Microbial deterioration and degradation of polymeric materials

S Krishna Mohan*, Tanu Srivastava

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Abstract

Polymeric materials due to its structural versatility are widely used in aerospace applications, aviation and space industries. As they are potential source of carbon and energy for heterotrophic microorganisms including bacteria and fungi in several ways their biodegradation affect these industries. The information on degradability can provide fundamental information facilitating design and life-time analysis of materials. Literature survey shows that polymers which are susceptible to biofilm formation includes paints, adhesives, plastics, rubbers, sealants, FRPCMs, lubricating materials, fuels etc. Even though the understanding of polymer degradation has been advanced in recent years the subject is still inadequately addressed because of the lack of information available. The review focuses on polymer biodeterioration and biodegradation and its mechanisms, the types of microorganisms involved the reactions of enzymes of importance in the biodegradation of polymers, consequences of biodegradation, the factors involved in biodegradation of polymers and its prevention and the tests used to evaluate it.

Keywords: Polymers, Biodegradation, Biodeterioration, Microorganisms, Enzymes, Biofilm.

Introduction

Polymeric materials have gained a wide influence due to their excellent mechanical and thermal properties and high stability. They are very unique in chemical composition, physical forms, mechanical properties and applications. Because of this structural versatility, polymeric materials are widely used in aerospace applications, aviation and space industries as paints, adhesives, sealants, plastics, composites, rubbers, lubricants, fuels, matrix materials for fiber reinforced polymeric composites (FRPCMs) etc. Polymeric materials are potential source of carbon and energy for heterotrophic microorganisms including bacteria and fungi in several ways. The actions of microorganisms on polymers are influenced by two different processes:

1. Direct action: The deterioration of plastics which serve as a nutritive substance for the growth of the microorganisms
2. Indirect action: The influence of metabolic products of the microorganisms, e.g., discoloration or further deterioration.

Biodegradation of a polymeric material is chemical degradation brought by the action of naturally occurring microorganisms such as bacteria and fungi via enzymatic action into metabolic products of microorganisms (e.g., H₂O, CO₂, CH₄, biomass etc.) (David et al. 1994; Chandra et al. 1998; Lenz 1993; Mohanty et al. 2000). In contrast to the biodegradation of polymers, where a near complete conversion of the material components takes place only a change in the polymer structure or the plastic composition is observed in many cases in polymer biodeterioration or biocorrosion (Gu et al. 2003). The ultimate result in the both the cases are a complete loss of structural integrity as a result of drastic decrease in molecular weight. In current times the term ‘biodegradable’ is considered an essential property of many manufactured materials to ensure that the particular material with stand its effect or not. Although biodegradation may be seen as a direct opposite to biodeterioration, they are usually the same processes, changed in meaning and significance solely by human need. Hence, in this review the term biodegradation also implicitly include biocorrosion or biodeterioration or microbially influenced corrosion (MIC). Microorganisms are involved in the degradation and deterioration of both synthetic and natural polymers forming biofilms (Gu et al. 2000). Polymers which are susceptible to biofilm formation include paints, adhesives, plastics, sealants, composites, lubricating materials, fuels etc (Gross et al. 1995; Gross et al. 1993; Gu et al. 1993; Gu et al. 1993; Gu et al. 1993; Gu et al. 1994; Gu et al. 1996; Albinas et al. 2003). This review article focuses on mode of biodegradation of polymeric materials, its mechanisms, consequences, factors...
involved, prevention and test methods to be followed for its evaluation.

Mode of biodegradation

The biological environment includes the biological agents such as bacteria, fungi and their enzymes responsible for the deterioration of polymeric substances. They consume a substance as a food source so that its original form disappears.

Microorganisms

Microorganisms are highly adaptive to environment and secrete both endoenzymes and exoenzymes that attack the substrate and cleave the molecular chains into segments (Albinas et al. 2003; Huang et al. 1990). The secreted enzymes are proteins of complicated chemical structure with high molecular weights possessing hydrophilic groups such as -COOH, -OH, and -NH₂ (Potts 1978) which can attack and eventually destroy almost anything. Several factors including the availability of water, temperature, oxygen usage, minerals, pH, redox potential, carbon and energy source influence the growth of microorganisms (Holmes 1988; Sand 2003) (Table 1). The degradative action of fungi and bacteria on the polymeric material is a result of enzyme production and resultant breakdowns to the non living substrate in order to supply nutrient materials. Differences between fungi and bacteria are illustrated in Table 2.

