Research Article

Biodegradation of Plastics – A Brief Review

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ABSTRACT

One of the most persistent pollutants left unchanged in the environment for centuries is plastics. They are resistant to attack by most microorganisms and hence remain non degradable. Their accumulation can be hazardous and can cause various environmental problems. Biodegradation refers to the physical or chemical changes induced in a material by any environmental factor such as light, moisture, heat or wind along with biological agents such as bacteria or fungi. Biodegradation of different types of plastics by different strains of bacteria under various conditions and factors affecting the process have been reviewed in this article. Biodegradation of plastics using non-conventional methods promises a future free of accumulation of commodity plastics used in packaging and commercial polymers, which are the most abundant form of plastic wastes.

Keywords: Biodegradation, plastics, bacteria, breakdown, degradation

INTRODUCTION

The use of plastics has transformed our life in many ways. The usage and production of plastics is ever increasing due to their versatility.

They are lightweight, strong, inexpensive, duration, corrosion resistant and have high thermal and electrical insulation properties. The production of plastic increased from 0.5 million tonnes in 1950 to over 260 million tonnes now.[1]
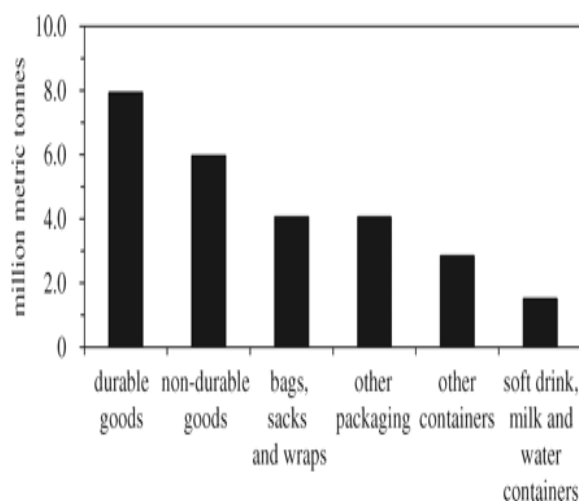
Figure 1: It shows the production of plastic products in the USA in 2005.[2]

One third of the plastic manufactured is used for packing and is therefore rapidly discarded. The discarded plastic gets accumulated in landfills, natural terrestrial habitats or in the ocean.[1]

Rate of accumulation depends on some factors like proximity of shore use, urban settlements, prevailing wind and ocean currents and region.[2]

The accumulation of plastics in terrestrial habitats led to its ingestion by the endangered California condor, *Gymnogyps californianus* and caused a further decline of its population.[1] The plastic debris that gets accumulated in the ocean poses a serious threat to marine flora and fauna. Marine animals get tangled in floating plastic debris which inhibits or limits their movement resulting in their drowning or they simply ingest suspended plastic debris along with their food. Plastic being non-degradable remains undigested and accumulates in their body. It may block digestive tracts, damage stomach linings, or lessen feeding drives.[3] Millimetre-sized marine plastics accumulated in the ocean act as a new pelagic habitat for microorganisms and invertebrates.

Diatoms, coccolithophores, bryozoans, barnacles, dinoflagellate, isopods, marine worms, marine insect eggs, bacteria, cyanobacteria, and fungi were found on its surface.[4]

Recycling of plastics is not always economically possible so it becomes necessary to study the various methods of biodegradation of plastics. Plastic waste might eventually end up in composts along with other biodegradable waste. Studying the biodegradation of plastic in mature composts will help in understanding the eventual fate of such plastic waste.[5]

Plastics can be degraded by chemical, thermal, photo or biological degradation. Any physical (like weight loss of sample, tensile strength) or chemical change (like carbon dioxide production) in the material suggests biological degradation by microorganisms. The degradation of a polymer is affected many factors like temperature, moisture, oxygen, sun light, stress, living organisms and contaminants.[6]

Polyhydroxybutyrate (PHB) and Polyhydroxyvalerate (P(HB-co-HV)) are examples of bioplastics.[7]

Table 1: It shows various polymer degradation routes.[6]

Factors (requirement/activity)	Photo-degradation	Thermooxidative degradation	Biodegradation
Active agent	UV-light or high-energy radiation	Heat and oxygen	Microbial agents
Requirement of heat	Not required	Higher than ambient required temperature	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

Table 2: It shows the different microorganisms reported to degrade different types of plastics.[6]

