue. Readily available exoenzymes from the colonized area can initiate the degradation process.

### 3.4 Biofilms

Communities of microorganisms attached to a surface are referred to as biofilms [31]. The microorganisms forming a biofilm undergo remarkable changes during the transition from planktonic (free-swimming) biota to components of a complex, surface-attached community (**Figure 3**). The process is quite simple with planktonic microorganism encountering a surface where some adsorb followed by surface release to final attachment by the secretion of exopolysaccharides which act as an adhesive for the growing biofilm [33]. New phenotypic characteristics are exhibited by the bacteria of a biofilm in response to environmental signals. Initial cell-polymer surface interactions, biofilm maturation, and the return to planktonic mode of growth have regulatory circuits and genetic elements controlling these diverse functions. Studies have been conducted to explore the genetic basis of biofilm development with the development of new insights. Compositionally, these films have been found to be a single microbial species or multiple microbial species with attachment to a range of biotic and abiotic surfaces [34, 35]. Mixed-species biofilms are generally encountered in most environments. Under the proper nutrient and carbon substrate supply, biofilms can grow to massive sizes. With growth, the biofilm can achieve large film structures that may be sensitive to physical forces such as agitation. Under such energy regimes, the biofilm can detach. An example of biofilm attachment and utility can be found in the waste water treatment sector where large polypropylene disks are rotated through industrial or agriculture waste water and then exposed to the atmosphere to treat pollutants through the intermediacy of cultured biofilms attached to the rotating polypropylene disk.

Biofilm formation and activity to polymer biodegradation are complex and dynamic [36]. The physical attachment offers a unique scenario for the attached microorganism and its participation in the biodegradation. After attachment as a biofilm component, individual microorganisms can excrete exoenzymes which can provide a range of functions. Due to the mixed-species composition found in most

