

Research review paper

Biological degradation of plastics: A comprehensive review

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Received 22 November 2007; received in revised form 31 December 2007; accepted 31 December 2007

Available online 26 January 2008

Abstract

Lack of degradability and the closing of landfill sites as well as growing water and land pollution problems have led to concern about plastics. With the excessive use of plastics and increasing pressure being placed on capacities available for plastic waste disposal, the need for biodegradable plastics and biodegradation of plastic wastes has assumed increasing importance in the last few years. Awareness of the waste problem and its impact on the environment has awakened new interest in the area of degradable polymers. The interest in environmental issues is growing and there are increasing demands to develop material which do not burden the environment significantly. Biodegradation is necessary for water-soluble or water-immiscible polymers because they eventually enter streams which can neither be recycled nor incinerated. It is important to consider the microbial degradation of natural and synthetic polymers in order to understand what is necessary for biodegradation and the mechanisms involved. This requires understanding of the interactions between materials and microorganisms and the biochemical changes involved. Widespread studies on the biodegradation of plastics have been carried out in order to overcome the environmental problems associated with synthetic plastic waste. This paper reviews the current research on the biodegradation of biodegradable and also the conventional synthetic plastics and also use of various techniques for the analysis of degradation in vitro.

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Keywords: Biodegradation; Synthetic plastics; Biodegradable plastics; Analysis of degradation

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1. Introduction

Plastics are man made long chain polymeric molecules (Scott, 1999). More than half a century ago synthetic polymers started to substitute natural materials in almost every area and nowadays plastics have become an indispensable part of our life. With time, stability and durability of plastics have been improved continuously, and hence this group of materials is now considered as a synonym for materials being resistant to many environmental influences. The word plastic comes from the Greek word “plastikos”, which means ‘able to be molded into different shapes’ (Joel, 1995). The plastics we use today are made from inorganic and organic raw materials, such as carbon, silicon, hydrogen, nitrogen, oxygen and chloride. The basic materials used for making plastics are extracted from oil, coal and natural gas (Seymour, 1989).

Plastics are resistant against microbial attack, since during their short time of presence in nature evolution could not design new enzyme structures capable of degrading synthetic polymers (Mueller, 2006). Nowadays, a wide variety of petroleum-based synthetic polymers are produced worldwide to the extent of approximately 140 million tons per year and remarkable amounts of these polymers are introduced in the ecosystem as industrial waste products (Shimao, 2001).

Synthetic plastics are extensively used in packaging of products like food, pharmaceuticals, cosmetics, detergents and chemicals. Approximately 30% of the plastics are used worldwide for packaging applications. This utilization is still expanding at a high rate of 12% per annum (Sabir, 2004). They have replaced paper and other cellulose-based products for packaging because of their better physical and chemical properties, such as their strength, lightness, resistance to water and most water-borne microorganisms. The most widely used plastics used in packaging are polyethylene (LDPE, MDPE, HDPE and LLDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC),

polyurethane (PUR), poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), nylons (Fig. 1 & Table 1). The widespread applications of plastics are not only due to their favorable mechanical and thermal properties but also mainly due to the stability and durability (Rivard et al., 1995). Because of their durability and visibility in litter, plastics (polymers) have attracted more public and media attention than any other component of the solid waste stream. In 1993, the total world demand for plastics was over 107 million tones and it was estimated about 146 million tones in 2000. The plastic industry in Pakistan is growing at an average annual growth rate of 15%. There are about 600–700 medium sized plastic processing units scattered all over Pakistan (Sabir, 2004).

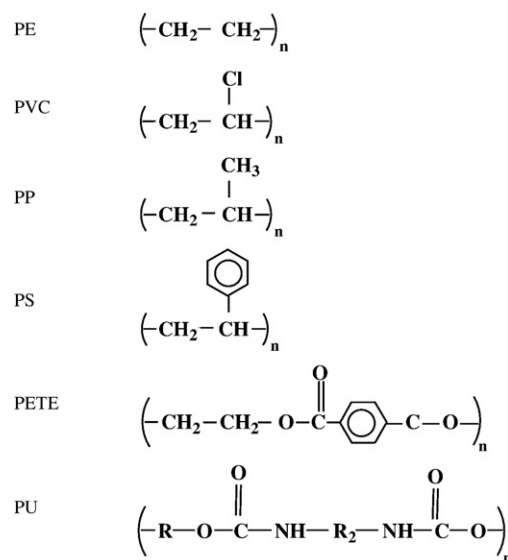


Fig. 1. Structures of conventional petrochemical plastics (adapted from Pavia et al., 1988). Polyethylene (PE), Polyvinyl chloride (PVC), Polypropylene (PP), Polystyrene (PS), Polyethylene Terephthalate (PET), Polyurethane (PU).

Table 1
Uses of synthetic plastics

Plastic	Use
Polyethylene	Plastic bags, milk and water bottles, food packaging film, toys, irrigation and drainage pipes, motor oil bottles
Polystyrene	Disposable cups, packaging materials, laboratory ware, certain electronic uses
Polyurethane	Tyres, gaskets, bumpers, in refrigerator insulation, sponges, furniture cushioning, and life jackets
Polyvinyl chloride	Automobile seat covers, shower curtains, raincoats, bottles, visors, shoe soles, garden hoses, and electricity pipes
Polypropylene	Bottle caps, drinking straws, medicine bottles, car seats, car batteries, bumpers, disposable syringes, carpet backings
Polyethylene terephthalate (PET)	Used for carbonated soft drink bottles, processed meat packages peanut butter jars pillow and sleeping bag filling, textile fibers
Nylon	Polyamides or Nylon are used in small bearings, speedometer gears, windshield wipers, water hose nozzels, football helmets, racehorse shoes, inks, clothing parachute fabrics, rainwear, and cellophane
Polycarbonate	Used for making nozzles on paper making machinery, street lighting, safety visors, rear lights of cars, baby bottles and for houseware. It is also used in sky-lights and the roofs of greenhouses, sunrooms and verandahs. One important use is to make the lens in glasses
Polytetrafluoroethylene (PTFE)	PTFE is used in various industrial applications such specialized chemical plant, electronics and bearings. It is met with in the home as a coating on non-stick kitchen utensils, such as saucepans and frying pans

(Vona et al., 1965).

The dramatic increase in production and lack of biodegradability of commercial polymers, particularly commodity plastics used in packaging (e.g. fast food), industry and agriculture, focused public attention on a potentially huge environmental accumulation and pollution problem that could persist for centuries (Albertsson et al., 1987). The plastic waste is disposed off through landfilling, incineration and recycling. Because of their persistence in our environment, several communities are now more sensitive to the impact of discarded plastic on the environment, including deleterious effects on wildlife and on the aesthetic qualities of cities and forests. Improperly disposed plastic materials are a significant source of environmental pollution, potentially harming life. In addition, the burning of polyvinylchloride (PVC) plastics produces persistent organic pollutants (POPs) known as furans and dioxins (Jayasekara et al., 2005). The estimated figure of plastic waste generation across the Pakistan is 1.32 million tons per annum. This considerable content of plastic in the solid waste generated in Pakistan is of great concern. Plastic waste is released during all stages of production and post consumption every plastic product is a waste (Sabir, 2004).

Some synthetic plastics like polyester polyurethane, polyethylene with starch blend, are biodegradable, although most commodity plastics used now are either non-biodegradable or even take decades to degrade. This has raised growing concern about degradable polymers and promoted research activity world wide to either modify current products to promote

degradability or to develop new alternatives that are degradable by any or all of the following mechanisms: biodegradation, photodegradation, environmental erosion and thermal degradation (Kawai, 1995).

In 1980's, scientists started to look if plastics could be designed to become susceptible to microbial attack, making them degradable in a microbial active environment. Biodegradable plastics opened the way for new considerations of waste management strategies since these materials are designed to degrade under environmental conditions or in municipal and industrial biological waste treatment facilities (Augusta et al., 1992; Witt et al., 1997).

Due to similar material properties to conventional plastics (Hocking and Marchessault, 1994; Steinbuchel and Fuchtenbusch, 1998), the biodegradable plastics (polyesters), namely polyhydroxyalkanoates (PHA), polylactides, polycaprolactone, aliphatic polyesters, polysaccharides and copolymer or blend of these, and have been developed successfully over the last few years (Fig. 2). The most important are poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate). Bioplastics (Biopolymers) obtained from growth of microorganisms or from plants which are genetically-engineered to produce such polymers are likely to replace currently used plastics at least in some of the fields (Lee, 1996). PHA's key properties are its biodegradability, apparent biocompatibility, and its manufacture from renewable resources. The global interest in PHAs is high as it is used in different packaging materials, medical devices, disposable personal hygiene and also agricultural applications as a substitute for synthetic polymers like polypropylene, polyethylene etc. (Ojumu et al., 2004) (Table 2) (Lee, 1996).

In the past 10 years, several biodegradable plastics have been introduced into the market. However, none of them is efficiently biodegradable in landfills. For this reason, none of the products has gained widespread use (Anonymous, 1999). At present, biodegradable plastic represents just a tiny market as compared with the conventional petrochemical material. Bioplastics will comparatively prove cheaper when oil prices will continue to hike up. Although not in use today, plastic shopping bags could be made from Polylactic acid (PLA) a biodegradable polymer derived from lactic acid. This is one form of vegetable-based bioplastic. This material biodegrades quickly under composting conditions and does not leave toxic residue. However, bioplastic can have its own environmental impacts, depending on the way it is produced (<http://en.wikipedia.org>). There is an urgent need to develop efficient microorganisms and their products to solve this global issue (Kathiresan, 2003).

This paper reviews the current research on the degradation of not only the biodegradable plastics but also the conventional synthetic (commodity) plastics and their blends, and also use of various techniques for the analysis of degradation in vitro.