Plastic	Microorganism
Polyethylene	*Brevibacillus borstelensis Rhodococcus rubber*
	Penicillium simplicissimum YK
	Comamonas acidovorans TB-35
Polyurethane	*Curvularia senegalensis*
	Fusarium solani
	Aureobasidium pullulans
	Cladosporium sp.
Polyvinylchloride	*Pseudomonas chlororaphis Pseudomonas putida* AJ *Ochrobactrum* TD
	Pseudomonas fluorescens B-22
	Aspergillus niger
	van Tieghem F-1119
Plasticized Polyvnyl chloride	*Aureobasidium* pullulans
BTA copolyester	*Thermomonspora*fusca
Naturalplastics	
Poly(3-hydroxybutyrate-co-3- mercaptopropionate)	*Schlegelellather mode polyerans*
Poly(3-hydroxybutyrate)	*Pseudomonas lemoignei*
Poly(3-hydroxybutyrate-co-3-mercaptopropionate)	*Pseudomonas indica* K2
Poly(3-hydroxybutyrate)Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	*Streptomyces sp.* SNG9
Poly(3-hydroxybutyrate-co-3- hydroxypropionate)	*Ralstoniapi ketti i*T1
Poly(3-hydroxybutyrate-co-3-hydroxypropionate)	*Acidovorax sp.* TP4
Poly(3-hydroxybutyrate) poly(3-hydroxypropionate) poly(4-hydroxybutyrate)	*Alcaligenes faecalis*
poly(ethylene succinate) poly(ethylene adipate)	*Pseudomonas stutzeri*
	Comamonas acidovorans
	Alcaligenes faecalis
	Schlegelellatherb mode polymerans Caenibacterium thermophilum
Poly(3-hydroxybutyrate)	*Clostridium botulinum*
Poly(3-hydroxybutyrate)	*Clostridium acetobutylicum*
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	
	Clostridium botulinum
	Clostridium acetobutylicum
Polycaprolactone	
	Fusariumsolani
	Fusariummoniliforme
	Penicilliumroquefort
Polycaprolactone	*Amycolatopsis sp.*
Polylactic acid	*Bacillus brevis*
	Rhizopusdelemer

Polymerblends	
Starch/polyethylene	*Aspergillus niger* *Penicillium funiculosm*
Starch/polyester	*Phanerochaete chrysosporium* *Streptomyces Phanerochaetechyrsosporium*

Different experiments were performed on different types of plastics and polymers; the following information was inferred by the studying the results of the experiments.

Susceptibility of NP, LDPE and HDPE

The degradation of NP (polyethylene films containing 9% of starch and commercial pro-oxidant (autoxidizable fatty acid ester, catalytic agents and transition metals) additives (Nature grad Plus, NP, 0.040 mm)), LDPE (Low Density Poly Ethylene) and HDPE (High Density Poly Ethylene) was compared. The bacterial growth rate was a maximum at 6 weeks, and then it started decreasing. LDPE and HDPE strongly inhibited cell growth. Disintegration of mechanical properties of NP films indicated biological degradation. The media of NP and LDPE became acidic after 3 weeks due to the accumulation of organic acids and gases released due to their biodegradation. The pH of the NP and LDPE media ranged between 3.5 and 4.5 but the pH of the HDPE medium remained between 6.0 and 6.5, unchanged. Maximum carbon dioxide evolution occurred at the lowest pH. Fungi require an acidic pH to grow. Optimal lignolytic activity was observed. This indicates that the NP and LDPE samples were not only degraded by bacteria but were also degraded by fungi.

The susceptibility and resistance of ND, LDPE and HDPE to microbial attack can be determined by the loss of their physical properties. Their decreasing order of susceptibility is: NP>>>LDPE>HDPE. This was inferred from the experimental results that showed the loss of tensile strength of NP, LDPE and HDPE to be 82.76%, 13.04% and 5.33% respectively. The increasing order of resistance to microbial attack is: HDPE>LDPE>>>NP. The resistance to microbial enzymatic attack is caused by the hydrophobicity of polyethylene. The starch present in NP allowed water absorption which in turn facilitated microbial colonisation. The microorganisms caused degradation of starch and esters thus disintegrating NP. The disintegration of NP depends on carbon dioxide production and microbial activity.[8]

Factors affecting Biodegradation of Plastics

The biodegradation of plastics by bacteria and fungi proceeds differently under different soil conditions according to their properties. The different factors that govern biodegradation are type of organism, polymer characteristics and nature of pre-treatment. Polymer characteristics refer to its tacticity, mobility, crystallinity, molecular weight, the type of functional groups and other substituents present in its structure and additives or plasticizers added to the polymer.[9] It was observed that

smaller fragments of plastics were biodegraded faster than bigger ones.[10]

Biological degradability of polymers by microorganisms decreases with increase in the molecular weight of the polymer. With increase in molecular weight, there is decrease in polymer solubility which makes it unfavourable for microbial attack as the polymer needs to be assimilated into the bacterial cell membrane and broken down by cellular enzymes. Repeating units of polymers like monomers, dimers and oligomers are easily degraded and mineralised.[6] Biodegradation is enhanced by abiotic hydrolysis, photo-oxidation and physical disintegration. These processes enhance the surface area of the polymer and reduce its molecular weight; facilitating microbial degradation.[9]

Amorphous regions are more susceptible to microbial degradation than crystalline regains.[11] The presence of a glucose source reduces the rate of biodegradation as glucose is a more preferred carbon source than plastic.[12]

Availability of Oxygen

In the presence of Oxygen, polymers are degraded by aerobic microorganisms with microbial biomass, carbon dioxide and water as end products. But under anoxic or anaerobic conditions, a consortium of anaerobic microorganisms are responsible for the degradation of the polymer with microbial biomass, water, methane and carbon dioxide as the end products (e.g. landfills, compost).

