

Polymer Biodegradation and Biodegradable Polymers – a Review

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Abstract

Synthetic polymers are important in many branches of industry, for example in the packaging industry. However, they have an undesirable influence on the environment and cause problems with waste deposition and utilization. Thus, there is a tendency to substitute such polymers with polymers that undergo biodegradable processes. Increasing interest in applying polymers based on natural materials such as starch has been observed.

This review describes biodegradation processes of xenobiotics such as aromatic compounds, plastics (PVA, polyesters, polyethylene, and nylon), and polymer blends (Starch/Polyethylene, Starch/Polyester, and Starch/PVA). Moreover, this review includes information about biodegradable polymers such as mixtures of synthetic polymers and substances that are easy digestible by microorganisms (chemically modified starch, starch-polymer composites, thermoplastic starch, and biodegradable packing materials), synthetic materials with groups susceptible to hydrolytic microbial attack (polycaprolactone), and biopolyesters (poly- β -hydroxyalkanoates). Production of this kind of material and introducing it to the market is important for the natural environmental. It may result in decreasing the volume of waste dumps.

Keywords: biodegradation, biodegradable polymers, xenobiotics

Introduction

Developments in science and technology, especially over the last two decades, have increased the amount of synthetic polymers produced worldwide each year. Each year approximately 140 million tonnes of synthetic polymers are produced [1]. In the United States, synthetic polymers are estimated to be approximately 20% of the volume of municipal solid waste. A similar situation has been observed in Germany. In Australia, most household waste ends up in municipal landfill sites, estimated to be 25% of total waste by weight [2]. The presence of these substances in the environment brings about important problems, including a challenge to wastewater treatment plants and

pollution of groundwater and surface water. Synthetic polymers are recognized as major solid waste environmental pollutants. Another problem is disposal of agricultural plastic wastes. Since 1990, the plastic industry has invested \$1 billion to support increased recycling, and to educate communities. Landfilling is the most common method for disposing of municipal solid waste. Many synthetic polymers, resistant to chemical and physical degradation, are produced and utilized. They present disposal problems when their usefulness ceases. Especially for agricultural plastic wastes, an alternative method of disposal is biodegradation. Biodegradation concerns specially designed so-called biodegradable polymers [3]. Increasing amounts of synthetic polymers produced results in increasing interest in polymer biodegradation. The recent incorporation of biological waste treatment (i.e., composting and biogasifica-

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tion) in an integrated approach to solid waste management has resulted in a growing commercial interest in the development of biodegradable materials for consumer products [4, 5]. On the market are a number of materials known as *biodegradable plastics* (i.e., starch-based materials, cellulose-derived polymers, bacterial polyesters and a range of synthetic polymers). The main problem associated with designing biodegradable polymers is the optimization of their chemical, physical and/or mechanical properties, as well as their biodegradability [5, 6].

Biodegradation

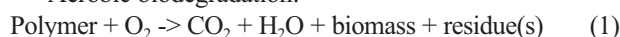
There is a world-wide research effort to develop biodegradable polymers as a waste management option for polymers in the environment. Biodegradation (i.e. biotic degradation) is a chemical degradation of materials (i.e. polymers) provoked by the action of microorganisms such as bacteria, fungi and algae. The most common definition of a biodegradable polymer is "a degradable polymer wherein the primary degradation mechanism is through the action of metabolism by microorganisms." Biodegradation is considered a type of degradation involving biological activity. Biodegradation is expected to be the major mechanism of loss for most chemicals released into the environment. This process refers to the degradation and assimilation of polymers by living microorganisms to produce degradation products. The most important organisms in biodegradation are fungi, bacteria and algae [7]. Natural polymers (i.e., proteins, polysaccharides, nucleic acids) are degraded in biological systems by oxidation and hydrolysis [3]. Biodegradable materials degrade into biomass, carbon dioxide and methane. In the case of synthetic polymers, microbial utilization of its carbon backbone as a carbon source is required [2].

Bacteria important in the biodegradation process include, *inter alia*, *Bacillus* (capable of producing thick-walled endospores that are resistant to heat, radiation and chemical disinfection), *Pseudomonas*, *Klebsiella*, *Actinomycetes*, *Nocardia*, *Streptomyces*, *Thermoactinomycetes*, *Micromonospora*, *Mycobacterium*, *Rhodococcus*, *Flavobacterium*, *Comamonas*, *Escherichia*, *Azotobacter* and *Alcaligenes* (some of them can accumulate polymer up to 90% of their dry mass) [2, 7-9]. Temperature is one of the

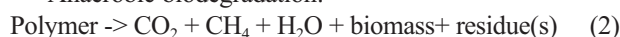
most important factors affecting microorganism growth. Also important are sources of carbon and nitrogen, and pH. Fungi active in the biodegradation process are *Sporotrichum*, *Talaromyces*, *Phanerochaete*, *Ganoderma*, *Thermoascus*, *Thielavia*, *Paecilomyces*, *Thermomyces*, *Geotrichum*, *Cladosporium*, *Phlebia*, *Trametes*, *Candida*, *Penicillium*, *Chaetomium*, and *Aerobasidium* [8, 10-12].

The biodegradation process can be divided into (1) aerobic and (2) anaerobic degradation (Fig. 1).

Aerobic biodegradation:



Anaerobic biodegradation:



If oxygen is present, aerobic biodegradation occurs and carbon dioxide is produced. If there is no oxygen, an anaerobic degradation occurs and methane is produced instead of carbon dioxide [3, 13, 14]. When conversion of biodegradable materials or biomass to gases (like carbon dioxide, methane, and nitrogen compounds), water, salts, minerals and residual biomass occurs, this process is called mineralization. Mineralization is complete when all the biodegradable materials or biomass are consumed and all the carbon is converted to carbon dioxide [3].