2. Degradation of plastics

Any physical or chemical change in polymer as a result of environmental factors, such as light, heat, moisture, chemical conditions or biological activity. Processes inducing changes in polymer properties (deterioration of functionality) due to

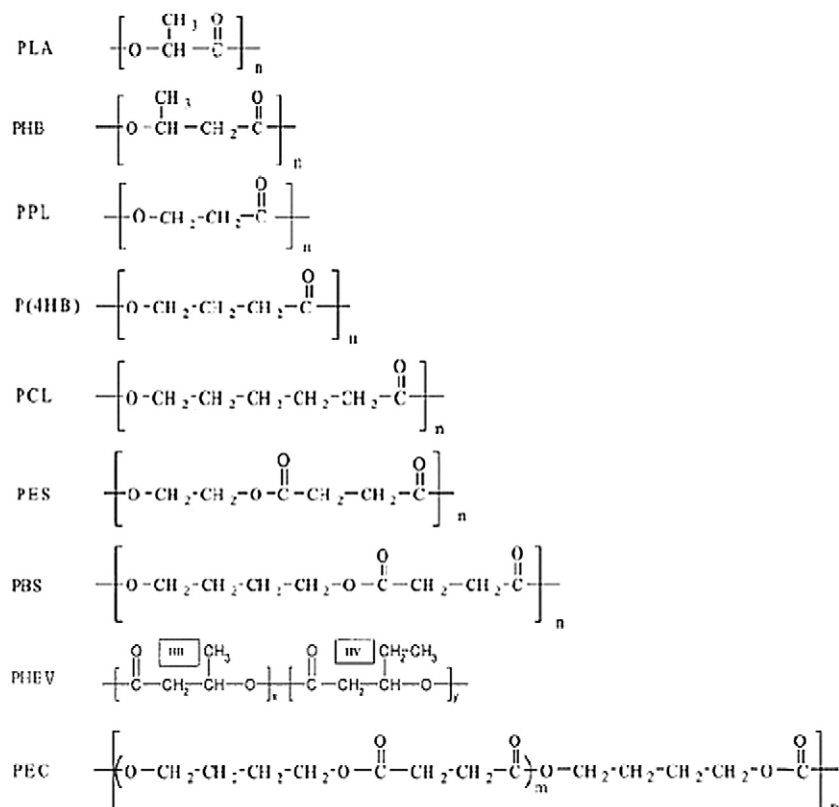


Fig. 2. Chemical structure of poly(lactide)(PLA), poly(3-hydroxybutyrate)(PHB), poly(propiolactone)(PPL), poly(ϵ -caprolactone)(PCL), poly(ethylene succinate) (PES), poly(butylenes succinate)(PBS), poly(3-hydroxybutyrate-co-3-hydroxyvalerate)(PHBV) and poly(ester carbonate)(PEC) (Tokiwa and Calabia 2004).

chemical, physical or biological reactions resulting in bond scission and subsequent chemical transformations (formation of structural inhomogeneities) have been categorized as polymer degradation. Degradation has been reflected in changes of material properties such as mechanical, optical or electrical characteristics, in crazing, cracking, erosion, discoloration, phase separation or delamination. The changes include bond scission, chemical transformation and formation of new functional groups (Pospisil and Nespurek, 1997). The degradation will either be photo, thermal or biological (Table 3).

Sensitivity of polymers to photodegradation is related to the ability to absorb the harmful part of the tropospheric solar radiation. This includes the UV-B terrestrial radiation (~295–315 nm) and UV-A radiation (~315–400 nm) responsible for the direct photodegradation (photolysis, initiated photooxidation). Visible part of sunlight (400–760 nm) accelerates polymeric degradation by heating. Infrared radiation (760–2500 nm) accelerates thermal oxidation (Gugumus, 1990; Pospisil and Nespurek, 1997). Most plastics tend to absorb high-energy radiation in the ultraviolet portion of the spectrum, which activates their electrons to higher reactivity and causes oxidation, cleavage, and other degradation (<http://composite.about.com/library/glossary/p/bldef-p3928.htm>, Photodegradation, 1989).

Thermal degradation of polymers is ‘molecular deterioration as a result of overheating’. At high temperatures the components of the long chain backbone of the polymer can

Table 2
Uses of biodegradable plastics

Plastics	Uses
Polyglycolic acid (PGA)	Specialized applications; controlled drug releases; implantable composites; bone fixation parts
Poly(lactic acid) (PLA)	Packaging and paper coatings; other possible markets include sustained release systems for pesticides and fertilizers, mulch films, and compost bags
Polycaprolactone (PCL)	Long-term items; mulch and other agricultural films; fibers containing herbicides to control aquatic weeds; seedling containers; slow release systems for drugs
Polyhydroxybutyrate (PHB)*	Products like bottles, bags, wrapping film and disposable nappies, as a material for tissue engineering scaffolds and for controlled drug release carriers
Polyhydroxyvalerate (PHBV)	Films and paper coatings; other possible markets include biomedical applications, therapeutic delivery of worm medicine for cattle, and sustained release systems for pharmaceutical drugs and insecticides
Polyvinyl alcohol (PVOH)	Packaging and bagging applications which dissolve in water to release Products such as laundry detergent, pesticides, and hospital washables
Polyvinyl acetate (PVAc)**	Adhesives, the packaging applications include boxboard manufacture, paper bags, paper lamination, tube winding and remoistenable labels

(<http://www.envis-icpe.com>, Plastics recycling-Economic and Ecological Options. ICPE 2006;4(4):1–12).

*<http://en.wikipedia.org/w/index.php?title=Polyhydroxybutyrate&oldid=189442759>. Accessed February 14, 2008.

**<http://www.chemquest.com/store/polyvinyl-acetate-european-adhesives.html>, 2006.

Table 3
Various polymer degradation routes

Factors (requirement/ activity)	Photo-degradation	Thermo- oxidative degradation	Biodegradation
Active agent	UV-light or high-energy radiation	Heat and oxygen	Microbial agents
Requirement of heat	Not required	Higher than ambient temperature required	Not required
Rate of degradation	Initiation is slow. But propagation is fast	Fast	Moderate
Other consideration	Environment friendly if high-energy radiation is not used	Environmentally not acceptable	Environment friendly
Overall acceptance	Acceptable but costly	Not acceptable	Cheap and very much acceptable

(<http://www.envis-icpe.com>, Plastics recycling-Economic and Ecological Options. ICPE 2006;4(4):1–12).

begin to separate (molecular scission) and react with one another to change the properties of the polymer. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include; reduced ductility and embrittlement, chalking, color changes, cracking and general reduction in most other desirable physical properties (Olayan et al., 1996).

Oxo-biodegradation process uses two methods to start the biodegradation. These methods are photodegradation (UV) and oxidation. The UV degradation uses UV light to degrade the end product. The oxidation process uses time, and heat to break down the plastic. Both methods reduce the molecular weight of the plastic and allow it to biodegrade (<http://www.willowridgeplastics.com/faqs.html>, 2005).

Biodegradation is the process by which organic substances are broken down by living organisms. The term is often used in relation to ecology, waste management, environmental remediation (bioremediation) and to plastic materials, due to their long life span. Organic material can be degraded aerobically, with oxygen, or anaerobically, without oxygen. A term related to biodegradation is biomineralisation, in which organic matter is converted into minerals (<http://en.wikipedia.org/wiki/Biodegradation>, Biodegradation, 2007). Plastics are biodegraded aerobically in wild nature, anaerobically in sediments and landfills and partly aerobically and partly anaerobically in composts and soil. Carbon dioxide and water are produced during aerobic biodegradation and carbon dioxide, water and methane are produced during anaerobic biodegradation (Gu et al., 2000a). Generally, the breakdown of large polymers to carbon dioxide (mineralization) requires several different organisms, with one breaking down the polymer into its constituent monomers, one able to use the monomers and excreting simpler waste compounds as by-

products and one able to use the excreted wastes (http://en.wikipedia.org/wiki/Microbial_metabolism, Microbial metabolism, 2007).

3. Biodegradation of plastics

Microorganisms such as bacteria and fungi are involved in the degradation of both natural and synthetic plastics (Gu et al., 2000a). The biodegradation of plastics proceeds actively under different soil conditions according to their properties, because the microorganisms responsible for the degradation differ from each other and they have their own optimal growth conditions in the soil. Polymers especially plastics are potential substrates for heterotrophic microorganisms (Glass and Swift, 1989).

Biodegradation is governed by different factors that include polymer characteristics, type of organism, and nature of pretreatment. The polymer characteristics such as its mobility, tacticity, crystallinity, molecular weight, the type of functional groups and substituents present in its structure, and plasticizers or additives added to the polymer all play an important role in its degradation (Artham and Doble, 2008; Gu et al., 2000b).

During degradation the polymer is first converted to its monomers, then these monomers are mineralized. Most polymers are too large to pass through cellular membranes, so they must first be depolymerized to smaller monomers before they can be absorbed and biodegraded within microbial cells. The initial breakdown of a polymer can result from a variety of physical and biological forces (Swift, 1997). Physical forces, such as heating/cooling, freezing/thawing, or wetting/drying, can cause mechanical damage such as the cracking of polymeric materials (Kamal and Huang, 1992). The growth of many fungi can also cause small-scale swelling and bursting, as the fungi penetrate the polymer solids (Griffin, 1980). Synthetic polymers, such as poly(caprolactone) (Toncheva et al., 1996; Jun et al., 1994), are also depolymerized by microbial enzymes, after which the monomers are absorbed into microbial cells and biodegraded (Goldberg, 1995). Abiotic hydrolysis is the most important reaction for initiating the environmental degradation of synthetic polymers (Göpferich, 1997) like polycarboxylates (Winursito and Matsumura, 1996), poly(ethylene terephthalate) (Heidary and Gordon, 1994), polylactic acids and their copolymers (Hiltunen et al., 1997; Nakayama et al., 1996), poly(α -glutamic acids) (Fan et al., 1996), and polydimethylsiloxanes, or silicones (Lehmann et al., 1995; Xu et al., 1998).