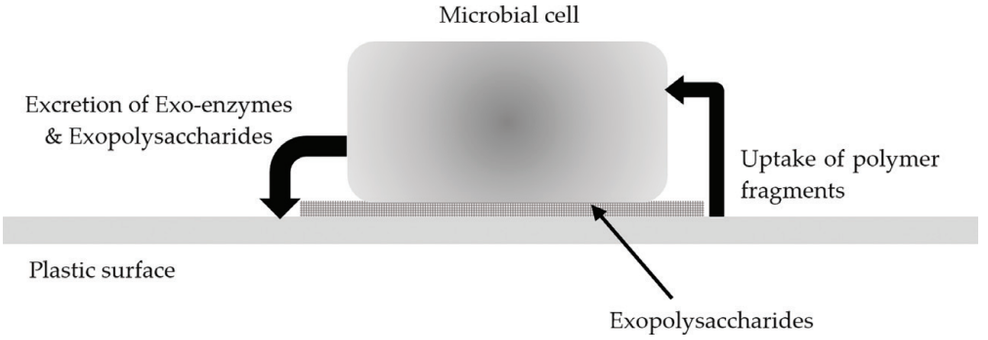


**Figure 3.**
*Microbial attachment processes to a polymer surface [32].*

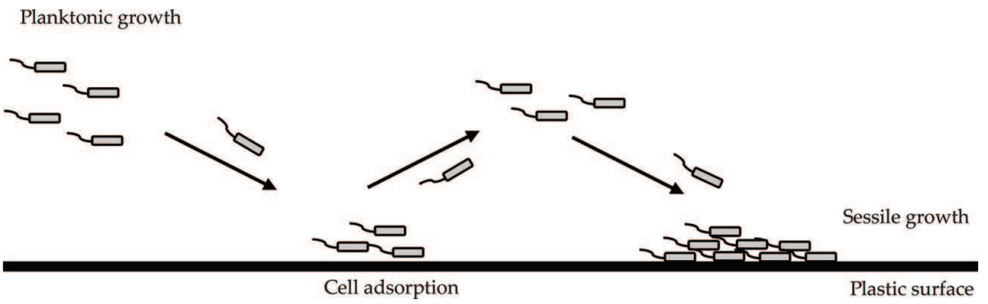


**Figure 4.**
*Biofilm formation and processes [34].*

environments, a broad spectrum of enzymatic activity is generally possible with wide functionalities. Biofilm formation can be assisted by the presence of pollutant chemical available at the polymer surface. The converse is also possible where surfaces contaminated with certain chemicals can prohibit biofilm formation. Biofilms continue to grow with the input of fresh nutrients, but when nutrients are deprived, the films will detach from the surface and return to a planktonic mode of growth. Overall hydrophobicity of the polymer surface and the surface charge of a bacterium may provide a reasonable prediction of surfaces to which a microorganism might colonize [37]. These initial cell-surface and cell-cell interactions are very useful to biofilm formation but incomplete (**Figure 4**). Microbial surfaces are heterogeneous, and can change widely in response to environmental changes. Five stages of biofilm development: have been identified as (1) initial attachment, (2) irreversible attachment, (3) maturation I, (4) maturation II, and (5) dispersion. Further research is required to provide the understanding of microbial components involved in biofilm development and regulation of their production to assemble to various facets of this complex microbial phenomenon [38].

The activities envisioned in this scenario (depicted in **Figure 4**) are the reversible adsorption of bacteria occurring at the later time scale, irreversible attachment of bacteria occurring at the second-minute time scale, growth and division of bacteria in hours-days, exopolymer production and biofilm formation in hours-days, and attachment and other organisms to biofilm in days-months.

### 3.5 Standardized testing methods

The evaluation of the extent of polymer biodegradation is made difficult by the dependence on polymer surface and the departure of degradation kinetics from the techniques available for small pollutant molecule techniques [39]. For applications for polymer biodegradation a variety of techniques have been applied. Visual observations, weight loss measurements, molar mass and mechanical properties, carbon dioxide evolution and/or oxygen consumption, radiolabeling, clear-zone formation, enzymatic degradation, and compost test under controlled conditions have been cited for their utility [27]. The testing regime must be explicitly described within a protocol of steps that can be collected for various polymers and compared on an equal basis. National and international efforts have developed such protocols to enable the desired comparisons using rigorous data collecting techniques and interpretation [40].

## 4. Environmental biodegradation of polymers

The conventional polymers such as (PE), (PP), (PS), (PUR), and (PET) are recognized for their persistence in the environment [41]. Each of these polymers is subject

to very slow fragmentation to form small particles in a process expected to require centuries of exposure to photo-, physical, and biological degradation processes. Until recently, the commercial polymers were not expected to biodegrade. The current perspective supports polymer biodegradation with hopeful expectation that these newly encountered biodegradation processes can be transformed into technologies capable of providing major assistance to the ongoing task of waste polymer management.

### 4.1 Polyolefins

The polyolefins such as polyethylene (PE) have been recognized as a polymer remarkably resistant to degradation [42]. Products made with PE are very diverse and a testament to its chemical and biological inertness. The biodegradation of the polyolefins is complex and incompletely understood. Pure strains elicited from the environment have been used to investigate metabolic pathways or to gain a better understanding of the effect that environmental conditions have on polyolefin degradation. This strategy ignores the importance of different microbial species that could participate in a cooperative process. Treatment of the complex environments associated with polymeric solid waste could be difficult with information based on pure strain analysis. Mixed and complex microbial communities have been used and encountered in different bioremediation environments [43].

A variety of common PE types, low-density PE (LDPE), high-density PE (HDPE), linear low-density PE (LLDPE) and cross-linked PE (XLPE), differ in their density, degree of branching and availability of functional groups at the surface. The type of polymer used as the substrate can strongly influence the microbial community structure colonizing PE surface. A significant number of microbial strains have been identified for the deterioration caused by their interaction with the polymer surface [44]. Microorganisms have been categorized for their involvement in PE colonization and biodegradation or the combination. Some research studies did not conduct all the tests required to verify PE biodegradation. A more inclusive approach to assessing community composition, including the non-culturable fraction of microorganisms invisible by traditional microbiology methods is required in future assessments. The diversity of microorganisms capable of degrading PE extends beyond 17 genera of bacteria and nine genera of fungi [45]. These numbers are expected to increase with the use of more sensitive isolation and characterization techniques using rDNA sequencing. Polymer additives can affect the kinds of microorganisms colonizing the surfaces of these polymers. The ability of microorganisms to colonize the PE surfaces exhibits a variety of effects on polymer properties. Seven different characteristics have been identified and are used to monitor the extent of polymer surface change resulting from biodegradation of the polymer. The characteristics are hydrophobicity/hydrophilicity, crystallinity, surface topography, functional groups on the surface, mechanical properties, and molecular weight distribution. The use of surfactants has become important to PE biodegradation. Complete solubilization of PE in water by a *Pseudomonas fluorescens* treated for a month followed by biosurfactant treatment for a subsequent month in the second month and finally a 10% sodium dodecyl sulfate treatment at 60°C for a third month led to complete polymer degradation. A combination of *P. fluorescens*, surfactant and biosurfactant treatments as a single treatment significantly exhibited polymer oxidation and biodegradation [46]. The metabolically diverse genus *Pseudomonas* has been investigated for its capabilities to degrade and metabolize synthetic plastics. *Pseudomonas* species found in environmental matrices have been identified to degrade a variety of polymers including PE, and PP [47]. The unique capabilities of *Pseudomonas* species related to degradation and metabolism of synthetic polymers requires a focus on: the interactions controlling cell surface