Mechanism of Biodegradation of Plastics

The polymer which is made of many monomers is converted into monomers and then these monomers are mineralised. This is done because the large polymers cannot pass through the cell membrane, so they are first depolymerised to enter into the cell and then they are mineralised or biodegraded inside the cell. This is observed in some synthetics polymers like polycaprolactone.

Initially various physical and biological forces act on the polymer to break it down. The physical forces include heating, cooling, freezing, thawing, wetting, drying and so on; they cause mechanical damage such as cracking of the polymer. The growth of fungi on the polymer can also cause swelling and bursting of the polymer to facilitate the fungi to penetrate into it.

Environmental degradation is initiated in synthetic polymers like poly carboxylates, polyethylene, poly terephthalate, poly lactic acids and their copolymers, poly dimethylsiloxanes, etc by abiotic hydrolysis.

Two types of enzymes are involved in biodegradation of polymers: intracellular and extracellular depolymerases. During degradation the exoenzymes or the extracellular depolymerases from the microorganisms convert the polymers into molecules having shorter chains. These molecules are monomers, dimers or oligomers that are small enough to pass through the semi permeable bacterial cell membrane. These are then utilised by the bacteria as sources of carbon and energy. This process is termed as depolymerisation. The process in which the end products are water, carbon dioxide or methane, is called mineralisation.[6]

Efficiency of Biodegradation

It is important to understand that the process of biodegradation is not 100% efficient, that is, the degradation of the polymer can rarely reach 100%. As observed in several experiments, even though complete degradation of plastics by microorganisms is not possible, there is a reduction in mechanical properties up to 98%.[13] This is due to the incorporation of a small part of the polymer into the microbial biomass, humus or other natural products.[6]

Microorganisms involved in Biodegradation of Plastics

Strains *Rhodococcus rhodochrous* ATCC 29672[14] and *R. rhodochrous* NCIMP 13259 are capable of growing on styrene as a sole carbon and energy source while *R. rhodochrous* stains CTM use 2-methylaniline as sole carbon and energy source.[15] Steroids are also degraded by some strains of *R. Rhodochrous*.[16]

Biodegradation of polyolefins

Synthetic polyolefins are inert and their backbone consists of long carbon chains. Their high hydrophobic nature and high molecular weight prevent their degradation by microorganisms.

However, some microorganisms were capable of breaking down polyolefins of low molecular weight after photodegradation and chemical degradation.

To make polyolefins susceptible to microbial degradation, their chain length and molecular weight must be reduced and their hydrophilic level must be improved by oxidation.

Polyethylene

Polyethylene can be made susceptible to microbial degradation by adding starch and pro oxidant. These are used in making biodegradable polyethylene. The starch improves the hydrophilic nature of polyethylene so that it can be catalysed by amylase enzymes. Microorganisms can easily degrade this part. When pro-oxidant is added to polyethylene, degradation is preceded by photodegradation and chemical degradation.[6]

Biotic and Abiotic hydrolysis

Biodegradation of plastics is preceded by biotic or abiotic degradation to give monomeric or oligomeric products.

Hydrobiodegradable polymers (E.g. polyesters and thermoplastic Starch) are degraded by biotic or abiotic hydrolysis whereas hydrophobic hydrocarbon polymers (E.g. Polyolefins) are resistant to hydrolysis and cannot be biodegraded. They are also resistant to oxidation. But by adding pro-oxidant additives, they can be made oxobiodegradable.

Pro-oxidants that are based on metal combinations capable of yielding two metal ions having similar stability and having oxidation number differing by only one unit are the most active or effective. E.g. Mn^{2+}/Mn^{3+}. The material uses Oxygen from the atmosphere to degrade by a free radical chain reaction. Hydroperoxidases are formed as the primary product; they either thermolyse or photolyse under the catalytic action of a pro-oxidant. This leads to chain scission that produces low molecular mass oxidation products such as carboxylic acids, alcohols, ketones and hydrocarbon waxes.