Biodegradable materials have the proven capability to decompose in the most common environment where the material is disposed, within one year, through natural biological processes into non-toxic carbonaceous soil, water or carbon dioxide [5]. The chemical structure (responsible for functional group stability, reactivity, hydrophylicity and swelling behaviour) is the most important factor affecting the biodegradability of polymeric materials. Other important factors are *inter alia*, physical and physico-mechanical properties, e.g., molecular weight, porosity, elasticity and morphology (crystalline, amorphous) [15, 16].

Xenobiotics Biodegradation

Xenobiotics are man-made compounds, frequently halogenated hydrocarbons, that are notoriously difficult for microbes to breakdown in the environment. Biodegradation of synthetic materials is complicated. Saturated alkanes are more susceptible to aerobic bacterial attack than unsaturated aliphatic hydrocarbons. Moreover, alkanes with a long carbon chains and straight structures are more prone to aerobic biodegradation. The most common aerobic pathway for alkane degradation is oxidation of the terminal methyl group into a carboxylic acid through an alcohol intermediate, and eventually complete mineralization through β -oxidation [5, 17-19].

Over the last two decades the increasing attention of xenobiotic biodegradation under anaerobic conditions such as in groundwater, sediment, landfill, sludge digesters and bioreactors, has been observed. Generally, anaerobic bacteria able to degrade xenobiotics are present in various anaerobic habitats, *inter alia* sediments, waterladen soils, reticu-

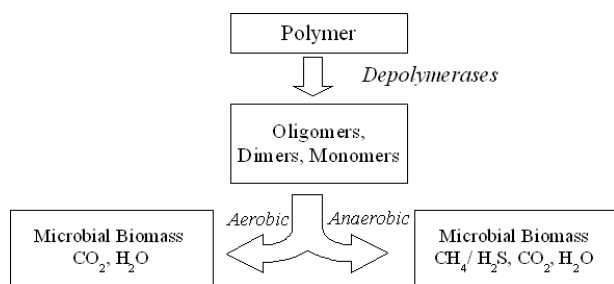


Fig. 1. Schema of polymer degradation under aerobic and anaerobic conditions [87].

lo-ruminal contents, gastrointestinal contents, sludge digesters, feedlot wastes, groundwater, and landfill sites [20]. Anaerobes use natural organics such as proteins, carbohydrates, and many others as carbon and energy sources. *D. oleovorans*, *G. metallireducens*, *D. acetonicum*, *Acidovorax*, *Bordetella*, *Pseudomonas*, *Sphingomonas*, *Variovorax*, *Veillonella alkalescens*, *Desulfovibrio* spp., *Desulfuromonas michiganensis*, and *Desulfitobacterium halogenans* are the major groups of anaerobic microorganisms involved in biodegradation of xenobiotic compounds. Pure cultures of this above-mentioned bacteria must be isolated under strict anaerobic conditions (sulfate-reducing and methanogenic) [19].

Biodegradation of Aromatic Compounds

Aromatic compounds are ubiquitous in nature. Although there is some debate as to their origin in the environment, it is generally accepted that most are not of biosynthetic origin but are derived from the pyrolysis of organic compounds. Indeed, next to glucosyl residues, the benzene ring is the most widely distributed unit of chemical structure in nature. Benzene, ethylbenzene, toluene, styrene, and the xylenes are among the 50 largest-volume industrial chemicals produced, with production figures of the order of millions of tons per year. These mentioned compounds are widely used as fuels and industrial solvents. Moreover, they and polynuclear aromatic compounds provide the starting materials for the production of pharmaceuticals, polymers, agrochemicals, and more [21].

Numerous studies have documented that aromatic compounds can be degraded under nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic conditions. Although biodegradation of aromatic compounds has been shown to occur under anaerobic conditions, information on the extent of this activity is limited [22].

Aerobic degradation of aromatic compounds involves their oxidation by molecular oxygen. Oxidation leads to the production of intermediates that enter central metabolic pathways including the Krebs Cycle and β -oxidation [23-25]. Microorganisms use oxygen (during aerobic respiration) to hydroxylate the benzene ring (Fig. 2), resulting in subsequent fission of the ring. Mono- and di-oxygenase enzymes incorporate one or two atoms of oxygen, respectively, into the ring [26]. The major reactions (catalyzed by di-oxygenases) is the cleavage of the aromatic double bond located between two hydroxylated carbon atoms (ortho pathway), or adjacent to a hydroxylated carbon atom (meta pathway), or in an indole ring [27].

In the benzene aerobic biodegradation process, three intermediates are present: catechol, protocatechuate, and gentisic acid. These compounds are broken down by similar pathways to simple acids and aldehydes that are readily used for cell synthesis and energy [28]. Polycyclic aromatic compounds (e.g. toluene, xylenes, naphthalene and ethylbenzene) are degraded by similar mechanisms as benzene. Di-oxygenase initiates an attack and it produces a dihydrodiol. Then, the dihydrodiol is converted to a catechol-like compound (Fig. 3) that can undergo *ortho* or *meta* ring fission. Enzyme di-oxygenase is indispensable to aerobic naphthalene transformation [25, 29, 30].

