

BIODEGRADABLE POLYMERS: ADVANCING CHEMISTRY FOR A SUSTAINABLE FUTURE

Dosdar Ali^{*1}, Sahrish Naheed², Umer Khitab³, Zahra Arshad⁴, Aneela Noreen⁵,
Ashique Ali Chohan⁶

^{*1}Department of Chemistry, Karakoram International University, Gilgit-Baltistan, Pakistan

²Department of Chemistry, University of Sargodha, Punjab Pakistan

³Huazhong University of Science and Technology 3BIO Lab, School of Life Science and Technology
China

⁴Department of Chemistry, Comsats University Islamabad, Lahore Campus Pakistan

⁵Institute of Biochemistry & Biotechnology Arid Agricultural University, Rawalpindi Pakistan

⁶Department of Energy and Environment, Faculty of Agricultural Engineering and Technology, Sindh
Agriculture University TandoJam Sindh, Pakistan

^{*1}dosdarchemist@gmail.com, ²sahrishnaheed9091@gmail.com, ³umerkhitab796@gmail.com,
⁴itszahra0437@gmail.com, ⁵Aneelaumarit@gmail.com, ⁶ashiqueakbar90@gmail.com

ABSTRACT

A potential remedy for the worldwide problem of plastic pollution and environmental deterioration is biodegradable polymers. Because they break down into non-toxic byproducts in the environment, these polymers—which come from both natural and manmade sources—offer a sustainable substitute for traditional plastics. The chemistry, production, and various uses of biodegradable polymers are examined in this overview, with a focus on how they contribute to sustainability. Important components including polylactic acid (PLA), polyhydroxyalkanoates (PHA), and polysaccharides are emphasized, along with cutting-edge green manufacturing techniques that reduce their negative effects on the environment. These materials' versatility and potential are demonstrated by their applications in biomedical sciences, packaging, agriculture, and environmental remediation. However, issues including scalability, mechanical performance, and production costs continue to be obstacles to broad adoption. A thorough overview of the field is provided in this review with the goal of stimulating more research and innovation in biodegradable polymer technology. This review also explores degradation mechanisms, life cycle analysis, and the environmental impact of biodegradable polymers, highlighting their advantages over conventional plastics. Developments in polymer chemistry, nanotechnology integration, and circular economy strategies hold promise for overcoming current limitations. Biodegradable polymers can play a paramount role in achieving a sustainable future by fostering interdisciplinary collaboration and policy support.

Keywords: Green Chemistry, Environmental Degradation, Biodegradable Polymers, Sustainable Materials

INTRODUCTION

Synthetic polymer pollution of the environment has reached alarming levels in developing nations. Plastics made from petroleum are not easily biodegradable and build up in the environment due to their resistance to

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microbial breakdown. Furthermore, oil costs have significantly climbed recently. The interest in biodegradable polymers has increased as a result of these findings. In the 1980s, biodegradable polymers and plastics were first made available. Over the past 20 years, there has been a growing interest in polymers derived from renewable resources, mostly because of two main factors: environmental concerns and the recognition that our petroleum supplies are limited. Biodegradable plastics come from a variety of sources, including natural and manmade polymers. Whereas synthetic polymers are made from non-renewable petroleum resources, natural polymers are abundant and derived from renewable sources.

The cleavage of hydrolytically or enzymatically sensitive linkages in the polymer causes polymer erosion during the biodegradation of polymeric biomaterials. Recently, a large number of biodegradable polymers have been created, and certain microbes and enzymes that can break them down have been found [1]. Economic success, social justice, and environmental preservation are the three pillars of sustainability, according to Wang et al. (2008). Plastic processes are reduced when well-enhanced and long-lasting biodegradable plastics are achieved. Resource management and sufficient ecological protection are the cornerstones of the goal of social economics and environmental sustainability consideration in biodegradable plastics.

Resource management and sufficient ecological protection are the cornerstones of the goal of social economics and environmental sustainability consideration in biodegradable plastics. To solve the basic ecological burdens of biodegradable plastics projects, attention must be paid to social, economic, and environmental sustainability principles due to the plastic industry's role in ecosystem degradation, climate change, and several interconnected challenges [2]. Developed in 1994, the Triple Bottom Line (abbreviated TBL) took social, financial, and environmental performance into account while executing projects [3]. According to this theory, biodegradable plastics would achieve sustainability in terms of their effects on the economy, society, and environment.

Human society and the environment are taken into account without endangering the financial rewards. The idea that society should choose an existent and achievable scale that future generations can likewise adopt forms the foundation of the sustainability principle. Thus, to reach this goal, development that will be successfully sustained requires the adoption of rigorous efforts concerning all facets of society and human activities [4]. In order to prevent the wasteful overuse of non-renewable resources that have significant environmental constraints, sustainable development of biodegradable plastics essentially involves controlling the relationship between human and environmental demands. However, this does not stop the existing ethics of basic civil rights and societal justice. In order to secure the survival of the present civilization and future generations, it can also entail preventing environmental and social failure. Adoption of sustainable, biodegradable plastics requires a set of comprehensive, process-oriented principles as well as social, economic, biophysical, and technical attributes [5]. The CPCB report claims that plastic waste's calorific value can be efficiently used to replace coal. In addition to lowering energy expenses, using plastic trash as an alternative fuel will also lower CO₂ emissions. Plastic garbage is entirely burned at high temperatures when it is combined with cement kilns and blast furnaces. The slag that is left over can be used to make cement and build roads. The procedure is safe in accordance with environmental standards, and there is no chance that burning plastic garbage would produce harmful emissions. For the purpose of disposing of the plastic garbage produced on their property, organizations such as the airport and railroads needed to build an environmentally acceptable waste management system. To reduce the burden of littered/discarded plastics, there is an urgent need for increased public awareness as people are responsible for the pollution caused by plastics [6]. In light of this, some suggestions have been made that could help shape future regulations for the handling of plastic trash. Additionally, modernizing the technique for disposing of plastic garbage is crucial. In accordance with IS 14535: 1998, the virgin plastic products must be tagged with the plastic identification code to facilitate sorting and segregation. The impact of excessive plastic material consumption on the environment and human well-being. Because plastic is not biodegradable, it is now considered a major global environmental and health hazard. Although plastic coatings and containers keep food fresher longer, they can also leave neurotoxins like BPA in the body [7]. PVC has been linked to male reproductive issues because it contains chemicals called phthalates, which are used in everything from flooring and pipes to

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clothing and furniture. Research has also demonstrated that exposure to environmental contaminants during childhood can have serious adverse consequences in later life. The need for novel analytical techniques appropriate for tracking multiple phthalates in diverse environmental, biological, and other matrices is always growing. The most common techniques are spectrometric and separation techniques, because of their high sensitivity, good selectivity, ease of automation and downsizing, and—most importantly—low investment and operating costs, contemporary electroanalytical methods can also be helpful in this field. This makes them appropriate for large-scale monitoring [8]. By lessening the environmental impact of conventional plastics, the project seeks to investigate the developments in biodegradable polymer chemistry and their potential to enhance sustainability. It focuses on the creation of biodegradable polymers from renewable resources, their use in a range of industries, and their advantages for the environment, such as lowering waste and reducing plastic pollution. There are still several unmet research needs, nevertheless, including the need for polymers that break down in a wider variety of environmental circumstances, enhancements to their mechanical strength and thermal stability, and affordable, scalable production techniques. Further research into hybrid and composite materials, as well as the long-term environmental impact of biodegradable polymers, is crucial for their widespread adoption. These gaps will help unlock the potential of biodegradable polymers in contributing to a more sustainable future. Other challenges include waste management, recycling, and locating sustainable raw materials.

