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Review Article

# Degradation of synthetic polymers: Microbial approach

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ABSTRACT

A synthetic polymer is a plastic, which is having wide applications in our day-to-day life. The packaging industries, agriculture, cosmetics, etc. Plastics are not easily degradable, it takes 1000 years to degrade a plastic or even more than that. The pollution caused by plastic is not only because of the waste disposal method but it is also because it releases carbon dioxide and dioxins while burning. Plastics are considered a threat to the environment as they are not easily degradable. Our review is based on the microbial approach for plastic degradation. The waste management method being used for plastic disposal is not effective enough. Nowadays biodegradable polymers are also being used as they are more easily degradable compared to synthetic polymers. The bacteria and fungi degrade most of the organic and inorganic components like starch, lignin, cellulose, and hemicelluloses.



## 1. Introduction

Plastic is a synthetic polymer that is abundantly found in every corner of the world. It is used almost in every sector for packaging, textiles, electrical gadgets, automotive, furniture to medical healthcare. Now the worldwide production of plastic has reached 367million tonnes, the industry produces approximately 150kilograms of polymers per person annually in the United States, with the increase of production in the plastic it has become an environmental hazard, impacting on health and threatening wildlife and even marine life.[1]

In the environment, we can find natural polymers, like cellulose. Latex was first chemically modified in $19^{th}$ century to form celluloid and vulcanized rubber. Bakelite the first synthetic polymer was produced in 1907 and rayon fiber was the first semisynthetic fiber developed by cellulose.[2] The polymers are resistant to chemicals, insulators of electricity, and heat. Resin is the raw material for the production of plastic products. Polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET) are the most commonly used resins, they are used in packaging.[3] Plastic takes years to decompose, the chemicals present in the plastic-like lead, mercury, and cadmium are carcinogens, when it comes into direct contact with humans it can cause cancer, immunological problems, and even congenital disabilities. The plastic in marine impacts the ingestion, suffocation, entanglement, and death of hundreds of species.[4]

Many plastics are non-biodegradable but few plastics are biodegradable which can be decomposed by the action of the microorganisms. In 2016 the Japanese scientists had discovered a bacterium that can break down the polyethylene terephthalate plastic, the bacterium *Ideonella sakaiensis* degrades polyethylene terephthalate by the two enzymes PETase and MHETase produce by the bacteria, the PETase breakdowns the polyester polymer by which polyethylene terephthalate is constructed into smaller pieces, during the process polyethylene terephthalate is

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converted into mono-(2-hydroxyethyl) terephthalate acid (MHET), terephthalate (TPA) and bis(2-hydroxyethyl) TPA (BHET).[5] The MHETase enzyme produced by the *Ideonella sakaiensis* converts the MHET into terephthalate and ethylene glycol. Environmental pollutants caused by the polyethylene terephthalate can be effectively solved by the bacterial enzymes. In 2017, biologist Federica Bertocchini at the Institute of Biomedicine and Biotechnology of Cantabria reported that wax worm caterpillars could break down polyethylene.[6]

After their initial observation, they exposed a paste made from mashed-up caterpillars to a sample of polyethylene film, which generated new peaks during a scan with an infrared spectrometer. Bertocchini and her team attributed the peaks to a breakdown product, ethylene glycol, likely generated by the caterpillar or by the microbe present in the guts of the caterpillar.[7] Microorganisms that are capable of degrading the polyolefins (Polyethylene, Polystyrene, and Polypropylene) polyvinyl chloride, polyethylene terephthalate are isolated from the open environment, the soil of plastic dumpsite, sewage sludge, landfills, marine water, and the plastic-eating worm.[8]

## 2. Preparation of Different Polymers

Types of synthetic polymer which forms hazardous to health and the environment is mostly the most common polyethylene, low-density polyethylene produced by free radical polymerization at high pressures above 1000atm, high temperatures of 200°C, and the high-density polymer are obtained by Ziegler-Natta catalysis at a temperature below 100°C, less than 100 atm of pressure. Polyethylene is produced more every year compared to any other plastics, they are relatively inexpensive and lightweight.[9] Polypropylene is rigid due to Ziegler-Natta catalyzed polymerization, they are thermally stable polymers with excellent resistance to stress and chemical reaction.

It costs more than polyethylene and it is much stronger than polyethylene. Polytetrafluoroethylene, it's a gas that is boiled at -76$^{0}$C and stored in cylinders at very high pressure. In 1938 Roy Plunkett received a cylinder of tetrafluoroethylene, that did not deliver as much gas as it should have, instead of returning the cylinder, he cut open with a hacksaw and discovered a white waxy powder that was the first polytetrafluoroethylene polymer. Later a less fortuitous route for this polymer was discovered, polytetrafluoroethylene or Teflon became commercially available.

Teflon has got the best resistance to the chemical attack of any polymer, it can withstand temperatures between -73°C to 260°C with no effect on its properties. It got a very low coefficient of friction, it has a waxy or even material as sticky as rubber, adhesives, bread dough, and candy. Insects get stuck to a Teflon-coated surface.