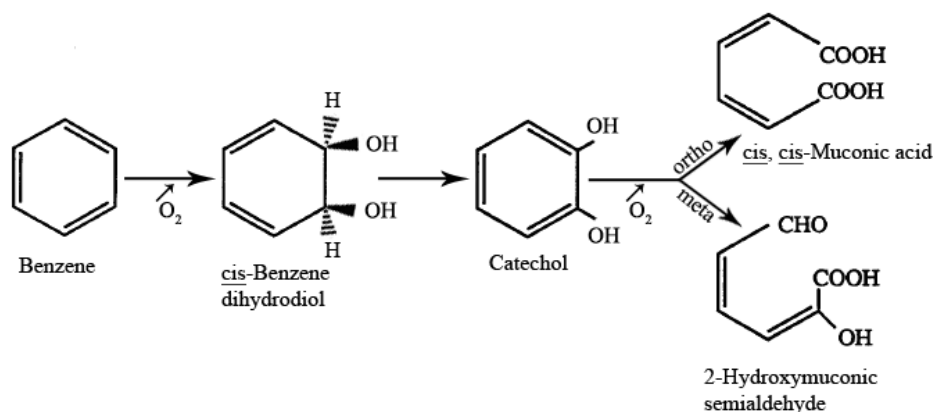


Fig. 2. Aerobic benzen biodegradation [25].

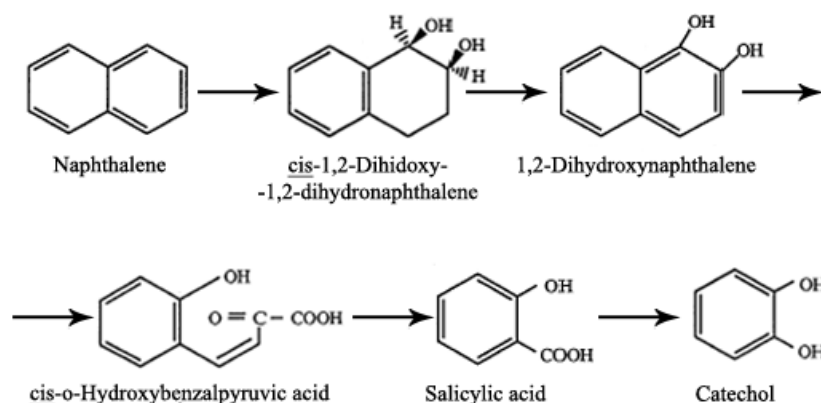


Fig. 3. Aerobic naphthalene biodegradation [25].

Some non-oxygenated aromatics, such as toluene, benzene, ethylbenzen, and xylenes, can be transformed under anaerobic conditions by denitrifying bacteria, in the presence of alternative electron acceptors. In the absence of oxygen, substituted aromatic compounds are more easily degraded than non-substituted compounds. The addition of a substituent group onto the benzene ring makes possible an alternative degradation method, including side-chain group attack (Fig. 4) [21, 25]. The first documented report for benzene and toluene degradation under anaerobic conditions appeared in 1980, concerning studies of biodegradation in microcosms containing samples from the site of the Amoco Cadiz oil spill. In 1984 and 1985, field evidence for anaerobic degradation was reported. Laboratory studies demonstrated that many different electron acceptors could replace oxygen in anaerobic degradation. Certain aromatic compounds have been shown to be degraded under denitrifying conditions, methanogenic conditions in microcosms, and by iron-reducing organisms. However, the existence of microbial communities capable of degrading aromatic materials with sulfate as the electron acceptor has not yet been proven. Some scientists have suggested that sulfate-reducing bacteria were involved in the biodegradation, although definitive proof to this effect has not been presented [31].

Biodegradation of Plastics

Increasing interest in plastic biodegradation is observed because of environmental pollution. Plastics are composed mainly of carbon, hydrogen, nitrogen, oxygen, chlorine and bromine, and are used in automobile production, space exploration, irrigation, agriculture, health and other industries [11, 32]. Generally, 2-3 million tons of plastics are used each year in agricultural applications. The Statewide Waste Characterization Study reported that approximately 350,000 tons of rigid plastic packaging containers were disposed of in California during 2003, which represents approximately 1% by weight of the overall waste stream. Plastic trash bags comprised 1% and plastic film, comprising 2.3% of the waste stream. The commercial sector generated about 50% of the waste, the residential sector 30% of the waste, and the self-hauled sector 20%. In 2003, plastics contributed to 12% by weight of the waste stream for commercial waste, 9.5% of the waste from residential waste, and 3.9% of the waste stream in self-hauled waste. Plastics are inert, that is resistant to biodegradation. But generally, the main environmental disadvantage of plastic materials is

that they do not readily break down in the environment and therefore can litter the natural environment [32]. Using biodegradable and compostable plastics can reduce the amount of plastics in landfills. The use of biodegradable polymers is increasing at a rate of 30% per year in some markets worldwide. Composting is a promising waste management option for degradable plastics because this process is designed to degrade wastes [33, 34].

Several organizations are involved in setting standards for biodegradable and compostable plastics: the U.S. Composting Council (USCC), the American Certification System of Biodegradable Products Institute (BPI), the Environment & Plastics Industry Council, the American Society for Testing and Materials (ASTM), the European Committee for Standardization (CEN), Japan's GreenPla program, and the British Plastics Federation. The restrictions from these organizations help create biodegradable and compostable products that meet the increasing worldwide demand for more environmentally friendly plastics [34].

Biodegradable polymers decompose into carbon dioxide, methane, water, inorganic compounds or biomass by the actions of microorganisms [34]. Biodegradable polymers used for producing biodegradable agricultural films include *inter alia*, copolyesters, poly(vinyl)alcohol, poly(vinyl)chloride, acylated starch-plastic, modified starch and vegetable oil [3].

