SCIEPublish

Review

Synthesize and Applications of Biodegradable Plastics as a Solution for Environmental Pollution Due to Non-Biodegradable Plastics, a Review

Samadhi Himantha Kelaniyagama, Asangi Gannoruwa * and A.H.L. Renuka Nilmini

Department of Materials and Mechanical Technology, Faculty of Technology, University of Sri Jayewardenepura, Homagama 10206, Sri Lanka; shklanka1997@gmail.com (S.H.K.); nilminil@sjp.ac.lk (A.H.L.R.N.)

* Corresponding author. E-mail: asangi@sjp.ac.lk (A.G.)

Received: 26 September 2024; Accepted: 3 December 2024; Available online: 9 December 2024

ABSTRACT: Biodegradable plastics are a potential sustainable alternative to conventional petrochemical-based non-degradable plastics. Due to their lightweight, flexibility, durability, versatile applications, chemical inertness, electrical and heat insulation, and conductivity, plastics have become an essential material for many industries, with annual production currently exceeding 450 million tons. However, these materials are non-biodegradable, leading to detrimental consequences such as the formation of microplastics from improper disposal and the generation of toxic gases, including furans, dioxins, mercury, and polychlorinated biphenyls, from burning plastic waste. This results in environmental pollution, affecting land, water bodies, and the atmosphere. In response, studies where the focus has been on creating bio-degradable polymers such as polylactic acid, polyhydroxy alkanoates, Polycaprolactone, Poly(butylene adipate-co-terephthalate), and Polybutylene succinate, which were extracted from renewable resources or chemically modified as biodegradable polymers. Biodegradable polymers exhibit a wide range of properties and can now be modified to be used in various applications suitable for substituting some conventional plastic products. Thus, the article highlights the critical issue of environmental pollution caused by non-biodegradable plastics and provides a comprehensive overview of the synthesis processes, properties, novel applications, and challenges associated with the use of biodegradable plastics.

Keywords: Biodegradable plastics; Environmental pollution; Plastic waste management; Polyhydroxyalkanoates; Poly(lactic acid); Renewable resources

© 2024 The authors. This is an open access article under the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/).

1. General Introduction

Plastics play an important role in the modern world due to their lightweight, versatility, chemical inertness, and favorable electrical and thermal properties. These attributes make plastics indispensable across various industrial applications, including household equipment, fittings, furniture, appliances, electrical components, medical devices, and packaging. By 2024, global plastic production surpassed 450 million tons per year and is expected to double by 2040 [1,2], with over 95% of single-use plastics [3]. Notably, more than 90% of raw materials used in the packaging industry are plastic-based. The synthesis of plastics, a 20th-century breakthrough [4], revolutionized industrial production. As a byproduct of the petroleum industry, plastic materials were inexpensive to manufacture and quickly earned the reputation of being 'the magic material'. Commonly used plastics in the production industry include polyethylene terephthalate (PET), high—density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC).

From 1950 to 1970, plastic production was manageable; however, the following two decades saw a significant increase in production, leading to unforeseen waste management challenges. Being non-degradable, plastic waste often disposed directly into the environment, creating massive landfills. In 2015, global plastic waste generation amounted to approximately 6300 Mt [5], where about 79% ended up in the landfills or spreading in the environment. Unless patterns change, plastic waste generation should increase almost twofold to approximately 12,000 Mt by 2050. Landfilling is the predominant waste management method in Europe, where EU landfills buried 7.2 million tons of plastic waste in

https://doi.org/10.70322/spe.2024.10011

2018 [6]. An examination of common polymers, low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) reveal that 48% to 60% of their total production from 1950–2016 flow to the landfills. In addition, landfills are hotbeds of microplastics; studies show that landfill refuse contains between 20,000 and 91,000 microplastic particles per kilogram [7], many more than in other environments such as sediments, sewage sludge, or agricultural soil. This points to the high accumulation of both macro- and microplastics in landfill sites, posing long-term environmental problems.

Under normal environmental conditions, these waste plastics will be broken down into microplastics due to weathering, espouse to sunlight, and burning. Microplastics pose severe hazards to both the environment and animals by disrupting food chains [8]. Furthermore, burning plastic waste releases harmful gases, such as furans, dioxins, and polychlorinated biphenyls, into the atmosphereThese toxic gases are known to be carcinogens, mutagens, or harmful to the central nervous system, causing various cancers, heart diseases, respiratory problems, neurological damage, and even affecting reproduction system [9]. Hence, the management of plastic waste becomes crucial for a healthy environment. Strategies like 3R concept has been developed to address this issue, however there are still problems associate with the waste management of conventional plastic. Consequently, research and development in renewable, biodegradable plastics are gaining significant attention.

Biodegradable materials can decompose gradually without harming the environment, offering a promising solution to the challenges posed by non-biodegradable plastics. These bio-degradable polymers (BDP) exhibit a wide range of properties, enabling them to compete with non-biodegradable thermoplastics in various fields. Polylactic acid (PLA) and polyhydroxyalkanoate (PHA), derived from bio-polyesters, are among the most commonly used biodegradable plastic materials [10]. This paper explores the synthesis and applications of biodegradable plastics as a solution to the environmental pollution caused by non-biodegradable plastics.

2. Biodegradable Plastics as a Sustainable Solution for Non-Degradable Plastics

2.1. Non-Degradable Plastic and Environment Pollution

With global plastic production increasing rapidly, many non-degradable plastics are being released into the environment throughout their life cycle. From one and a half million tons in the 1950s, global plastic production surged to 450 million tons by 2024 and is expected to double by 2040. According to UN environmental global reports, 79% of one time use plastic products are not efficiently managed and eventually end up in massive landfills [11]. Landfills are a source of many environmental challenges. “Leachate” liquid that percolates through the landfill often contains hazardous substances, such as heavy metals, organic pollutants, and pathogens, which can seep into the surrounding soil and contaminate the groundwater nearby if not managed [12]. This leachate can be a big risk to local water supplies and ecosystems. Furthermore, landfill sites take up so much land, resulting in habitat destruction and loss of biodiversity in surrounding areas. In addition, the waste of plastics in landfills also causes long-term pollution since the plastics do not degrade for hundreds of years and break down into microplastics, which are transported into the surrounding land and water.

Plastics can break down into small particles through photodegradation, thermal oxidation, or hydrolysis mechanisms [13]. In the early 1970s, researchers identified micro-size plastic particles in coastal water [14]. Later, Thompson RC and co-workers coined the term ‘microplastic’ for plastic particles smaller than 5 mm [15]. Most microplastics are generated from the partial degradation of PE, PP, PVC, PET, and PS, which are extremely hard to decompose and persist in the environment for extended periods fully. The low degradation rate of plastics is primarily due to their very high molecular weights, resistance to mid-chain attack, comparative water resistance, and low surface area to volume ratio [16]. According to Do Sul et al., plastics are dispersed in aquatic, atmospheric, and terrestrial systems [17], entering these environments through various pathways, such as being transported from land to rivers and eventually reaching the ocean [18]. Nearly eight million tons of non-degradable plastics are disposed of in the oceans each year by coastal countries, equivalent to covering every foot of seaboard on Earth with five trash bags [19]. This non-degradable plastic waste leads to the loss of millions of animals yearly, including fish, birds, and other marine life. Around 700 species are known to be impacted by plastics, including some that are endangered. Plastics have also become a threat to land animals; and they have consumed plastics, leading to their painful deaths. Plastic bottles significantly contribute to this environmental pollution.

Burning waste plastics is often used as a waste reduction method by local communities, as it reduces the large volume of material destined for landfills. Waste plastic incineration could provide energy recovery potential by harnessing the heat produced by combustion for electricity generation [20] or for heating buildings as an alternative energy source [21]. Waste generated from polyolefin-based polymers such as PE and PP is suitable for the energy

generation via incineration process [22–24]. The cost of transporting waste to a landfill may make incineration a cost-effective waste management solution for municipalities compared to recycling other options. However, burning plastic waste harms the environment, animals, and humans. For instance, incineration or simple burning of plastic waste containing PVC, CPVC and polycarbonate releases dioxins, furans, mercury, and polychlorinated biphenyls to the environment especially to the atmosphere [9,25]. These poisonous gases are known to cause different diseases, such as cancer, neurological damage, reproductive complications, and damage to the immune system [26–28]. Emission from plastics burning that contains halogens such as PVC greatly emits dioxane, polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and large quantities of hydrochloric acid (HCl) could have a greater impact on human health, and affect the respiratory system [25]. For instance, chromatographic signals measured among 88 of the most abundant VOCs in emissions from burning PVC, 54% are from benzene, a known carcinogen, and this is far greater than the 4.8% from emissions from burning biomass. Another major emission is hydrogen chloride (HCl), detected at 2.3 ± 0.1 ppmv and acting as a sensory and pulmonary irritant. Also of high concern are chloromethane (3007 ppbv), vinyl chloride or chloroethene (25 ppbv), and 1,3 butadiene, whose toxicological impacts, in addition to human health, include ecosystem health. Furthermore, depending on burning conditions, chlorine dioxide, a strong oxidant, has been observed at elevated levels [25,29,30]. The dioxins generated can blow onto crops or enter waterways, where toxins find their way into the food chain and ultimately humans [31]. In addition, from incineration in plastics on 2015 is estimated at 5.9 million metric tons of CO_2 emotion and simple burning of plastic emitted 1.8 billion tons of CO_2 in 2019 which is 3.3% of global emissions. This may lead to climate change since it discharges huge amounts of carbon dioxide (CO_2) [32–34]. These results demonstrate the necessity of alternative plastic waste management techniques that prevent the hazardous environmental and health threats contributed by plastic waste burning.

2.2. Waste Management through 3R Concept

Strategies like the 3Rs—Reduce, Reuse, and Recycle—have been implemented to address the problems allied with the rising use of non-degradable plastics. Nevertheless, these initiatives encounter several challenges [35]. A large number of plastic wastes of different types and huge quantities are challenging to handle by recycling facilities, which results in the manufacturing of poor-quality recycled products or the disposal of such products in landfills. Also, it is hard to promote the reduction of the use of plastic products, especially for necessary products, without affecting the supply chain system [36].

In 2016, the consumption of plastic bottles was about 500 billion, meaning that one million bottles were used every minute. This is projected to rise by 20% by 2021 [37]. Although the number of plastic bottles produced is very high, only a small fraction is recycled. Of this small fraction, just 5–7% is turned into new plastic products. The economic factor also becomes an issue when it comes to recycling plastic bottles because the cost of recycling is usually higher than the cost of producing new plastic bottles. This is due to the economic disparity between recycling and using virgin plastics, thus making people continue using virgin plastics [38].

In addition, consumer preferences are vital to the success of the 3R concept. Most of the population uses plastic bottles more than the delicate glass and heavy metal types, mainly because plastic bottles are lighter and easier to lift. This preference only intensifies the issues with plastic waste since throwaway plastics remain a popular choice. Minimizing the use of plastic items, especially for basic needs, is daunting without altering existing production systems and consumer practices.

The chart in Figure 1 shows the data on the annual plastic waste by disposal from the year 2000 up to the year 2019. This implies that despite the enhanced recycling activities, the major chunk of plastic waste is either burnt or disposed of in landfills. This development highlights the need for better waste management strategies and the adoption of the 3 R's model to prevent environmental pollution. A number of strategies have to be employed. Improvement of recycling, increasing the awareness of biodegradable plastics [39].

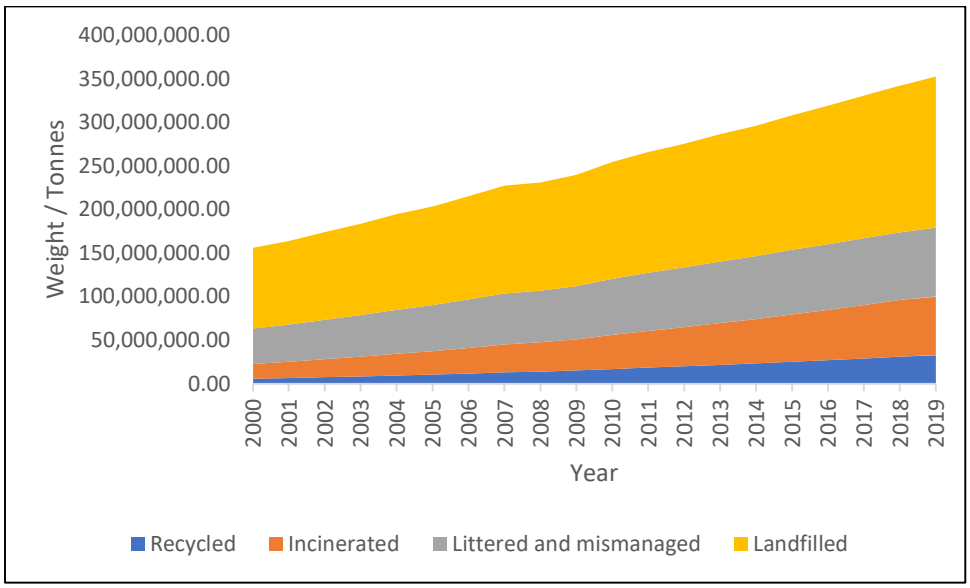

Figure 1. Annual Plastic waste management using 3R method from 2000 to 2019 data adapted from [40].

Overall, plastic recycling provides economic and environmental benefits. One such example is post-consumer recycled plastics (PCRP) [41]. PCRP is very important in reducing plastic waste contaminated with landfills and establishing a circular economy [42] by reprocessing plastic waste; that is, plastic waste from household and commercial sources, in order to give a second life to plastic waste and reduce waste and ultimately result in savings of net energy and emissions, relative to landfilling plastic waste. The use of PCR plastics has shown to cut down emissions of CO_2, carbon monoxide, and dioxins [41–43], and is an environmentally preferable alternative. Moreover, the growth and decentralization of recycling activities may enhance employment opportunities [44]. The widespread use of PCR plastics for non-degrading applications, such as buckets, tubs and bins, for flowerpot manufacture and bags, where properties are adequate for appropriate service life and functionality, without exposure to harsh environmental conditions is noted. Additionally, the production of PCR plastics utilizes less land, energy, water and chemicals and results in less pollution than treatment from other methods, including landfilling and burning. However, plastic recycling has its challenges; for mixed plastics, the process is complex. It involves collection, sorting, cleaning, and compatibilization and is extremely expensive. A second issue is that polymers are incompatible with each other; some plastic types cannot be recycled into a blend with others without the quality of the resulting material being degraded. During recycling, plastics commonly show lower quality than fresh ones, and lower clarity, mechanical characteristics, and color constancy restrict their applications. The economic viability of recycling also depends on oil price fluctuation, recycling costs and the market demand for recycled plastics, whose prices are often ruled by the basic virgin plastic price [45–47].