Generally, an increase in molecular weight results in a decline of polymer degradability by microorganisms. In contrast, monomers, dimers, and oligomers of a polymer's repeating units are much easily degraded and mineralized. High molecular weights result in a sharp decrease in solubility making them unfavorable for microbial attack because bacteria require the substrate to be assimilated through the cellular membrane and then further degraded by cellular enzymes. At least two categories of enzymes are actively involved in biological degradation of polymers: extracellular and intracellular depolymerases (Doi, 1990; Gu et al., 2000b). During degradation, exoenzymes from microorganisms break down complex polymers yielding smaller molecules of short chains,

e.g., oligomers, dimers, and monomers, that are smaller enough to pass the semi-permeable outer bacterial membranes, and then to be utilized as carbon and energy sources. The process is called depolymerization. When the end products are CO_2 , H_2O , or CH_4 , the degradation is called mineralization (Frazer, 1994; Hamilton et al., 1995). It is important to note that biodeterioration and degradation of polymer substrate can rarely reach 100% and the reason is that a small portion of the polymer will be incorporated into microbial biomass, humus and other natural products (Atlas and Bartha, 1997; Narayan, 1993). Dominant groups of microorganisms and the degradative pathways associated with polymer degradation are often determined by the environmental conditions. When O_2 is available, aerobic microorganisms are mostly responsible for destruction of complex materials, with microbial biomass, CO_2 , and H_2O as the final products. In contrast, under anoxic conditions, anaerobic consortia of microorganisms are responsible for polymer deterioration. The primary products will be microbial biomass, CO_2 , CH_4 and H_2O under methanogenic (anaerobic) conditions (Barlaz et al., 1989) (e.g. landfills/compost) (Fig. 3).

The list of different microorganisms degrading different groups of plastics is given in Table 4.

4. Standard testing methods

4.1. Visual observations

The evaluation of visible changes in plastics can be performed in almost all tests. Effects used to describe degradation include roughening of the surface, formation of holes or cracks, de-fragmentation, changes in color, or formation of bio-films on the surface. These changes do not prove the presence of a biodegradation process in terms of metabolism, but the parameter of visual changes can be used as

a first indication of any microbial attack. To obtain information about the degradation mechanism, more sophisticated observations can be made using either scanning electron microscopy (SEM) or atomic force microscopy (AFM) (Ikada, 1999). After an initial degradation, crystalline spherulites appear on the surface; that can be explained by a preferential degradation of the amorphous polymer fraction, etching the slower-degrading crystalline parts out of the material. In another investigation, (Kikkawa et al., 2002) used AFM micrographs of enzymatically degraded PHB films to investigate the mechanism of surface erosion. A number of other techniques can also be used to assess the biodegradability of polymeric material. These include; Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD), contact angle measurements and water uptake. Use of these techniques is generally beyond the scope of this review, although some are mentioned in the text.

4.2. Weight loss measurements: determination of residual polymer

The mass loss of test specimens such as films or test bars is widely applied in degradation tests (especially in field- and simulation tests), although again no direct proof of biodegradation is obtained. Problems can arise with correct cleaning of the specimen, or if the material disintegrates excessively. In the latter case, the samples can be placed into small nets to facilitate recovery; this method is used in the full-scale composting procedure of DIN V 54900. A sieving analysis of the matrix surrounding the plastic samples allows a better quantitative determination of the disintegration characteristics. For finely distributed polymer samples (e.g., powders), the decrease in residual polymer can be determined by an adequate separation

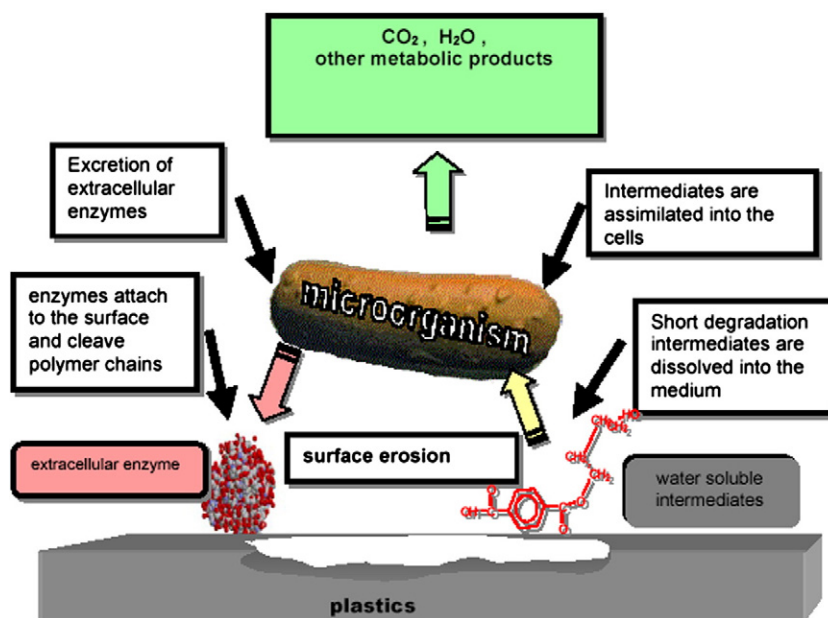


Fig. 3. General mechanism of plastic biodegradation under aerobic conditions (Mueller, 2003).

Table 4
List of different microorganisms reported to degrade different types of plastics

Synthetic Plastics		
Plastic	Microorganism	Reference
Polyethylene	<i>Brevibacillus borstelensis</i> <i>Rhodococcus rubber</i>	Hadad et al. (2005) Sivan et al. (2006); Gilan et al., 2004
Polyurethane	<i>Penicillium simplicissimum</i> YK <i>Comamonas acidovorans</i> TB-35 <i>Curvularia senegalensis</i> <i>Fusarium solani</i> <i>Aureobasidium pullulans</i> <i>Cladosporium</i> sp.	Yamada-Onodera et al., 2001 Akutsu et al., 1998 Howard (2002)
Polyvinyl chloride	<i>Pseudomonas chlororaphis</i> <i>Pseudomonas putida</i> AJ <i>Ochrobactrum</i> TD <i>Pseudomonas fluorescens</i> B-22 <i>Aspergillus niger</i> van Tieghem F-1119	Zheng et al. (2005) Anthony et al. (2004) Mogil'nitskii et al. (1987)
Plasticized Polyvinyl chloride	<i>Aureobasidium pullulans</i>	Webb et al. (2000)
BTA-copolyester	<i>Thermomonaspora fusca</i>	Kleeberg et al. (1998)
Natural plastics		
Poly(3-hydroxybutyrate-co-3- mercaptopropionate)	<i>Schlegelella thermodepolymerans</i>	Elbanna et al. (2004)
Poly(3-hydroxybutyrate)	<i>Pseudomonas lemoignei</i>	Jendrosseck et al. (1995)
Poly(3-hydroxybutyrate-co-3-mercaptopropionate)	<i>Pseudomonas indica</i> K2	Elbanna et al. (2004)
Poly(3-hydroxybutyrate) Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	<i>Streptomyces</i> sp. SNG9	Mabrouk and Sabry (2001)
Poly(3-hydroxybutyrate-co-3-hydroxypropionate)	<i>Ralstonia pikettii</i> T1	
Poly(3-hydroxybutyrate-co-3-hydroxypropionate)	<i>Acidovorax</i> sp. TP4	Wang et al. (2002)
Poly(3-hydroxybutyrate) poly(3-hydroxypropionate) poly(4-hydroxybutyrate) poly(ethylene succinate) poly(ethylene adipate)	<i>Alcaligenes faecalis</i> <i>Pseudomonas stutzeri</i> <i>Comamonas acidovorans</i>	Kasuya et al. (1999)
Poly(3-hydroxybutyrate)	<i>Alcaligenes faecalis</i>	Kita et al. (1997)
Poly(3-hydroxybutyrate)	<i>Schlegelella thermodepolymerans Caenibacterium thermophilum</i>	Romen et al. (2004)
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	<i>Clostridium botulinum</i> <i>Clostridium acetobutylicum</i>	Abou-Zeid et al. (2001)
Polycaprolactone	<i>Clostridium botulinum</i> <i>Clostridium acetobutylicum</i>	Abou-Zeid et al. (2001)
Polycaprolactone	<i>Fusarium solani</i>	Benedict et al., 1983
Poly(lactic acid)	<i>Fusarium moniliforme</i> <i>Penicillium roquefort</i> <i>Amycolatopsis</i> sp. <i>Bacillus brevis</i> <i>Rhizopus delemere</i>	Torres et al., 1996 Pranamuda et al., 1997; Pranamuda and Tokiwa, 1999 Tomita et al., 1999 Fukuzaki et al., 1989
Polymer blends		
Starch/polyethylene	<i>Aspergillus niger</i> <i>Penicillium funiculosm</i> <i>Phanerochaete chrysosporium</i>	Lee et al., 1991
Starch/polyester	<i>Streptomyces</i> <i>Phanerochaete chrysosporium</i>	Lee et al., 1991

or extraction technique (polymer separated from biomass, or polymer extracted from soil or compost). By combining a structural analysis of the residual material and the low molecular weight intermediates, detailed information regarding the degradation process can be obtained, especially if a defined synthetic test medium is used (Witt et al., 2001).

4.3. Changes in mechanical properties and molar mass

As with visual observations, changes in material properties cannot be proved directly due to metabolism of the polymer material. However, changes in mechanical properties are often used when only minor changes in the mass of the test specimen

are observed. Properties such as tensile strength are very sensitive to changes in the molar mass of polymers, which is also often taken directly as an indicator of degradation (Erlandsson et al., 1997). Whilst, for an enzyme-induced depolymerization the material properties only change if a significant loss of mass is observed (the specimen become thinner because of the surface erosion process; the inner part of the material is not affected by the degradation process), for abiotic degradation processes (which often take place in the entire material and include the hydrolysis of polyesters or oxidation of polyethylenes) the mechanical properties may change significantly, though almost no loss of mass due to solubilization of degradation intermediates occur at this stage. As a consequence, this type of measurement is often used for materials where abiotic processes are responsible for the first degradation step (Breslin, 1993; Tsuji and Suzuyoshi, 2002).