Classification of biodegradable polymer:

Biodegradable polymers are generally divided into two groups, natural and synthetic based on their origin. Synthetic origin polymers offer advantages over natural polymers by being versatile with a wide spectrum of applications, having the capability to tailor mechanical properties and altering the rate of degradation according to the need. On the other hand, natural polymers seem to be attractive due to their excellent biocompatibility, but they have not been fully investigated due to their undesirable properties like antigenicity and batch-to-batch variation [9]. The instability of the polymers leading to biodegradation has proven to be immensely important in many medical applications[10]. Biodegradable polymers offer tremendous potential in many exciting applications like drug delivery, tissue engineering, gene therapy, regenerative medicine, temporary implantable devices, coatings on implants, etc [11]. The basic criteria for selecting a polymer for use as a degradable biomaterial are to match the mechanical properties and the degradation rate to the needs of the application, non-toxic degradation products, biocompatibility, shelf life/stability, processability, and cost [12].

NATURAL BIODEGRADABLE POLYMERS

Biopolymers are polymers formed in nature during the growth cycles of all organisms; hence, they are also referred to as natural polymers. Their synthesis generally involves enzyme-catalyzed, chain-growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes.

Polysaccharides

For material applications, the primary polysaccharides of interest are cellulose and starch, with growing attention to complex carbohydrate polymers produced by bacteria and fungi, such as xanthan, curdlan, pullulan, and hyaluronic acid. These polymers often have branched structures and diverse carbohydrate units, unlike starch, which combines branched (amylopectin) and linear (amylose) polymers of glucose. Both cellulose and starch consist of d-glucopyranoside units linked by acetal bonds, formed between the C1 of one glucose unit and the hydroxyl group of another at C3 (cellulose and amylose) or C6 (amylopectin). Glucose in these polysaccharides exists in cyclic hemiacetal forms, with starch containing the α -isomer and cellulose the β -isomer, influencing their biodegradability by specific enzymes. polysaccharides are different and are not interchangeable. Fig. 1 shows the structures of some polysaccharides.

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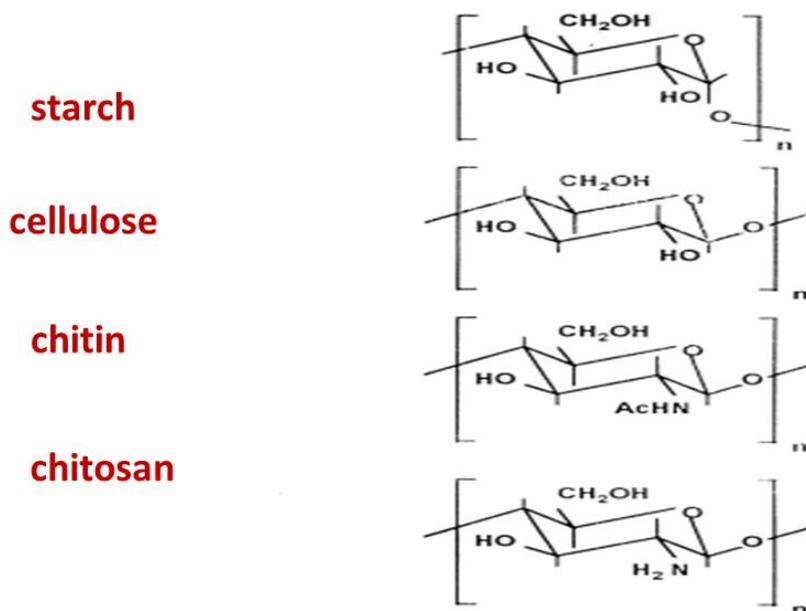


Figure 1: Structures of polysaccharides.

Starch, a widely occurring plant polymer, is primarily sourced from crops like potatoes, corn, and rice, forming granules composed of linear amylose (~20%) and branched amylopectin (~80%). While amylose is crystalline and soluble in boiling water, amylopectin is insoluble but hydrolyzed by enzymes targeting its α -1,4 and α -1,6 acetal bonds. Starch has gained attention as a film-forming material due to its low permeability, making it suitable for food packaging and biodegradable agricultural mulch films. However, challenges like brittleness, retrogradation, and low thermal stability limit its direct use. To enhance its properties, starch undergoes chemical modifications such as acetylation, improving hydrophobicity, solubility, and tensile strength in aqueous environments. Acetylated starch films maintain wet strength and are enzymatically degradable, showing promise for bioreactor membranes. Starch is also blended with polymers like polyethylene and polyvinyl alcohol to produce biodegradable films with properties similar to conventional plastics. Techniques like starch-xanthate integration and crosslinking with isocyanates have enabled its use as a filler, compatibilizer, and crosslinking agent, reducing costs and enhancing biodegradability. These advances highlight starch's potential as a sustainable material for diverse applications, though further optimization is needed for large-scale adoption.

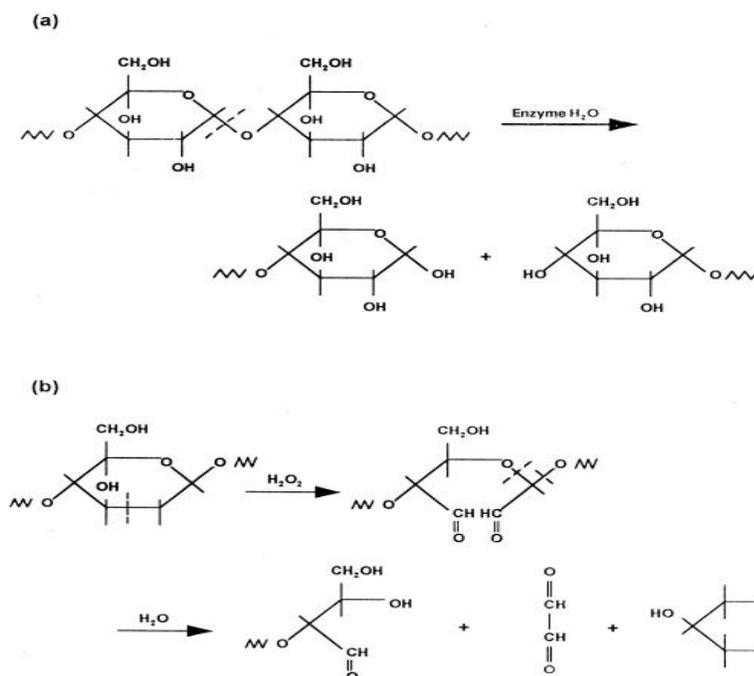
Chitin and chitosan

Chitin is a macromolecule found in the shells of crabs, lobsters, shrimps and insects. It consists of 2-acetamide-2-deoxy-b-d-glucose through the b-(1-4)-glycoside linkage. Chitin can be degraded by chitinase. Chitin fibers have been utilized for making artificial skin and absorbable sutures.³⁰ Chitin is insoluble in its native form but chitosan, the partly deacetylated form, is water soluble. The materials are biocompatible and have antimicrobial activities as well as the ability to absorb heavy metal ions. They also find applications in the cosmetic industry because of their water-retaining and moisturizing properties. Using chitin and chitosan as carriers, a water-soluble prodrug has been synthesized. [13] Modified chitosans have been prepared with various chemical and biological properties.[14] N-carboxymethylchitosan and N-carboxybutylchitosan have been prepared for use in cosmetics and wound treatment. ³³ Chitin derivatives can also be used as drug carriers, ³⁴ and a report of the use of chitin in absorbable sutures shows that chitins have the lowest elongation among suture materials consisting of chitin, poly(glycolic acid) (PGA), plain catgut and chromic catgut.[15] The tissue reaction of chitin is similar to that of PGA.