2.3. Introducing Biodegradable Plastics as a Solution for Non-Degradable Plastic

As a solution to the environmental concerns posed by petroleum-based plastics, researchers have begun investigating biodegradable plastics. Currently, there are three types of biodegradable plastics, classified according to their stage of development. The first type involves blending polymers and additives degraded by microorganisms [48]. In these blended biodegradable plastics, nondegradable polymers are mixed with specific additives or plasticizers that facilitate partial or complete biodegradation. These plastics are not inherently biodegradable, but they contain additives that promote biodegradation through microbial activity. These plastics need specific environmental conditions for the metabolization of microorganisms. However, the degradation rate of blended polymers depends on the type of additives, exposure to oxygen, moisture content, and microbial activity. The second type consists of synthetic polymer materials with grafted groups that undergo hydrolysis through microbial attack. The synthetic polymers are chemically grafted with biodegradable segments within the polymer chain. The grafted segments enable enzymatic and hydrolytic degradation of the plastic. The third and most efficient method synthesizes polymers from naturally occurring materials through fermentation, such as well-known poly(lactic acid) (PLA), poly(hydroxybutyrate) (PHB) and poly(hydroxyalkanoate) (PHA) [16]. These are mainly synthesized from renewable resources. These plastics are oken down into carbon dioxide, water, and biomass under composting conditions.

These biodegradable plastics in Figure 2 are primarily replacing traditional petroleum-derived plastics in the packaging industry. Starch is the major raw material used to produce biodegradable polymers. Annually, Europe produces 50 million tons of starch [1,49], with more than 25 million tons utilized for biodegradable polymer synthesis [49]. A significant disadvantage of these biodegradable polymers is that they require the addition of other additives or elastomers to achieve the necessary properties for packaging. Consequently, researchers are focusing on developing compatibilizers or coupling agents that prevent the separation of biodegradable polymers and additives.

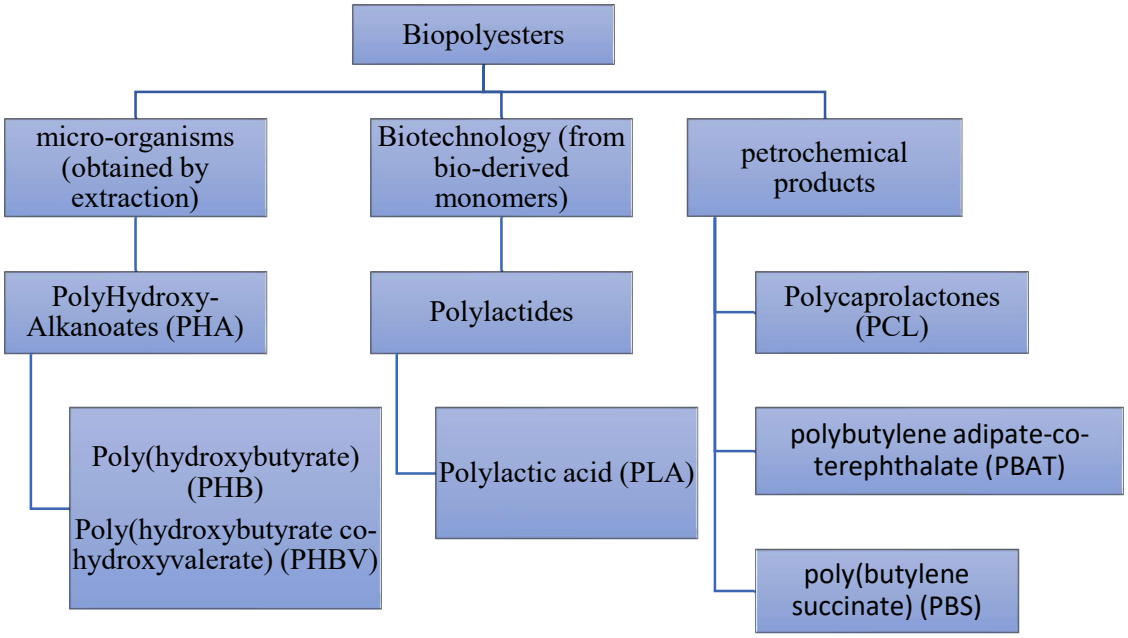

Figure 2. Classification of Bio- degradable polyester based on extraction method.

3. Synthesize, Properties and Applications of Biodegradable Plastics

3.1. Poly(lactic acid)

3.1.1. Synthesize, Properties and Applications of Poly(lactic acid)

Poly(lactic acid) is a vastly used alternative for non-degradable plastics. PLA is one of the most important biopolymers because it can be sourced from renewable and non-toxic feedstocks, mainly sugar and starch [50]. Until the early 2010s, the applications of PLA were primarily limited to the biomedical field [51] due to its features that permit use in the human body. In the late 2010s, PLA was introduced to the packaging industry as a biodegradable packaging material because it possesses essential properties like biodegradability, mechanical strength, and processability [52].

The production of polylactic acid (PLA) begins with the fermentation of sugars derived from natural sources such as corn, sugarcane, and various food components as in Figure 3 [50]. The initial stage in the synthesis of PLA entails the creation of lactic acid (2-hydroxypropanoic acid), the most prevalent hydroxycarboxylic acid identified by a Swedish chemist in 1970. Lactic acid (LA) can be synthesized through fermentation or chemical means and is naturally present in a variety of food items, as well as being a byproduct of in situ microbial fermentation, for instance, sauerkraut, yogurt, buttermilk, sourdough bread, and numerous other fermented products. LA serves as a crucial metabolic intermediate in most living organisms, ranging from anaerobic prokaryotes to humans [51].

LA has traditionally been used in the food industry for preservation, flavoring, pH buffering, or as a bacterial spoilage inhibitor in a wide range of processed foods [53]. Technical-grade lactic acid was additionally utilized in leather production. LA's two functional groups enable a range of chemical reactions. These reactions are classified into four types: condensation, esterification, reduction, and alcohol substitution. Through such reactions, LA can be used to produce items that possibly have a large-volume use in industrial and consumer products [54]. The major products of these chemical reactions include polymers for prepared plastic and plastic-based fibers. PLA can form linear polyesters through intramolecular or self-esterification due to its hydroxyl and carboxyl functional groups.

LA isomers are classified as either L-lactic acid (L-LA) or D-lactic acid (D-LA) as in Figure 4. Among these isomers, L-LA is the most desirable feedstock for dilactate production because it delivers a high dilactate yield and a HMW-polymer with a high degree of crystallinity and strength [55].

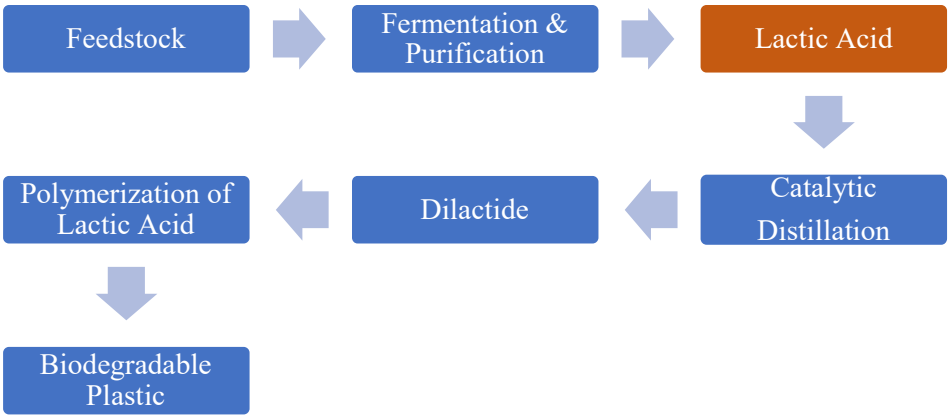

Figure 3. Polymerization process of the Lactic acid synthesized through fermentation.

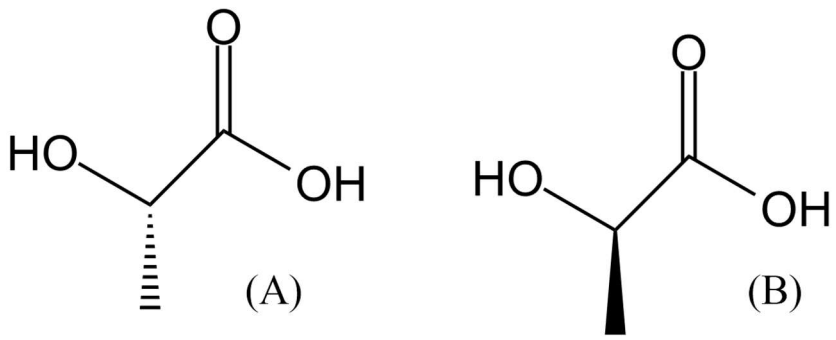

Figure 4. Structures of (**A**) L-lactic acid (**B**) D-lactic acid.

The polymerization of LA (as in Figures 5–7) is the initial step in producing PLA, a biopolymer with properties similar to traditional plastics. The most cost-effective polymerization technique used in PLA synthesis is condensation polymerization. However, this method struggles to produce high molecular weight polymers [50] and solvent-free polymers [10]. Thus, the preparation of high molecular weight PLA (HM-PLA) generally calls for the use of coupling agents or esterification-promoting agents. Plasticizers that interact with the hydroxyl or carboxyl end-groups of PLAS are used in lesserquantities in terms of the PLA weight.

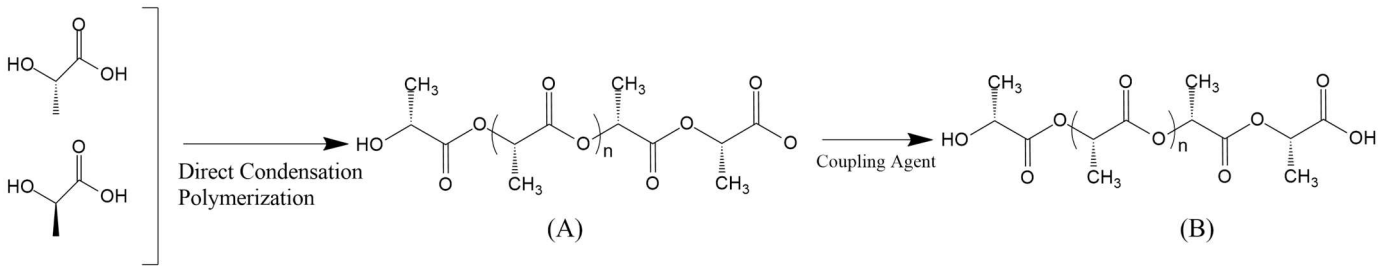

Figure 5. Polymerization of Lactic acid Through Direct Condensation Polymerization (**A**) Low MW PLA (**B**) High MW PLA.

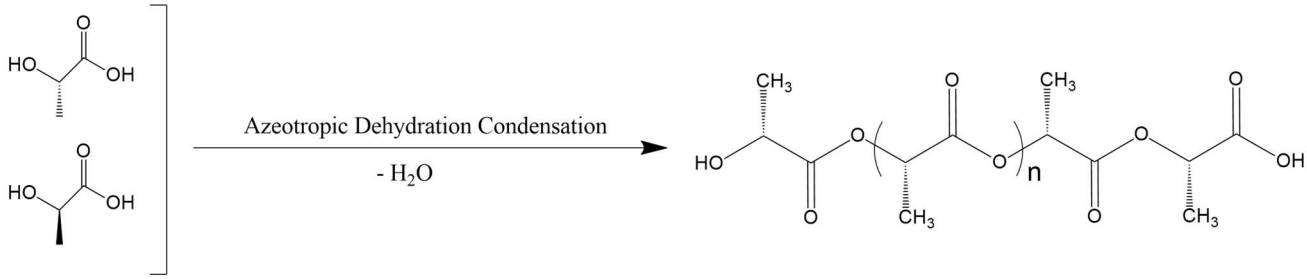

Figure 6. Polymerization of Lactic Acid Through Azeotropic Dehydration Condensation.

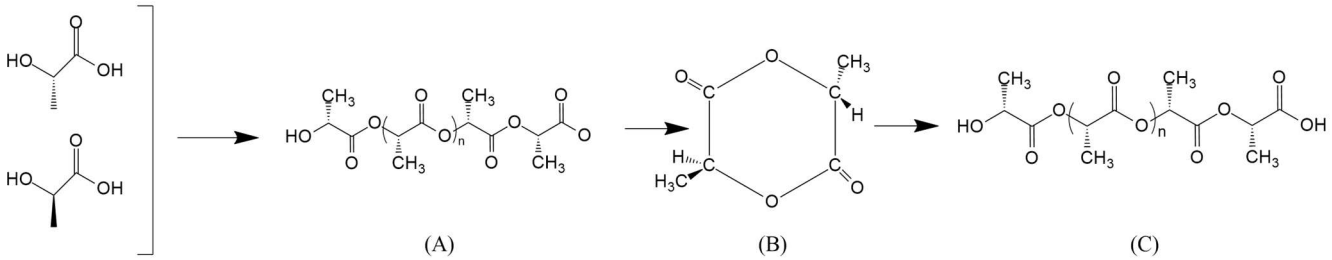

Figure 7. Polymerization of Lactic Acid Through Ring Opening Polymerization (**A**) PLA Oligomer (**B**) Lactide (**C**) High MW-PLA.

A disadvantage of chain extenders is that after adding the extenders, the subsequent reaction might not complete and some might remain in the PLA, causing more metal impurities to be deposited. In the same minute, some chain extenders cut down PLA's biodegradability to a large extent. Examples of chain extenders are: epoxides, isocyanates, and anhydrides. However, isocyanates with which PLA is used are toxic, which is a major drawback as PLA is mostly used in food packaging.

Another relevant method for synthesizing HM-PLA is ring-opening polymerization, although this process can be costly when implemented on an industrial scale. It involves breaking the LA cyclic dimer (lactide) using a catalyst to initiate polymerization. Polycondensation, depolymerization, and ring-opening polymerization are recognized as popular in the process of polymerization [56]. Catalysts like tin, aluminum, lead, zinc, bismuth, iron, and yttrium are incorporated to manage the extent of polymerization regarding their concentration, reaction time, and temperatures [50].

However, chemical polymerization, such as ring-opening polymerization, uses heavy metals that are dangerous to the environment. Enzymatic polymerization is comparatively greener than conventional chemical polymerization. Using this technique, one can synthesize PLA with a fine structure starting from cheap monomers; simultaneously, it outperforms ring-opening and condensation polymerization. The complete process of biosynthesis that entails the application of microbes as reaction catalysts is still underway. The synthesized PLA is a co-polymer of L-lactic acid and D-lactic acid. These isomers affect PLA's optical purity, which determines its crystalline, thermal, barrier, and mechanical properties.

Lower optical purity results in a more amorphous polymer, and a reduced concentration of L-lactic acid lowers the melting and glass transition temperatures. The crystallinity of PLA can be classified into three forms: Alpha, Beta, and Gamma PLA [57]. These forms exhibit distinct thermal properties, with the melting temperatures of the alpha and beta structures being 185 °C and 175 °C, respectively [58]. According to Bigg, D.M., the melting temperature (T_m) and glass transition temperature (T_g) of PLA are reduced with respect to the decreasing of L-lactic acid concentration, as shown in Table 1.