| Table 1: Spectrum of conditions under which microbial life is observed |
|---|---|---|
| S.No | Parameter | Conditions |
| 1 | pH | 0 to 13 |
| 2 | Temperature | -5°C to +116°C |
| 3 | Pressure | To 1.000 bar |
| 4 | Redox potential | -500 mV to +850 mV |
| 5 | Salinity | Ultrapure water to almost saturated water |
| 6 | Radiation | Biofilms on Ultra violet lamps, irradiation units and nuclear power plants |
| 7 | Nutrient concentration | From 10 µgL to plants |

Factors affecting polymer biodegradation

All polymers are more or less biodegradable to some extent due to the organic nature of their principle elements like resin and hardener. Polymeric materials complexity, structures and compositions is one of the important aspects which govern polymer biodegradation. Polymer biodegradation is a heterogeneous process. Polymers do not consist simply of only one chemical homogenous component, but contain different polymers (blends) or low MW additives (plasticizers) which can serve as good nutrients for the ambient microorganisms developed on polymer surfaces (Kyrikou et al. 2007). Moreover, within one polymer itself different structural elements can be present (copolymers), and these may either be distributed statistically along the polymer chains (random copolymers) which or alternatively (alternating copolymers). Another structural characteristic of a polymer is the possible branching of chains or the formation of networks (cross linked polymers). Despite having the same overall composition these different structures of a polymer can directly influence accessibility of the material to the enzyme catalyzed polymer chain cleavage, and also have a crucial impact on the higher ordered structures of the polymers. In recent years a considerable amount of qualitative and semi-quantitative information has been accumulated to draw some conclusions about the following important factors (Chandra et al. 1998; Baljit et al. 2008; Gijpferich 1996) which are affecting the rate of degradation of synthetic polymers in a biological environment.

- Polymer structure and morphology
- Molecular weight
- Hydrophobic and hydrophilic characteristics
- Additives
- Methods of synthesis
- Environmental conditions

Enzymes

Wide range of microorganisms utilizes enzymes which are structurally high specialized proteins with complex three dimensional structures as carbon and energy sources. In the presence of enzymes, a rise in reaction rate of 10⁶–10²⁰ without creating undesirable products can be often observed (Lenz 1993). In general many different types of enzymes (over 2000) exist in a biological system and each enzyme performs one chemical function. Susceptibility of the polymers to microbial attack generally depends on enzyme availability, availability of a site in the polymers for enzyme attack and enzyme specificity for that polymer and the presence of coenzyme if required. The type of reaction which is probably of most importance in the enzymatic degradation of polymers is the bimolecular reaction in which the enzyme catalyzes the interaction of the polymer and a low molecular reagent. These reactions can occur by either single displacement mechanism or double displacement mechanism. In the single displacement mechanism both substrates, A and B are bound to the free enzyme E₀ by consecutive reversible reactions. After that the final complex E₀AB dissociates into the products C, D and the free enzyme E₀ (Fig 1). Whereas, in the double displacement mechanism only one substrate at a time is bound to the enzyme but the complex of the first bound substrate, E₀AY undergoes unimolecular dissociation at an appropriate functional group to form a new complex E₀Y between the enzyme and a fragment Y of AY. This intermediate complex combines with the second substrate B and transfers the Y fragment to B (Fig 2).

\[ E₀ + A \rightarrow E₀A \rightarrow E₀AB \rightarrow C + D + E \]

Single displacement mechanism

Double displacement mechanism

Environmental conditions
Generalization concerning biodegradation

Biodegradability is primarily dependent on hydrolyzable and oxidizable chemical structures, balance of hydrophobicity, and molecular weights. Physical properties such as crystallinity, orientation, Tm or Tg, and morphological properties such as surface area or thickness affect the rate of degradation. The following guidelines were made for the relationship between polymer structure and biodegradation (Swift 1993; Kawai 1995).