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Starch

Starch is a polymer which occurs widely in plants. The principal crops used for its production include potatoes, corn and rice. In all of these plants, starch is produced in the form of granules, which vary in size and somewhat in composition from plant to plant. In general, the linear polymer, amylose, makes up about 20 wt% of the granule, and the branched polymer, amylopectin, the remainder. Amylose is crystalline and can have a number average molecular weight as high as 500 000, but it is soluble in boiling water. Amylopectin is insoluble in boiling water, but in their use in foods, both fractions are readily hydrolyzed at the acetal link by enzymes. The α -1,4-link in both components of starch is attacked by amylases (Fig. 2a) and the α -1,6-link in amylopectin is attacked by glucosidases. Starch has been widely used as a raw material in film production because of increasing prices and decreasing availability of conventional film-forming resins.[16] Starch films possess low permeability and are thus attractive materials for food packaging. Starch is also useful for making agricultural mulch films because it degrades into harmless products when placed in contact with soil microorganisms. Research on starch includes investigation of its water adsorptive capacity, the chemical modification of the molecule, its behavior under agitation and high temperature, and its resistance to thermomechanical shear. Although starch is a polymer, its stability under stress is not high. At temperatures higher than 150°C, the glucoside links start to break, and above 250°C the starch grain endothermally collapses. At low temperatures, a phenomenon known as retrogradation is observed. This is a reorganization of the hydrogen bonds and an aligning Figure 2. Enzymatic hydrolysis of (a) starch and (b) cellulose. BIODEGRADABLE POLYMERS 1277 of the molecular chains during cooling. In extreme cases under 10°C, precipitation is observed. Thus, though starch can be dispersed into hot water and cast as films, the above phenomenon causes brittleness in the film. In its application in biodegradable plastics, starch is either physically mixed in with its native granules, kept intact, or melted and blended on a molecular level with the appropriate polymer. In either form, the fraction of starch in the mixture which is accessible to enzymes can be degraded by either, or both, amylases and glucosidases. The starch molecule has two important functional groups, the $-OH$ group which is susceptible to substitution reactions, and the $C-O-C$ bond which is susceptible to chain breakage. The hydroxyl group of glucose has a nucleophilic character. By the reaction of its $-OH$ group, modification of various properties can be obtained. One example is the reaction with silane to improve its dispersion in polyethylene.[17] Crosslinking or bridging of the $-OH$ groups changes the structure into a network while increasing the viscosity, reducing water retention and increasing its resistance to thermomechanical shear.



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Figure 2: Enzymatic hydrolysis of (a) starch and (b) cellulose

SYNTHETIC POLYMERS

Polyesters Poly (α -hydroxy acids) This class of polyesters is most extensively investigated for biomedical applications due to their excellent biocompatibility and tunable degradation properties. They laid the foundation for the development of the first synthetic suture material based on polyglycolide. The category of poly (α -hydroxy acids) includes poly (glycolic acid), poly (lactic acid), and a range of copolymers (poly (lactic-co-glycolic acid)). These polymers are synthesized by ring-opening or condensation polymerization depending on the starting monomer units.[18] Poly (α -hydroxy acids) undergo degradation by non-enzymatic hydrolysis of ester linkages along the backbone into lactic acid and glycolic acid which are resorbed through natural metabolic pathways. The emergence of these polymers from initial resorbable sutures into the most preferred materials for controlled drug delivery makes them the representative class of biodegradable polymers.[19] The first FDA-approved biodegradable synthetic suture based on polyglycolide DEXON® was developed in 1970. Polyglycolide with high crystallinity shows low solubility in organic solvents and good mechanical properties due to which it is indicated for orthopedic applications (Biofix®). Despite many advantages, its application is limited due to the higher rate of degradation, solubility, and accumulation of acidic degradation products.[20] Poly lactides unlike polyglycolides are present in many forms due to the optical isomerism of lactic acid. Polymerization of isomers of lactide (L-lactide and D-lactide) results in crystalline polymers with about 40% crystallinity, whereas polymerization of racemic mixture (DL-lactic acid) results in amorphous polymers with lower mechanical strength. Poly (L-lactic acid) and poly (DL-lactic acid) are more preferred for biomedical applications in which the former is used for bone fixation devices (Bio Interference Screw®, BioScrew®, Bio-Anchor®) and the latter is a suitable candidate as a drug delivery vehicle.[21] The rate of degradation depends on the molecular weight of the polymer, crystallinity and porosity of the matrix. Being more hydrophobic compared to polyglycolide, it shows a slower rate of degradation.[22] Copolymers of poly lactides and polyglycolides [poly (lactide-co-glycolide)] were developed to overcome the demerits of individual polymers and for better property modulation. The properties of these copolymers like crystallinity and rate of degradation are decided by the proportion of each of the polymers. Synthetic versatility obtained by different LA/GA ratios makes it suitable for different applications (PuraSorb®PLG: 80 L/20G; Vicryl®: 90G/10L; Vicryl Mesh®; Dermagraft®). PLGA is being extensively investigated for their potential in tissue regeneration, drug and protein delivery which is proven successful by CYTOPLAST Resorb® and LUPRON DEPOT®. As bulk degrading polymers like poly (α -hydroxy acids) cannot follow zero-order kinetics, surface eroding polymers were developed to overcome this disadvantage.[23]

Poly lactones

Polycaprolactone (PCL) is a semicrystalline polymer with solubility in common solvents making it easily processable. Hydrolytically labile ester linkages are responsible for its slow degradation (2–3 years). Copolymer blends and mixtures of polycaprolactone with other polymers, low molecular weight polyols and macromers alter the rate of degradation and other properties which broaden their potential in a range of applications.[24] For instance, a copolymer of PCL with polyglycolide or polylactide results in rapid degradation and less stiffer fibers (MONACRYL®). The property of slow degradation leads to investigation of PCL as a vehicle for the long-term delivery of drugs/vaccines (Capronor®) and cell-based therapies. Capronor® is a long-term contraceptive device loaded with levonorgestrel.[25] Poly (p-dioxanone) [PDS], another poly lactone, was used in the development of the first commercial monofilament suture in the 1980s. It is a semicrystalline polymer with a very low T_g of 10°C to 0°C.[26] The slow to moderately degrading PDS breaks down by non-specific scission of ester backbone in to glyoxylate which is further converted into glycine. Bone fixation screws based on PDS are available as Orthosorb Absorbable Pins®[27]