PVA Biodegradation

The chemical structure of poly(vinyl) alcohol (PVA) is composed mainly of head-to-tail 1,3-diol units. However, only 1-2% of head-to-head 1,2-diol units exist in PVA. The 1,2-diol content influences some properties of PVA, *inter alia* its biodegradability. Factors affecting PVA biodegradability include the degree of polymerization (DP), the degree of saponification (hydrolysis; DS), tacticity of the main chain, ethylene content, and 1,2-glycol content. In general, DP and DS did not have a significant influence on the biodegradation of PVA [35].

Poly(vinyl)alcohol historically has been produced industrially by the hydrolysis of poly(vinylacetate). As the vinyl alcohol monomer it cannot exist due to its tautomerization into acetaldehyde. PVA was discovered in 1924, when a PVA solution was obtained by saponifying poly(vinyl ester) with caustic soda solution. PVA has such physical properties as viscosity, film forming, emulsifying, dispersing power, adhesive strength, tensile strength, and

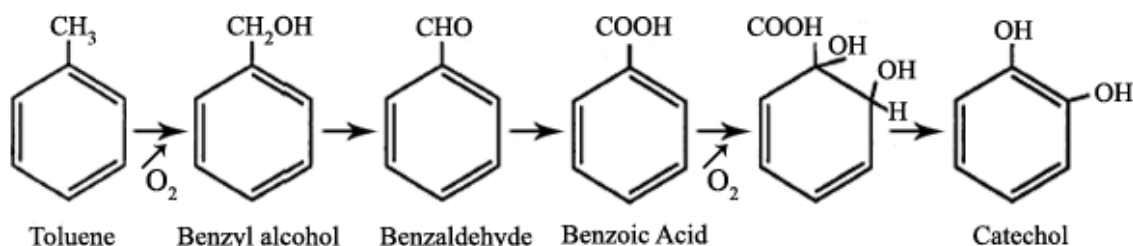


Fig. 4. Aerobic toluene biodegradation: side group attack [25].

flexibility. PVA is resistant to water, oil, grease, and solvent. It was widely used, especially in fabric and paper sizing, fiber coating, adhesives, emulsion polymerization, films for packing and farming, and the production of poly(vinylbutyral). The production of PVA peaked as the volume of synthetic, water-soluble polymers in the world amounted to about 1,250 kt in 2007. Asia (especially China and Japan), Western Europe, and the USA aspire to be the greatest producers and consumers of poly(vinyl)alcohol. About 76% of worldwide PVA production is in Asia [35].

Poly(vinyl)alcohol is a vinyl polymer in which the main chains are joined by only carbon-carbon links. The history of PVA biodegradation extends back more than 70 years, since the first report of degradation by *Fusarium lini* B [35, 36]. Recently, it was reported that 55 species of microorganisms (including bacteria, fungi, yeast and mould) participate in degradation of poly(vinyl)alcohol. Scientists have isolated the *Pseudomonas* bacteria from soil bacterium growing on PVA as the source of carbon. *Pseudomonas* is the main PVA degrader. This bacterium produces and secretes an enzyme that degrades PVA. This enzyme was isolated, purified and characterized. Polyvinyl alcohol dehydrogenase (PVADH) from *Pseudomonas* ssp. 113P3 catalyzed an oxidation reaction of PVA to produce beta-diketone structure on PVA. The degradation mechanism included two steps: the conversion of the 1,3-glycol structure of two successive repeating units to a β -diketone by a random oxidative dehydrogenation reaction or oxidation of one hydroxyl group yielding monoketone structures. This process was catalyzed by an extracellular secondary alcohol oxidase enzyme. And the second step was a reaction that broke the carbon-carbon bond and converted one of the ketone groups to a carboxylic group. This results in chain scission (Fig. 5) [3]. But according to the products produced by the first step of PVA degradation, there are two possible pathways for this second step: either hydrolysis of β -diketone structures of oxidized PVA (oxiPVA) by a β -diketone hydrolase (oxiPVA hydrolase) or the aldolase reaction involving the monoketone structures of oxiPVA [35].

Polyesters

In polyesters, monomers are bonded by ester linkages. Enzymes that degrade this polymer are ubiquitous in living organisms (e.g., *Thermomonospora Fusca* and *Streptomyces albus*) [1, 37], so it may be degraded in several biotic environments. The most important factors affecting biodegradability are molecular mass and crystallinity [38].

Poly(ϵ -Caprolactone)

PCL is a synthetic linear polyester with almost 50% crystallinity. It is biologically degradable and consists of 6-hydroxyhexanoates. The environmental degradation of PCL is affected by the actions of bacteria that are widely distributed in the ecosystem [38]. Recent studies have shown that some filamentous fungi and yeasts also can hydrolyze PCL to water-soluble products. Scientists have reported that *Pullularia pullulans* can efficiently degrade a lower molecular weight PCL film (Mw=1,250), but the extent of decomposition of a PCL film with Mw above 15,000 by the fungus was negligible. PCL with higher Mws (25,000 and 35,000) is degraded by *Penicillium* sp. strain and a yeast. However, increasing the Mw of the polyester reduced its degradability. One of the most important factors influencing PCL biodegradation are the PCL degrading microorganisms that produce different types of PCL hydrolases, even though the biodegradability of a polymer is related to its Mw. PCL could be hydrolyzed by esterases and lipases [39]. Synthetic polyesters such as PCL, poly(ethylene dicarboxylic acids), and poly(butylene dicarboxylic acids) could be degraded by lipases of *R. delemar* and *Rhizopus arrhizus*. During the degradation process in a biotic environment, the amorphous fraction of PCL is degraded before the degradation of the crystalline fraction. Ester linkages are easy to hydrolyze [2]. PCL is not susceptible to bacterial and fungal PHB depolymerases [36, 39-41]. Some of the fungal phytopathogens (*Fusarium* spp.) produce cutinase that degrades a cutin polyester (the structural component of a plant cuticle) [36].