attachment of biofilms to polymer surfaces, extracellular polymer oxidation and/or hydrolytic enzyme activity, metabolic pathways mediating polymer uptake and degradation of polymer fragments within the microbial cell through catabolism, and the importance of development of the implementation of enhancing factors such as pretreatments, microbial consortia and nutrient availability while minimizing the effects of constraining factors such as alternative carbon sources and inhibitory by-products. In an ancillary study, thermophilic consortia of *Brevibacillus* sps. and *Aneurinibacillus* sp. from waste management landfills and sewage treatment plants exhibited enhanced PE and PP degradation [48].

The larval stage of two waxworm species, *Galleria mellonella* and *Plodia interpunctella*, has been observed to degrade LDPE without pretreatment [49, 50]. The worms could macerate PE as thin film shopping bags and metabolize the film to ethylene glycol which in turn biodegrades rapidly. The remarkable ability to digest a polymer considered non-edible may parallel the worm's ability utilize beeswax as a food source. From the guts of *Plodia interpunctella* waxworms two strains of bacteria, *Enterobacter asburiae* YP1 and *Bacillus* sp. YP1, were isolated and found to degrade PE in laboratory conditions. The two strains of bacteria were shown to reduce the polymer film hydrophobicity during a 28-day incubation. Changes to the film surface as cavities and pits were observed using scanning electron microscopy and atomic-force microscopy. Simple contact of ~100 *Galleria mellonella* worms with a commercial PE shopping bag for 12 hours resulted in a mass loss of 92 mg. The waxworm research has been scrutinized and found to be lacking the necessary information to support the claims of the original *Galleria mellonella* report [51].

Polypropylene (PP) is very similar to PE, in solution behavior and electrical properties. Mechanical properties and thermal resistance are improved with the addition of the methyl group but chemical resistance decreases. There are three forms of propylene selectively formed from the monomer isotactic, syndiotactic, and atactic due to the different geometric relationships achievable through polymerization technology. PP properties are strongly directed by tacticity or the methyl group orientation as related the methyl groups in neighboring monomer units. Isotactic PP has a greater degree of crystallinity than atactic and syndiotactic PP and therefore more difficult to biodegrade. The high molar mass of PP prohibits permeation through the microbial cell membrane which thwarts metabolism by living organisms. It is generally recognized that abiotic degradation provides a foothold for microorganisms to form a biofilm. With partial destruction of the polymer surface by abiotic effects the microbes can then start breaking the damaged polymer chains [52].

### 4.2 Polystyrene

PS is a sturdy thermoplastic commonly used in short-lifetime items that contribute broadly to the mass of poorly controlled polymers [53]. Various forms of PS such as general purpose (GPPS)/oriented polystyrene (OPS), polystyrene foam, and expanded polystyrene (EPS) foam are available for different commercial leading to a broad solid waste composition. PS has been thought to be non-biodegradable. The rate of biodegradation encountered in the environment is very slow leading to prolonged persistence as solid waste. In the past, PS was recycled through mechanical, chemical, and thermal technologies yielding gaseous and liquid daughter products [54]. A rather large collection of studies has shown that PS is subject to biodegradation but at a very slow rate in the environment. A sheet of PS buried for 32 years. in soil showed no indication of biotic or abiotic degradation [55]. The hydrophobicity of the polymer surface, a function of molecular structure and composition, detracts from the effectiveness of microbial attachment [56, 57]. The general lack of water solubility of PS prohibits the transport into microbial cells for metabolism.