1. Naturally occurring polymers are biodegradable. Chemically modified natural polymers may biodegrade depending on the extent of modification and the kind of modifying group.
2. Synthetic addition polymers except polyvinyl alcohol with carbon-chain backbones do not biodegrade at molecular weights greater than 1000.
3. Synthetic addition polymers include polyacetals and polyesters with hetero-atoms in their backbones may biodegrade.
4. Synthetic condensation polymers are generally biodegradable to a greater or lesser extent depending on the following factors
   - Chain coupling (ester > ether > amide > urethane)
   - Molecular weight (lower is faster than higher)
   - Morphology (Tm) (amorphous is faster than crystalline)
   - Hardness (Tg) (softer is faster than harder) and
   - Hydrophilicity vs hydrophobicity (hydrophilic is faster than hydrophobic).
5. Water solubility does not guarantee biodegradability.

General mechanism of biodeterioration and biodegradation

Biodeterioration

Biodeterioration of polymers involves primarily enzyme-catalyzed chemical reactions which can occur due to endoenzymes and exoenzymes (Lenz 1993; Ranjith et al. 2005). The former results in random chain cleavage with a substantial decrease in molecular weight whereas the later in which the immediate effect on molecular weight of the residual polymer will be much less results in removal of only terminal units, which are generally either monomers, dimers or trimers (A, A, A) (Fig 3). Here, A represents both the internal repeating units and the terminal units, the subscript represent the number of such units in the product formed.

Biodegradation

Microorganisms are not able to transport the polymers directly through their outer cell membranes into the cells where most of the biochemical processes take place due to the lack of water-solubility and the length of the polymer molecules. In order to use such materials as a carbon and energy source, microorganisms have developed a special strategy. The microbes excrete extracellular enzymes which depolymerize the polymers outside the cells. Extracellular and intracellular depolymerases enzymes are actively involved in biological degradation of polymers. Anaerobic and aerobic biodegradation mechanism pathways are given in Fig 4 (Gu 2003). During degradation, exoenzymes from microorganisms break down complex polymers yielding short chains or smaller molecules, e.g., oligomers, dimers, and monomers, that are smaller enough (water soluble) to pass the semi-permeable outer bacterial membranes and then to be utilized as carbon and energy sources (Gu 2003). This initial process of polymer breaking down is called depolymerization. When the end products are inorganic species, e.g., CO₂, H₂O, or CH₄, the degradation is called mineralization.

When O₂ is available, aerobic microorganisms are mostly responsible for destruction of complex materials with microbial biomass, CO₂, and H₂O as the final products. In contrast, in the absence of O₂ i.e. under anoxic conditions, anaerobic consortia of microorganisms are responsible for polymer deterioration. In this case the primary products will be microbial biomass, CO₂, CH₄ and H₂O under methanogenic conditions (Barlaz et al. 1989; Barlaz et al. 1989; Gu et al. 2001) or H₂S, CO₂ and H₂O under sulfidogenic conditions. Since thermodynamically O₂ is a more efficient electron acceptor than SO₄²⁻ and CO₂, aerobic processes yield much more energy and are capable of supporting a greater population of microorganisms than anaerobic processes. It is important to understand that biodeterioration and degradation of polymer substrate can rarely reach 100% because a small portion of the polymer will be always incorporated into microbial biomass, humus and other natural products (Alexander 1977; Atlas et al. 1997; Narayan 1993; Gu et al. 2006).

Properties deterioration

Biodegradation of polymers results in the deterioration of some of the mechanical, optical and electrical properties given in the Table 3. Since usually mechanical properties of polymers are predominantly determined by the length of the polymer chains in the...
material, scission of polymer chains is one major reason for changes in mechanical properties. Even just a single endo cleavage in a polymer chain can reduce the molar mass to 50%, and hence cause significant changes in mechanical properties. The small variations in the chemical structures will result in large differences in term of biodegradability. When plasticizers are removed from the plastic materials by micro organisms, embrittlement can also occur.

The changes in electrical properties often are due to principally surface growth, its associated moisture and to pH changes caused by excreted metabolic products. Removal of susceptible plasticizers, modifiers, and lubricants, results in increased modulus, changes in weight, dimensions, other physical properties, and deterioration of electrical properties such as insulation resistance, dielectric constant, power factor, and dielectric strength.