4.4. CO₂ evolution/O₂ consumption

Under aerobic conditions, microbes use oxygen to oxidize carbon and form carbon dioxide as one of the major metabolic end product. Consequently, the consumption of oxygen (respirometric test) (Hoffmann et al., 1997) or the formation of carbon dioxide (Sturm test) are good indicators for polymer degradation, and are the most often used methods to measure biodegradation in laboratory tests. Due to the normally low amount of other carbon sources present in addition to the polymer itself when using synthetic mineral media, only a relatively low background respiration must be identified, and the accuracy of the tests is usually good. In particular, the type of analytical methods, especially for the determination of CO₂ have been modified. Besides conventional trapping of CO₂ in Ba(OH)₂ solution, followed by manual titration, infrared and paramagnetic O₂ detectors can also be used to monitor O₂ and CO₂ concentrations in the air stream. Although, the automated and continuous measurements have advantages, they also have disadvantages. For example, the exact air flow must be measured, the signals of the detectors must be stable for long periods of time and, if slow degradation processes are to be determined, the CO₂ concentration or fall in O₂ concentration to be detected is very small, thereby, increasing the likelihood of systematic errors. Under these circumstances, other concepts (e.g., trapping CO₂ in a basic solution, $\pm$ pH 11.5) with continuous titration or detection of the dissolved inorganic carbon (Pagga et al., 2001) may be useful alternatives. Other attempts to overcome problems with CO₂ detection are based on non-continuously aerated, closed systems. Here, either a sampling technique in combination with an infrared-gas analyzer (Calmon et al., 2000) or a titration system (Mueller, 1999) was applied. Another closed system with a discontinuous titration method has been described by (Solaro et al., 1998). Tests using small closed bottles as degradation reactors and analyzing the CO₂ in the headspace (Itavaara and Vikman, 1995) or by the decrease in dissolved oxygen (closed-bottle test) (Richterich et al., 1998) are simple and relatively insensitive to leakages, but may cause problems due to the low amounts of material and inoculums used.

Although used originally in aqueous test systems for polymer degradation, CO₂ analysis was also adapted for tests

in solid matrices such as compost (Pagga, 1998), and this method has now been standardized under the name, controlled composting test (ASTM, 1998; DIN, 1998; ISO 14855, 1999; JIS, 2000). For polymer degradation in soil, CO₂ detection proved to be more complicated than in compost because of slower degradation rates that led not only to long test durations (up to 2 years) but also low CO₂ evolution as compared to that from the carbon present in soil. One means of overcoming problems with background CO₂ evolution from the natural matrices compost or soil is to use an inert, carbon-free and porous matrix, wetted with a synthetic medium and inoculated with a mixed microbial population. This method proved practicable for simulating compost conditions (degradation at $\sim$ 60 °C) (Bellina et al., 2000), but has not yet been optimized for soil conditions.

4.5. Radiolabeling

In contrast to residue analysis, net CO₂ and ¹⁴CO₂ evolution measurements are simple, non-destructive and measure ultimate biodegradation. If appropriately ¹⁴C labelled test material is available, the measurements and their interpretations are relatively straightforward. Materials containing a randomly distributed ¹⁴C marker can be exposed to selected microbial environments. The amount of ¹⁴C carbon dioxide evolved is estimated using a scintillation counter. This method is not subject to interference by biodegradable impurities or additives in the polymer. Biodegradability investigations using this technique for polymeric materials in different microbial environments show a high degree of precision and consistency (Sharabi and Bartha, 1993). However, labeled materials are expensive and not always available. The licensing and the waste disposal problems connected with radioactive work may also be a drawback.

4.6. Clear-zone formation

A very simple semi-quantitative method is the so-called clear-zone test. This is an agar plate test in which the polymer is dispersed as very fine particles within the synthetic medium agar; this results in the agar having an opaque appearance. After inoculation with microorganisms, the formation of a clear halo around the colony indicates that the organisms are at least able to depolymerize the polymer, which is the first step of biodegradation. This method is usually applied to screen organisms that can degrade a certain polymer (Nishida and Tokiwa, 1993; Abou-Zeid, 2001), but it can also be used to obtain semi-quantitative results by analyzing the growth of clear zones (Augusta et al., 1993).

4.7. Enzymatic degradation

The enzymatic degradation of polymers by hydrolysis is a two-step process: first, the enzyme binds to the polymer substrate then subsequently catalyzes a hydrolytic cleavage. PHB can be degraded either by the action of intracellular and extracellular depolymerases in PHB-degrading bacteria and fungi. Intracellular

degradation is the hydrolysis of an endogenous carbon reservoir by the accumulating bacteria themselves while extracellular degradation is the utilization of an exogenous carbon source not necessarily by the accumulating microorganisms (Tokiwa and Calabia 2004). During degradation, extracellular enzymes from microorganisms break down complex polymers yielding short chains or smaller molecules, e.g., oligomers, dimers, and monomers, that are smaller enough to pass the semi-permeable outer bacterial membranes. The process is called depolymerization. These short chain length molecules are then mineralized into end products e.g. CO₂, H₂O, or CH₄, the degradation is called mineralization, which are utilized as carbon and energy source (Gu, 2003).

4.8. Controlled composting test

The treatment of solid waste in controlled composting facilities or anaerobic digesters is a valuable method for treating and recycling organic waste material (Biological Waste Management Symposium, 1995; OECD, 1994). Composting of biodegradable packaging and biodegradable plastics is a form of recovery of waste which can cut the increasing need of new landfilling sites. Only compostable materials can be recycled through biological treatment, since materials not compatible with composting could decrease the compost quality and impair its commercial value. The environmental conditions of the composting test are the following: high temperature (58 °C); aerobic conditions; proper water content (about 50%). Mature compost is used as a solid matrix, as a source of thermophilic microorganisms (inoculum), and as a source of nutrients. The test method is based on the determination of the net CO₂ evolution, i.e. the CO₂ evolved from the mixture of polymer-compost minus the CO₂ evolved from the unamended compost (blank) tested in a different reactor (Bellina et al., 1999). A very important requisite is that the packaging material under study must not release, during degradation, toxic compounds into the compost which could hinder plants, animals, and human beings by entering the food chain (Tosin et al., 1998).

5. Biodegradation of natural plastics

5.1. Biodegradation of polyhydroxyalkanoates

Microorganisms that produce and store PHA under nutrient limited conditions may degrade and metabolize it when the limitation is removed (Williams and Peoples, 1996). However, the ability to store PHA does not necessarily guarantee the ability to degrade it in the environment (Gilmore et al., 1990). Individual polymers are much too large to be transported directly across the bacterial cell wall. Therefore, bacteria must have evolved extracellular hydrolases capable of converting the polymers into corresponding hydroxyl acid monomers (Gilmore et al., 1990). The product of PHB hydrolysis is R-3-hydroxybutyric acid (Doi et al., 1992), while extracellular degradation of PHBV yields both 3-hydroxybutyrate and 3-hydroxyvalerate (Luzier, 1992). The monomers are water soluble but small enough to passively diffuse through the cell

wall, where they are metabolized by β -oxidation and tricarboxylic acid cycle (TCA) to produce carbon dioxide and water under aerobic conditions (Scott, 1999). Under anaerobic conditions, methane is also produced (Luzier, 1992). In general, no harmful intermediates or by-products are generated during PHA degradation. In fact, 3-hydroxybutyrate is found in all higher animals as blood plasma (Lee, 1996). For this reason, PHAs have been considered for medical applications, including long-term controlled drug release, surgical pins, sutures, and bone and blood vessel replacement.

A number of aerobic and anaerobic microorganisms that degrade PHA, particularly bacteria and fungi, have been isolated from various environments (Lee, 1996). *Acidovorax faecilis*, *Aspergillus fumigatus*, *Comamonas* sp., *Pseudomonas lemoignei* and *Variovorax paradoxus* are among those found in soil, while in activated sludge *Alcaligenes faecalis* and *Pseudomonas* have been isolated. *Comamonas testosteroni* has been found in seawater, *Ilyobacter delafieldii* is present in the anaerobic sludge. PHA degradation by *Pseudomonas stutzeri* in lake water has also been observed. Because a microbial environment is required for degradation, PHA is not affected by moisture alone and is indefinitely stable in air (Luzier, 1992). PHAs have attracted industrial attention for use in the production of biodegradable and biocompatible thermoplastics (Takaku et al., 2006). Poly (3-hydroxybutyrate) (PHB) and Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) degrading organisms were isolated from sewage sludge and evaluated their efficiency to degrade PHB and PHBV in solid-plate assay. In our study we have isolated a *Streptomyces* strain, identified as *Streptovorticillium kashmeriense* AF1, capable of degrading PHB and PHBV, and a bacterial strain *Bacillus megaterium* AF3, capable of degrading PHBV, from the soil mixed with active sewage sludge on the basis of producing clear zones of hydrolysis on PHB and PHBV containing mineral salt agar plates (Shah et al., 2007; Shah, 2007).

The microbial degradation rate of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) films in soil appeared to be dependent on the microbial population and distribution, and the degradation ability of the PHBV-degrading microorganisms colonizing the surface of incubated PHBV films (Sang et al., 2000). In one of our studies, the scanning electron micrographs of the PHBV film buried in soil mixed with sewage sludge for 120 days showed clear evidences of degradation with pits, surface roughening, grooves, cavities and disintegration (Fig. 4). Later on *S. kashmirensis* AF1 was recovered from the surface of PHBV film (Shah, 2007). Sang et al. (2002) also reported various traces, cavities, and grooves as observed on the dented surface of PHBV films demonstrating that the degradation was a concerted effect of a microbial consortium colonizing the film surface, including fungi, bacteria, and actinomycetes. Numerous irregular erosion pits have also been observed by Molitoris et al. (1996) on the surface of poly polyhydroxyalkanoate by *Comamonas* sp.