Peroxidation causes hydrophilic surface modification which favours microorganisms. They can bio-assimilate the low molecular mass oxidation products. Thus pro-oxidants enable thermo-oxidative degradation of Polyethylene. Temperature, the type and amount of additives, partial pressure of Oxygen and the type of polymer affects the rate of degradation. Temperature is the most important factor that affects degradation of Polyethylene. Low partial pressure of Oxygen can drastically slow down the rate of degradation.[17]

Polyvinylchloride (PVC)

PVC is strong and has low moisture absorption. It resists abrasion. PVC can be degraded by chemical and photodegradation but there are very few reports on biodegradation of PVC.

It has many commercial and industrial applications like rigid pipes, shoe soles, garden hoses, textiles, electrical wire insulation, pipes and fittings, synthetic leather products and floor coverings.

Polystyrene

Polystyrene is a synthetic plastic that gives products like styrene, benzene, toluene and acrolein on thermal or chemical degradation. There are very few instances of biodegradation of polystyrene reported so far but biodegradation of its monomer styrene has been reported a few times.

It has many commercial and industrial applications like manufacturing of disposable cups, packaging material, electronics and laboratory ware due to its properties like lightweight, stiffness and thermal insulation.

### Biodegradation of Natural Plastics (Polyhydroxylkanoates)

PHA is produced and stored in their cells by microorganisms under nutrient limited conditions. This PHA is degraded and metabolized when the nutrients become available. But the ability to store PHA does not

ensure the degradation of PHA in the environment. Polymers cannot pass through the semi permeable cellular membrane unless they are broken down into their smaller subunits or monomers. For this purpose, bacteria have evolved to produce extracellular hydrolases that can convert the polymers into corresponding hydroxyl acid monomers. Hydrolysis of PHB gives R-3-hydroxybutyric acid and hydrolysis of PHBV gives both 3-hydroxybutyrate and 3-hydroxyvalerate. These monomers are both water soluble and are small enough to pass through the cell wall. Once they enter the cell, they are metabolised by Beta oxidation and TCA cycle to produce carbon dioxide and water in aerobic conditions. But in the absence of Oxygen or in anaerobic conditions, methane is produced along with the other products. Most of the PHA degrading bacteria produce only one PHA depolymerase except P. lemoignei which produces at least 7 different extracellular PHA depolymerases which have slightly different biochemical properties.

Usually, no harmful by products are produced in this process. 3-hydroxybutyrate is also found as blood plasma in higher organisms. Since it is totally harmless, PHA has a number of medical applications like surgical pins, bone and blood vessel replacement, sutures and long-term controlled drug release. Due to the stability of PHA, they have been used in industrial applications in producing biodegradable and biocompatible thermoplastics.[6]
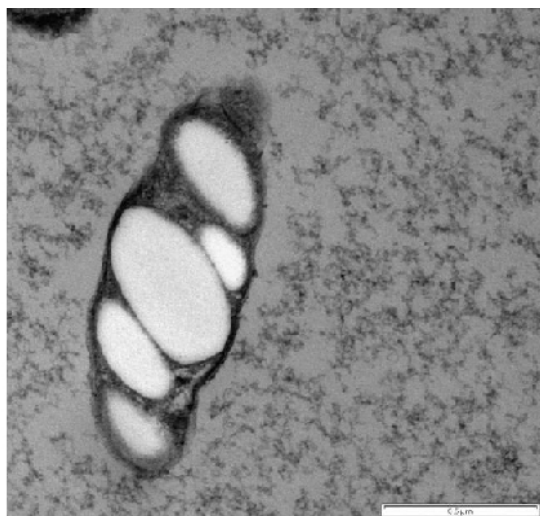
Figure 2: It shows the presence of PHA granules in cells of *Comamonas sp.* EB172 viewed under TEM. Scanning electron microscopy.[18]

Biodegradation of Polyurethane

Polyurethanes belong to a synthetic class of polymers which are made of urethane linkages. An alcohol functional group and an isocyanate functional group react together to form a urethane linkage. Polyurethanes have a wide variety of commercial applications. They are used in paints, thermal insulating materials. Polyurethane is susceptible to biodegradation despite its xenobiotic origins.[19] A bacterial strain, *Comamonasacidovorans* TB-35, utilises polyester polyurethane polymers containing

Polydiethyleneglycol Adipate as a carbon source. It has polyester polyurethane (PUR)-degrading enzyme, PUR esterase, bound to its cell surface that can degrade Polyurethane.[20] Biodegradation by other bacteria is incomplete as they are not able to use this as the sole carbon source; they require additional carbon sources as well.[21] Biodegradation of polyurethane is indicated by an increase in the number and size of pores on its surface that can be seen under an electron microscope.[22]

CONCLUSION

Many different strains of bacteria are involved in the degradation of plastics; the most common ones belong to the genus Bacillus. Biodegradation of plastics by bacteria can be made most efficient by altering the factors that govern the process. It promises a reduction in plastic pollution in the future.

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