Poly(L-Lactide)

PLA is a biocompatible thermoplastic with a melting temperature of 175°C and a glass transition temperature of 60°C. It is synthesized by the polymerization of L-lactic acid. PLA can be hydrolyzed by the lipase from *R. delemar* and the proteinase K from *Tritirachium album* and also by the polyester polyurethane depolymerase from *Comamonas acidovorans* [42]. PLA is more resistant to microbial attack in the environment than other microbial and synthetic polyesters [36, 43, 44].

Aliphatic Polyalkylene Dicarboxylic Acids

A variety of aliphatic polyesters such as PEA, PES, polypropylene adipate (PPA), PBA, PBS, and polyhexylene carbonate have been widely produced commercially.

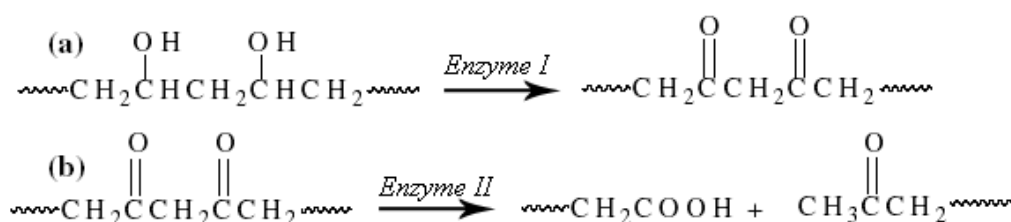


Fig. 5. Degradation mechanism of polyvinyl alcohol: (a) enzyme-catalyzed oxidation of the 1,3-glycol structure to a β -diketone; (b) chain scission of the β -diketone.

Biodegradation of these polymers is measured by microbial growth on an agar plate containing the respective emulsified polymer substrate [45, 36], or by enzymatic degradation tests using fungal hydrolases (e.g., lipase, PEA depolymerase, and PHB depolymerase). These polyesters can also be hydrolyzed by several filamentous fungi such as *Aspergillus flavus*, *A. niger*, *A. versicolor*, *Aureobasidium pullulans*, *P. funiculosum*, and *Chaetomium globosum*. However, increasing the Mw and hydrocarbon content in the polymers consisting of dicarboxylic acid units reduces their biodegradability [36].

Polyethylene (PE)

Polyethylene is widely used for various one-trip applications like food packaging, retail industry uses and agricultural uses. These applications lead to a large quantity of plastic waste, causing serious environmental problems [46].

PE is the most problematic plastic that is resistant to microbial attack. Polyethylene subjected to 26 days of artificial UV irradiation before being buried in soil evolved less than 0.5% carbon by weight after 10 years. Without prior irradiation, less than 0.2% carbon dioxide was produced. Similarly, a polyethylene sheet that had been kept in contact with moist soil for a period of 12 years showed no evidence of biodeterioration. However, some studies demonstrated partial biodegradation of polyethylene after shorter periods of time. It showed that UV photooxidation, thermal oxidation or chemical oxidation with nitric acid of polyethylene prior to its exposure to a biotic environment did enhance biodegradation [47].

Polyethylene is a synthetic polymer with $-\text{CH}_2-\text{CH}_2-$ repeating units in the polymer backbone. This polymer is resistant to biodegradation, which results from highly stable C-C and C-H covalent bonds and high molecular weight. The mechanism of biodegradability of polyethylene includes alteration by adding a carbonyl group (C=O) in the polymer backbone. The altered polyethylene molecule undergoes biotic oxidation. In the process of biodegradation, PE molecules containing carbonyl groups first get converted to alcohol by the monooxygenase enzyme. After that, alcohol is oxidized to aldehyde by the alcohol dehydrogenase enzyme. Next, aldehyde dehydrogenase converts aldehyde to the fatty acid. This fatty acid undergoes β -oxidation inside cells [11]. Biotic factors that may bring about polyethylene biodegradation included inter alia bacteria, fungi, biosurfactants produced by microbes to attach on PE surface, biofilm growth on PE surface, uptake of shorter chain PE polymers membranes, and assimilation of such short chains via β -oxidation pathway inside cells using intracellular enzymes. And abiotic factors are: sunlight and photooxidation, the addition of carbonyl radicals into $-\text{CH}_2-\text{CH}_2-$ backbone due to photooxidation and propagation of Norrish type I and II degradation, diffusion of O_2 into PE crystals, and PE chain scission [11].

Nylon

Nylons are produced in large quantities as fibers and plastics all over the world. Nylon is one of the most important synthetic polymers. However, nowadays little attention

has been given to its biodegradation. The very poor biodegradability of nylon in comparison with aliphatic polyester is assumed to be due to its strong intermolecular cohesive force caused by hydrogen bonds between molecular chains of nylon [48].

Nylon is a synthetic polyamide with repeating amide groups ($-\text{CONH}-$) in its backbone. Some forms of nylons have been shown to biodegrade by fungi and bacteria. Bacterium *Geobacillus thermocatenulatus* is used to biodegrade nylon 12 and nylon 66. Some scientists have shown that bacterial degradation of nylon 12 is associated with the enzymatic hydrolysis of amine bonds, which is accompanied by the formation of 12-amino dodecanoic acid. Also, they have proposed that further oxidation would result in the degradation of 12-Imino dodecanoic acid into carboxyl and other degradation products (Fig. 6) [11, 49].

Biodegradation of Polymer Blends

The degradation of the more readily biodegradable component controls the rate of degradation of polymer blends [2].