Table 1. Effect of L/D lactic acid ratio to T_g and T_m of PLA.

L/D Lactic Acid Ratio	T_g/°C	T_m/°C
100/0	63	178
95/5	59	164
90/10	56	150
85/15	56	140
80/20	56	125

Schwach, E., and coworkers investigated how the surface energy of PLA varies with different amounts of L-lactic acid and D-lactic acid. Surface energy is important for operations such as printing and multilayering, as it influences PLA's interfacial tension. For example, a PLA composition containing 92% L-lactide and 8% meso-lactide has a surface

energy of 49 mJ m^{-2}, with dispersive and polar components of 37 and 11 mJ m^{-2}, respectively [59,60]. Given PLA's widespread use in packaging, improving its barrier characteristics to carbon dioxide, oxygen, and water vapor is critical. PLA typically has lower CO_2 permeability coefficients than crystalline polystyrene at 25 °C and 0% relative humidity but higher than PET. The oxygen permeability of PLA is shown in Figure 8.

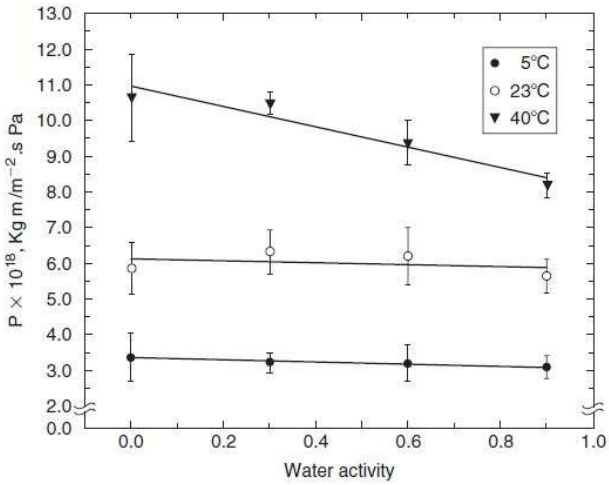

Figure 8. Oxygen permeability coefficient as a function of water activity for poly(L-LA). Adapted from [57].

The rheological behavior of PLA is heavily influenced by factors such as temperature, molecular weight, and shear rate, necessitating careful consideration during processing. High molecular weight PLA exhibits melt viscosities ranging from 500 to 1000 Pas at 10–50 s^{-1} shear rates. These melts behave as pseudoplastic, non-Newtonian fluids. Conversely, low molecular weight PLA (~40,000 Da) demonstrates Newtonian-like behavior at typical film extrusion shear rates [61,62]. Semi-crystalline PLA generally has higher shear viscosity compared to amorphous PLA under similar manufacturing conditions. Furthermore, PLA melts exhibit significant decreases in viscosity with increasing shear rates, indicating shear-thinning behavior.

To meet processing requirements, PLA's rheological properties can be tailored by introducing branching into the polymer chain architecture [63]. Various techniques can achieve this, including multifunctional polymerization initiators, hydroxycyclic ester initiators, multicyclic esters, and crosslinking via free radical addition. Palade, L.I. and co-workers have demonstrated that high L-content PLA with molecular weights ranging from 100,000 to 120,000 Mw exhibits strain-hardening behavior during polymer deformation. This characteristic is crucial for applications like fiber spinning, film casting, and film blowing, where PLA can sustain large Hencky strains without breaking due to its extensional viscosities [64].

PLA exhibits a range of mechanical and physical properties critical to its applications. The density of PLA is 1.21–1.25 g/cm^3, making it suitable for lightweight applications [65]. PLA can have both amorphous and semi–crystalline forms, impacting its strength and melting point. The semi—crystalline PLA has enhanced stiffness and a higher melting point. Glass transition temperature (Tg) of PLA is between 50 °C to 80 °C, and melting temperature is in the range of 150 °C to 180 °C [63], which is directly affected to its thermal stability. The tensile strength of PLA ranges from 21 to 60 MPa, and its modulus varies from 0.35 to 3.5 GPa [66]. Away from its promising properties, PLA has some drawbacks. PLA is more brittle compared to traditional plastics, with an elongation at break of less than 10%. This limits the application of PLA in areas requiring plastic deformation under high stress. Additionally, PLA is relatively hydrophobic, leading to low cell affinity and potential inflammatory responses in biological settings. Finally, the lack of reactive side-chain groups lowers PLA's ability to graft with additives or elastomers, making both surface and bulk modifications difficult [67–69].

PLA's versatility allows it to be used in various industries. PLA has been primarily utilized in the biomedical field for targeted drug delivery systems, drug encapsulation, and tissue engineering due to its biocompatibility. A major advancement is in PLA stereo-complexes (sc-PLA) synthesized by combining both poly L-lactic acid and poly D-lactic acid [64,70,71], which gives improved thermal stability and make PLA suitable for heat resistance application. Recent studies focusing on the incorporation of microfillers, nanofillers, and elastomers into PLA aim to improve its elasticity, rigidity, thermal stability, flame retardancy, and tailored electrical properties, thereby expanding PLA's usability in electronic applications. Furthermore, the preparation of PLA/natural fiber composites offers a better alternative to

synthetic fibers. Additionally, PLA is widely used in the packaging industry and in 3D printing applications, particularly in Fused Deposition Modeling (FDM) [72–75].

3.1.2. Synthesize, Properties, and Applications of Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are biopolymers synthesized primarily by microorganisms that have sparked broad interest due to their distinct physicochemical features and potential to replace non-degradable plastics. Research on bacterial storage materials began with the discovery of lipid-like inclusions in Azotobacter chroococcum and Bacillus megaterium, later identified as poly(3-hydroxybutyric acid) (P[3HB]). Initially believed to contain only 3-hydroxybutyrate (3HB), subsequent identification of other hydroxyalkanoates (HA), such as 3-hydroxyvalerate (3HV) and 3-hydroxyhexanoate ($3HH_x$), expanded the potential applications of PHA [76]. There are three key points in the development of PHA. The identification of 3HB inclusions in certain bacteria marked the beginning of PHA research. The discovery of other HA units broadened the scope of PHA applications [77]. PHA synthesis was observed in various bacteria, such as Azohydromonas australica, C. necatora, and *Pseudomonas putida*, as well as photosynthetic organisms and some archaebacteria [78]. This stage involved characterizing different HA units and understanding their biosynthetic pathways. Cloning and characterization of genes responsible for PHA biosynthesis provided deeper insights into the molecular mechanisms underlying PHA production. Current research focuses on understanding the tertiary and quaternary structures of PHA synthases to unravel their catalytic mechanisms and substrate specificities [76,79,80]. The most simplified synthesize process of the PHA is illustrated in Figure 9.

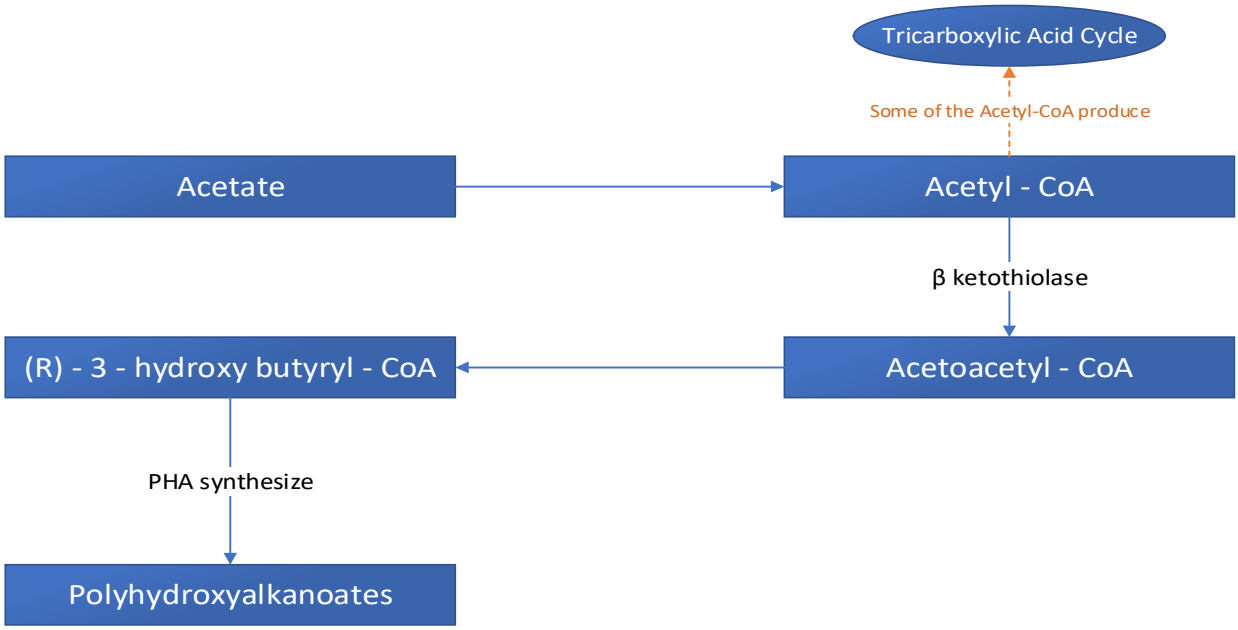

Figure 9. Pathway for the biosynthesis of polyhydroxyalkanoates (PHA)—Simplified.

Polyhydroxyalkanoates (PHA) production and recovery methods highlight the need for alternate carbon sources in order to reduce dependency on food-derived glucose and vegetable oils. The synthesis of PHA within a biorefinery is being investigated, particularly in conjunction with bioethanol production from lignocellulose, plant oils, lipids, and plant starch [81]. Second-generation industrial biorefineries are expected to process lignocellulosic materials, such as agricultural and forestry residues, to produce sugars that can be converted into PHAs. The problems of PHA recovery are inextricably tied to bacterial biomass, necessitating extra isolation and purification procedures. PHA can be recovered using a variety of methods, including solvent extraction, enzymatic cell disruption, mechanical disruption, and supercritical fluid extraction [82–84]. Emphasis is placed on economically friendly and reliable raw materials, including crude oil, in the production of biodegradable polymers. Synthetic and catalytic routes are also gaining attention for PHA production [85,86].

PHAs can be derived from different hydrocarbon sources. Certain microorganisms, such as *Pseudomonas* strains and *Rhodococcus aetherivorans IAR1*, can grow on hydrocarbons and accumulate medium-chain-length PHAs (mcl-PHAs). PHAs derived from hydrocarbons have alkyl groups ranging from propyl to dodecyl, depending on the substrate

utilized. *Pseudomonas* strains effectively produce surfactants that aid in solubilizing and emulsifying hydrocarbons, facilitating their transport through cell waslls. However, the productivity of PHAs from hydrocarbons is currently lower compared to other strategies, requiring improvements for large-scale production. Pyrolysis oils derived from shredded plastic particles can also serve as substrates for hydrocarbon-utilizing bacterial strains like *Pseudomonas* sp. and *Ralstonia eutropha* for PHA production. Type II methylotrophs can use methane, a commonly available hydrocarbon found in oilfields, and through organic matter breakdown. *Methylocystis* ssp. had a yield of 0.55 g PHB g^{-1} CH_4 and a productivity of 0.031 g PHB L^{-1} h^{-1}, which was consistent with the process's theoretical potential [81,87–90].

Another way of synthesizing PHA is the utilization of carbohydrates [91], specifically monosaccharides, oligosaccharides, and polysaccharides, for PHA production. Polysaccharides such as starch, cellulose, and hemicellulose can be hydrolyzed into monosaccharides or disaccharides, which can be fermented to produce PHAs. Bacterial strains like Azeobacter vinelandii, Alcaligenes latus, and Hydrogenophaga pseudoflava can produce PHAs from sucrose and lactose obtained from sugar-bearing raw materials or whey. Recombinant strains of *Escherichia coli* have also been used for PHA production from lactose. Starch-derived glucose has been used by ICI and Chemie Linz for commercial PHA production. Attention has shifted towards deriving glucose and simple sugars from lignocellulose for large-scale PHA production. Lignocellulose, consisting of cellulose, hemicellulose, and lignin, can be hydrolyzed to obtain pentoses that can serve as substrates for fermentable PHA production.

Pseudomonas cepacia and *Pseudomonas pseudoflava* have identified as bacteria that can use pentose to produce PHA. *E coli* with PHA synthesis genes of *Ralstonia eutropha* has reported the efficient production of PHB from xylose. PHAs are synthesized by accumulating 3-hydroxyvalerate (3HV) from the employed co-substrate, namely, liquefied wood along with glucose.

To utilize triacylglycerols to synthesize PHA, certain bacteria along with their lipases, can ferment the substance into polyhydroxyalkanoates (PHAs), according to Rosenberg, E. and Ron, E. Z., 1999. The triacylglycerols are broken down by lipase to fatty acids, which then enter cells and, in the process of β-oxidation are converted to PHA monomers and polymers [92]. For example, Aeromonas caviae and *Chromobacterium* sp. have been used to convert triacylglycerols from plant oils into PHAs. Additionally, *Ralstonia eutropha* H16 can utilize plant oils to synthesize P3HB homopolymers. Besides, animal fats and glycerol, which are among biodiesel by-products, can also be used for PHA production. Experiments with various types of industrial waste, including waste frying oil, which contains various nutrients, showed very high productivity and yield for PHA production under batch fermentation conditions [93].

PHA is produced mainly by bio-fermentation and has only the isotactic configuration [81,90,94]. PHA characteristics are highly dependent on the nature of the polymer, which is determined by the chain length and the number of carbon atoms within the polymer chain. The monomer with five or fewer carbon atoms is short-chain-length (SCL) PHA, whereas the monomer present in MCL PHA has five or more carbon atoms in the chain. Crystallinity is more prominent in SCL-PHA compared to MCL-PHA, which exhibits a higher degree of amorphousness. This is supported by the comparison between PHB and isotactic polypropylene in Young's modulus, tensile strength, impact strength, UV resistance, and oxygen permeability, which showed that PHA has a strong factor as a packaging material similar to iPP. However, some issues associated with PHA include reduced toughness over time due to ongoing crystallization, as well as lower strain elongation compared to iPP. As for the problems described above, one can use nucleating agents and post-treatment.

The high melting temperature of PHB (174–179 °C) near its decomposition temperature can result in thermal degradation, requiring a lower melting temperature for PHA to replace commodity plastics [95,96]. In 1982, ICI introduced random copolymers of PHA with 3-hydroxybutyrate (3-HB) and hydroxyvalerate (HV) or 4-hydroxybutyrate units to overcome these problems. The copolymer was produced using the microorganism Alcaligenes eutrophus, allowing the production of materials with different property profiles [97,98].