A narrow range of microorganisms have been elicited for the environment and found to degrade PS [53]. *Bacillus* and *Pseudomonas* strains isolated from soil samples have been shown to degrade brominated high impact PS. The activity was seen in weight loss and surface changes to the PS film. Soil invertebrates such as the larvae of the mealworm (*Tenebrio molitor* Linnaeus) have been shown to chew and eat Styrofoam [57]. Samples of the larvae were fed Styrofoam as the sole diet for 30 days and compared with worms fed a conventional diet. The worms feeding Styrofoam survived for 1 month after which they stopped eating as they entered the pupae stage and emerged as adults after a subsequent 2 weeks. It appears that Styrofoam feeding did not lead to any lethality for the mealworms. The ingested PS mass was efficiently depolymerized within the larval gut during the retention time of 24 hours and converted to $CO_2$ [51]. This remarkable behavior by the mealworm can be considered the action of an efficient bioreactor. The mealworm can provide all the necessary components for PS treatment starting with chewing, ingesting, mixing, reacting with gut contents, and microbial degradation by gut microbial consortia. A PS-degrading bacterial strain *Exiguobacterium* sp. strain YT2 was isolated from the gut of mealworms and found to degrade PS films outside the mealworm gut. Superworms (*Zophobas morio*) were found to exhibit similar activity toward Styrofoam. Brominated high impact polystyrene (blend of polystyrene and polybutadiene) has been found to be degraded by *Pseudomonas* and *Bacillus* strains [58]. In a complementary study, four non-pathogenic cultures (*Enterobacter* sp., *Citrobacter sedlakii*, *Alcaligenes* sp. and *Brevundimonas diminuta*) were isolated from partially degraded polymer samples from a rural market setting and each were found to degrade high impact polystyrene [59].

### 4.3 Polyvinyl chloride

PVC is manufactured in two forms rigid and flexible. The rigid form can be found in the construction industry as pipe or in structural applications. The soft and flexible form can be made through the incorporation of plasticizers such as phthalates. Credit cards, bottles, and non-food packaging are notable products with a PVC composition. PVC has been known from its inception as a polymer with remarkable resistance to degradation [60]. Thermal and photodegradation processes are widely recognized for their role in the weathering processes found with PVC [61, 62]. The recalcitrant feature of polyvinyl chloride resistance to biodegradation becomes a matter of environmental concern across the all processes extending from manufacturing to waste disposal. Few reports are available relating the extent of PVC biodegradation. Early studies investigated the biodegradation of low-molecular weight PVC by white rot fungi [63]. Plasticized PVC was found to be degraded by fungi such as *As. fumigatus*, *Phanerochaete chrysosporium*, *Lentinus tigrinus*, *As. niger*, and *Aspergillus sydowii* [64].

Modifying the PVC film composition with adjuvants such as cellulose and starch provided a substrate that fungi could also degrade [65]. Several investigations of soil bacteria for the ability to degrade PVC from enrichment cultures were conducted on different locations [66]. Mixed cultures containing bacteria and fungi were isolated and found to grow on plasticized PVC [67]. Significant differences were observed for the colonization by the various components of the mixed isolates during very long exposure times [68]. Significant drift in isolate activity was averted through the use of talc. Consortia composed of a combination of different bacterial strains of *Pseudomonas otitidis*, *Bacillus cereus*, and *Acanthopleurobacter pedis* have the ability to degrade PVC in the environment [64]. These results offer the opportunity to optimization conditions for consortia growth in PVC and use as a treatment technology to degrade large collections of PVC. PVC film blends were shown to degrade by partnering biodegradable polymers with PVC [69].

### 4.4 Polyurethane

PUR encompass a broad field of polymer synthesis where a di- or polyisocyanate is chemically linked through carbamate (urethane) formation. These thermosetting and thermoplastic polymers have been utilized to form microcellular foams, high performance adhesives, synthetic fibers, surface coatings, and automobile parts along with a myriad of other applications. The carbamate linkage can be severed by chemical and biological processes [70].