Sturm test has been used by many researchers to study the biodegradation of biodegradable polymers (Whitchurch and Terence, 2006), the aliphatic and aromatic compounds (Kim et al., 2001). We have gravimetrically calculated CO₂ evolved

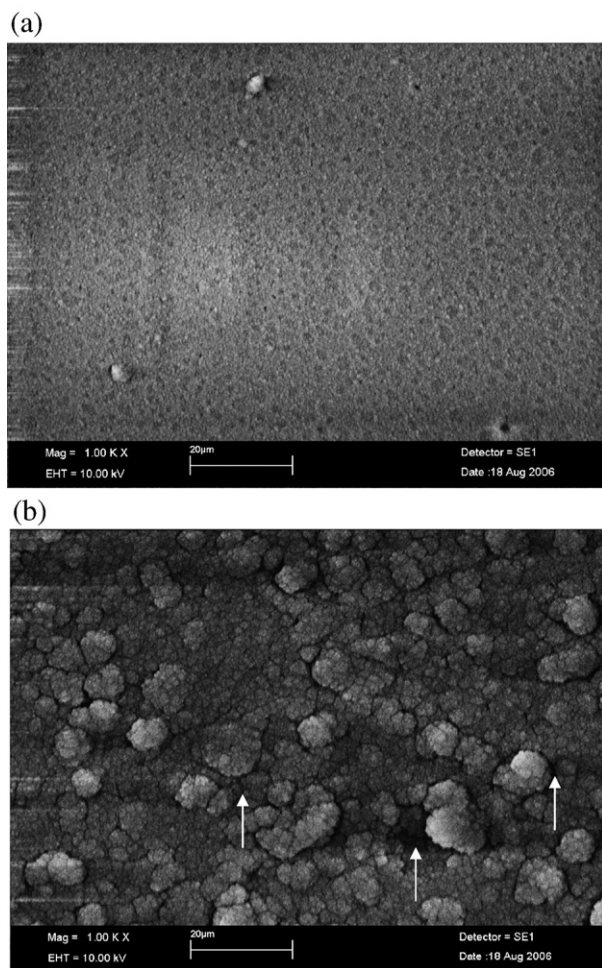


Fig. 4. Scanning Electron Micrograph of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) film (a) Before soil burial; (b) After soil burial for 120 days.

as a result of PHB and PHBV biodegradation by *S. kashmirensis* AF1 and *B. megaterium* AF3, through Sturm Test. The results showed that in all the cases the amount of CO₂ evolved in test was more than in control.

5.2. Enzymatic degradation of polyhydroxalkanoates

At least two categories of enzymes are actively involved in biological degradation of polymer: extracellular and intracellular depolymerases (Doi, 1990; Gu et al., 2000b). Extracellular PHB depolymerases are secreted from various microorganisms and play an important role in the metabolism of PHB in the environment. Several PHB depolymerases have been isolated and purified from various microorganisms belonging to the *Alcaligenes* (Bachmann and Seebach, 1999), *Comamonas* (Jendrossek et al., 1993; Kasuya et al., 1994) and *Pseudomonas* species (Nakayama et al., 1985; Mukai et al., 1994; Schober et al., 2000). This shows that extracellular PHB depolymerases are ubiquitous in the environment. Analysis of their primary structures revealed that the enzymes are composed of substrate-binding domain, catalytic domain, and a linker region connecting the two domains. The substrate-binding domain plays a role in binding to the solid PHB. The catalytic domain contains the catalytic

machinery composed of a catalytic triad (Ser-His-Asp). The serine is part of a lipase box pentapeptide Gly-X-Ser-X-Gly, which has been found in all known hydrolases such as lipases, esterases and serine proteases (Jaeger et al., 1994). The properties of PHB depolymerases have been studied extensively and share several biochemical properties such as: relatively small molecular weight, below 100 kDa and most PHA depolymerases are between 40 and 50 kDa; do not bind to anion exchangers such as DEAE but have strong affinity to hydrophobic materials such as butyl-Toyopel and phenyl-Toyopel; optimum pH is between 7.5–9.8, only the depolymerase of *Pseudomonas picketti* and *Penicillium funiculosum* have pH optima between 5.5 and 7; highly stable at a wide range of pH, temperature, ionic strength, etc; most PHA depolymerases are inhibited by serine esterase inhibitors such as diisopropyl-fluorophosphate or acylsulfonamide compounds, which have been shown to bind covalently to the active site serine of serine hydrolases (Jendrossek, 1998). In our study we have isolated a PHBV depolymerase from *Bacillus* sp. AF3, with molecular size 37 kDa, at pH 7 and temperature 37 °C (Shah et al., 2007).

Apparently, most PHA-degrading bacteria that have been analyzed produce only one PHA depolymerase. *P. lemoignei*, one of the best-studied PHA-degrading bacteria, however, produces at least seven different extracellular PHA-depolymerases which differ slightly in their biochemical properties. The three PHA-depolymerases (PHB depolymerases A, B and D) are specific for PHB and P(3HB-co-3HV) with a low 3-HV content. The other two PHA depolymerases (PHB depolymerase C and poly(D-3-hydroxyvalerate) depolymerase) also degrade both PHB and PHV (Jendrossek and Handrick, 2002). A strain of *A. faecalis* T1, isolated from activated sludge, excreted D-3-hydroxybutyrate oligomer hydrolase and an extracellular PHB depolymerase (Shirakura et al., 1983). We have isolated two different types of PHB and PHBV depolymerases from *S. kashmirensis* AF1, having molecular sizes 35–37 and 45 kDa (Shah, 2007).

In 1990 the British-based company Imperial Chemical Industries (ICI) released a material called Biopol. Biopol is made from PHBV. When thrown away, this material is broken down by the microorganisms present in waste and decomposed completely within a couple of months. Other versions of biodegradable plastics have been developed in the United States. In 1991 Procter and Gamble, Du Pont, and Exxon funded bacteria-based plastic research at the University of Massachusetts at Amherst. In addition, Battelle, a private research company, produced a completely biodegradable plastic from vegetable oils. Plastics can be made from other glucose-intensive materials such as potato scraps, corn, molasses, and beets (Kings et al., 1992; Sharpley and Kaplan, 1976).

By 1997, compostable bags still sold for more than non-degradable bags. One synthetic polymer used in biodegradable plastic bags was aliphatic polyester called polycaprolactone, marketed by Union Carbide. Another biodegradable plastic film called MaterBi contained corn starch and other proprietary ingredients. Corn was also used to make polylactic acid for Cargill's EcoPLA biopolymer. University of Michigan worked on a material called Envar consisting of an alloy of caprolactone

and a thermoplastic starch. One research group at the University of Utah at Salt Lake City in 1997, for instance, synthesized an injectable polymer that forms a non-toxic biodegradable hydrogel that acts as a sustained release matrix for drugs (Kings et al., 1992; Sharpley and Kaplan, 1976).

6. Biodegradation of synthetic plastics

The degradation of most synthetic plastics in nature is a very slow process that involves environmental factors, followed by the action of wild microorganisms (Albertsson, 1980; Cruz-Pinto et al., 1994; Albertsson et al., 1994). The primary mechanism for the biodegradation of high molecular weight polymer is the oxidation or hydrolysis by enzyme to create functional groups that improves its hydrophilicity. Consequently, the main chains of polymer are degraded resulting in polymer of low molecular weight and feeble mechanical properties, thus, making it more accessible for further microbial assimilation (Albertsson and Karlsson, 1990; Albertsson et al., 1987; Huang et al., 1990). Examples of synthetic polymers that biodegrade include poly(vinyl alcohol), poly(lactic acid), aliphatic polyesters, polycaprolactone, and polyamides. Several oligomeric structures which biodegrade are known: oligomeric ethylene, styrene, isoprene, butadiene, acrylonitrile, and acrylate. Physical properties such as crystallinity, orientation and morphological properties such as surface area, affect the rate of degradation (Huang et al., 1992).

6.1. Biodegradation of thermoplastic polyolefins

6.1.1. Polyethylene

Synthetic polyolefins are inert materials whose backbones consist of only long carbon chains. The characteristic structure makes polyolefins non-susceptible to degradation by microorganisms. However, a comprehensive study of polyolefin biodegradation has shown that some microorganisms could utilize polyolefins with low molecular weight (Yamada-Onodera et al., 2001). The biodegradation always follows photodegradation and chemical degradation.

Polyethylene is one of the synthetic polymers of high hydrophobic level and high molecular weight. In natural form, it is not biodegradable. Thus, their use in the production of disposal or packing materials causes dangerous environmental problems (Kwpp and Jewell, 1992). To make PE biodegradable requires modifying its crystalline level, molecular weight and mechanical properties that are responsible for PE resistance towards degradation (Albertsson et al., 1994). This can be achieved by improving PE hydrophilic level and/or reducing its polymer chain length by oxidation to be accessible for microbial degradation (Bikiaris et al., 1999).

The degradation of polyethylene can occur by different molecular mechanisms; chemical, thermal, photo and biodegradation. Some studies (Lee et al., 1991; Glass and Swift, 1989; Imam et al., 1992; Gu, 2003) have assessed the biodegradability of some of these new films by measuring changes in physical properties or by observation of microbial growth after exposure to biological or enzymatic environments, but mostly by CO₂ evolution.

Since polyethylene (PE) is widely used as packaging material, considerable work not only on biodegradable polyethylene but also on biodegradation of polyethylene has been conducted (Bonhomme et al., 2003; Wang et al., 2004). The results of these studies indicated that polyethylene was biodegraded following photodegradation and/or chemical degradation.