The mechanical properties of PHAs mainly depend on the molecular weight, monomer composition, and crystallinity [99], PHB is a highly crystalline homopolymer and is stiff and brittle with high tensile strength but low elongation at break. However, copolymerization with other hydroxyalkanoates (especially 3-hydroxyvalerate (3HV) or 4-hydroxybutyrate (4HB)) significantly lowers crystallinity and increases flexibility and elongation so that the mechanical characteristics are similar to those of polypropylene. As example, P(3HB-co-3HV) containing in excess of 20 mol% 3HV can range in elasticity of films and fibers, and P(4HB) is a strong, flexible thermoplastic with as much as 1000% elongation at break, demonstrating superior properties over other degradable thermoplastics such as PGA and PLLA. Higher molecular weight PHAs show better tensile strength and elongation, especially up to 1320 MPa tensile strength in ultra-high molecular weight PHB [76,99,100]. Crystallinity levels influence stiffness, flexibility, and biodegradability; for instance, PHB has a crystallinity index of 44%, while P (3HB: On the other hand, medium-

chainlength HAs (mclHAs) lower that index even further to 40%, and cause mclHA (30% 30% 3HV) to be more amorphous, flexible [100]. The range of elastic modulus in PHA spans orders of magnitude, from 0.002 GPa for flexible mcl-PHAs to about 3.5 GPa for brittle scl-PHAs, with PHB exhibiting the highest modulus (1.1–3.5 GPa). At the same time, 3HV or 4HB copolymers have much lower moduli, consistent with the trend in greater flexibility. Tensile strength is from 19–40 MPa for PHB, and ranges from 20–48 MPa for 3HV or 4HB copolymers, the latter having lower tensile strength owing to low crystallinity, while ultra-high molecular weights (Mw > 1 million) achieve anomalously high strengths (150 MPa). The material stretchability measured in terms of elongation at the break before breaking is the lowest for PHB (0.4–5.0%) and increases with the higher 3HV or 4HB content up to 740–833% [101] in the case of mcl-PHAs, thus indicating high flexibility. Through control of monomer composition, molecular weight, and crystallinity, researchers can tune the mechanical properties of PHAs for alternative applications beyond conventional plastics.

PHA has applications in several fields because of its environmentally friendly nature. PHA can be used in various products such as bottles, containers, trays, cups, and plates due to its biodegradability under both aerobic and anaerobic conditions. Flexible films made from biodegradable polymers are particularly established and find applications in compostable waste bags, carrier bags for organic waste, and agricultural films, reducing labor and disposal costs. PHA is also used in packaging for (snack) foods due to its barrier properties, competing with polyethylene in applications where biodegradability is not a strict requirement. Overall, these applications contribute to reducing landfill waste and improving the efficiency of composting processes. Different approaches, such as incorporating polar groups, block-copolymerization, and graft copolymerization, can be used to make polymers hydrophilic. Hydrophilic modification can also be achieved by attaching hydrophilic polyethylene glycol (PEG) through synthetic or biological procedures known as PEGylation [102]. Supramolecular hydrogels have been created using PEG-PHB-PEG triblock copolymers coupled with cyclodextrins, forming inclusion complexes with the potential for controlled long-term release applications in medical applications [103,104]. Furthermore, hydrophilic PHA/PEG systems stimulate the adhesion and proliferation of neuronal olfactory ensheathing cells (OECs) in tissue engineering applications. The material's hydrophilicity facilitated cell adhesion while retaining good cell viability [105]. PHAs have further medicinal applications, such as fluorescent bile acid PHB-PEG nanoparticles for drug administration and PHB bio-PEGylation, which enhances nerve cell health and migration [106]. Finally, mixed microspheres of poly(3-hydroxybutyrate) and cellulose acetate phthalate were used for colon delivery of the anticancer medicine 5-fluorouracil [107], providing a useful supplement to previous drug targeting methods.

However, many challenges stand in the way of using polyhydroxyalkanoates (PHAs) instead of petroleum-based plastics. The main obstacle is high production and recovery costs, of which 50% is the cost of the carbon sources [108]. Other factors affecting the cost include fermentation, process productivity, and downstream processing. Large-scale production of medical-grade PHAs will incur additional costs for purification, particularly continuous dissolution and re-precipitation. Extracting PHAs from bacterial cells is complex and expensive, usually accomplished using solvent extraction with chlorinated solvents, which are costly and environmentally harmful. Furthermore, the properties of these materials present several challenges. For instance, PHB, the most common PHA, has low thermal and mechanical properties [109]. Two factors that complicate processing and may limit the biodegradability of HMDT are a high crystallinity and a melting temperature of 180 °C, which make HMDT stiff but brittle. Furthermore, a high degree of purified product is frequently required for medical applications such as those mentioned above, and waste derived PHAs are likely to contain impurities such as endotoxins, proteins, and lipids, which would require additional purification steps and hence increase the expense of the product. PHA adoption is hindered by the lack of industrial infrastructure for large scale PHA production and processing, as there are presently very few facilities for the recycling and separating PHAs, which is vital for a circular economy [110]. Moreover, PHAs have been slow to develop and commercialize due to the lack of strong legislative support. Their availability is limited, and they do not yet meet the performance characteristics required to serve as substitutes for petroleum-based plastics in various applications. Given the high production costs, material limitations, impurities, and deficiencies in the infrastructure required to produce PHAs, it is crucial to address these challenges for PHAs to remain competitive and viable as a sustainable alternative to conventional plastics.

3.1.3. Synthesize, Properties and Applications of Polycaprolactone

Polycaprolactone (PCL) is a polymer that was first synthesized in the early 1930s and became commercially available because of its biodegradable properties [111]. It can be prepared through various methods, including ring-opening polymerization. PCL is a hydrophobic, semi-crystalline polymer with good solubility and a low melting point.

It gained attention in the biomedical field [112] during the resorbable polymer boom of the 1970s and 1980s for its advantageous properties [113], such as tailorable degradation kinetics, mechanical properties, and controlled drug delivery. However, PCL was overshadowed by other resorbable polymers that offered faster degradation rates. PCL has regained interest in tissue engineering in recent years due to its superior rheological and viscoelastic properties, making it suitable for scaffold fabrication [114]. Its relatively low production cost and existing FDA approval and CE Mark registration for certain drug-delivery devices provide an advantage for market availability. Despite its advantages, PCL has not been widely used in clinical applications.

The preparation of PCL starts with the polymerization of its monomer as in Figure 10. Several microorganisms oxidize cyclohexanol into adipic acid. The production of ε-caprolactone (ε-CL) and 6-hydroxyhexanoic acid involves an intermediate process. Industrially, ε-CL is obtained by oxidizing cyclohexanone using peracetic acid [115,116]. There are two polymerization techniques to polymerize the PCL. 6-hydroxycaproic (6-hydroxyhexanoic) is polymerized through polycondensation, and ε-CL is polymerized through Ring Opening Polymerization (ROP). Braud C. and coworkers have investigated the method that involves the polycondensation of 6-hydroxyhexanoic acid under vacuum, resulting in PCL oligomers. No catalyst was used, and the reaction was completed within 6 h at a gradually increased temperature range of 80 to 150 °C [117]. Another approach involves the polymerization of 6-hydroxycaproic acid using lipase from *Candida antarctica* under a vacuum. This method produces polymers with an average molecular weight of 9000 g/mol and a polydispersity below 1.5 within 2 days. Similarly, the use of lipase from *Pseudomonas* sp. at 45 °C to polymerize ethyl 6-hydroxyhexanoate yields polymers with an average molecular weight of 5400 g/mol and a polydispersity below 2.26 after 20 days with 82% monomer conversion. In this case, ethanol is generated as a byproduct but can be removed under a vacuum [118,119]. ROP has more advantages over the polycondensation.

The process of ROP can be classified into four main types of catalysts; anionic, cationic, monomer activated, and coordination-insertion ROP. Anionic ring-opening polymerization (ROP) involves the generation of an anionic species that attacks the carbonyl carbon of the monomer, breaking the acyl-oxygen bond and generating an alkoxide species [120]. However, a limitation of this method is the back-biting issue, an intramolecular transesterification that leads to the formation of low molecular weight or cyclic polymers. On the other hand, cationic ROP is based on the generation of a cation, which is then nucleophilically attacked by the carbonyl oxygen of the monomer via and SN2 type mechanism [120]. This type of ROP is initiated by the monomer molecules, which are first activated by a catalyst and then react with the polymer chain end. Coordination-insertion ROP which is the most frequent type of ROP, involves the binding of the monomer to the catalyst and then the insertion of the monomer into the metal-oxygen bond of the catalyst. In the propagation step the growing chain is anchored on the metal through an alkoxide bond.

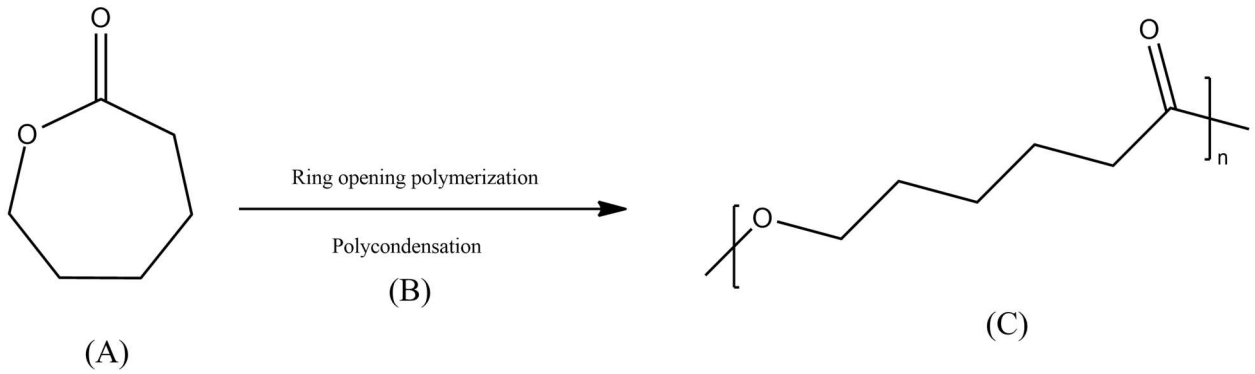

Figure 10. Synthesis pathway of Polycaprolactone (**A**) ε-caprolactone (**B**) Polymerization Technique (**C**) Polycaprolactone.

Introducing an initiator and a catalyst for Ring-Opening Polymerization (ROP) of ε-caprolactone (ε-CL) involves several undesirable side reactions [121,122], namely inter-molecular transesterification indicated in Figure 11 and intra-molecular transesterification indicated in Figure 12. Such reactions are generally noted at the advanced state of polymerization and on heating conditions. They cause an increase in the polydispersity of the obtained polymer and a failure of the regulation of the polymerization process. These are; alkali-based catalysts, alkaline earth-based catalysts, poor metal-based catalysts, transition metal-based catalysts, and rare earth metals-based catalysts.

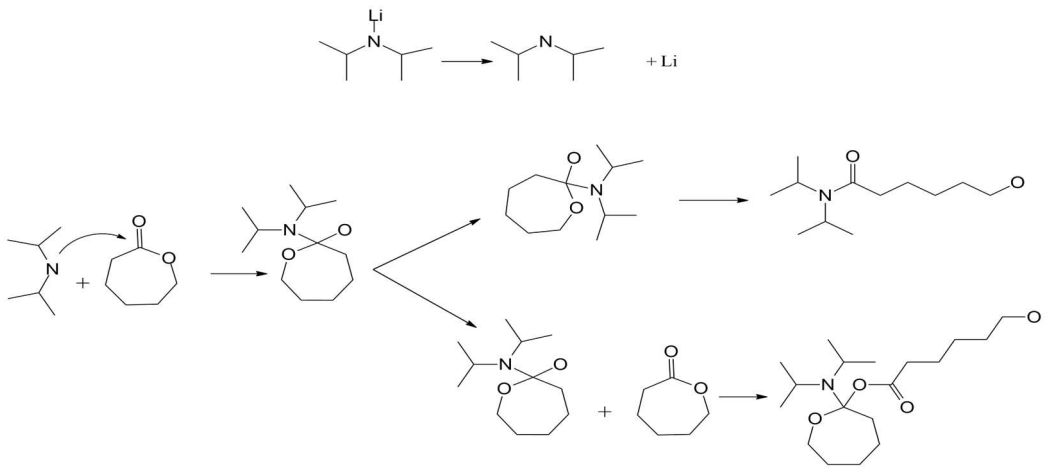

Figure 11. Mechanism of Ring opening polymerization using lithium diisopropylamide (LDA).

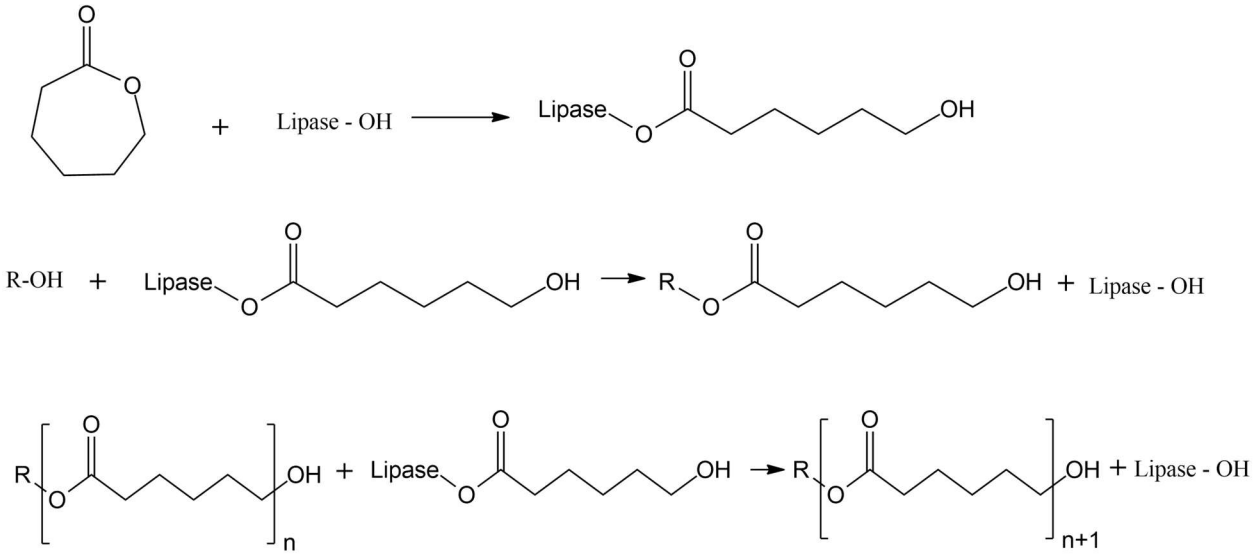

Figure 12. Mechanism of enzymatic Ring opening Polymerization of e-CL.