### Table 3: Deteriorated mechanical, optical and electrical properties

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Electrical properties</th>
<th>Optical properties</th>
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<tbody>
<tr>
<td>Tensile strength</td>
<td>Dielectric strength</td>
<td>Optical transmission</td>
</tr>
<tr>
<td>Stiffness</td>
<td>Dielectric constant</td>
<td>Haze</td>
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<tr>
<td>Hardness</td>
<td>Insulation resistance</td>
<td>Water vapour</td>
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<tr>
<td>Weight loss</td>
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<td>Embrittlement</td>
<td>Arc resistance</td>
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<td>Impact resistance</td>
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<tr>
<td>Gloss</td>
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### Biofilms

Deterioration of polymeric materials is caused by adhering microorganisms that colonize their surfaces, forming biofilm (Mitchell et al. 1996; Viktorov et al. 1992). The formation of a biofilm is a prerequisite for substantial corrosion and deterioration of these materials to take place. Biofilm is a slimy layer where bacterial cells can encase themselves in a hydrated matrix of polysaccharides and protein which is composed of water (80-95%), extracellular polymer substances (EPS) that contribute 85-98% of the organic matter, the microorganisms, entrapped organic and inorganic particles (e.g. humic substances, debris, clay, silica, gypsum, etc.), substances sorbed to EPS, cells or particles and substances dissolved in the interstitial water (Flemming 1998). The process of establishment of complex community of microorganisms on surface attachment as biofilm is known as biofouling or microfouling. The major five damaging mechanisms (both direct and indirect) through which the structure and function of synthetic polymeric materials can be damaged by biofilms can be very high. This includes (Flemming 1998) (1) Coating the surface, masking surface properties and contaminating adjacent media such as water, (2) Increasing the leaching additives and monomers out of the polymer matrix, (3) Attack by enzymes or radicals of biological origin to polymer and additives; leading to both embrittlement and loss of mechanical stability, (4) Accumulating water and penetrating the polymer matrix with microbial filaments, causing swelling and increased conductivity and (5) Excretion of lipophilic microbial pigments that lead to unwanted colours in the polymer.

### Biocides

Polymer biodegradation can be treated by Physical-mechanical, biological, electrochemical and chemical methods (Videla 2002). Among which chemical methods are most frequently employed in which using biocides is the most profound characteristic of chemical treatment. The biocides are single compounds (or a mixture of compounds) capable of killing microorganisms or inhibiting microbial growth. They are also employed to remove populations from either within the matrix of a material or on the surfaces of a material and are divided into Oxidising biocides and Non-oxidising biocides where the latter being more effective because of their overall control of bacteria, algae and fungi. Moreover, they have greater persistence, as many of them are pH independent. Frequently, a combination of oxidizing biocides and non-oxidizing biocides is used to optimize the microbiological control. The action of a biocide used to disinfect any system should be bactericidal, fungicidal and algicidal, thus requiring the application of broad-spectrum biocide compounds. Although the intrinsic activity of biocidal agents is important the more concern is the interaction between them and the material/system which they are designed to protect. The spectrum of activity must be appropriate to the challenge the materials and the biocide must be compatible with the material as well as be able to provide protection for a suitable period of service.

### Test methods for biodegradable polymers

While biodeterioration test aims to characterize changes in the material properties (which can even be caused by minor chemical changes in the polymers such as extraction of plasticizer or oxidation, etc.), biodegradable tests for plastics material is finally transformed into natural biological products. Due to the following facts multiple test procedures are necessary in evaluating the biodegradability of a material:

- Observed weight loss may result not from polymer degradation, but from the leaching of additives, including plasticizers.
- Carbon dioxide production might result from the degradation of low molecular weight fraction of the polymer, with no degradation of longer chains.
- A large loss of material strength might come from a very small change in its chemical makeup.
- Strength is often disproportionately affected by the loss of additives and 90% decrease of strength can result from as little as 5% mineralization.

The current available methods are not adequate to address the wide array of polymers utilized under different environmental conditions (Gu 2003; Gu et al. 2005). In addition, available test methods offer very little flexibility because the objectives of these methods are in the development stage. The extent of degradation of the advanced polymers used in aviation and electronics cannot be determined quantitatively with the existing techniques. When testing degradation phenomena of plastics in the environment one has to face a general problem concerning the kind of tests applied and the conclusions which can be drawn. Besides reproducibility, the shortening of test durations and minimization of the material needed is a crucial point when performing extended systematic investigation for biodegradation testing. In principle the degradation tests can be classified into three categories.