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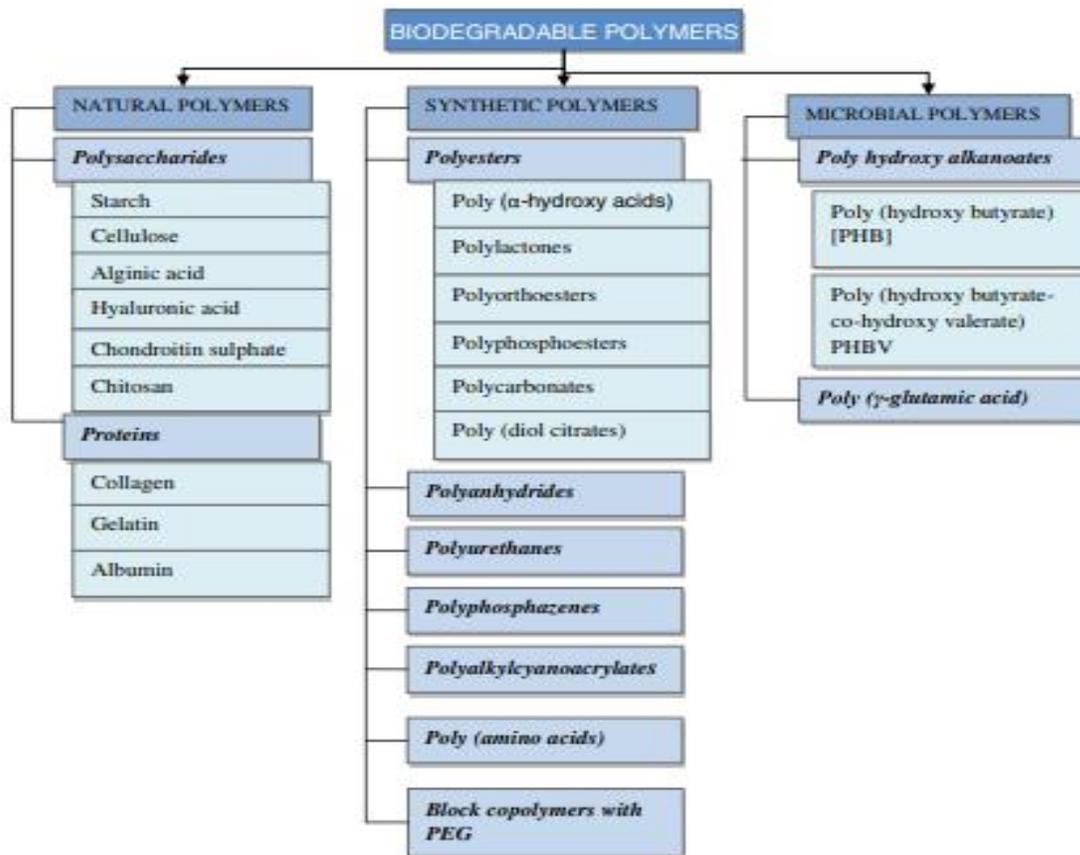


Figure 3: Classification of Biodegradable polymers

Poly (glycolic acid), poly(lactic acid), and their copolymers are among the most widely studied biodegradable polymers in the polyester family. PGA is a rigid thermoplastic material with high crystallinity (46–50%). The glass transition and melting temperatures of PGA are 361C and 2251C, respectively. Because of high crystallinity, PGA is not soluble in most organic solvents; the exceptions are highly fluorinated organic solvents such as hexafluoro isopropanol [28]. Although common processing techniques, such as extrusion, injection and compression molding can be used to fabricate PGA into various forms, its high sensitivity to hydrolytic degradation requires careful control of processing conditions [29]. Porous scaffolds and foams can also be fabricated from PGA, but the properties and degradation characteristics are affected by the type of processing technique. Solvent casting, particulate leaching method and compression molding are used to fabricate PGA based implants. The preferred method for preparing high molecular weight PGA is ringopening polymerization of glycolide (Fig. 1), the cyclic dimer of glycolic acid, and both solution and melt polymerization methods can be used. The common catalysts used include organo tin, antimony or zinc. If stannous octoate is used, temperature of approximately 1751C is required for a period of 2–6 h for polymerization. Although it is possible to synthesize these polymers by acid-catalyzed polycondensation of respective acids, the resulting polymers generally have a low molecular weight, broad molecular weight distribution and consequently poor mechanical properties. The second stage of degradation involves largely the crystalline areas of the polymer, which becomes predominant when the majority of the amorphous regions have been eroded.

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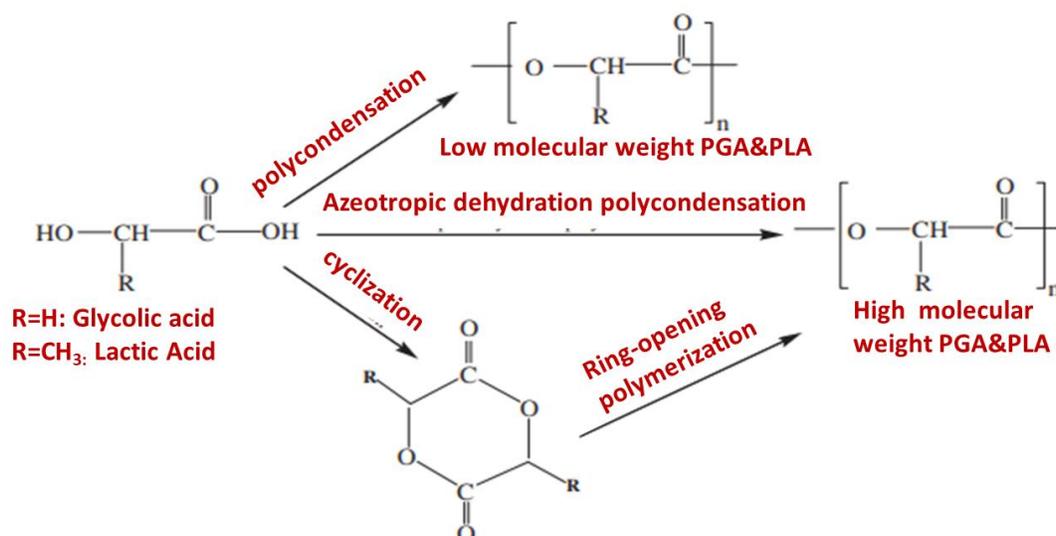


Figure 3: Synthetic routes to poly(glycolic acid) and poly(lactic acid).

The Synthesis of PHAs—Types of Microorganisms That Accumulate PHA and the Processes Within.

PHAs are macromolecules, allowing for the storage of carbon and energy in PHA producing microorganisms[30]. In nature, PHA synthesis can occur through a number of different metabolic pathways, with these pathways determined by the microorganism producing it and the conditions in which this microorganism lives. The synthesis of PHAs is regulated through three genes and three enzymes and is one of the simplest biosynthetic pathways. One of the most common, and shorter pathways for PHA production is that of polyhydroxybutyrate (PHB) (Figure 3). Out of the 150 plus monomers that can be produced by PHA producing bacteria, only a small number of these, under natural conditions, can be formed into the homopolymers and copolymers required for the formation of PHAs. Due to this natural bottleneck for inhibiting polymer formation, sclPHAs such as PHB and P(3HB:HV) are more commonly found in more typical physiological conditions due to their shorter metabolic pathways. With over 300 microorganisms capable of producing PHA, there are relatively few that can synthesize PHA at a level that is sufficient for scaling up to an industrial level. There are several bacterial species that can produce PHA at sufficient levels, though (Table 1). Although PHA can be formed by bacteria, fungi, and microalgae, there is significantly more research and promise for the efficiency of bacteria to produce PHA[31]. *P. putida strain* KT2440, is one of the most studied bacterial strains in the pseudomonas genus. *P. putida* KT2440 is a Gram-negative bacterium that has been extensively studied due to its ability to degrade aromatic compounds and accumulate mcl-PHA. It is one of the most studied bacteria strains as it can synthesize high quantities of polymer per cell mass, amounts up to 75% w/w make it an attractive strain for production scaleup of PHA. *P. putida* KT2440 also has advantageous features for biotechnology due to its metabolic diversity and genetic tractability. It is capable of utilizing a wide range of carbon sources such as glucose, glycerol and fatty acids. PHA accumulation in KT2440 from sugars requires nitrogen limitation but high levels of PHA can be accumulated, without nitrogen limitation while utilizing fatty acids as the carbon source. *P. putida* KT2440 has two main metabolic pathways that provide precursor molecules for the synthesis of mcl-PHA's (Figure 3) namely de novo fatty acid synthesis when using substrates such as glucose and glycerol and β -oxidation when using fatty acids. Another mcl-PHA producing bacterial strain that has been studied extensively is *Pseudomonas oleovorans* ATCC 29347. This strain type can grow on substrates such as n-alkane, n-alkene and longchain fatty acids to accumulate copolymers of mcl-PHA. Monomer units ranging from C6 to C14 are produced via β -oxidation of acyl-CoA, with monomers below C6 bypassing the PHA producing phase with these monomers converted into acetyl-CoA. These monomers below C6 are then harnessed via the TCA cycle for energy and as a carbon source for cell growth [32]. *Burkholderia sacchari* (strain IPT101 in the case