Alkali metal-based catalysts exhibit some activity in the ROP process. However, due to their ionic nature and the anionic mechanism of ROP, polymerization control is limited by the occurrence of transesterification. Additionally, alkali-based compounds tend to form aggregates, leading to reduced solubility [123]. Catalysts based on alkaline earth metals, such as magnesium and calcium, offer high activity and low toxicity, making them appealing for various applications. Magnesium, being biologically benign and abundant, shows particular promise for the synthesis of biomedical polymers. Alkyl-containing magnesium complexes and magnesium alkoxide complexes yielded high molecular weight polymers with low to moderate polydispersity. The initiation of polymerization involved alkyl transfer or insertion of the alkoxy group into the monomer. A magnesium aryloxide catalyst demonstrated a "living" character of polymerization without intramolecular transesterification. Similarly, calcium, known for its benign nature, was explored as a catalyst. The calcium-based system displayed wide molecular weight distribution, but the addition of alcohol led to controlled polymerization. The mechanism involved rupturing the acyl-oxygen bond of the monomer and insertion into the Ca-O bond of calcium alkoxide. Calcium ammoniate and strontium-based systems also exhibited polymerization but with higher polydispersity due to considerable transesterification. The proposed reaction mechanisms and termination steps were detailed for each case.

Bhaw-Luximon A. and coworkers studied the polymerization of ε-caprolactone (ε-CL) in dioxane using lithium diisopropylamide (LDA) as the catalyst. Figure 13 depicts the hypothesized anionic polymerization pathway [124]. The procedure was completed in a few minutes at 25 °C, generating a medium molecular weight polymer (Mn = 5700 g/mol) with an ε-CL to LDA ratio of 50. After a few hours of exposure to 170 °C, phenyl lithium produced high molecular weight polymers. Yuan et al. employed cyclopentadienyl sodium in bulk and non-polar solvents, yielding an average molecular weight of 130,000 g/mole. However, when using polar solvents, only oligomers occurred [119].

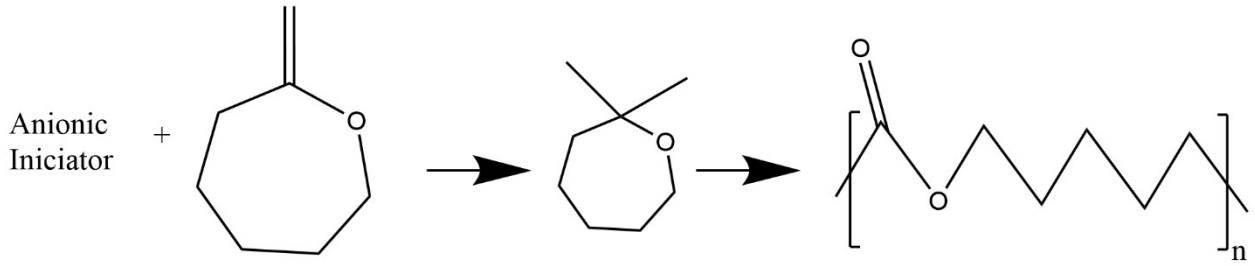

Figure 13. Anionic Polymerization Pathway of ε-Caprolactone (ε-CL).

Metal-based compounds, particularly those based on aluminum and tin, are widely used as catalysts for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). In the case of aluminum-based catalysts, aluminum(III) triflate and copper(II) triflate demonstrated superior performance, resulting in high molecular weight polymers. Conversely, lanthanum(III) and samarium(III) triflates produced oligomers, while sodium(I) and magnesium(II) triflates exhibited no catalytic activity. Diethylaluminum alkoxide and triethylaluminum-amine systems led to specific PCL structures, indicating initiation by both alkoxide and amino groups. However, the methyl aluminoxane-trimethylaluminum system showed inadequate control over polymerization, accompanied by back-biting reactions. Aluminum alkoxides with bulkier alkyl substituents exhibited enhanced polymerization efficiency. Notably, aluminum(III) isopropoxide, existing as trimers or tetramers in certain solvents, acted as the catalyst-initiator, with the tetramer demonstrating greater stability. Coordination between the ester groups of PCL and the aluminum center facilitated controlled polymerization. The presence of alcohols influenced the reaction rate and enabled controlled polymerization. Notably, aluminum isopropoxide catalysis in supercritical carbon dioxide ($scCO_2$) resulted in high polydispersity due to the formation of various reactive species, including carbonates, during the reaction with CO_2 [125–129].

Instead of using metal-based catalysts, enzymes can be used as an alternative. Nobes, G.A., et al., MacDonald, R.T., et al., Kobayashi, S., et al., 2001, and Kobayashi, S., 1999, have proposed a mechanism for the enzymatic ring-opening polymerization (eROP) of ε-caprolactone (ε-CL) using lipases [130–133], as shown in Figure 12. In this mechanism, the lipase initially interacts with the monomer to form a lipase-activated complex with ε-CL. Subsequently, the alcohol component reacts with the complex. Modeling studies focused on ε-CL eROP have indicated that polymerization, degradation, and enzyme deactivation take place concurrently.

Compared to other polymers, PCL has a low melting point (59–64 °C) and a Tg of −60 °C, which allows for easy polymer processing through methods such as conventional extrusion or injection molding, and foaming [134]. Its crystallinity is about 67%, and the crystallization rate can be enhanced by adding starch as a nucleating agent for PCL. Crystallinity is often assessed by measuring the melting enthalpy of PCL relative to that of pure, 100% crystalline PCL (139.5 J/g). PCL has superior rheological and viscoelastic properties than other aliphatic polyesters with a modulus of 190 MPa, elongation at break in excess of 500%, and tensile stress at break of 14 MPa [135]. PCL can be blended with polymers such as PLA or starch or reinforced with fibers to enhance its mechanical strength. For example, the addition of starch increases stiffness by raising the storage modulus and enhances damping properties, making it useful in biomedical applications that require energy dissipation [136,137]. The hydrolyzable ester linkages in PCL's structure make it biodegradeable: it breakdowns bacterial and fungal, but not human enzymes, and is biodegradeable to varying rates based on its molecular weight, crystallinity, and environmental conditions. PCL can also be blended with other polymers, for example starch, for tailoring its degradation rate. Although versatile, PCL's hydrophobicity can reduce cell adhesion and modification of the surface is often needed for better *in-vivo* integration; however, the water and gas barrier properties of nanocomposites, for example, carbon nanotubes, are enhanced. It declines the biodegradation rate though with the increase in molecular weight, the crystallinity of polyvinyl alcohol decreases. PCL is a versatile biomaterial due to its combination of mechanical, thermal, and customizable degradation properties, but occasional modifications in order to optimize cell compatibility and mechanical performance are often required.

PCL is mainly used in the biomedical field because of its biodegradability. The concepts of biodegradability and bioresorbability in the context of biopolymers, particularly in biomedical applications, are important. The distinction between biodegradability and bioresorbability is highlighted in Table 1, emphasizing that biodegradability does not necessarily imply removal from the body [138]. Bioresorbability refers to the complete elimination of foreign materials and degradation products without residual side effects. The degradation mechanisms of poly(ε-hydroxy) esters, such as PCLs, involve surface erosion and bulk degradation pathways. Surface erosion involves the cleavage of the polymer at the surface level, while bulk degradation occurs within the polymer matrix [139,140]. This form of controlled release

has many benefits, including the fact that the rate can be easily and accurately estimated, which is useful if the substance that is being released is a medicine [141]. In contrast, bulk degradation can create an acidic gradient, which may lead to inflammatory reactions. The degradation process of PCL occurs in two stages: non-enzymatic hydrolysis of the ester linkages, followed by intracellular metabolism of the high molecular weight product once its molecular weight has been reduced. Several *in vitro* and *in vivo* degradation studies support these mechanisms [142,143]. Other works concerning the thermal degradation and degradation rates of PCL containing block copolymers are also found. For instance, the studies that were carried out in rats show a progressive decrease in molecular weight and elimination of PCL from the body.

Thus, the biodegradable characteristics make tissue engineering one of the important applications of PCL [144]. Some of the latest developments in tissue engineering are characterized by tissue replacement and implementation methodology. The field has seen a vast improvement in the services rendered in biomaterials, stem cells, growth factors, and biomimetic substrates. These developments have opened new opportunities for engineering laboratory-grown tissues using the extracellular matrix, engineered cells, and bioactive molecules. When it comes to the choice of scaffolds, some of the features are considered more valuable than others. These are the requirement for 3D structures with interconnected pore channels to accommodate cell development and deliver nutrition and waste products through the scaffold's interconnected pores. The scaffolds should also be biocompatible and bioresorbable; that is, the degradation and resorption of the scaffold should occur in a manner that can be regulated to match the growth of the cells and tissue either *in-vitro* or *in-vivo*. In addition, the chemistry of the scaffold surface should promote cell adhesion, growth, and differentiation. Finally, the mechanical characteristics of the scaffolds must closely resemble those of the target tissue at the implantation site [145]. Surface treatment methods are applied with the purpose of modifying a surface while retaining or even improving the characteristics of the rest of the volume of the material. These changes can be either chemical or physical, meaning they involve the creation of new compounds or structures on the existing surface. However, the surface modification can also be done with the help of the coating technique in which the original surface is covered with a layer of another material possessing the required characteristics. The goal is to tailor the surface for better biocompatibility without compromising the overall properties of the material [146]. Photothermal agents with biocompatibility were synthesized by Kim and coworkers using polymeric nanoparticles containing gold nanorods. Seed-mediated growth was employed in the preparation of the gold nanorods to make them sensitive to near-infrared light, enabling the elicitation of the photothermal effect. The hydroxyl groups of PCL diol were esterified with mercaptopropionic acid with the formation of PCL dithiol, which acted as a phase transfer and capping agent for the formation of polymeric nanoparticles. The loading and/or unloading process of hexadecyltrimethylammonium bromide was done using PCL dithiol. The gold nanorods were first coated with dithiol, followed by a layer of PCL to enhance the stability of the nanocomposite, and finally covered with the hydrophilic polymer F127. The synthesized newly developed gold nanorods were highly stable in water. They had the recommended maximum absorbance in the near-infrared (NIR) region,which clearly showed a high surface plasmon resonance effect. These characteristics make the gold nanorods suitable for use as photothermal agents [147].

The role of scaffold surface chemistry and degradation rate has been extensively studied, and it is well-established that these parameters play a crucial role in tissue formation. Besides these aspects, there are other factors specifically related to scaffolds' mechanical properties, such as elasticity, which have also been cited. Research has shown that mechanical signals are essential in tissue growth and remodeling. For instance, cyclic mechanical strain promoted the formation and function of the engineered smooth muscle tissues. Hence, when intending to fashion tissues subjected to regular mechanical stimulation, the physical characteristics of the scaffold have to be contemplated. On the other hand, aliphatic biodegradable polyesters such as PGA, PLA, and PLGA, which are commonly used in tissue engineering, often fail under cyclic strain and exhibit signs of plastic deformation. Lacunae of this nature is a major drawback when it comes to engineering elastomeric tissues. As a result, researchers have explored using composites and copolymers to address this issue and develop scaffolds with the desired elastic properties [148].

Thomas and coworkers have investigated bone engineering using PCL. The researchers observed that higher rotation speeds resulted in increased fiber alignment and tensile strength. Conversely, as the rotation speeds increased, they observed a decrease in hardness and Young's modulus. These variations in mechanical properties were attributed to both microscopic and macroscopic factors, including the crystallinity of the fibers, improved alignment, and tighter packing density. This study emphasizes the importance of investigating specific parameters within a production process to achieve optimized mechanical properties tailored to a particular application [149].

Biodegradation rates of polycaprolactone (PCL), a stably radical polymer formed by an FDA approved synthetic process, are currently too slow to support its use as a sustainable alternative for many products based on petroleum given adequate biodegradability and product performance are necessary. Its relatively low hydrophobicity limits cell

attachment and therefore reduces its suitability for some tissue engineering applications and retards its biodegradation through lack of water infiltration [113,150]. Cell compatibility can be improved by: blending with hydrophilic polymers, such as starch or PEO, to enhance hydrophilicity, and surface modifications, such as coating with extracellular matrix proteins or plasma treatment, to improve control of degradation rates. Thirdly, PCL's relatively low mechanical strength (elastic modulus), for example, limits PCL's suitability for load-bearing applications. This can be solved by blending in stiffer materials like fibers and nanofillers or by blending with stronger polymers (such as PLA). However, this usually involves adjusting the compatibility between components, particularly by surface treatment or the use of compatibilizers. The slow degradation rate of PCL, while beneficial for long-term implants, presents a challenge in applications that require rapid decomposition, such as disposable packaging. The degradation profile of PCL can be tailored by modification to its composition, molecular weight, or crystallinity, or by blending with other polymers. Furthermore, the high production cost of this polymer, compared to conventional plastics, makes it commercially unappealing, especially since cost-saving efforts, such as blending with starch, can alter its material properties. However, its poor barrier properties to water and gas limit PCL use in packaging, though carbon nanotubes as nanofillers can ameliorate some of this effect at increased cost and complexity. While the PCL is FDA approved for some medical uses, its clinical adoption is hindered by a lack of clinical data to confirm its long-term safety and effectiveness [151]. The expansion of PCL's role through various industries will require addressing these challenges through innovations in cost-effective production, property modification, and clinical validation.

3.1.4. Synthesize, Properties and Applications of Poly(butylene adipate-co-terephthalate)

Poly (Butylene Adipate-co-Terephthalate) (PBAT) is a biodegradable synthetic polyester synthesized by sophisticated two-step polycondensation reaction of polycondensation reaction of Butanediol (BDO) Adipic acid (AA) and Terephthalic Acid (PTA) [152]. The simplified process of synthesizing PBAT is show in Figure 14.

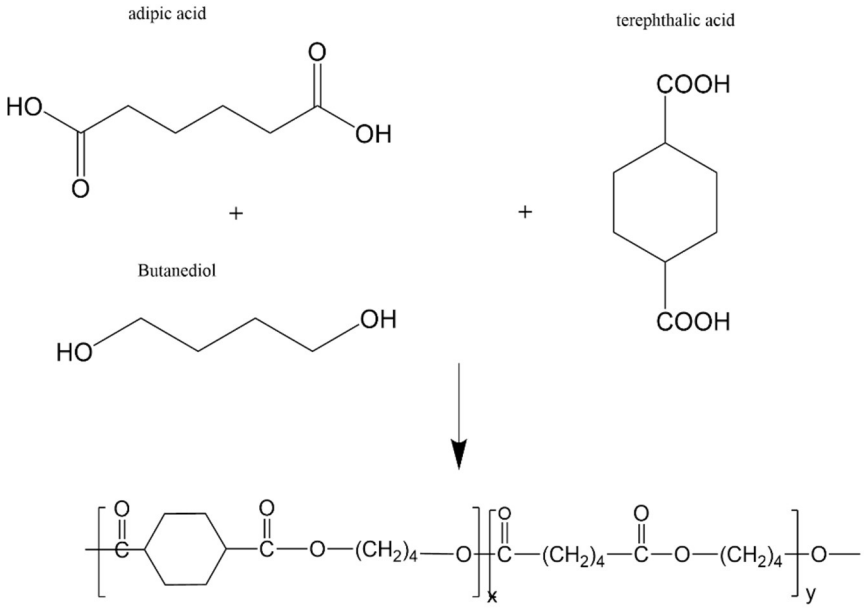

Figure 14. Simplified Schematic diagram of synthesis of PBAT.