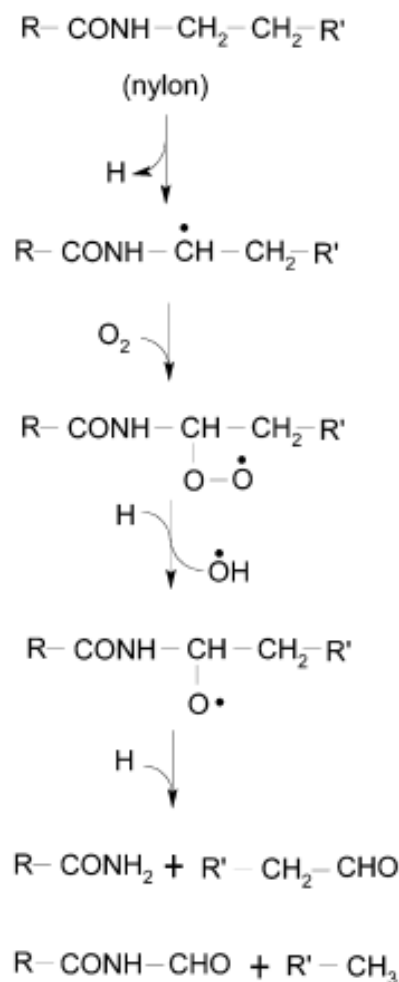


Fig. 6. Proposed mechanism of nylon biodegradation by fungus peroxidase. Methylene group adjacent to the nitrogen atom in the nylon polymer backbone is first oxidized by the enzyme fungus peroxidase. The $-\text{CH}-$ radical undergoes a stepwise oxidation process releasing various degradation products [11].

Synthetic materials (e.g., polyolefins) are not degraded by microorganisms in the environment, which contribute to their long life. Therefore, recycling and degradation of plastics is an important issue for environmental and economic reasons. Blending has become an economical and versatile route to obtain polymers with a wide range of desirable properties. Partially biodegradable polymers obtained by blending biodegradable and non-biodegradable commercial polymers can effectively reduce the volume of plastic waste by partial degradation. They are more useful than completely biodegradable polymers due to the economic advantages and superior properties imparted by the commercial polymer used as a blending component [50].

Starch, an omnipresent bio-material, is one of the most abundant and inexpensive polysaccharide sources which have the unique characteristic of biodegradability and easily dissolve in water. Blends of synthetic polymers and starches have been extensively studied since these blends can be prepared so they are biodegradable. Biodegradable polymer films are made *inter alia* from low density polyethylene (LDPE), rice starch and potato starch [51].

Starch/Polyethylene Blends

With the development of the plastics industry, starch/polyethylene plastics with good degradability and compatibility are increasingly desired. The dry native starch was directly mixed in the polyethylene matrix with blends used for many products [52].

Starch is a highly hydrophilic macromolecule. It is often used as the degradable additive in the preparation of biodegradable polyethylene film. Polyethylene is resistant to microbial breakdown. The possibility of biodegradation is connected with molecular size (the higher the molecular size, the smaller the possibility of biodegradation). The great difference between starch and polyethylene in their properties results in poor compatibility of starch/polyethylene blends [52].

The biodegradation of polyethylene is affected by preliminary irradiation in the ultraviolet range, the presence of photodegradative enhancers, its morphology and surface area, additives and antioxidants [2, 53, 54]. The degradation of the carbon-carbon backbone may be enhanced by the addition of readily biodegradable compounds, such as starch, to a low-density polyethylene matrix [55]. The rate of biodegradation of starch-filled polyethylene depends on starch content and is sensitive to environmental conditions [2, 56]. The most important trigger for the biodegradation of polyethylene is oxidation of impurities such as fats and oils [55]. The biodegradation rate-limiting component is the oxygen concentration at the surface of the films [2].

Starch/Polyester Blends

Blends of starch and polyester are completely biodegradable when each component in the blend is biodegradable, as well as compostable [40]. The type of

microorganisms and their populations are the main factors influencing the degree of degradation. Enzymes capable of cleaving the ester bonds of poly-(hydroxyalkanoate) are poly-(hydroxybutyrate) depolymerases and lipases [2, 58, 59]. It is well-known that the addition of starch filler improves the rate of degradation of polyesters [60].

Mani and Bhattacharya have reported that biodegradable blends of starch and aliphatic polyester give excellent properties when small amounts of compatibilizers (anhydride functionalized polyesters) are added. The tensile strengths are comparable to that of synthetic polyester, even at a starch level of 70% by weight. The elongation is drastically reduced as the percentage of starch is increased (2001) [61].

Starch/PVA Blends

PVA is compatible with starch and blends are expected to have good film properties. If both components are biodegradable in various microbial environments, PVA and starch blends are biodegradable. The hydrophilic nature of PVA enhances compatibility with starch, making it suitable for the preparation of polymer blends. The use of PVA with starch improves the mechanical properties of the blends [62]. Starch/polyvinyl alcohol blends are one of the most popular biodegradable plastics, and are widely used in packaging and agricultural applications [51]. Although the processing and mechanical properties of starch/PVA blends have been investigated extensively, there is only a limited number of publications about it [2, 63].