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of UCD), is a Gram-negative bacterium that was originally isolated from sugarcane crops in Brazil. It is capable of utilizing Figure 3. Biosynthesis pathways of short chain length (scl) PHA, medium chain length (mcl) PHA and short-medium-chain length (scl-mcl) PHA from sugars and oils. PhaA, β -ketothiolase; PhaB, NADPH-dependent acetoacetyl-CoA reductase; PhaC, PHA synthase; PhaG, 3-hydroxyacyl-ACPCoA transferase; PhaJ, (R)-enoyl-CoA hydratase; FabD, malonyl-CoA-ACP transacylase; FabG, 3-ketoacyl-CoA reductase. Table 1. Microorganisms extensively studied for their ability to accumulate PHA. Microorganism PHA Type Reference *P. putida* KT2440 mcl *P. oleovorans* ATCC 29347 mcl *Burkholderia sacchari* LFM 101 scl *Cupriavidus necator* H16/DSM 428 scl *P. putida* strain KT2440, is one of the most studied bacterial strains in the *Pseudomonas* genus. *P. putida* KT2440 is a Gram-negative bacterium that has been extensively studied due to its ability to degrade aromatic compounds and accumulate mcl-PHA. It is one of the most studied bacteria strains as it can synthesize high quantities of polymer per cell mass, amounts up to 75% w/w make it an attractive strain for production scaleup of PHA. *P. putida* KT2440 also has advantageous features for biotechnology due to its metabolic diversity and genetic tractability. It is capable of utilizing a wide range of carbon sources such as glucose, glycerol and fatty acids. PHA accumulation in KT2440 from sugars requires nitrogen limitation but high levels of PHA can be accumulated, without nitrogen limitation while utilizing fatty acids as the carbon source. *P. putida* KT2440 has two main metabolic pathways that provide precursor molecules for the synthesis of mcl-PHA's (Figure 3) namely de novo fatty acid synthesis when using substrates such as glucose and glycerol and β -oxidation when using fatty acids. Another mcl-PHA producing bacterial strain that has been studied extensively is *Pseudomonas oleovorans* ATCC 29347. This strain type can grow on substrates such as n-alkane, n-alkene and long-chain fatty acids to accumulate copolymers of mcl-PHA [32]. Monomer units ranging from C6 to C14 are produced via β -oxidation of acyl-CoA, with monomers below C6 bypassing the PHA producing phase with these monomers converted into acetyl-CoA. These monomers below C6 are then harnessed via the TCA cycle for energy and as a carbon source for cell growth. *Burkholderia sacchari* (strain IPT101 in the case of UCD), is a Gram-negative bacterium that was originally isolated from sugarcane crops in Brazil. It is capable of utilizing the components of lignocellulose (cellulose, hemicellulose, lignin) to produce high-value chemicals and products such as poly-3-hydroxybutyrate [P(3HB)]. The capability of *B. sacchari* to produce such high-value products from the most abundant renewable resource worldwide (lignocellulose) was the driving force for its use as a strain for the industrial scale-up of PHA production processes. This is particularly apparent in studies that have shown this bacterium can accumulate P(3HB) up to 80% of its cell dry weight from sucrose. It also grows efficiently on glucose, glycerol, organic acids and hydrolyzed straw. Another well-studied PHB-producing bacterial strain is *Cupriavidus necator* H16, previously known as *Ralstonia eutropha*. This bacterium is considered a model organism due to the availability of its complete genome sequence as well as its genetic tractability. On top of its metabolic diversity, *C. necator* can achieve high cell densities aerobically under both heterotrophic and chemolithoautotrophic growth conditions. Under heterotrophic conditions, *C. necator* can utilize substrates such as fructose, fatty acids and N-acetylglucosamine in tandem with oxygen. Under chemolithoautotrophic conditions, *C. necator* can utilize carbon dioxide as its substrate in tandem with hydrogen and oxygen. When carbon dioxide is the single available source of carbon *C. necator* can assimilate via the reductive pentose phosphate cycle, otherwise known as the Calvin-Benson-Bassham cycle. Due to its capability to produce a variety of valuable chemicals and polymers from an array of sources, *C. necator* is considered a good candidate for biotechnological processes [33].

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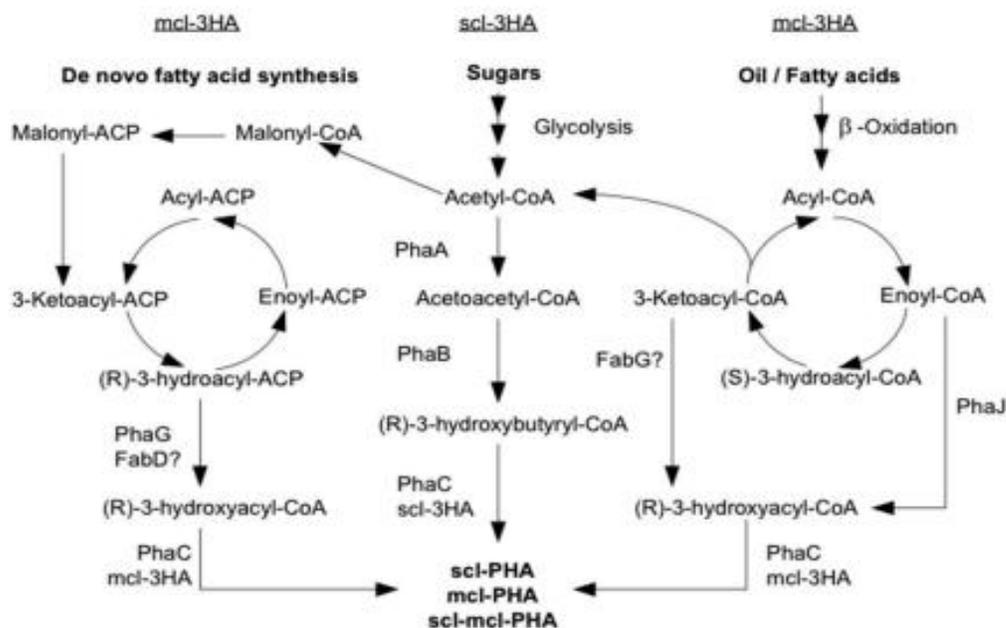


Figure 4: Biosynthesis pathways of short chain length (scl) PHA, medium chain length (mcl) PHA, and short-medium-chain length (scl-mcl) PHA from sugars and oils. PhaA, β -ketothiolase; PhaB, NADPH-dependent acetoacetyl-CoA reductase; PhaC, PHA synthase; PhaG, 3-hydroxyacyl-ACPCoA transferase; PhaJ, (R)-enoyl-CoA hydratase; FabD, malonyl-CoA-ACP transacylase; FabG, 3- ketoacyl-CoA reductase [34].