This starts with the transesterification of DMT with BDO in the presence of a rare earth stearate catalyst e.g., Dysprosium, Neodymium or yttrium stearates at 170C under a nitrogen flow. This step is carried out in an inert environment created with nitrogen so that unwanted side reactions do not occur and methanol, a product of the step, is continuously removed. Furthermore, the high production cost of this polymer, compared to conventional plastics, makes it commercially unappealing, especially since cost-saving efforts, such as blending with starch, can alter its material properties. First, the mixture is heated to 210 °C under nitrogen flow to release water byproduct, then is heated to 270 °C with gradually reduced pressure (below 70 Pa) to drive the polycondensation reaction. A high-temperature, low-pressure environment removes byproducts such as water and methanol, increasing the equilibrium to the high molecular weight PBAT. Upon cooling, the PBAT liquid forms a highly viscous liquefied form that solidifies [86,152,153].

Catalysts are essential in PBAT synthesis. Dysprosium stearate, among rare earth stearates, exhibited the best performance, resulting in PBAT with bimodal molecular weight distribution, relatively high molecular weight, and

good mechanical properties, with tensile strength of up to 24.4 MPa, which were superior to those prepared with conventional catalysts, such as tetrabutyl titanate. The synthesis process takes about 8 h, and additives are added to enhance polymer performance. Introducing nucleating agents (talc or silicon oxides) during the final polymerization encourages crystallization and reduces tackiness. Phosphorous compounds are used as color stabilizers but may retard the rate of condensation. Moreover, via long chain branching (LCB) by including multifunctional monomers, the melt strength of PBAT is further improved for better processability [154].

After synthesis, PBAT polymer is ready for use in film extrusion or injection molding. This integrated catalyst selection, temperature and pressure conditions, as well as additives, comprehensive synthesis approach optimizes PBAT effective mechanical properties and degradation characteristics for use as a promising sustainable alternative to conventional plastics in biodegradable applications [152].

PBAT has a unique combination of thermal, mechanical, and functional properties, making it ideal for use in a variety of applications. PBAT is mechanically very flexible, with high elongation at break, which is notably similar to density polyethylene (LDPE), which makes it suitable for applications requiring elasticity. The rubbery texture, which can be controlled over a broad range by adjusting the monomer ratios of butylene adipate and butylene terephthalate or by changing the molecular weight of the polymer, is a consequence of its moderate tensile strength and low Young's modulus. For instance, greater amounts of terephthalate improve the stiffness (Young's modulus) at the expense of elongation, and a higher molecular weight increases the tensile properties, except that they sacrifice elongation [155,156]. Mechanical properties of PBAT are enhanced by processing methods, including fiber spinning at higher take-up velocities, which induce higher molecular orientation and crystallinity, thereby increasing tensile strength and modulus and lowering elongation. The melting temperature of PBAT (Tm 121–123 °C) is lower than polybutylene terephthalate (PBT) because of the flexible butylene adipate units but higher than polybutylene adipate (PBA). PBAT has a glass transition temperature (Tg) of around −29 °C, is flexible at room temperature, and is semi-crystalline with moderate crystallinity and well-defined crystal structures due to the mixed crystallization of both butylene adipate and butylene terephthalate units [157]. Moreover, PBAT exhibits reversible alpha-beta transitions of the crystal structure under tensile stress, like with PBT, albeit at higher strains because of the lower modulus of PBAT. One of the most important advantages of PBAT is that it is functionally fully biodegradable in environmental conditions with microorganisms (in compost and soil environments), breaking down into CO_2, water, and biomass. Integration into existing plastic processing frameworks is facilitated by its processability with standard techniques such as extrusion, injection molding, film blowing, *etc.*, and its compatibility with other biodegradable polymers (e.g., starch or PLA) to form performance enhanced composites. Good compatibility in PBAT blends can be achieved but may require compatibilizers or surface modifications to prevent phase separation. Moreover, they expand the potential applications of PBAT due to its improved moderate gas and water vapor barrier properties, which can be further enhanced by blending with other polymers (e.g., PBS) or incorporating fillers. As such, PBAT's biodegradable and flexible properties and adaptability make it a promising alternative to fossil-based plastics. At the same time, the prospects for expanding its market presence depend on continued research to lower production costs and improve specific properties, thereby enhancing its performance in various applications [158].

PBAT and its composites are currently and potentially applied to a wide range of applications, owing to their biodegradability, flexibility, and compatibility with existing processing methods. In packaging, PBAT is particularly promising: Starch PBAT blends are used in shopping bags such as those used in Chinese supermarkets, compostable bags that degrade within organic waste, and for food packaging, where PBAT composites and even composites with torrefied coffee grounds can increase thermal and moisture resistance [159]. However, cost is a challenge for market penetration of PBAT beyond these applications to a wider scale. Regarding the biomedical sector, PBAT is biocompatible and biodegradable and could be applied to antimicrobial fabrics for use in infection control in hospitals and biocompatible nanocomposites with non-cytotoxic properties in medical implants. Antimicrobial properties suitable for wound dressings were also observed in some PBAT nanocomposites (such as PBAT/CMMT (cetyltrimethylammonium bromide modified montmorillonite) [159,160]. In addition to PBAT, mulch films with PLA and nanoparticles are used to improve the durability and decomposition rate post-growing season for agricultural use to minimize plastic waste. PBAT is speculated to exhibit biodegradable properties and can benefit industrial applications such as in disposable components or packaging materials. In the future, PBAT is expected to meet the needs of advanced applications, driven by research in new areas such as tissue engineering, drug delivery, and biodegradable sensors. Meanwhile, efforts are underway to develop bio-based PBAT using monomers sourced from renewable materials (e.g., bio-based butanediol and FDCA, or 2,5-furandicarboxylic acid) to enhance sustainability [161]. However, there are challenges to PBAT adoption, including a high production cost and property enhancement required, where ongoing

research focuses on improving PBAT's mechanical strength and barrier performance through advanced blending and processing techniques. The inherent biodegradability of PBAT along with suitable mechanical and processability properties make PBAT a versatile material in the move towards environmentally acceptable materials, with potential for growth in applications fostered by developments in bio-based polymer technologies.

3.1.5. Synthesize, Properties and Applications of Polybutylene Succinate

Polybutylene succinate (PBS) is synthesized by a polycondensation reaction between succinic acid (SA) or its dimethyl ester (dimethyl succinate) and 1,4 butanediol (BDO) as base material. The synthesis occurs in two main steps: esterification (or transesterification if dimethyl succinate is used) [162], and polycondensation constitute important steps to arrive at the high molecular weight polymer. The first step combines SA and BDO under controlled temperatures between 150–200 ° C [163,164] and reacts to form low molecular weight oligomers along with water as a by-product as shown in the following esterification reaction in Figure 15.

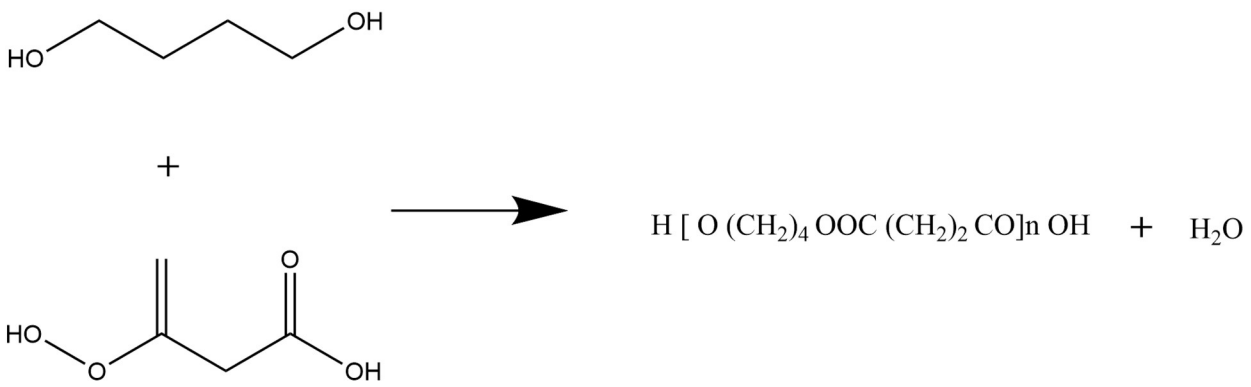

Figure 15. Esterification of succinic acid and butanediol.

In the case of dimethyl succinate as a starting material, transesterification occurs with methanol as a byproduct, which is similarly removed via distillation to drive the reaction forward, as in Figure 16.

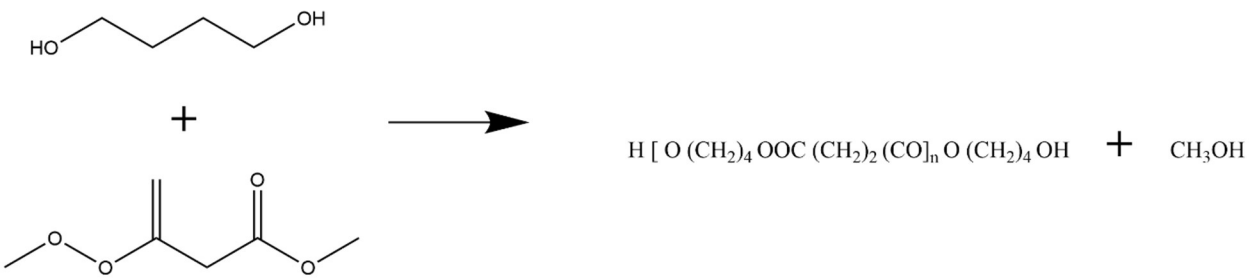

Figure 16. Transesterification of dimethyl succinate and butanediol.

To facilitate these reactions, catalysts such as titanium (IV) n-butoxide, zirconium (IV) n-butoxide, tin (II) 2-ethylhexanoate, or metal oxides like germanium oxide (GeO_2) are commonly used, sometimes with chelating agents like lactic or glycolic acid to enhance their activity [165]. Effective removal of water or methanol byproducts during esterification or transesterification is vital, as incomplete removal can hinder the formation of high-molecular-weight PBS in subsequent steps. Following esterification or transesterification, the polycondensation step proceeds under high vacuum at elevated temperatures of 220–240 °C. This step links the oligomers into long polymer chains, releasing additional BDO as a byproduct. The high vacuum environment aids in the removal of BDO, driving the reaction toward forming PBS with a high molecular weight as in Figure 17.

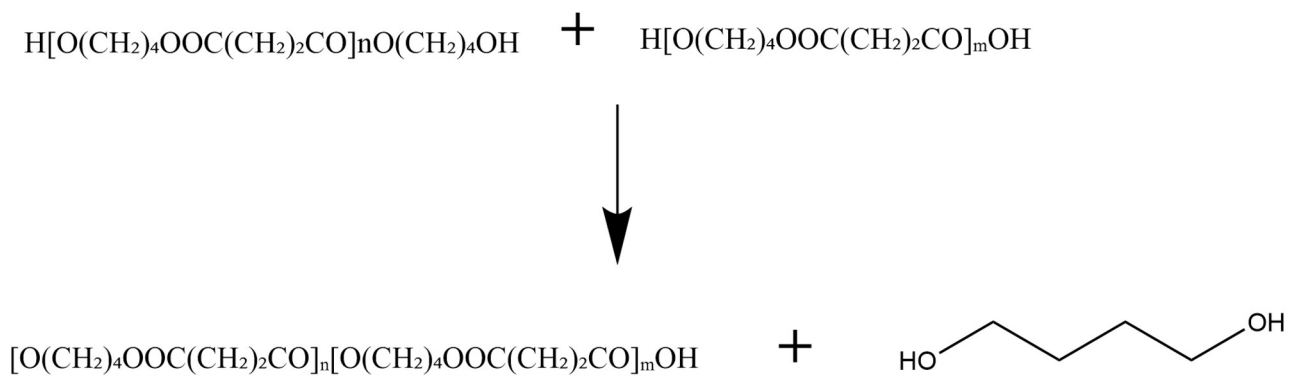

Figure 17. Polycondensation reaction in PBS synthesis.

An inert nitrogen atmosphere is maintained for both stages, to prevent polymer degradation and to produce a high-quality product. The molecular weight would then be determined by carefully monitored reaction parameters such as vacuum, temperature, and removal of byproducts. In the event of high-temperature reactions, excess BDO may be used to make up for such losses, and chain extenders such as hexamethylene diisocyanate may be added to increase molecular weight. Azeotropic distillation employing solvents such as azeotropic distillation, employing solvents decalin or dimethylbenzene, is also utilized for removing water and pushing the reaction equilibrium towards a high molecular weight of PBS formation [166].

PBS is a semicrystalline polyester with mechanical properties similar to polyethylene [167], possessing good tensile strength, impact resistance, moderate rigidity and hardness. The Young's modulus and rigidity of PBS are lower than that of polylactic acid (PLA), but PBS is also tougher than PLA [168]. The molecular weight, copolymerization, and filler content can all affect the mechanical properties of PBS. PBS with a molecular weight less than 100,000 g/mol is brittle, with an elongation at break of around 10% and an Izod impact strength of less than 40 J/m. In contrast, PBS having a molecular weight above 180,000 g/mol shows improved ductility and allows for processing through blowing. PBS produced through copolymerization with less than 30 mol% comonomer content exhibits lower crystallinity and higher elongation and impact strength, but reduced tensile strength. In general, the addition of fillers, such as organic or inorganic materials, increases the elastic modulus and decreases elongation at break, while the effect on tensile strength is not consistent. PBS has a melting temperature (T_m) of approximately 112–116 °C, which is dependent upon molecular weight and thermal history range, as well as a glass transition temperature (T_g) of −32 °C which broadens its workability for processes such as extrusion and injection molding [169]. The heat distortion temperature is 97 °C. Typical copolymerization results include lower T_m, degree of crystallinity and heat distortion temperature and higher elongation and impact strength. Fillers like hydroxyapatite and chitosan can also decrease the melting point and slightly increase crystallinity. PBS is a fully biodegradable thermoplastic through hydrolytic and enzymatic degradation and is amenable to extrusion, injection molding, and thermoforming. It is brittle, has good clarity and has a shiny appearance. The materials crystallize slowly and have low melt viscosity, which makes processing difficult and results in poor gas barrier properties. PBS absorbs water, and its rate increases with increasing temperatures. Biocompatible and non-toxic, its density is between 1.23 and 1.26 g/cm^3. Blending with natural fibers can reduce the cost of PBS, but it's still more costly than petroleum-based plastics—although making plastics from reprocessed PBS can offset some of that price differential. By blending it with other polymers (e.g., PLA), its strength, flexibility, and ductility can be improved, making it suitable for food packaging applications. Tailoring the thermal, mechanical, and biodegradation properties of PBS is possible through copolymerization, while surface treatments such as plasma treatment can improve its hydrophilicity for biomedical applications [170]. The properties and modifications of PBS we outline here suggest its potential as a sustainable and versatile material for many applications.