Biodegradation of polyethylene is known to occur by two mechanisms: hydro-biodegradation and oxo-biodegradation (Bonhomme et al., 2003). These two mechanisms agree with the modifications due to the two additives, starch and pro-oxidant, used in the synthesis of biodegradable polyethylene. Starch blend polyethylene has a continuous starch phase that makes the material hydrophilic and therefore, catalyzed by amylase enzymes. Microorganisms can easily access, attack and remove this part. Thus the hydrophilic polyethylene with matrix continues to be hydro-biodegraded. In case of pro-oxidant additive, biodegradation occur following photodegradation and chemical degradation. If the pro-oxidant is a metal combination, after transition, metal catalyzed thermal peroxidation, biodegradation of low molecular weight oxidation products occurs sequentially (Bonhomme et al., 2003; El-Shafei et al., 1998; Yamada-Onodera et al., 2001). El-Shafei et al. (1998) investigated the ability of fungi and *Streptomyces* strains to attack degradable polyethylene consisting of disposed polyethylene bags containing 6% starch. He has isolated 8 different strains of *Streptomyces* and two fungi *Mucor rouxii* NRRL 1835 and *Aspergillus flavus*. In a study, Low density polyethylene pieces buried in soil mixed with sewage sludge were examined microscopically after 10 months, fungal attachment was found on the surface of the plastic, indicating possible utilization of plastic as a source of nutrient (Shah, 2007). The isolated fungal strains were identified as *Fusarium* sp. AF4, *Aspergillus terreus* AF5 and *Penicillium* sp. AF6. The ability of the fungal strains to form a biofilm on polyethylene was attributed to the gradual decrease in hydrophobicity of its surface (Gilan et al., 2004).

The structural changes in the form of pits and erosions observed through scanning electron microscopy indicated surface damage of PE incubated with *Fusarium* sp. AF4. That suggested that the fungal strains, especially *Fusarium* sp. AF4, was able to adhere to the surface of LDPE and can cause surface damage (Shah, 2007). In a study by Bonhomme et al. (2003), SEM evidence confirmed that microorganisms (fungi) build up on the surface of the polymer (polyethylene) and after removal of the microorganisms, the surface became physically pitted and eroded. The surface of the polymer after biological attack was physically weak and readily disintegrates under mild pressure. Otake et al. (1995) reported the changes like whitening of the degraded area and small holes on the surface of PE film after soil burial for 32 years. Biodegradation of LDPE film was also reported as 0.2% weight loss in 10 years (Albertsson, 1980). Ohtaki et al. (1998) tested LDPE bottles exposed in aerobic soil for over 30 years, and observed some evidences of biodegradation using SEM of the degraded parts and as reduction in molecular weight by Time of Flight Mass Spectrometry (TOF-MS).

Yamada-Onodera et al. (2001) isolated a strain of fungus *Penicillium simplicissimum* YK to biodegrade polyethylene

without additives. UV light or oxidizing agents, such as UV sensitizer, were used at the beginning of the process to activate an inert material, polyethylene. Polyethylene was also treated with nitric acid at 80 °C for 6 days before cultivation with inserted functional groups that were susceptible to microorganisms. Bonhomme et al. (2003) has reported that with the fungal activity, polyethylene with a starting molecular weight in the range of 4000 to 28,000 was degraded to units with a lower molecular weight of 500 after three months of liquid cultivation, which indicated the biodegradation of that polyethylene. In a similar study the Polyethylene pieces were treated by exposing it to UV light and also nitric acid. That pretreated polymer was then applied to microbial treatment using *Fusarium* sp. AF4 in a mineral salt medium containing treated plastic as a sole source of carbon and energy. An increase in the growth of fungus and some structural changes as observed by FTIR, were observed in case of treated PE which according to Jacinto indicated the break down of polymer chain and presence of oxidation products of PE. Non-degraded polyethylene exhibits almost zero absorbancy at those wave numbers (<http://www.dasma.dlsu.edu.ph/offices/ufro/sinag/Jacinto.htm>). Absorbance at 1710–1715 cm^{-1} (corresponding to carbonyl compound), 1640 cm^{-1} and 830–880 cm^{-1} (corresponding to $\text{C}=\text{C}$), which appeared after UV and nitric acid treatment, decreased during cultivation with microbial consortia (Hasan et al., 2007). Typical degradation of PE and formation of bands at 1620–1640 cm^{-1} and 840–880 cm^{-1} was also reported by Yamada-Onodera et al. (2001), attributed to oxidation of polyethylene. Overall, polyethylene degradation is a combined photo- and bio-degradation process. First, either by abiotic oxidation (UV light exposure) or heat treatment, essential abiotic precursors are obtained. Secondly, selected thermophilic microorganisms degrade the low molar mass oxidation products to complete the biodegradation (Bonhomme et al., 2003).

6.1.2. Polyvinyl chloride

Polyvinyl chloride (PVC) is a strong plastic that resists abrasion and chemicals and has low moisture absorption. Mostly, PVC is used in buildings for pipes and fittings, electrical wire insulation, floor coverings and synthetic leather products. It is also used to make shoe soles, rigid pipes, textiles and garden hoses. There are many studies about thermal and photodegradation of PVC (Braun and Bazdadea, 1986; Owen, 1984) but there only few reports available on biodegradation of PVC. According to Kirbas et al. (1999) PVC having low molecular weight can be exposed to biodegradation by the use of white-rot fungi.

6.1.3. Polystyrene

Polystyrene (PS) is a synthetic plastic used in the production of disposable cups, packaging materials, in laboratory ware, in certain electronic uses. PS is used for its lightweight, stiffness and excellent thermal insulation. When it is degraded by thermal or chemical means it releases products like; styrene, benzene, toluene and acrolein. There are very few reports on the biodegradation of polystyrene but the microbial decomposition of its monomer; styrene, have been reported by few researchers (Tsuchii et al., 1977).

7. Biodegradation of polymer blends

The rate of degradation of polymer blends is initially controlled by the degradation of the more readily biodegradable component. The initial degradation process interferes with the structural integrity of the polymer and increases the surface area considerably for enzyme attack on the less affected area. The exposure of the remaining polymer to microbes and secreted degradative enzymes is then enhanced. Work has been carried out to understand the degradation mechanisms of different polymer blends and their degradation products by microorganisms.

There are several categories of biodegradable starch-based polymers including:

1. Thermoplastic starch products;
2. Starch synthetic aliphatic polyester blends;
3. Starch PBS/PBSA polyester blends; and
4. Starch PVOH blends.

7.1. Starch/polyethylene blends

Polyethylene is reported to be an inert polymer with strong resistance to microbial breakdown (Weiland et al., 1995). Biodegradation is decreased with an increase in molecular size (Tung et al., 1999). Linear paraffin molecules below a molecular size of about 500 Da can be utilised by several microorganisms (Albertsson and Karlsson, 1993). Scott (1990) concluded that microbial attack on polyethylene is a secondary process where an initial oxidation step results in the reduction of molecular size to a size sufficiently small for biodegradation to occur. Addition of readily biodegradable compounds, such as starch, to a low-density polyethylene matrix may enhance the degradation of the carbon–carbon backbone (Griffin, 1977). The biodegradability of starch/polyethylene blends, and chemically modified samples of blends has been investigated (Johnson et al., 1993; Bikiaris et al., 1998). The aerobic and anaerobic biodegradability of starch-filled polymer blends has been evaluated. Carbon removal from a starch polyethylene blend was low compared to pure starch and the rate of removal was higher under aerobic conditions. Similar results were obtained by Chandra and Rustgi (1997) for the biodegradation of maleated linear low-density polyethylene starch blends in a soil environment composed of a mixed fungal inoculum consisting of *Aspergillus niger*, *Penicillium funiculom*, *Chaetomium globosum*, *Gliocladium virens* and *Pullularia pullulans*. Biodegradation of starch polyethylene films containing a pro-oxidant and 6% starch showed evidence of polyethylene degradation in the presence of lignin degrading bacteria of the genus *Streptomyces* and also in the presence of the white-rot fungus *Phanerochaete chrysosporium* (Lee et al., 1991). The rate of degradation of starch-filled polyethylene depended on the starch content, and was very sensitive to the environmental conditions and other ingredients in the formulation (Albertsson and Karlsson, 1993). Oxidation of impurities, such as fats and oils, would seem to be an important trigger for the biodegradation of polyethylene. The production of reactive oxygen species such as peroxides is a likely source of initiators of molecular

breakdown although other radicals may be involved (Cornell et al., 1984).

The degradation of 11 commercially produced degradable starch/polyethylene blended compost bags was evaluated in a municipal yard waste compost site (Johnson et al., 1993) by chemical degradation, photodegradation and biodegradation of each product. The oxygen concentration at the surface of the films appeared to be the rate-limiting component. A pro-oxidant additive (transition metal) was critical in promoting the oxidative degradation of the polyethylene. Several researchers have investigated the use of modified starch in starch/low-density polyethylene blends (Evangelista et al., 1991). The modified starches enhanced the miscibility and adhesion of starch in those blends. However, the poor biodegradability of modified starches leads to a very slow rate of biodegradation compared with unmodified starch/polyethylene blends. Other investigations have been carried out to evaluate the biodegradability of films containing starch, polyethylene and EAA (Shogren et al., 1992). The results indicated that rapid and appreciable starch depletion led to deterioration of the mechanical properties of the films leaving a rather weak matrix which was prone to further physical disruption by biotic and abiotic factors.