Biodegradable Polymers

In Poland, synthetic materials constitute 3 to 10% of the mass of waste materials and every year it rises 3%. It results in increasing the surface of waste dumps. The solution to the problem may be biodegradable polymers. Biodegradable materials may be divided into three groups: the mixtures of synthetic polymers and substances which are easy digestible by microorganisms (*inter alia*, modified natural polymers, natural polymers such as starch and cellulose), synthetic materials with groups that are susceptible to hydrolytic microbial attack (for example, polycaprolactone) and the biopolyesters from bacterial sources. The most popular and important biodegradable polymers are aliphatic polyesters [e.g., polylactide, poly(ϵ -caprolactone), polyethylene oxide, poly(3-hydroxybutyrate), polyglycolic acid] and thermoplastic proteins [64]. The major advantages of biodegradable plastics are that they can be composted with organic wastes and returned to enrich the soil, their use will not only reduce injuries to wild animals caused by dumping of conventional plastics, but will also lessen the labor cost for the removal of plastic wastes in the environment because they are degraded naturally, their decomposition will help increase the longevity and stability of landfills by reducing the volume of garbage, they could be recycled to useful monomers and oligomers by microbial and enzymatic treatment [65].

Mixtures of Synthetic Polymers and Substances that are Easy Digestible by Microorganisms

Chemically Modified Starch

Native starch films are hydrophilic and have poor mechanical strength. They cannot be used for packaging applications [66]. The addition of amylopectin to the films adversely affects their flexibility, tensile strength and elongation to a breaking point [67]. In the case of altered starch physical and chemical properties, modifications are used. The glucopyranose units of starch molecules have free hydroxyl groups at C-2, C-3 and most C-6 carbon atoms. Derivatization of the glucosidic hydroxyl group can be carried out using mild conditions. The nature of the attached group and the degree of substitution (number of substitutions per D-glucopyranosyl structural unit) are the main factors that influence the properties of modified starch. Commercial starches have a degree of substitution less than 0.2, while a fully substituted starch has a degree of substitution of 3 [68]. Derivatives can be prepared as starch esters. This is usually done by an acetylation reaction in which active chloride in a pyridine solvent is used. The ester group acts as an internal plasticizer to increase the fatty acid chain length, which results in greater internal plasticization [2].

Starch-Polymer Composites

Starch is often used as a biodegradation additive. The major role of starch has been found to provide higher oxygen permeability as it is consumed by microorganisms [69].

Starch components are more rapidly degraded by microorganisms than the synthetic polymers in the blends. Biodegradable packaging materials may be divided into two types. The first type includes starch-filled and the second type includes starch-based polymers. The starch content of starch-filled polymers is normally less than 15% by weight. In traditional plastics, particularly in polyolefins such as starch/high density polyethylene, starch is used as natural filler. These films biodegrade on exposure to microbial environments. [2, 54, 70]. Starch-based polymers contain relatively higher percentages of starch (more than 40%), mixed with synthetic components. It makes them attractive for biodegradability and several blends have been prepared and tested for packaging applications. The range of mechanical properties of these polymers falls short of the required properties, but improvements have been made by blending, co-polymerization, grafting and cross-linking [2, 71].

Thermoplastic Starch

Starch is often used to make biodegradable polymers but is difficult to process thermoplastically. It results from limited internal mobility of the polyanhydroglucose chain which prevents thermal transition in the chemical stable temperature range, so plasticizers are used to enable melting. Water and glycerol are the most common plasticizers [2, 72].

Thermoplastic starch is processed like synthetic plastics through extrusion and injection units. Unfortunately, it is a very hydrophilic product. Some authors tried to modify the starch structure, e.g. by acetylation, to reduce the hydrophilic character of the chains [73, 74].

Biodegradable Packing Materials

A wide range of materials are used for packaging applications including metal, glass, wood, paper or pulp-based materials, plastics or combination of more than one materials as composites. They are applied in three broad categories of packaging: primary packaging (in contact with the goods and taken home by consumers), secondary packaging (covers the larger packaging, i.e., boxes, used to carry quantities of primary packaged goods), tertiary packaging (used to assist transport of large quantities of goods, i.e., wooden pallets and plastic wrapping). Secondary and tertiary packaging materials have less material variation and they are relatively easier to collect and sort for recycling purposes. Primary packaging materials are dispersed into households and also they are largely mixed, contaminated and often damaged and thus pose problems in recycling or reuse of the materials [75].

Over 67 million tonnes of packaging waste is generated annually in the EU, comprising about one-third of all municipal solid waste. In the UK, 3.2 million tons of household waste produced annually are packaging, which equates to over 12% of the total household waste produced. In developed countries, food packaging represents 60% of all packaging. This is due primarily to strict food packaging regulations and also the drive to enhance appearance and so increase sales. In the UK, the proportion of food that is unfit for consumption before it reaches the consumer is 2%, whereas in developing countries, where packaging is not as widespread, this loss can be in excess of 40% [75-78].

Starch is the most commonly used natural polymer in biodegradable packing production (it is abundant, inexpensive, readily available and biodegradable in many environments). Often, blends of starch and polyethylene are used to produce biodegradable bags [79].

The Synthetic Materials with Groups Susceptible to Hydrolytic Microbial Attack

Polycaprolactone

Polycaprolactone (PCL) is a semi crystalline aliphatic polyester derived from a ring opening polymerization of caprolactone. It has a relatively low melting point of 60°C. It is completely biodegradable by microorganisms (including some phytopathogens) in marine, sewage sludge, soil and compost ecosystem. Many phytopathogens secrete cutinase (serine hydrolase) that degrades cutin, the structural polymer of the plant cuticle. Due to its biodegradability and biocompatibility, PCL has attracted much attention in the medical field mainly as controlled release drug carriers [80-82].

Polycaprolactone is degraded in at least two stages. The first stage involves non enzymatic hydrolytic ester cleavage, autocatalyzed by carbon end groups of the polymer chains. When the molecular weight is reduced to 5,000, the second stage starts with a slowing down of the rate of chain scission and the beginning of weight loss because of the diffusion of oligomeric species from the bulk. The polymer becomes prone to fragmentation and either enzymatic surface erosion or phagocytosis contributes to the absorption process [41].