1. Field tests: Complex environment and variable conditions
2. Simulation tests: Complex environment and defined conditions
3. Laboratory tests: Synthetic environment and defined conditions

### Field tests

Field tests such as burying plastic samples in soil, river or full-scale composting performed represent ideal practical environmental conditions, but there are some serious disadvantages of such kinds of tests. One is that environmental conditions such as temperature,
pH, or humidity, cannot be efficiently controlled in nature and secondly, analytical methods for monitoring the degradation process are very limited. In most cases it is only possible to evaluate visible changes of the polymer samples or to determine the disintegration by measuring the weight loss. Analysis of residues and intermediates is complicated due to the complex and undefined environment. Since a pure physical disintegration of a plastic material is not regarded as biodegradation these tests alone are not suitable to prove whether a material is biodegradable or not.

**Simulation tests**

Various simulation tests have been developed to overcome the problems at least partially with field tests. Here, the degradation takes place in a real environment (e.g. compost, soil or sea water), but the exposure to the environment is performed in a laboratory reactor. The important external parameters which can affect the degradation process (e.g. temperature, pH, humidity, etc.) can here be controlled and adjusted. Examples for such tests include the soil burial test (Pantke 1990), the so-called controlled composting test (Pagga et al. 1995; Tosin et al. 1996; Ohtaki et al. 1998; Tuominen et al. 2002; Degli-Innocenti et al. 1998), test simulating landfills (McCartin et al. 1990; Smith et al. 1990; McCarthy et al. 1992), or aqueous “aquarium tests (Pichner et al. 1995). Nutrients are sometimes added in these tests with the aim to accelerate degradation and to reduce the duration of the degradation tests.

**Laboratory tests**

The most reproducible biodegradation tests are laboratory tests, where defined media are used which then are inoculated with a mixed microbial population. In some cases individual microbial strains or mixtures of some strains are used for inoculation. Such tests often take place under conditions optimized for the activity of the particular microorganisms (e.g. temperature, pH, humidity, etc.) with the effect, that polymers often exhibit a much higher degradation rate in laboratory tests than observed under natural conditions.

The most reproducible degradation tests directly use the isolated extracellular enzymes of the microorganisms which are responsible for the first step of the degradation process, the molar mass reduction of the polymers by depolymerization (Tokiwa et al. 1977; Marten et al. 2003; Marten et al. 2005; Walter et al. 1995; Vikman et al. 1995). Even though with laboratory tests it is not possible to prove biodegradation in terms of metabolization by microorganisms, the shorter test durations and the reproducible test conditions makes them especially useful for systematic investigation when studying basic mechanisms of polymer biodegradation. However, conclusions on the absolute degradation rate in a natural environment can only be drawn to a limited extent. Examples for such tests include Rapid detection method, Closed bottle test, Environmental chamber method, Petri dish screen, Gravimetry, Respirometry, Measurement of Biogas and Surface hydrolysis.

**Conclusions**

In recent years the issue of degradable polymers and plastics with particular emphasis on biodegradation has received a great deal of attention. Naturally occurring polymers are readily biodegradable in the environment but most of the synthetic high polymers biodegrade only very slowly under comparable exposure conditions. There are, however, exceptions to this observation and several classes of synthetic polymers that undergo ready environmental biodegradation are known. Protection of the materials from biodegradation can be achieved to some extent through surface engineering and control of the physical, chemical and biological environments. Biocides have been widely used for the protection but the development of resistant bacteria and fungi is becoming a serious problem than expected. Assessment of biodegradability is a key consideration in the development of biodegradable polymers. Strict definitions do not exist about the constituent of abiotic environment to carry out such testing and criteria to be followed to establish biodegradability of a polymer in the laboratory. The test results are sensitive to a variety of factors, particularly the consortia of micro-organisms used. It is, therefore, often difficult to appreciate the full significance of the reported data and to test results relate to each other. Material biodeterioration is highly undesirable to material integrity as these are used mostly in structural designs of aerospace vehicles. Damage to the structure may result in premature weakening which is often translated to system failure and enormous economic losses. This review thus stresses for the need of microbial susceptibility studies for all types of synthetic polymeric materials before using in the actual hardware.

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**Nomenclature**

<table>
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<tr>
<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>FRPCM</td>
<td>Fiber reinforced polymeric composites</td>
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<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Melting point temperature</td>
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<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass transition temperature</td>
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<tr>
<td>EPS</td>
<td>Extracellular polymer substances</td>
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</table>

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