7.2. Starch/polyester blends

Blends of starch and Polycaprolactone (PCL) are assumed to be completely biodegradable since each component in the blend is readily biodegradable as well as compostable (Tokiwa et al., 1994; Bastioli, 1994). Biodegradability of different grades of the commercial polyester Bionolle™ has been studied in activated sludge, soils and compost (Nishioka et al., 1994). Bionolle™ 3000 was degraded more easily than Bionolle™ 1000 and Bionolle™ 6000. Moulds did not degrade Bionolle™ 6000 and some Gram-negative bacteria did not degrade Bionolle™ 1000. The degree of degradation mainly depended on the type of microorganism and their population. It is known that poly-(hydroxybutyrate) depolymerases and lipases are both capable of cleaving the ester bonds 4 poly-(hydroxyalkanoate) (Doi et al., 1992). Because of structural similarity, these enzymes are expected to degrade Bionolle™. Biodegradation of Bionolle™ by compost has been studied and shown to be complete (Jayasekara et al., 2005). Furthermore, the products were shown to be non-toxic to the earthworm, *Eisenia fetida*. Blending of Bionolle with low cost starch has been investigated in order to improve its cost competitiveness whilst maintaining other properties at an acceptable level. It has been shown that the addition of starch filler significantly improved the rate of degradation of the Bionolle™ component (Ratto et al., 1999). A study of the biodegradation of cellulose, a poly(-caprolactone) starch blend and an aliphatic–aliphatic copolyester was undertaken in a ring test (Pagga et al., 2001) involving several laboratories using standards like; ISO 14852 (1999), and ISO 14852. According to both criteria (the biological oxygen demand (BOD) and CO₂ released) the cellulose was more degraded than the poly(-caprolactone)-starch blend which in turn was more degraded (on average) than the copolyester.

7.3. Starch/PVA blends

The water-soluble synthetic polymer, polyvinyl alcohol (PVA) has excellent compatibility with starch and blends are expected to have good film properties. Several such blends have been developed and tested for biodegradable packaging applications and appear to have potential for use (Tudorachi et al., 2000). PVA and starch blends are assumed to be biodegradable since both components are biodegradable in various microbial environments. The processing and mechanical properties of starch/PVA blends have been well investigated (Park et al., 1994; Bastioli, 1994; Haschke et al., 1998) but only a limited number of publications are available regarding the biodegradability of such blends. Data on the biodegradability of starch, PVA, glycerol and urea blends by bacteria and fungi isolated from the activated sludge of a municipal sewage plant and landfill indicated that microorganisms consumed starch and the amorphous region of PVA as well as the glycerol and urea plasticisers (Tudorachi et al., 2000). The crystalline region of PVA was unaffected. A biodegradability study of starch, PVA and glycerol blends has also been carried out by Park et al. (1994). ASTM D 5271-92 (1992) was used to evaluate the rate and degree of biodegradation of PVA blends which were reported as biodegradable. In a separate study of PVA and poly-(3-hydroxybutyric acid) blended films, the solubility of the PVA component in water was found to effect the biodegradability of the blend (Ikejima et al., 1999).

7.4. Polylactic acid (PLA) (renewable resource) polyesters

Polylactic acid (PLA) is linear aliphatic polyester produced by poly-condensation of naturally produced lactic acid or by the catalytic ring opening of the lactide group. Lactic acid is produced (via starch fermentation) as a co-product of corn wet milling. The ester linkages in PLA are sensitive to both chemical hydrolysis and enzymatic chain cleavage. PLA is often blended with starch to increase biodegradability and reduce costs. However, the brittleness of the starch-PLA blend is a major drawback in many applications. To remedy this limitation, a number of low molecular weight plasticisers such as glycerol, sorbitol and triethyl citrate are used. A number of companies produce PLA, such as Cargill Dow LLC. PLA produced by Cargill Dow was originally sold under the name EcoPLA, but now is known as NatureWorks PLA, which is actually a family of PLA polymers that can be used alone or blended with other natural-based polymers (Developing Products that Protect the Environment, 2007).

The applications for PLA are thermoformed products such as drink cups, take-away food trays, containers and planter boxes. The material has good rigidity characteristics, allowing it to replace polystyrene and PET in some applications. PLA is fully biodegradable when composted in a large-scale operation with temperatures of 60 °C and above. The first stage of degradation of PLA (two weeks) is via hydrolysis to water-soluble compounds and lactic acid. Rapid metabolism of these products into CO₂, water and biomass by a variety of microorganisms. There have been reports on the degradation

of PLA oligomers (molecular weight ~1000) by *Fusarium moniliforme* and *Penicillium Roquefort* (Torres et al., 1996) and the degradation of PLA by *Amycolatopsis* sp. (Pranamuda et al., 1997; Pranamuda and Tokiwa, 1999) and by *Bacillus brevis* (Tomita et al., 1999). In addition, enzymatic degradation of low molecular weight PLA (molecular weight ~2000) has been shown using esterase-type enzymes such as *Rhizopus delemere* lipase (Fukuzaki et al., 1989). McCarthy (1999) showed that A-PLA presents a soil degradation rate much slower compared to PBSA.

7.5. Polybutylene succinate (PBS) (synthetic aliphatic) polyesters

Polybutylene succinate (PBS) is a biodegradable synthetic aliphatic polyester with similar properties to PET. PBS is generally blended with other compounds, such as starch (TPS) and adipate copolymers (to form PBSA), to make its use economical. PBS has excellent mechanical properties and can be applied to a range of end applications via conventional melt processing techniques. Applications include mulch film, packaging film, bags and ‘flushable’ hygiene products. PBS is hydro-biodegradable and begins to biodegrade via a hydrolysis mechanism. Hydrolysis occurs at the ester linkages and this results in a lowering of the polymer’s molecular weight, allowing for further degradation by microorganisms. Data from SK Chemicals (Korea), a leading manufacturer of PBS polymers, quotes a degradation rate of 1 month for 50% degradation for 40 µm thick film in garden soil.

7.6. Aliphatic–aromatic (AAC) copolyesters

Aliphatic–aromatic (AAC) copolyesters combine the biodegradable properties of aliphatic polyesters with the strength and performance properties of aromatic polyesters. This class of biodegradable plastics is seen by many to be the answer to making fully biodegradable plastics with property profiles similar to those of commodity polymers such as polyethylene. To reduce cost AACs are often blended with TPS. Although AACs have obvious benefits, their market potential may be affected by legislation, such as that in Germany, which distinguishes between biodegradable plastics made from renewable resources and those, like AAC, which use basically the same raw materials as commodity plastics and petrochemicals. Currently in Germany, biodegradable plastics must contain greater than 50% renewable resources to be accepted (Biodegradable Plastics-Developments and Environmental Impacts, 2002).

The two main types of commercial AAC plastics are Ecoflex™ produced by BASF and Eastar Bio™ produced by Eastman. Under each trade name are a number of specific grades. Each grade of polymer has been designed with controlled branching and chain lengthening to match its particular application. AACs come closer than any other biodegradable plastics to equalling the properties of low density polyethylene, especially for blown film extrusion. AACs also can meet all the functional requirements for cling film such as

transparency, flexibility and anti-fogging performance, and therefore this material has great promise for use in commercial food wrap for fruit and vegetables, with the added advantage of being compostable. Whilst being fossil fuel-based, AACs are biodegradable and compostable. AACs fully biodegrade to carbon dioxide, water and biomass. Typically, in an active microbial environment the polymer becomes invisible to the naked eye within 12 weeks (Biodegradable Plastics-Developments and Environmental Impacts, 2002).

7.7. Modified polyethylene terephthalate (PET)

Modified PET (polyethylene terephthalate) is PET which contains co-monomers, such as ether, amide or aliphatic monomers that provide ‘weak’ linkages that are susceptible to biodegradation through hydrolysis. The mechanism involves a combination of hydrolysis of the ester linkages and enzymatic attack on ether and amide bonds. With modified PET it is possible to adjust and control degradation rates by varying the co-monomers used. Depending on the application, up to three aliphatic monomers are incorporated into the PET structure. Typical modified PET materials include PBAT (polybutylene adipate/terephthalate) and PTMAT (polytetramethylene adipate/terephthalate). DuPont have commercialised Biomax™ which is a hydro-biodegradable modified PET polyester. Certain Biomax™ grades also contain degradation promoters to provide tailored combinations of performance properties and degradation rates. The options available for modified PET provide the opportunity to produce polymers which specifically match a range of application physical properties whilst maintaining the ability to adjust the degradation rate by the use of copolyesters.

8. Other degradable polymers

8.1. Ethylene vinyl alcohol (EVOH)

EVOH is another water-soluble synthetic plastic, and is used as an oxygen barrier layer in multilayer film packaging. The high cost of EVOH is a significant barrier to its widespread use in other biodegradable plastics applications.

8.2. Photo-biodegradable plastics

Photodegradable plastics are thermoplastic synthetic polymers into which have been incorporated light-sensitive chemical additives or copolymers for the purposes of weakening the bonds of the polymer in the presence of ultraviolet radiation. Photodegradable plastics are designed to become weak and brittle when exposed to sunlight for prolonged periods. Photosensitisers used include diketones, ferrocene derivatives (aminoalkylferrocene) and carbonyl-containing species. These plastics degrade in a two-stage process, with UV light initially breaking some bonds leaving more brittle lower molecular weight compounds that can further degrade from physical stresses such as wave action or scarification on rocks. The effectiveness is dependent on exposure intensity and will vary with factors such as the season, geography, dirt or water

cover, and shading. A new approach to making photodegradable plastics involves adding catalytic metal salts or chelates to initiate the breakdown process. In photodegradable systems, biodegradation occurs only after an initial photodegradation stage. Degradation of the polymer is triggered by UV light, and assisted by the presence of UV sensitizers in the polymer. The polymer is initially converted to low molecular weight material (i.e. waxes), and then converted to carbon dioxide and water by bacterial action.