Green Chemistry Approaches for the synthesis of biodegradable polymer:

Solvent Free Processing:

Fabrication of polymer composites using solvent-free melting processes has also been reported. In the studies of Yu et al., high-conductivity polymer composites were prepared by a one-step solvent-free melting process, based on powder mixing and in situ polymerization (**Figure 5**) [35]. The uniform dispersion of the graphene nanoplatelet (GNP) fillers in the composite films was confirmed by a 3D nondestructive X-ray microcomputed tomography (micro-CT) analysis technique which can be used for analyzing the internal structures of composite films. The conductive behavior of the prepared composite films was highly dependent on the GNP filler dispersion. This study provides a promising platform for fabricating low-cost conductive polymer films. Tan et al. developed solvent-free porous composite scaffolds that have applications in tissue engineering (TE) using rapid prototyping (RP) techniques. The polyetheretherketone (PEEK)-hydroxyapatite (HA) biocomposite blends were made using a selective laser sintering (SLS) rapid prototyping system. The microstructure of the prepared three-dimensional TE scaffolds can be controlled using the SLS process parameters like scan speed, laser power, and part bed temperature. In addition, different amounts of hydroxyapatite can be incorporated into the polymer blends, and it can be used as tissue engineering scaffolds, especially as bone scaffolds. The computational design and fabrication of polycaprolactone (PCL) scaffolds were carried out by Williams et al. using selective laser sintering. The mechanical characteristics, microstructure, tissue in-growth, and biological properties of the PCL scaffolds were analyzed in the study. The PCL scaffolds prepared using SLS have shown suitable mechanical properties as required for their bone tissue engineering applications. The in vivo studies have proven the ability of these PCL scaffolds to enhance the tissue in-growth which can be utilized in bone and cartilage tissue engineering applications. Yuan et al. prepared multi-walled carbon nanotubes/polymer composites using the SLS technique. The study has shown that laser-sintered composites (s-CNT/PA12 and s-CNT/PU) are electrically conductive at less than 1 wt.% concentration of CNTs whereas the thermal conductivity was deleteriously affected by the inevitable pores. These conductive polymer composites can have applications in

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various fields like automobile, aerospace electronic packaging, etc. Badalov et al. proposed a new method for fabricating thin-film composite membranes by using interfacial polymerization and ink-jet printing techniques[36]. The synthesized composites formed by the incorporation of fluorinated diamine into m-phenylenediamine-based polyamide have resulted in membranes with better salt rejection due to an increase in selective layer hydrophobicity. The incorporation of the fluorinated monomer provides improved ion separation properties to the membrane. The usage of other functional monomers in the inkjet PAF methods is a future aspect of the study. The composite membranes prepared by this technique can be used for water treatment and desalination. Our group recently reported the fabrication of a polycaprolactone scaffold using fused deposition modeling without any solvent. The polymer surface was modified by plasma polymerization after which gold nanoparticles were incorporated into the PCL surface using a surface immobilization technique [37]. The PCL scaffolds exhibited enhanced mechanical properties because of interface properties and uniform dispersion of gold nanoparticles (Au-PCL). The combination of the fused deposition method and plasma technology resulted in the successful fabrication of 3D-printed PCL scaffolds having sufficient biomechanical properties to be used in biomedical applications as seen from the nanoindentation studies. The plasma-modified scaffolds containing gold nanoparticles (Au-PCL) showed greater proliferation of HFF2 cells than amine-modified PCL (A-PCL) and neat PCL as seen in Figure 7. Thus, this study clearly shows that FDM is a potential method that can be used for fabricating tissue-engineered scaffolds for biomedical applications.

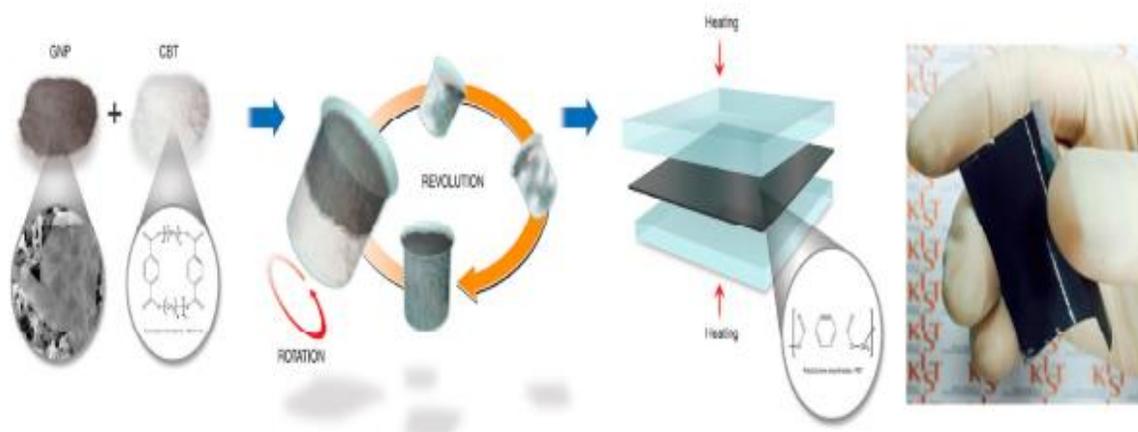


Figure 5: Schematic of solvent-free one-step synthesis based on powder mixing and in situ polymerization for a composite film filled with highly dispersed GNP fillers. Reproduced with permission from[38].

Production of Bio-Based Polymers from Renewable Sources and Agro-Waste

The production of bio-based polymers from agro-waste depends on the availability, cost, and abundance of raw materials. India and China, as major producers of fruits and vegetables, are well-positioned to lead in this field. Renewable sources like lignocellulosic fibers, cellulose esters, polylactic acid, and polyhydroxyalkanoates (PHA) are commonly used for bio-based polymers. These materials, derived from plants like curaua, pineapple, and jute, provide mechanical strength but may have limited biodegradability due to substitution levels. Agricultural waste such as fruit peels, seeds, and coconut shells, traditionally discarded, is now a vital resource for bio-based plastics, plasticizers, and antioxidants. Natural plasticizers, derived from polysaccharides in vegetable-based wastes, improve polymer elasticity and strength, but their performance relative to synthetic alternatives remains underexplored. Natural antioxidants like pomegranate peel extracts and essential oils show promise in replacing synthetic, potentially harmful additives like butylated hydroxytoluene, although commercial applications are limited. The utilization of agro-waste for bio-based polymer production is more sustainable than composting, which generates significant CO₂ emissions [39]. In 2018, global production of bio-based plastics was 2.1 million tons, far below the demand projected to reach 7 million tons by 2020. Bio-based polymers offer advantages in food packaging, such as

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antimicrobial properties, UV protection, and recyclability. However, many bio-based plastics are non-biodegradable due to synthetic additives. Challenges include low production capacity, limited technology, and the need for region-specific approaches to utilizing locally available waste. Biodegradable polymers like poly (butylene adipate-co-terephthalate) and polyhydroxyalkanoates are promising but have limitations based on chain length and mechanical properties. Selection criteria for agro-waste include starch, cellulose, lignin content, and environmental impact. While plant cellulose enhances mechanical strength, it reduces biodegradation rates, a challenge addressed by replacing plant cellulose with bacterial cellulose[40]. These innovations highlight the tradeoffs and opportunities in developing sustainable bio-based polymers.