Teflon is extremely slippery that they used to spray on plants so prey on the plants fall off.

Polyvinyl Chloride, the chlorine substituents on the polymer chain make polyvinyl chloride more fire-resistant than polyethylene, they also increase the force of attraction between polymer chains, which increases the hardness of the plastic. PVC has got a wide range of uses by adding in plasticizers, stabilizers, fillers, and dyes making PVC one of the most versatile plastics.[10]

Acrylics, acrylic acid is the common name for 2-propenoic acid, Orlon is the acrylic fibers made by polymerizing the derivative of acrylic acid known as acrylonitrile. Some other acrylic polymers are formed by polymerizing an ester of methyl acrylate.

Polymethyl methacrylate is the most important acrylic polymer, it is a lightweight, crystal-clear, glasslike polymer that is used in airplane windows, taillight lenses, and light fixtures. As it is hard and stable to sunlight and extremely durable. The transparency of PMMA makes the polymer ideal for hard contact lenses, PMMA is impermeable to oxygen and water. By copolymerizing, the mixture of acrylic acid and the sodium salt of acrylic acid the product called Sodium polyacrylate is formed, the polymer network and the solution in which the polymer is immersed generate an osmotic pressure that draws water into the polymer.[11] The amount of liquid that can be absorbed depends on the ionic strength of the solution, the total concentration of positive and negative ions in the solution, this is a superabsorbent polymer that can be found in disposable diapers.

The first plastic Celluloid and the first artificial fiber Rayon were produced from cellulose. The first truly synthesized plastic was Bakelite, which starts with the reaction between formaldehyde and phenol to form a mixture of ortho- and para-substituted phenols. If the temperature is above 100°C, these phenols condense to form a linkage.

The families of condensation polymers known as polyamides and polyesters were obtained by reacting a diacyl chloride with a diamine[12] and the polyesters are made by reacting the diacyl chloride with alcohol. It was soon realized that playful exercise had oriented the polymer molecules in two dimensions and produced a new material with superior properties. The first polyester fibers were produced by reacting ethylene glycol and either terephthalic acid or one of its esters to give polyethylene and poly terephthalate, this polymer is still used to make thin films Mylar and textile fibers Dacron and Fortrel.[13]

Phosgene reacts with alcohols to form esters that are analogous to those formed when acyl chlorides react with alcohols. The product formed is called carbonate ester because it is the diester of carbonic acid, polycarbonates are produced when one of the esters reacts with appropriate alcohol has got very high resistance to impact and is used in safety glass, bullet-proof windows, and motorcycle helmets. Weathering of microplastics is a major process to determine the polymer degradation rate and process in the ecosystem.[14] The combined process of photo-1oxidation, soil pH, and temperature only deteriorate these plastic wastes to a small degree and occur at a very slow yet gradual pace. The exposure of photo-oxidation towards the soil-incorporated microplastics compared to the surface aggravates the situation. Microbial biodegradation seems to be the most likely method of accelerating the deterioration processes.[15] Microorganisms that are found in the deep soil colonize the plastic and where biodegradation is initiated through the adherence of microorganisms to the plastic surfaces which facilitated the formation of biofilm.[16] In the soil, if once colonized, these microbes secrete proteinases to catalyze the hydrolysis of plastics resulting in the formation of oligomers, monomers, and metabolic intermediates which are ultimately mineralized into carbon dioxide and water.[17] The biodegradation of plastics in the soil environment and some other factors should be taken into consideration. The characteristics of soils are associated with uncontrolled biotic and abiotic factors which are highly correlated with geographical aspects. The microbial biodegradation processes vary from one environment to another and are highly dependent on different climates.[18] Polypropylene is utilized in a wide range of applications of single-use disposables to long-lasting durables due to its excellent features, mechanical properties, simple manufacturing, reasonable price, and the improvement to the transparency, strength, and shelf-life in polypropylene manufacturing have significantly increased its usage.[19] The repetitive methylene units form a continuous chain that creates a hydrophobic polymer that is resistant to degradation. The addition of the methyl side chain repetitively in every unit will decrease the potential of polypropylene to undergo a degradation process. The microorganism which can grow under extreme temperatures is capable of using microplastic as an energy source.[20]

## 3. Mechanism of Polymer Degradation

The degradation of the polymer by microbes undergo several steps of mechanism like, the aerobic biodegradation of the PE by the bacteria forms a carbonyl–groups by the action of oxidative enzymes released by the microorganisms or the exterior agents, the number of carbonyl-groups and carboxylic acids are subsequently reduced and oxidized then it undergoes fragmentation and hydrolysis of the polymer carbon chains and then release the intermediate products which are mediated by enzymes secreted by microorganisms, the small fragments of hydrocarbon are released by bio fragmentation and metabolized by microbes.[21] The hydrolysed product is then transferred to the cell wall, the intracellular conversion of hydrolysis products to microbial biomass with an associate to release of carbon dioxide and water out of the cell. The fragmentation and bio assimilation of LDPE into biomass by the bacterial species, such as P*seudomonas putida* IRN22, *P. putida* LS46, *Micrococcus luteus* IRN20, and *Acinetobacter pittii* IRN19.[22] These bacteria were able to utilize the untreated LDPE as a sole source of carbon and energy for growth and generate alkane hydrolysis products and accumulate biodegradable polymers in form of short-chain length and medium-chain length polyhydroxyalkanoates.[23] The *Acinetobacter calcoaceticus* and *Pseudomonas aeruginosa* were found to metabolize only alkane hydrocarbons and not LPDE.[24]