Aromatic esters and the extent of the crystalline fraction of the polymer have been identified as important factors affecting the biodegradation of PUR [71, 72]. Acid and base hydrolysis strategies can sever the carbamate bond of the polymer. Microbial ureases, esterases and proteases can enable the hydrolysis the carbamate and ester bonds of a PUR polymer [71, 73, 74]. Bacteria have been found to be good sources for enzymes capable of degrading PUR polymers [75–82]. Fungi are also quite capable of degrading PUR polymers [83–85]. Each of the enzyme systems has their preferential targets: ureases attack the urea linkages [86–88] with esterases and proteases hydrolyzing the ester bonds of the polyester PUR as a major mechanism for its enzymatic depolymerization [89–92]. PUR polymers appear to be more amenable to enzymatic depolymerization or degradation but further searches and inquiry into hitherto unrecognized microbial PUR degrading activities is expected to offer significant PUR degrading activities.

### 4.5 Polyethylene terephthalate

PET is a polyester commonly marketed as a thermoplastic polymer resin finding use as synthetic fibers in clothing and carpeting, food and liquid containers, manufactured objects made through thermoforming, and engineering resins with glass fiber. Composed of terephthalic acid and ethylene glycol through the formation of ester bonds, PET has found a substantial role in packaging materials, beverage bottles and the textile industry. Characterized as a recalcitrant polymer of remarkable durability, the polymer's properties are reflective of its aromatic units in its backbone and a limited polymer chain mobility [91]. In many of its commercial forms, PET is semicrystalline having crystalline and amorphous phases which has a major effect on PET biodegradability. The environmental accumulation of PET is a testament of its versatility and the apparent lack of chemical/physical mechanisms capable of attacking its structural integrity show it to be a major environmental pollution problem.

The durability and the resulting low biodegradability of PET are due to the presence of repeating aromatic terephthalate units in its backbone and the corresponding limited mobility of the polymer chains [92]. The semicrystalline PET polymer also contains both amorphous and crystalline fractions with a strong effect on its biodegradability. Crystallinity exceeding 30% in PET beverage bottles and fibers having even higher crystalline compositions presents major hurdles to enzyme-induced degradation [93, 94]. At higher temperatures, the amorphous fraction of PET becomes more flexible and available to enzymatic degradation [95, 96]. The hydrolysis of PET by enzymes has been identified as a surface erosion process [97–100]. The hydrophobic surface significantly limits biodegradation due to the limited ability for microbial attachment. The hydrophobic nature of PET poses a significant barrier to microbial colonization of the polymer surface thus attenuating effective adsorption and access by hydrolytic enzymes to accomplish the polymer degradation [101].

A wide array of hydrolytic enzymes including hydrolases, lipases, esterases, and cutinases has been shown to have the ability to hydrolyze amorphous PET polymers

and modify PET film surfaces. Microbes from a vast collection of waste sites and dumping situations have been studied for their ability to degrade PET. A subunit of PET, diethylene glycol phthalate has been found to be a source of carbon and energy necessary to the sustenance of microbial life. Enzyme modification may be effectively employed to improve the efficiency and specificity of the polyester degrading enzymes acknowledged to be active degraders of PET [102]. Significant efforts have been extended to developing an understanding of the enzymatic activity of high-performing candidate enzymes through selection processes, mechanistic probes, and enzyme engineering. In addition to hydrolytic enzymes already identified, enzymes found in thermophilic anaerobic sludge were found to degrade PET copolymers formed into beverage bottles [103].

Recently, the discovery of microbial activity capable of complete degradation of widely used beverage bottle plastic expands the range of technology options available for PET treatment. A microorganism isolated from the area adjacent to a plastic bottle-recycling facility was shown to aerobically degrade PET to small molecular daughter products and eventually to $CO_2$ and $H_2O$. This new research shows that a newly isolated microbial species, *Ideonella sakaiensis* 201-F6, degrades PET through hydrolytic transformations by the action of two enzymes, which are extracellular and intracellular hydrolases. A primary hydrolysis reaction intermediate, mono (hydroxy-2-ethyl) terephthalate is formed and can be subsequently degraded to ethylene glycol and terephthalic acid which can be utilized by the microorganism for growth [104–109].