PBS is a promising alternative to synthetic petroleum-based materials because of its biodegradability, flexibility, transparency, and high elongation at break. Another way PBS can be used is to blend it with other polymers [171], like PLA or chitosan, to improve its properties making food shelf life longer. It is additionally used in compostable bags and as a direct melt coating on paperboard for convenience food packaging. In mulching films, PBS is used to maintain soil moisture, control weed growth, and regulate soil temperature in agriculture. Similarly, in vegetation nets, it provides an enhanced habitat for climbing plants. PBS is used in catering products, foams, tableware, and textiles, including nonwoven sheets and garments. PBS is becoming increasingly attractive in the biomedical field for its biodegradability, biocompatibility, and non-toxicity, especially as the matrix for drug delivery systems; for instance, PBS microspheres

were developed for drug delivery of L-dopa and PBS/PEG blends have been studied for controlled praziquantel release. The antibacterial properties and triggered release of adsorbed drug molecules from PBS based nanospheres and electrospun fibers are explored [172]. Additionally, PBS has applications in tissue engineering, where it can be processed into scaffolds for skin, cartilage, heart tissue, and nerve regeneration. Blending it with other polymers or adding fillers can enhance the mechanical properties of the scaffold. Additionally, shape memory polymers (SMPs) in the form of PBS based polymers seem to have interesting potential for biomedical devices such as stents and implants. Further to these uses, PBS is being investigated in raw wastewater treatment to remove the dye, in oil spill cleaning using a composite containing maghemite, and as a thermal insulation material in a composite with cellulose nanocrystals. While promising, complications for PBS include high production costs, poor properties for certain applications, and scarcity—particularly of medical grade PBS. To date, however, research is ongoing to further expand the application of PBS by means of 3D and 4D printing [173], wound dressings, and smart, bioactive materials that exhibit a lethal antimicrobial property, stimuli responsiveness, or both. Because production costs decrease and its properties are optimized further, PBS can replace petroleum-based plastics in all kinds of sectors and will become a more sustainable solution.

Many challenges and limitations prevent PBS from being extensively adopted and used. The high production cost is one of the main obstacles since the material is more expensive than conventional petroleum-based plastics, preventing its widespread competition in many applications. Further, pure PBS has inherent property limitations which limit its use in some applications. This makes PBS brittle, leading to cracking or breaking under stress. It also has a slow crystallization rate, which lengthens processing times; low melt viscosity, complicating molding; softness, limiting its use in rigid applications; and poor gas barrier properties, reducing its potential for packaging. Additionally, medical-grade PBS is not available in all regions, posing a challenge for the supply chain [174]. Due to these challenges, PBS is frequently modified via blending other polymers as an effort to enhance properties, reinforcing with fillers or fibers to improve mechanical strength, or copolymerization to tailor the thermal, mechanical, and degradation properties. owever, modifications to these properties can add complexity and cost, along with challenges such as blend compatibility and filler agglomeration. Poor consumer awareness of the environmental impact of traditional plastics, together with inadequate waste management infrastructure that in many cases does not enable PBS to enter the appropriate waste flows that allow PBS to be composted, also hampers the adoption of PBS as some PBS does end up in landfills. In terms of biomedical applications, these polyesters display specific challenges with regard to their insufficient osteoblast compatibility and bioactivity on one hand, hydrophobicity preventing different cell attachment on the other hand, and slower degradation rates which could not meet the requirements of certain applications in addition to the absence of reactive centers for including binding to drugs, demanding subsequent modifications of these thermoplastics for successful use in drug delivery and tissue engineering [175,176]. Moreover, PBS-based medical products cannot be clinically translated and commercialized in part due to the unavailability or limited availability of medical grade PBS and the lack of approval from FDA [177] for some biomedical applications. Nevertheless, this limitation is being harnessed by current research with efforts to lower production costs, enhance material properties, and extend applications so that PBS can compete as a sustainable alternative to conventional plastics in the future. Overall the the technical definitions for biodegarability can be shown as in Table 2 and the applications of biodegradable polymers can sumerize as shown in Figure 18.

Table 2. Definitions for biodegradability [36,178–180].

Biodegradables	Biodegradable materials can be defined as solid polymeric materials or devices that break down through the process of macromolecular degradation and which are distributed throughout the body without definite indications of excretion from the body (exclusion of environmental, fungal or bacterial degradation). Biologic factors can be problematic to biodegradable polymeric system or device; the system's coherence and sometimes even integrity of the macromolecular components can be threatened, leading to formation of fragments or other forms of degradation products. If at all they relocate, they do so within the body without necessarily migrating to another region in the body.
Bioresorbable	Bioresorbables are solid polymeric materials and methods that degrade in their bulk and then resorb *in vivo*.
Bioerodibles	Bioerodible materials are bioactive solid polymers or devices in which the main feature is surface erosion in relation to the body environment and complete dissolution. Hence, the term bioerosion is reserved for complete removal of the initial foreign material and degradation by products from the surface, and complete disappearance of the low molecular weight molecules without any lasting effects.
Bioabsorbable	Bioabsorbables are solid polymeric materials or devices that dissolve in body fluids without resulting in polymer chain cleavage or molecular mass loss.

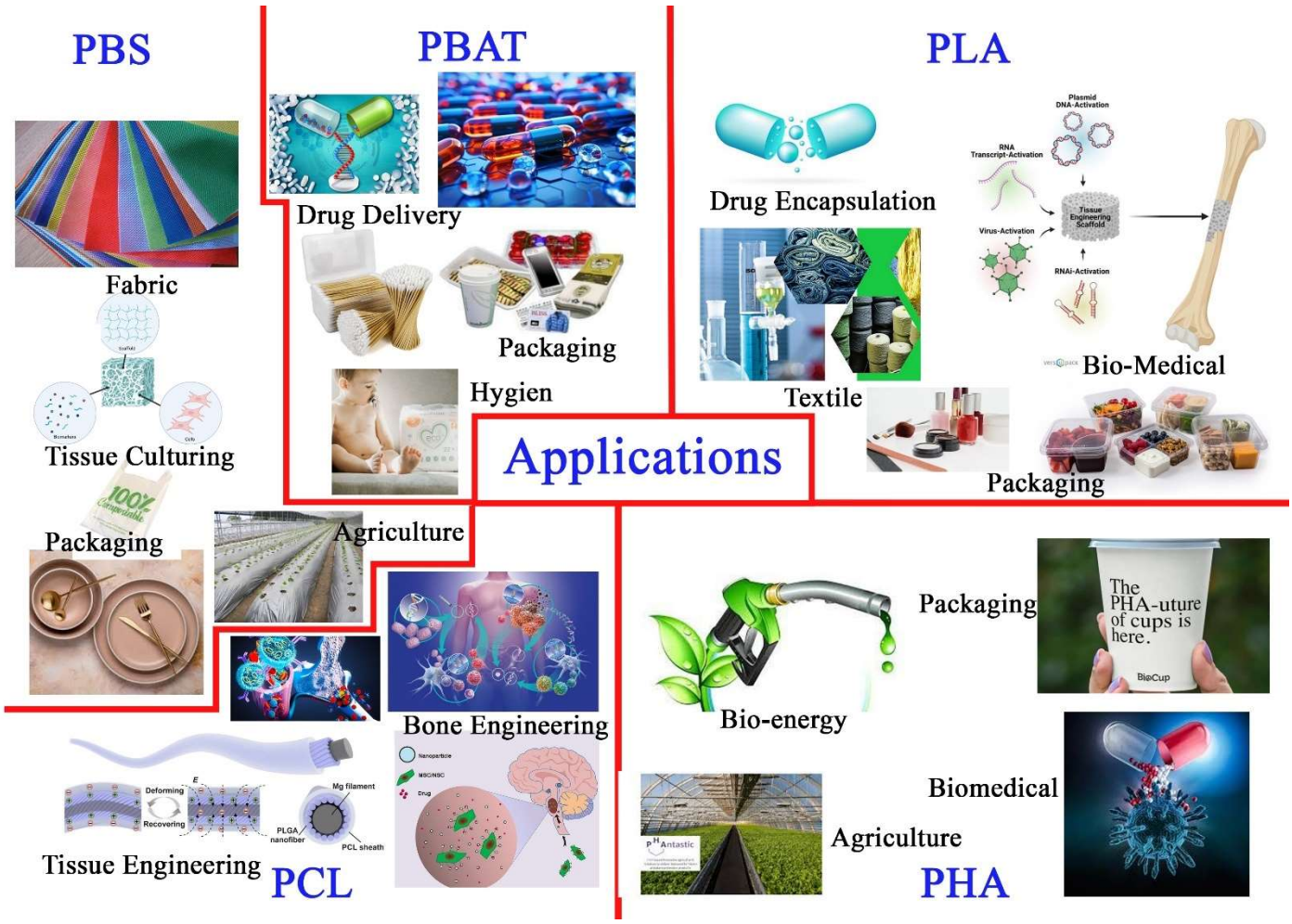

Figure 18. Summary of Applications of Biodegradable Plastics.

4. Conclusions

The formulation of biodegradable plastics and its use can be overcome the pollution brought by non-biodegradable plastics. This paper clearly shows that biodegradable plastics derived from renewable resources, such as PLA, PHA, PCL, PBS, and PBAT, offer a promising alternative to traditional petroleum-based plastics. They not only reduce the use of fossil resources but also help address the global issue of plastic pollution. Biodegradable plastics have various characteristics that qualify them for use in various industries, although they are mainly used in packaging. Due to their biodegradability under natural environmental conditions, they provide relief to ecosystems that are burdened by conventional plastics. Also, efforts to improve the synthesis of biodegradable polymers to produce new blends and composites have improved their mechanical and thermal performances to approximate non-biodegradable plastics. However, going for biodegradable plastics also has its own drawbacks. Currently, the cost of manufacturing biodegradable plastics is still high compared to conventional plastics, thus ranking a major challenge to biodegradable plastics. Also, the structure of waste management that is already in place should be modified to properly sort biodegradable materials to facilitate composting or recycling activities that would unlock the potential impacts of the materials, particularly on the environment.

Acknowledgments

This review article is based on the work supported by University Research Grants (Grant No. ASP/01/RE/TEC/2022/64), University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka.

Author Contributions

All three authors contibuted to manuscript in all sections in similler level.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Funding

This research was funded by University Research Grants (Grant No. ASP/01/RE/TEC/2022/64), University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka.

Declaration of Competing Interest

No potential conflict of interest was reported by the authors.

References

1. Sarah P, Julien BMG, Melissa IG, Paolo M, Adrienne G, Noémie V. *Plastic Overshoot Day Report 2024*; EA-Earth Action: Lausanne, Switzerland, 2024.
2. Association ISW. *Global Waste Management Outlook 2024: Beyond an Age of Waste, Turning Rubbish into a Resource*; Association ISW: Washington, DC, USA, 2024.
3. Environment U. *Putting the Environment at the Heart of People'S Lives [EN/AR/RU/ZH]—World*; United Nations: New York, NY, USA, 2018.
4. Bordes P, Pollet E, Avérous L. Nano-biocomposites: Biodegradable polyester/nanoclay systems. *Prog. Polym. Sci.* **2009**, *34*, 125–155.
5. Babayemi JO, Nnorom IC, Osibanjo O, Weber R. Ensuring sustainability in plastics use in Africa: Consumption, waste generation, and projections. *Environ. Sci. Eur.* **2019**, *31*, 1–20.
6. Mossman S. Plastics and social responsibility. In *Provocative Plastics: Their Value in Design and Material Culture*; Palgrave Macmillan: London, UK, 2020; pp. 275–295.
7. Hess KZ. *Open Dumping and Burning: A Source of Terrestrial Microplastics in Underserved Communities*; Oklahoma State University: Stillwater, OK, USA, 2023.
8. Wabnitz C, Nichols WJ. Plastic pollution: An ocean emergency. *Mar. Turt. Newsl.* **2010**, *129*, 1–4.
9. Verma R, Vinoda K, Papireddy M, Gowda A. Toxic pollutants from plastic waste-a review. *Procedia Environ. Sci.* **2016**, *35*, 701–708.
10. Avérous L. Polylactic acid: Synthesis, properties and applications. In *Monomers, Polymers and Composites from Renewable Resources*; Elsevier: Amsterdam, The Netherlands, 2008; pp. 433–450.
11. Nations U. *UNEP Annual Report 2019*; UNEP: Nairobi, Kenya, 2019.
12. Zhou Y, Wang J, Zou M, Jia Z, Zhou S, Li Y. Microplastics in soils: A review of methods, occurrence, fate, transport, ecological and environmental risks. *Sci. Total Environ.* **2020**, *748*, 141368.
13. Li P, Wang X, Su M, Zou X, Duan L, Zhang H. Characteristics of plastic pollution in the environment: A review. *Bull. Environ. Contam. Toxicol.* **2021**, *107*, 577–584.
14. Carpenter EJ, Smith KL. Plastics on the Sargasso Sea Surface. *Science* **1972**, *175*, 1240–1241. doi:10.1126/science.175.4027.1240.
15. Thompson RC, Olsen Y, Mitchell RP, Davis A, Rowland SJ, John AW, et al. Lost at sea: Where is all the plastic? *Science* **2004**, *304*, 838.
16. Huang JC, Shetty AS, Wang MS. Biodegradable plastics: A review. *Adv. Polym. Technol.* **1990**, *10*, 23–30.
17. do Sul JAI, Costa MF. The present and future of microplastic pollution in the marine environment. *Environ. Pollut.* **2014**, *185*, 352–364.
18. Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, et al. Plastic waste inputs from land into the ocean. *Science* **2015**, *347*, 768–771.
19. Parker L. *The World's Plastic Pollution Crisis Explained*; National Geographic Society: Washington, DC, USA, 2019.
20. Al-Salem S. Energy production from plastic solid waste (PSW). In *Plastics to Energy*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 45–64.
21. Fahim I, Mohsen O, ElKayaly D. Production of fuel from plastic waste: A feasible business. *Polymers* **2021**, *13*, 915.
22. Gupta A, Lilley D. Incineration of plastics and other wastes for efficient power generation: A review. In Proceedings of the 41st Aerospace sciences meeting and exhibit, Reno, VA, YSA, 6–9 January 2003; p. 334.