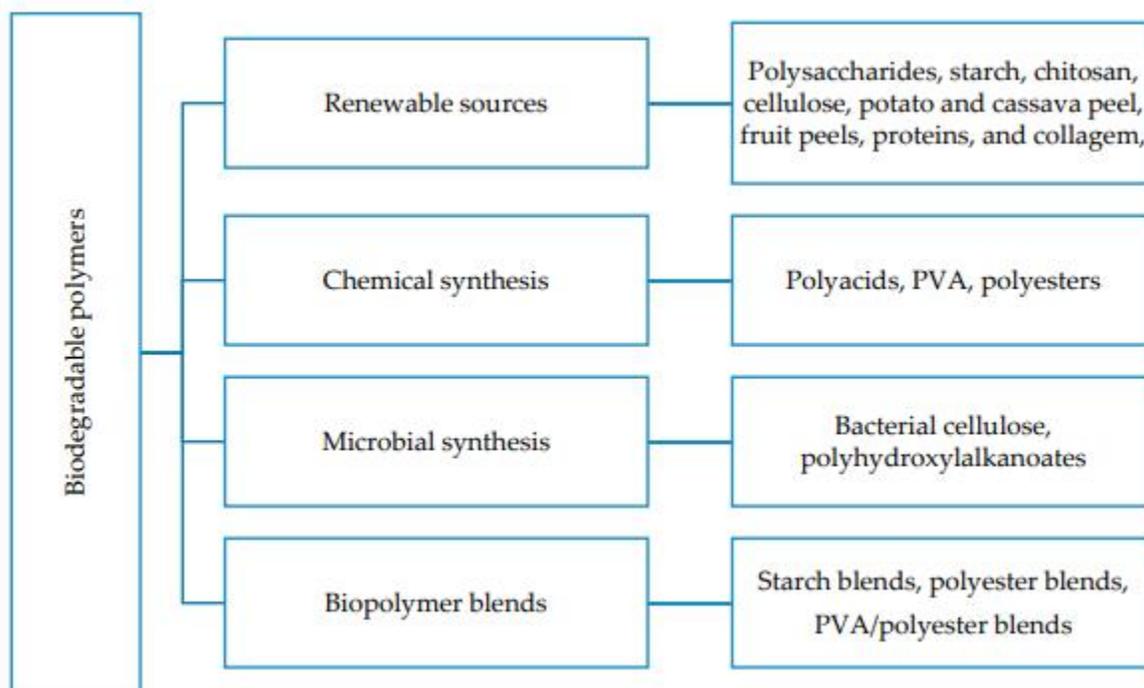


Figure 6: Classification of production processes for biodegradable polymers (reproduced with permission from the publisher.[41])

Biodegradable polymer in the environment:

Conventional polymers such as polyethylene and polypropylene persist for many years after disposal. Built for the long haul, these polymers seem inappropriate for applications in which plastics are used for short periods and then disposed of. Furthermore, plastics are often soiled by food and other biological substances, making physical recycling of these materials impractical and generally undesirable. In contrast, biodegradable polymers (BPs) disposed in bioactive environments degrade by the enzymatic action of microorganisms such as bacteria, fungi, and algae. Their polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. BPs are often derived from plant processing of atmospheric CO₂. Biodegradation converts them to CO₂, CH₄, water, biomass, humic matter, and other natural substances. BPs are thus naturally recycled by biological processes (Fig. 1). The worldwide consumption of biodegradable polymers has increased from 14 million kg in 1996 to an estimated 68 million kg in 2001. Target markets for BPs include packaging materials (trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable nonwovens (engineered fabrics) and hygiene products (diaper back sheets, cotton swabs), consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys), and agricultural tools (mulch films, planters). BP commercialization is, however, hampered by competition with commodity plastics that are inexpensive and familiar to the customer. Also, an infrastructure for the disposal of BPs in bioactive environments must be developed and will require capital investments. Without an extensive network of efficient composting and other bioconversion facilities

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that, in addition to compost, yield other valuable chemical intermediates, BPs and other biodegradables (food, yard-waste, nonrecycled paper) are destined to be entombed in dry landfill environments designed to retard biodegradation.

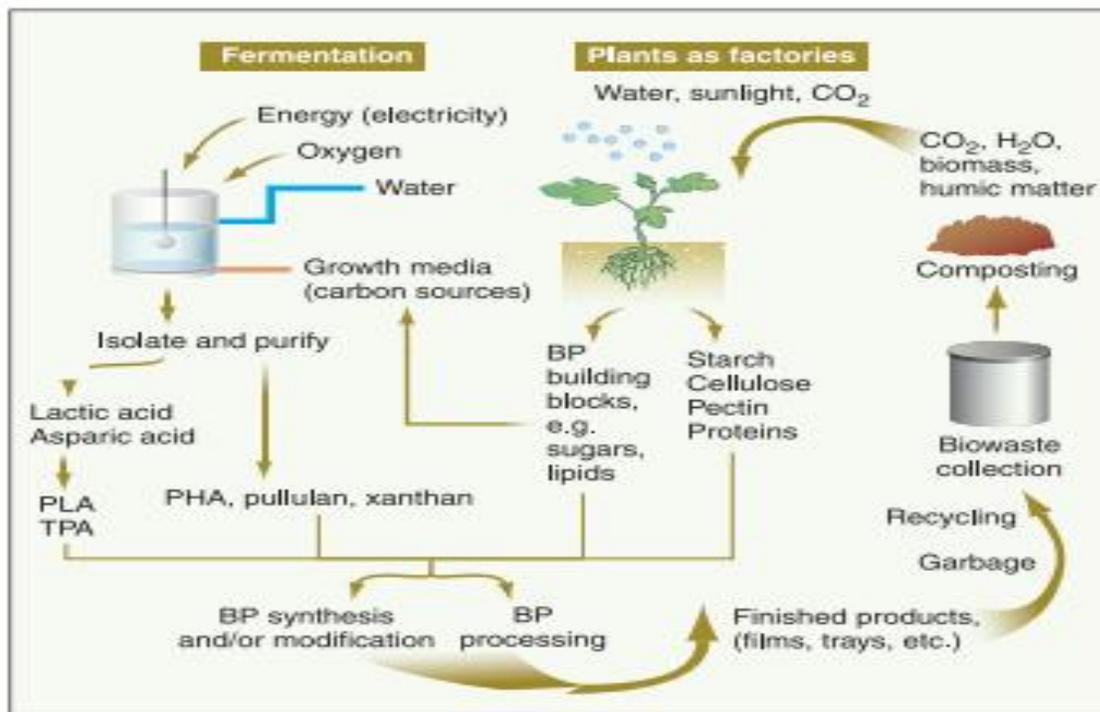


Figure 7: Cyclic process by which agricultural products and fermentative routes can yield biodegradable polymers. BPs will biodegrade to natural substances such as CO₂, water, humic matter, and biomass upon disposal in bio-bins and exposure to a bioactive environment. New crops, using nutrients from compost and fixing CO₂, will produce new polymer building blocks, monomers, and polymers [42].

In the medical field:

Biodegradable polymers can be applied in the medicinal arena and are mainly classified into drug delivery systems, wound healing products, and surgical implant devices. The advancement of biopolymeric drug delivery systems now attains remarkable interest, especially in controlled delivery. More importantly, drug delivery inside humans can be regulated through biodegradable capsules. Particularly, biodegradable polymers are used to prepare novel formulations, and the high permeability of buccal mucosa is an appropriate target for drug delivery. In this regard, drug delivery combined with biopolymers and buccal routes is shielding, safe, and rapidly functioning. Similarly, in the case of wound healing, bioresorbable non-wovens to substitute human tissue repair, and simple sutures, staples, or meshes, are accessible. Comparatively, the usage of biological resorbable scaffolds for tissue engineering is worth revealing. Further, biodegradable polymers are renewable, cost-effective, and found in various varieties. Notably, biodegradable polymers are considered an exceptional candidate for wound healing due to their bioactive features, facilitating cell growth and regeneration potential, and providing antimicrobial conditions and immunomodulation[43]. In addition, biodegradable polymers are a probable candidate for wound care because they can absorb a massive amount of water. In recent years, these polymers are capable of releasing drugs at the site of damage and making them appropriate for healing applications. Many biopolymers have good film-forming features, making them applicable for conventional commodity applications. Notably, they are used in foodstuff containers (bottles, jars), soil retention sheeting, farming film, garbage bags, and wrapping material. Additionally, biodegradable polymers in non-woven form can be used in farming, filtration, hygiene, and protecting wear [44].