Biodegradable polyesters which have been developed commercially and are in commercial development are as follows:

PHA	Polyhydroxyalkanoates	PHB	Polyhydroxybutyrate
PHH	Polyhydroxyhexanoate	PHV	Polyhydroxyvalerate
PLA	Poly(lactic acid)	PCL	Polycaprolactone
PBS	Polybutylene succinate	PBSA	Polybutylene succinate adipate
AAC	Aliphatic–Aromatic copolyesters	PET	Polyethylene terephthalate
PBAT	Polybutylene adipate/terephthalate	PTMAT	Polymethylene adipate/terephthalate

8.3. Biodegradation of thermoset plastics

8.3.1. Polyurethane

Polyurethane (PUR) is commonly utilized as a constituent material in many products including furniture, coating, construction materials, fibers, and paints. Structurally, PUR is the condensation product of polyisocyanate and polyol having intramolecular urethane bonds (carbonate ester bond, —NHCOO—) (Sauders and Frisch, 1964). The urethane bond in PUR has been reported to be susceptible to microbial attack. The hydrolysis of ester bonds in PUR is postulated to be the mechanism of PUR biodegradation. The breakdown products of the biodegradation are derived from polyester segment in PUR when ester bonds are hydrolyzed and cleaved (Nakajima-Kambe et al., 1999).

Three types of PUR degradations have been identified in literature: fungal biodegradation, bacterial biodegradation and degradation by polyurethanase enzymes (Howard, 2002). For example, four species of fungi, *Curvularia senegalensis*, *Fusarium solani*, *Aureobasidium pullulans* and *Cladosporium* sp, were obtained from soil and found to degrade ester-based polyurethane. Kay et al. (1991) isolated and investigated 16 different bacteria with their ability to degrade PUR. In another comprehensive study in Japan, PUR was biodegraded as a sole carbon and nitrogen source by *Comamonas acidovorans* (Nakajima-Kambe et al., 1999; Akutsu et al., 1998). Shah (2007) has reported 5 bacterial strains that were isolated after soil burial of Polyurethane film for 6 months. Those bacteria were identified as *Bacillus* sp. AF8, *Pseudomonas* sp. AF9, *Micrococcus* sp. AF10, *Arthrobacter* sp. AF11 and *Corynebacterium* sp. AF12 (Table 4). The bacterial isolates were listed for polyurethanolytic activity by clear zones formation around the bacterial colonies when Coomassie blue R-250 was added to bacterial cultures in mineral media containing polyurethane. This is a rapid and sensitive screening assay for polyurethanolytic bacteria. The method was used to count the viable

polyurethane degrading bacteria and also to screen and characterize PU degrading enzymes. The detection of polyurethanase in a PU gel is based on the ability of enzymes to depolymerise the substrate. Thus by hydrolyzing the substrate, the interaction of the Coomassie blue with the polyurethane is diminished resulting in a zone of clearing within a blue background (Howard et al., 1999).

FTIR spectroscopy was used to confirm that the mechanism of polyurethane biodegradation was the hydrolysis of the ester bond in polyurethane. Results obtained by Nakajima-Kambe et al. (1995) and Howard et al. (1999) indicated that the polyurethane biodegradation was due to the hydrolysis of ester bonds. The decrease of the ratio of ester bond over ether bond was also approximately 50%, which agreed with the measured amount of polyurethane degraded. In our study the PUR plastic films were buried in soil for about 6 months. FTIR analysis of these PUR films showed a slight decrease in the peak from wavelength 2963 cm^{-1} (control) to 2957 cm^{-1} (test) indicating the cleavage of C–H bonds and formation of C=C at the region of $1400\text{--}1600\text{ cm}^{-1}$. Pettit and Abbott (1975) were also of the opinion that the decomposition of urea units by release of ammonia contributes to the degradation of polyurethane. Sequentially the ester bonds of the urethane groups ($\text{H}_2\text{N-CO-OR}$) at 1715 cm^{-1}

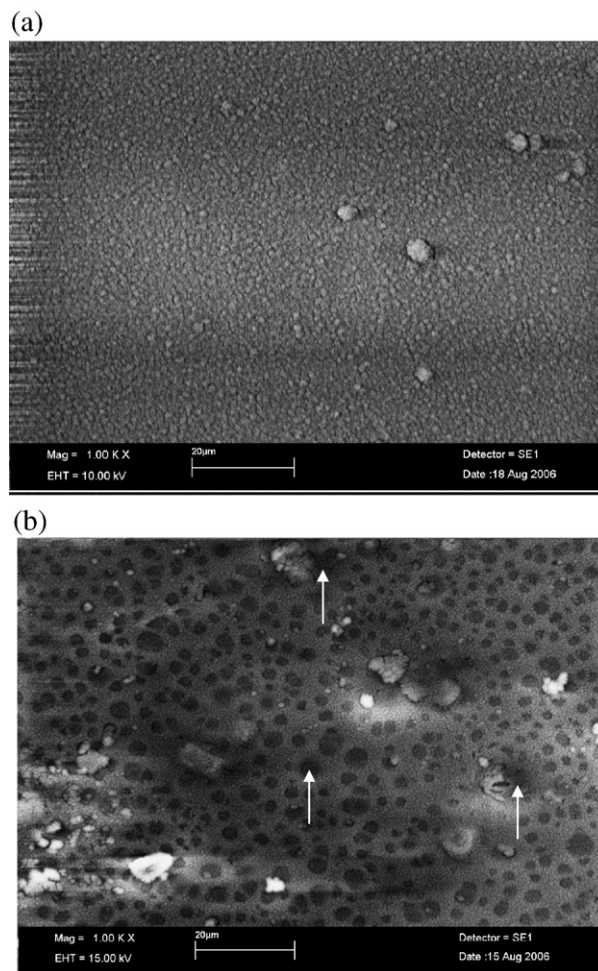


Fig. 5. Scanning Electron Micrographs of Polyurethane film treated with bacterial consortia, (a) Control; (b) Test.

could be broken by the hydrolytic effects of microbial esterases. PUR breakdown products were analyzed by FTIR using *Corynebacterium* sp. and reported that PUR degradation was caused by the hydrolysis of ester bonds (Fig. 5) (Kay et al., 1993).

Two kinds of PUase enzymes were isolated and characterized by Howard et al. (1999), Allen et al. (1999) and Vega et al. (1999). These were shown to be a cell-associated membrane bound PU-esterase and an extracellular PU-esterase. These two enzymes play different roles in polyurethane biodegradation. The membrane bound PU-esterase provides cell-mediated access to the hydrophobic polyurethane surface. Then the extracellular PU-esterase sticks on the surface of the polyurethane. Under these enzymatic actions, bacteria could adhere to the surface of polyurethane and hydrolyze PU substrate to metabolites. The enzyme esterase can hydrolyze polyester chains in PU to diethylene glycol and adipic acid (Akutsu et al., 1998). Results obtained by Nakajima-Kambe et al. (1995) and Howard et al. (1999) indicated that the polyurethane biodegradation was due to the hydrolysis of ester bonds. Pathirana and Seal (1985) reported that some polyester-PUR degrading fungi produce extracellular esterases, proteases or ureases in the presence of PUR. Esterase activity has been determined in the culture supernatant of *Corynebacterium* sp. (Kay et al., 1993) *C. acidovorans* (Nakajima-Kambe et al., 1997) and in fungus like *C. senegalensis* (Crabbe et al., 1994).

Bacteria known to degrade polyester PU also produce PU degrading enzymes such as polyurethanases (Ruiz et al., 1999; Rowe and Howard, 2002). Purified polyurethanase enzymes, PueA and PueB, were used to assay enzyme activity towards polyurethane-rhodamine agar plates, poly(ester-urethane) (PEU) and poly(carbonate-urethane) (PCU). The lipase-catalyzed polymerization of low molecular weight and biodegradable urethanedioles with short chain dialkyl carbonate and alkanedioates produced PCU and PEU, respectively. They were readily degraded in an organic solvent into the repolymerizable cyclic oligomers by lipase as a novel chemical recycling (Degli-Innocenti et al., 1998).

9. Composting

Composting is a managed process that controls the biological decomposition and transformation of biodegradable materials into a humus-like substance called compost. The controlled biooxidation process proceeds through mesophilic and thermophilic phases and results in the production of carbon dioxide, water, minerals and stabilized organic matter (compost or humus). Another benefit of this process is that the heat produced can result in destruction of pathogens that may be present in the waste stream. For most operations, including plastic biodegradation, a combination of sludge and solid waste provides the best operation.

The plastic product or material must disintegrate during composting such that the residual plastic is not readily distinguishable from other organic materials in the finished compost. A plastic material or product is considered to have demonstrated satisfactory disintegration if after lab-scale

composting, no more than 10% of its original dry weight remains after sieving on a 2.0 mm sieve. That is, 90% of the test sample must pass through a 2.0 mm sieve (Degli-Innocenti et al., 1998; Korner et al., 2005).

10. Conclusions

This review has covered the major concerns about the natural and synthetic polymers, their types, uses and degradability. It has looked at the disposal methods and the standards used in assessing polymer degradation. Another area examined has been the developments in the biodegradation of some of the newer polymers, either alone or in blended films.

There are a large number of tests which are used to determine the extent of degradation of polymers either alone or in blended forms. Many are respirometric, determining the amount of carbon dioxide released on exposure to fungi, bacteria, activated sludge (aerobically or anaerobically), compost or soil. Some tests use loss of weight or change in physical properties such as tensile strength and comparison of spectroscopic (FTIR, DSC, NMR, SEM, AFM, XRD) data. It is important to have comparable international standard methods of determining the extent of biodegradation. Unfortunately, the current standards have not, so far, been equated to each other and tend to be used in the countries where they originated [e.g. ASTM (USA), DIN (Germany), JIS (Japan), ISO (international standards), CEN (Europe)]. Many, which are otherwise harmonious, differ in the fine details of the testing. There is an urgent need to standardize all details so that researchers may know that they have all worked to the same parameters. It is clear that most recalcitrant polymers can be degraded to some extent in the appropriate environment at the right concentration. By judicious blending their persistence may be minimised environmentally. Screening of organisms which degrade polymers, or produce enzymes or enzyme systems that degrade polymers, may prove as environmentally profitable in the 21st century, as the screening program for antibiotics in the 1950 s and 1960 s. A screening program for such organisms and enzymes is required but will require more universally uniform standards for assessment of their degradative ability.

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