The Biopolyesters

Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are a diverse family of intracellular biopolymers synthesized by a wide range of microorganisms under conditions of nutrient stress. PHAs play an important role in encystment and sporulation [82]. Polyhydroxyalkanoates (PHAs) are synthesized as cellular and energy storage materials. They are usually accumulated as a result of a nutrient limitation. PHAs have similar properties to conventional plastics and are completely biodegradable [83]. PHAs have potential as biodegradable replacements for conventional bulk commodity plastics and therefore promote sustainable development [82]. One of the PHAs is polyhydroxybutyrate (PHB), which is accumulated in various bacteria including *Alcaligenes eutrophus* and *Azotobacter vinelandii* [83].

Poly-β-Hydroxyalkanoates

Biopolyesters are natural macromolecules, from bacterial sources. Though they are relatively expensive, an increasing interest in using them is observed. It results from their environmentally friendly nature in terms of manufacture, use and disposal. In 1994, 500 tons of biopolyesters were produced. The simplest and most common poly-β-hydroxyalkanoate is poly-β-hydroxybutyrate (PHB). PHB is synthesized as a storage material by a large number of resting bacteria. The amount of PHB in bacteria normally is 1 up to 30% of their dry weight. Under controlled fermentation conditions, some *Azotobacter* and *Alcaligenes* ssp. can accumulate polymer up to 90% of their dry mass [2, 84].

PHB has two limitations in its use: a narrow processability window, and a relatively low-impact resistance due to its high degree of crystallinity. These drawbacks have hampered the utilization of PHB as a common plastic. Blends of PHB with other polymers can offer opportunities to extend and explore their many useful and interesting properties and to modify its undesirable properties. For example, PHB has been blended with poly(ethylene oxide), poly(vinyl butyral), poly(vinyl acetate), poly(vinylphenol), cellulose acetate butyrate, chitin and chitosan [85].

Aliphatic Polyester Blends

Poly(Hydroxyalkanoate)

Aliphatic polyesters are biodegradable and susceptible to hydrolytic degradation. Examples of this group include

poly(hydroxyalkanoate)s (PHAs) that occur widely in nature. They are produced by a wide variety of microorganisms as an internal carbon and energy storage, as part of their survival mechanism. Up to now, over 90 different types of PHA consisting of various monomers have been reported and the number is still increasing [86]. Bacterially synthesized PHAs can be produced from a variety of renewable resources, and are truly biodegradable and highly biocompatible thermoplastic materials. Therefore, PHAs are expected to contribute to the construction of an environmentally sustainable society. Some PHAs behave similarly to conventional plastics such as polyethylene and polypropylene, while others are elastomeric. Thus, blending offers much scope for expanding their range of applications. The most representative member of this family is poly(3-hydroxybutyrate) (PHB). Blending of polymers is an effective alternative to acquiring new materials with desired properties. PHA occurs in blends with such polymers as hydroxybutyrate (HB), 3-hydroxyvalerate (3HV), 3-hydroxypropionate (3HP), 3-hydroxyhexanoate (3HH), and 4-hydroxybutyrate (4HB) [86].

Blends of Poly(d,l)Lactide Family

PLA are produced from renewable resources such as starch, are biodegradable and compostable, and they have very low or no toxicity and high mechanical performance, comparable to those of commercial polymers. However, the thermal stability of PLAs is generally not sufficiently high enough for them to be used as an alternative in many commercial polymer applications. The various PLA blends were studied to improve their thermal properties. A stereocomplex is formed from enantiomeric PLAs, poly(L-lactic acid) (PLLA) and poly(D-lactide) (i.e., poly(D-lactic acid) (PDLA)) due to the strong interaction between PLLA and PDLA chains. The stereocomplexed PLLA/PDLA blend has a melting temperature (T_m) (220-230°C) ca. 50°C higher than those of pure PLLA and PDLA (170-180°C), and can retain a non-zero strength in the temperature range up to T_m . Moreover, the PLLA/PDLA blend has a higher hydrolysis resistance compared with that of the pure PLLA and PDLA, even when it is amorphous-made, due again to the strong interaction between PLLA and PDLA chains. PLLA is usually hard and brittle, which hinders its usage in medical applications, i.e. orthopedic and dental surgery. Poly DL-lactic acid (PDLLA) can degrade quickly due to its amorphous structure, thus the degradation time of PLLA/PDLLA blends can be controlled through various blending ratios [86].

Conclusion

This review has covered the major concerns about the natural and synthetic polymers, their types, uses and degradability. Technical and economical problems connected with materials recycling has induced scientists to search for new materials that may be organically recycled. Synthetic polymers' negative influence on the natural environment creates many problems with waste deposition and

utilization. Nowadays, there are few biodegradable water-soluble polymers available commercially, in spite of the obvious and pressing need for environmental protection. Biodegradable polymers have been researched, but polymers based on renewable sources (especially on starch) are most desirable. The major advantages of biodegradable polymers are that they can be composted with organic wastes and returned to enrich the soil, their use will not only reduce injuries to wild animals caused by dumping of conventional plastics but will also lessen the labor cost for the removal of plastic wastes in the environment because they are degraded naturally, their decomposition will help increase the longevity and stability of landfills by reducing the volume of garbage, they could be recycled to useful monomers and oligomers by microbial and enzymatic treatment. Recently, the development of the manufacture of such polymers has been observed.

Using biodegradable polymers in many fields of industry, instead of synthetic materials, may significantly help protect the natural environment.

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