The biodegradability of pre-treated polyethylene materials includes LDPE, HDPE, and linear low-density polyethylene films of different thickness by *Rhodococcus rhodochrous,* which is one of the most efficient bacteria for PE biodegradation.[25] The species known to degrade PE are capable of hydrolyzing and metabolizing linear n-alkanes like paraffin molecules. Alkane hydroxylase is the key enzyme involved in the aerobic degradation of alkanes by bacteria. In the first hydroxylation of C-C bonds release primary or secondary alcohols, which get oxidized to ketones or aldehydes and hydrophilic carboxylic acids. The microbial oxidation reduces the number of carbonyl groups due to the formation of carboxylic acids. The carboxylated-alkanes are analogous to fatty acids, which are catabolized by bacteria the β-oxidation system pathway has demonstrated the microbial oxidation of n-alkanes by bacteria the β-oxidation pathway, and subsequently to the tricarboxylic cycle. The oxidation pores released by the action of enzymes in the process may be absorbed by microbial cells where they are catabolized. The extracellular mechanisms that lead to enzymatic oxidation and hydrolysis of chains of PE polymers are also significant to oligomers production with a maximum of 55 carbons from PE films that are adsorbed by bacteria after 240 days of incubation,[26] Amidohydrolase forms the key enzyme in the alkane hydroxylase system pathway, which are involved in PE degradation in the -oxidation pathway and known to degrade linear alkanes. The important enzymes that are interested in the alkane hydroxylase system are the monooxygenases, the number and types of Amidohydrolase vary greatly in different bacteria which itself differs in the amount of carbon in the alkane chains. *Rhodococcus ssp.* TMP2 genome encodes 5 AHs (alkB1, alkB2, alkB3, alkB4, and alkB5) while the *Pseudomonas aeruginosa* genome encodes two Amidohydrolase: alkB1 and alkB2. Alkane hydroxylase is involved in the hydroxylation of the terminal carbon-first step of the n-alkane oxidation pathway.[27] The AlkB enzyme of *P. aeruginosa* strain E7 played a central role in the mineralization and biodegradation of LMWPE into carbon dioxide. The alkB gene was cloned in *Pseudomonas sp.* E4 and the AlkB enzyme expressed from the recombinant strain from LMWPE biodegradation.

The class of multi-copper enzymes, the Laccase enzymes expressed by *Rhodococcus sp.* rubber which also shows an important role in PE biodegradation.[28]

Microorganisms are not capable to transport the polymers through their outer membranes into the cells and due to the lack of water solubility and the length of the polymer molecules all the biochemical processes take place in the cell.[29] The microorganisms have developed an advanced program to utilize the materials like carbon and other energy sources. To depolymerize the polymers outside the cells the microbes excrete extracellular enzymes on the polymers. The extracellular and intracellular depolymerized enzymes actively take part in the biological degradation of polymers. During degradation, the exoenzymes from microorganisms break down complex polymers yielding short chains molecules, e.g., monomers, dimers, and oligomers, they are compact enough and also water-soluble which helps to pass the semi-permeable outer bacterial membranes.[30] This preliminary process of polymer breaks down is called depolymerization, the end products are inorganic species, e.g., Carbon dioxide, water, or methane, and this degradation is called mineralization.[31] When oxygen is accessible, the aerobic microorganisms are responsible for the disintegration of complex materials with microbial biomass, carbon dioxide, and water as the end products. In the absence of oxygen, under anoxic conditions, anaerobic consortia of microorganisms are responsible for polymer deterioration,[32] the primary products of this will be microbial biomass, carbon dioxide, methane, and water under methanogenic conditions or hydrogen sulfide, carbon dioxide, and water under sulfidogenic situation.[33] Thermodynamically oxygen is a more efficient electron acceptor than sulfur dioxide and carbon dioxide,[34] aerobic procedures yield more energy and are capable enough to support great inhabitants of microorganisms than the anaerobic procedure.[35]

## 4. Conclusion

In this review, we have shown the degradation of types of synthetic polymers used in our day to day life for a different purpose which is then thrown as trash which becomes hazardous to the environment and creates pollution so to reduce and solve the problem different microorganisms are used for the degradation which does not harm the nature and it is eco-friendly. Properties and nature of different polymers are mentioned, the mechanism by which the microorganism will degrade the polymers is also summarised. In the future, we will see that we are using mutated microorganisms and other natural factors which can be time-saving and eco-friendly.

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## 6. Conflict of Interest

The authors declare no conflict of interest.

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