This discovery could be a candidate as a single vessel system that could competently accomplish PET hydrolysis as an enzyme reactor. This may be the beginning of viable technology development applicable to the solution of the global plastic problem recognized for its terrestrial component as well as the water contamination problem found in the sea. These remarkable discoveries offer a new perspective on

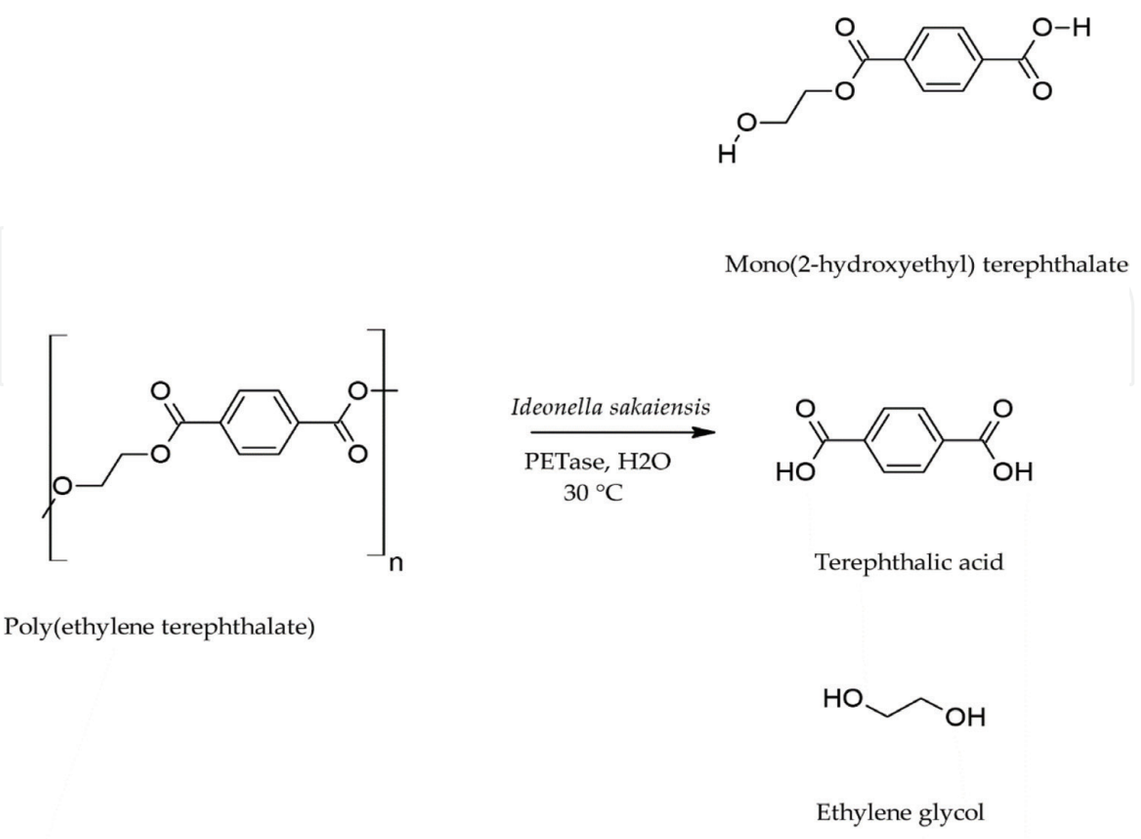


**Figure 5.**
*Microbial depolymerization of poly(ethylene terephthalate).*

the recalcitrant nature of PET and how future environmental management of PET waste may be conducted using the power of enzymes. The recognition of current limiting steps in the biological depolymerization of PET are expected to enable the design of a enzymes-based process to reutilized the natural assets contained in scrap PET [110] (**Figure 5**).

## 5. Conclusions

The major commercial polymers have been shown to be biodegradable in a variety of circumstances despite a strong predisposition suggesting that many of these polymers were recalcitrant to the effects of biodegradation. The question of whether bioremediation can play a significant role in the necessary management of polymer waste remains to be determined. Treatment technology for massive waste polymer treatment must be sufficiently robust to be reliable at large scale use and adaptable to conditions throughout the environment where this treatment is required. The status of information relating to the application of biodegradation treatment to existing and future polymer solid waste is at early stages of development for several waste polymers. The discovery of that invertebrate species (insect larvae) can reduce the size of the waste polymer by ingesting and degradation in the gut via enzymes which aid or complete degradation is rather amazing and requires additional scrutiny. There is an outside change that a polymer recycling technology based on these findings is a future possibility.

## Disclaimer

The views expressed in this book chapter are those of the author and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

## Conflict of interest

No "conflict of interest" is known or expected.

## Author details

John A. Glaser
U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, Ohio, USA

*Address all correspondence to: glaser.john@epa.gov

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