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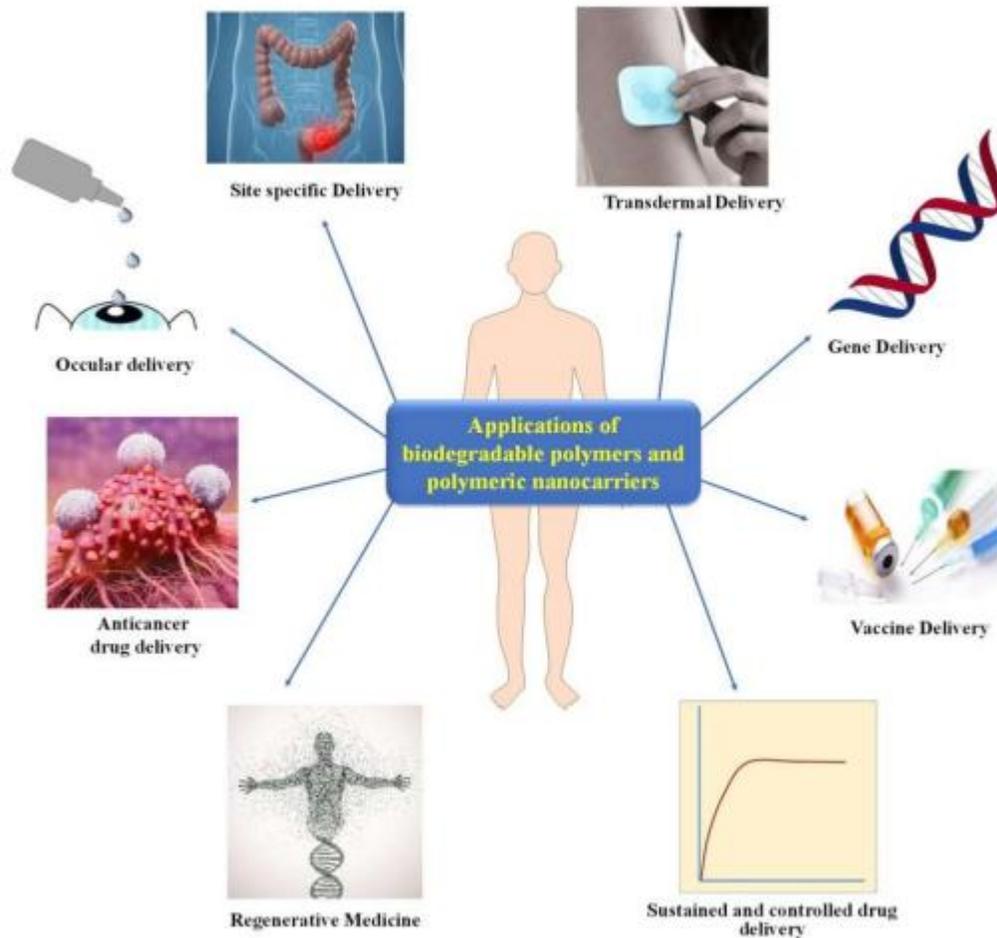


Figure 8: Different kinds of biopolymer applications and polymeric nanocarriers [45].

Food Industry Application:

Mostly biodegradable bioplastics are used for flexible packaging and non-degradable bioplastics are used for rigid packaging. The future of bioplastics focuses on the market for compostable, semi-durable, and durable bioplastics used in consumer and industrial applications. Biodegradable polymers can be used for modified atmospheric storage (MAP) of fruits and vegetables instead of conventional polymers. In MAP it is often desirable to generate an atmosphere low in O₂ and/or high in CO₂ to influence the metabolism of the product being packaged and the activity of decay-causing organisms to increase storability and/or shelf life. In addition to atmosphere modification, MAP vastly improves moisture retention, which can have a greater influence on preserving quality than O₂ and CO₂ levels [46]. Figure 1 represents the global scenario of bioplastics application in different sectors at present and a future estimation [47]. Packaging is an integral component of the food processing sector. Food packaging is a combination of art, science, and technology of enclosing a product for achieving safe transportation and distribution of the products in wholesome conditions to the users at least price. Most of the conventional packaging materials are products of petrochemicals like PVC, PET, polystyrene (PS), polypropylene (PP), polyamide (PA). The properties which make them unique for packaging of food are low cost, excellent physical properties (density, molecular weight), mechanical properties (tensile strength), transmission properties (O₂, CO₂), which not only increase the shelf-life of the product but also add functionality in terms of convenience and attractiveness to the consumers [48].

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Application in agriculture: The investigation of green materials such as bio-based plastics is validated by the contribution of synthetic plastic materials to anthropogenic contamination of the environment in each phase of the life cycle—from monomer synthesis to disposal in landfills or recycling. The current rate of global plastic production is unsustainable, considering more than 400 million tons of waste are generated each year. Additionally, the rate is expected to increase fourfold by 2050 and there has been a concomitant increase in agricultural plastic waste. The agricultural plastic waste originates from shading nets, mulching materials, and pesticide containers. The volume of agricultural plastic waste would surge in line with the global demand for food cultivated in controlled environments[49]. Considering that only a small fraction of the waste is utilized in the production of animal feeds, manure, and other value-added products, there is a potential for the production of biodegradable polymers from agricultural waste. The recycling of plastic waste is not favorable using current technologies due to the risk of leakage of toxic and synthetic chemicals such as anti-oxidants, plasticizers, and stabilizers [50]. The absence of facile, scalable, and environmentally favorable recycling processes has impacted the rate of recycling of global plastics waste—only 9% of the plastics are recycled[51]. The threat of plastics to the environment extends beyond the lack of suitable recycling methods; the synthesis of eco-friendly polymer composites has been impacted by unsuitable synthetic routes.

Future perspective:

Biodegradable polymers have enormous promise to advance sustainability in the future. Developments in polymer chemistry are concentrating on creating polymers with improved mechanical qualities, antibacterial and self-healing properties, and customized rates of breakdown. To reduce waste and energy consumption, these polymers are increasingly being manufactured utilizing bio-based feedstocks, which lessens dependency on fossil fuels and aligns with green chemistry concepts. The performance and breadth of applications of biodegradable polymers are anticipated to be further improved by emerging technologies like nanotechnology and 3D printing, opening up a variety of industries for their use, including consumer goods, packaging, medical devices, and agriculture. To guarantee that these materials blend in perfectly with natural degradation processes and support a circular economy, effective end-of-life strategies—such as recycling and composting systems—are essential. Furthermore, to spur innovation and promote broad adoption, partnerships between governments, businesses, and academia—backed by incentives and regulations—are crucial. Biodegradable polymers offer a promising way to combat environmental pollution and lower carbon emissions, paving the way for a more sustainable future.

Conclusion:

To sum up, biodegradable polymers are a revolutionary development in materials science that provides environmentally friendly substitutes for traditional plastics. These spontaneously degrading polymers tackle important environmental issues like resource depletion and plastic pollution. Their production lessens environmental effects and dependency on fossil fuels by using bio-based feedstocks and following green chemistry principles. Their applications in a variety of industries, including medical, packaging, and agriculture, are increased by advancements in their design and processing, which include customized degradation rates and improved performance. Their adaptability is further increased by the use of cutting-edge technologies like 3D printing and nanotechnology, opening the door for high-performance, environmentally friendly materials. To maximize their environmental benefits and promote a circular economy, effective waste management systems—such as recycling and composting—are essential. To get over present obstacles like cost and scalability and to encourage worldwide adoption, cooperation between researchers, businesses, and legislators is crucial. Biodegradable polymers have the potential to strike a balance between industrial demands and environmental responsibility as the world moves toward more sustainable practices. They are essential to a sustainable future because of their capacity to reduce environmental pollution and provide creative solutions for a range of businesses. We can make a substantial contribution to a healthier, greener Earth by advancing research and development in this area.

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