23. Bora RR, Wang R, You F. Waste polypropylene plastic recycling toward climate change mitigation and circular economy: Energy, environmental, and technoeconomic perspectives. *ACS Sustain. Chem. Eng.* **2020**, *8*, 16350–16363.
24. Kannan P, Al Shoaibi A, Srinivasakannan C. Energy recovery from co-gasification of waste polyethylene and polyethylene terephthalate blends. *Comput. Fluids* **2013**, *88*, 38–42.
25. Buekens A, Cen K. Waste incineration, PVC, and dioxins. *J. Mater. Cycles Waste Manag.* **2011**, *13*, 190–197.
26. Velis CA, Cook E. Mismanagement of plastic waste through open burning with emphasis on the global south: A systematic review of risks to occupational and public health. *Environ. Sci. Technol.* **2021**, *55*, 7186–7207.
27. Valavanidis A, Iliopoulos N, Gotsis G, Fiotakis K. Persistent free radicals, heavy metals and PAHs generated in particulate soot emissions and residue ash from controlled combustion of common types of plastic. *J. Hazard. Mater.* **2008**, *156*, 277–284.
28. Park YK, Kim W, Jo YM. Release of harmful air pollutants from open burning of domestic municipal solid wastes in a metropolitan area of Korea. *Aerosol Air Qual. Res.* **2013**, *13*, 1365–1372.
29. Buekens A, Cen K. PVC and waste incineration-modern technologies solve old problems. In Proceedings of the 6th International Conference on Combustion, Incineration/Pyrolysis and Emission Control: Waste to Wealth, Kuala Lumpur, Malaysia, 26–29 July 2010.
30. Chong NS, Abdulramoni S, Patterson D, Brown H. Releases of fire-derived contaminants from polymer pipes made of polyvinyl chloride. *Toxics* **2019**, *7*, 57.
31. Mai L, He H, Zeng EY. Plastic pollution in waterways and in the oceans. In *Water and Climate Change*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 179–195.
32. Lemieux PM, Lutes CC, Santoianni DA. Emissions of organic air toxics from open burning: A comprehensive review. *Prog. Energy Combust. Sci.* **2004**, *30*, 1–32.
33. Jones MW, Glen PP, Thomas G, Robbie MA, Clemens S, Johannes G, et al. National contributions to climate change due to historical emissions of carbon dioxide, methane and nitrous oxide. *Sci. Data* **2023**, *10*, 155.
34. Hamilton LA, Feit S. Plastic & Climate: The Hidden Costs of a Plastic Planet. 2019. Available online: https://policycommons.net/artifacts/2485040/untitled/3507468/ (15 October 2024).
35. Aadal H, Rad KG, Fard AB, Sabet PGP, Harirchian E. Implementing 3R concept in construction waste management at construction site. *J. Appl. Environ. Biol. Sci* **2013**, *3*, 160–166.
36. Liu L, Liang Y, Song Q, Li J. A review of waste prevention through 3R under the concept of circular economy in China. *J. Mater. Cycles Waste Manag.* **2017**, *19*, 1314–1323.
37. Dauvergne P. Why is the global governance of plastic failing the oceans? *Glob. Environ. Chang.* **2018**, *51*, 22–31.
38. Truelove HB, Yeung KL, Carrico AR, Gillis AJ, Raimi KT. From plastic bottle recycling to policy support: An experimental test of pro-environmental spillover. *J. Environ. Psychol.* **2016**, *46*, 55–66.
39. Nuangjakchim MR, Patterson PG. *Awareness, Understanding & Attitude towards Biodegradable Plastic and How It Affects Purchase Decision and Corporate Image*; Thammasat University: Bangkok, Thailand, 2019.
40. OECD. *Plastic Waste by Region and End-of-Life Fate*; OECD: Paris, France, 2022.
41. Dahlbo H, Poliakova V, Mylläri V, Sahimaa O, Anderson R. Recycling potential of post-consumer plastic packaging waste in Finland. *Waste Manag.* **2018**, *71*, 52–61.
42. Schulte A, Kampmann B, Galafton C. Measuring the circularity and impact reduction potential of post-industrial and post-consumer recycled plastics. *Sustainability* **2023**, *15*, 12242.
43. Hahladakis JN, Iacovidou E. An overview of the challenges and trade-offs in closing the loop of post-consumer plastic waste (PCPW): Focus on recycling. *J. Hazard. Mater.* **2019**, *380*, 120887.
44. Chawla S, Varghese BS, Chithra A, Hussain CG, Keçili R, Hussain CM. Environmental impacts of post-consumer plastic wastes: Treatment technologies towards eco-sustainability and circular economy. *Chemosphere* **2022**, *308*, 135867.
45. Ágnes N, Rajmund K. The environmental impact of plastic waste incineration. *AARMS–Acad. Appl. Res. Mil. Public Manag. Sci.* **2016**, *15*, 231–237.
46. Hopewell J, Dvorak R, Kosior E. Plastics recycling: Challenges and opportunities. *Philos. Trans. R. Soc. B Biol. Sci.* **2009**, *364*, 2115–2126.
47. Bernardo C, Simões CL, Pinto LMC. Environmental and economic life cycle analysis of plastic waste management options. A review. In Proceedings of the AIP Conference Proceedings, Atlanta, GA, USA, 17–22 July 2016.
48. Joseph TM, Unni AB, Joshy K, Kar MD, Haponiuk J, Thomas S. Emerging Bio-Based Polymers from Lab to Market: Current Strategies, Market Dynamics and Research Trends. *C* **2023**, *9*, 30.
49. Agriculture and rural development—European Commission. In Proceedings of the Meeting of the CDG Arable Crops—Starch Sector, Brussels, Belgium, 20 October 2022.
50. Singhvi M, Zinjarde S, Gokhale D. Polylactic acid: Synthesis and biomedical applications. *J. Appl. Microbiol.* **2019**, *127*, 1612–1626.
51. Datta R, Henry M. Lactic acid: Recent advances in products, processes and technologies—A review. *J. Chem. Technol. Biotechnol. Int. Res. Process Environ. Clean Technol.* **2006**, *81*, 1119–1129.

52. Godavitarne C, Robertson A, Peters J, Rogers B. Biodegradable materials. *Orthop. Trauma* **2017**, *31*, 316–320.
53. Schreurs VV, Schaafsma G. Lactic acid and lactates: In health and wellness. *Nutrafoods* **2010**, *9*, 7–16.
54. Holten CH. *Lactic Acid. Properties and Chemistry of Lactic Acid and Derivatives*; Verlag Chemie: Weinheim, Germany, 1971.
55. Kister G, Cassanas G, Bergounhon M, Hoarau D, Vert M. Structural characterization and hydrolytic degradation of solid copolymers of d, l-lactide-co-ε-caprolactone by Raman spectroscopy. *Polymer* **2000**, *41*, 925–932.
56. Gupta B, Revagade N, Hilborn J. Poly (lactic acid) fiber: An overview. *Prog. Polym. Sci.* **2007**, *32*, 455–482.
57. Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. *Macromol. Biosci.* **2004**, *4*, 835–864.
58. Urayama H, Moon SI, Kimura Y. Microstructure and thermal properties of polylactides with different L-and D-unit sequences: Importance of the Helical nature of the L-sequenced segments. *Macromol. Mater. Eng.* **2003**, *288*, 137–143.
59. Averous L. Biodegradable multiphase systems based on plasticized starch: A review. *J. Macromol. Sci. Part C Polym. Rev.* **2004**, *44*, 231–274.
60. Schwach E, Averous L. Starch-based biodegradable blends: Morphology and interface properties. *Polym. Int.* **2004**, *53*, 2115–2124.
61. Cooper-White JJ, Mackay ME. Rheological properties of poly (lactides). Effect of molecular weight and temperature on the viscoelasticity of poly (l-lactic acid). *J. Polym. Sci. Part B Polym. Phys.* **1999**, *37*, 1803–1814.
62. Garlotta D. A literature review of poly (lactic acid). *J. Polym. Environ.* **2001**, *9*, 63–84.
63. Lim L-T, Auras R, Rubino M. Processing technologies for poly (lactic acid). *Prog. Polym. Sci.* **2008**, *33*, 820–852.
64. Farah S, Anderson DG, Langer R. Physical and mechanical properties of PLA, and their functions in widespread applications—A comprehensive review. *Adv. Drug Deliv. Rev.* **2016**, *107*, 367–392.
65. Hiroi R, Ray SS, Okamoto M, Shiroi T. Organically modified layered titanate: A new nanofiller to improve the performance of biodegradable polylactide. *Macromol. Rapid Commun.* **2004**, *25*, 1359–1364.
66. Sanchez-Garcia M, Gimenez E, Lagaron J. Novel PET nanocomposites of interest in food packaging applications and comparative barrier performance with biopolyester nanocomposites. *J. Plast. Film Sheeting* **2007**, *23*, 133–148.
67. Miletić A, Ristić I, Coltelli M-B, Pilić B. Modification of PLA-based films by grafting or coating. *J. Funct. Biomater.* **2020**, *11*, 30.
68. Hassouna F, Raquez J-M, Addiego F, Dubois P, Toniazzo V, Ruch D. New approach on the development of plasticized polylactide (PLA): Grafting of poly (ethylene glycol)(PEG) via reactive extrusion. *Eur. Polym. J.* **2011**, *47*, 2134–2144.
69. Wu F, Lan X, Ji D, Liu Z, Yang W, Yang M. Grafting polymerization of polylactic acid on the surface of nano-SiO_2 and properties of PLA/PLA-grafted-SiO_2 nanocomposites. *J. Appl. Polym. Sci.* **2013**, *129*, 3019–3027.
70. Balla E, Daniilidis V, Karlioti G, Kalamas T, Stefanidou M, Bikiaris ND, et al. Poly (lactic Acid): A versatile biobased polymer for the future with multifunctional properties—From monomer synthesis, polymerization techniques and molecular weight increase to PLA applications. *Polymers* **2021**, *13*, 1822.
71. Mathew AP, Oksman K, Sain M. The effect of morphology and chemical characteristics of cellulose reinforcements on the crystallinity of polylactic acid. *J. Appl. Polym. Sci.* **2006**, *101*, 300–310.
72. Beltrán FR, Arrieta MP, Moreno E, Gaspar G, Muneta LM, Carrasco-Gallego R, et al. Evaluation of the technical viability of distributed mechanical recycling of PLA 3D printing wastes. *Polymers* **2021**, *13*, 1247.
73. Subramaniam S, Samykano M, Selvamani S, Ngui W, Kadirgama K, Sudhakar K, et al. 3D printing: Overview of PLA progress. In Proceedings of the AIP Conference Proceedings, Bodrum, Turkey, 4–8 September 2019.
74. Tirado-Garcia I, Garcia-Gonzalez D, Garzon-Hernandez S, Rusinek A, Robles G, Martinez-Tarifa JM, et al. Conductive 3D printed PLA composites: On the interplay of mechanical, electrical and thermal behaviours. *Compos. Struct.* **2021**, *265*, 113744.
75. Spiridon I, Darie RN, Kangas H. Influence of fiber modifications on PLA/fiber composites. Behavior to accelerated weathering. *Compos. Part B Eng.* **2016**, *92*, 19–27.
76. Sudesh K, Abe H, Doi Y. Synthesis, structure and properties of polyhydroxyalkanoates: Biological polyesters. *Prog. Polym. Sci.* **2000**, *25*, 1503–1555.
77. Dhania S, Bernela M, Rani R, Parsad M, Grewal S, Kumari S, et al. Scaffolds the backbone of tissue engineering: Advancements in use of polyhydroxyalkanoates (PHA). *Int. J. Biol. Macromol.* **2022**, *208*, 243–259.
78. Muneer F, Rasul I, Qasim M, Sajid A, Nadeem H. Optimization, production and characterization of polyhydroxyalkanoate (PHA) from indigenously isolated novel bacteria. *J. Polym. Environ.* **2022**, *30*, 3523–3533.
79. Kaniuk Ł, Stachewicz U. Development and advantages of biodegradable PHA polymers based on electrospun PHBV fibers for tissue engineering and other biomedical applications. *ACS Biomater. Sci. Eng.* **2021**, *7*, 5339–5362.
80. Stubbe J, Tian J. Polyhydroxyalkanoate (PHA) homeostasis: The role of the PHA synthase. *Nat. Prod. Rep.* **2003**, *20*, 445–457.
81. Winnacker M. Polyhydroxyalkanoates: Recent Advances in Their Synthesis and Applications. *Eur. J. Lipid Sci. Technol.* **2019**, *121*, 1900101. doi:10.1002/ejlt.201900101.
82. Madkour MH, Heinrich D, Alghamdi MA, Shabbaj II, Steinbüchel A. PHA recovery from biomass. *Biomacromolecules* **2013**, *14*, 2963–2972.

83. Kannah RY, Kumar MD, Kavitha S, Banu JR, Tyagi VK, Rajaguru P, et al. Production and recovery of polyhydroxyalkanoates (PHA) from waste streams–A review. *Bioresour. Technol.* **2022**, *366*, 128203.
84. Kunasundari B, Sudesh K. Isolation and recovery of microbial polyhydroxyalkanoates. *Express Polym. Lett.* **2011**, *5*, 620–634.
85. Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind. Eng. Chem. Res.* **2009**, *48*, 3713–3729.
86. Jiang G, Hill DJ, Kowalczuk M, Johnston B, Adamus G, Irorere V, et al. Carbon sources for polyhydroxyalkanoates and an integrated biorefinery. *Int. J. Mol. Sci.* **2016**, *17*, 1157.
87. de Smet MJ, Eggink G, Witholt B, Kingma J, Wynberg H. Characterization of intracellular inclusions formed by Pseudomonas oleovorans during growth on octane. *J. Bacteriol.* **1983**, *154*, 870–878.
88. Ni Y-Y, Chung MG, Lee SH, Park H-Y, Rhee YH. Biosynthesis of medium-chain-length poly (3-hydroxyalkanoates) by volatile aromatic hydrocarbons-degrading Pseudomonas fulva TY16. *Bioresour. Technol.* **2010**, *101*, 8485–8488.
89. Guzik MW, Kenny ST, Duane GF, Casey E, Woods T, Babu RP, et al. Conversion of post consumer polyethylene to the biodegradable polymer polyhydroxyalkanoate. *Appl. Microbiol. Biotechnol.* **2014**, *98*, 4223–4232.
90. Winnacker M, Rieger B. Copolymers of polyhydroxyalkanoates and polyethylene glycols: Recent advancements with biological and medical significance. *Polym. Int.* **2017**, *66*, 497–503. doi:10.1002/pi.5261.
91. Yalpani M, Marchessault RH, Morin FG, Monasterios CJ. Synthesis of poly (3-hydroxyalkanoate)(PHA) conjugates: PHA-carbohydrate and PHA-synthetic polymer conjugates. *Macromolecules* **1991**, *24*, 6046–6049.
92. Rosenberg E, Ron EZ. High- and low-molecular-mass microbial surfactants. *Appl. Microbiol. Biotechnol.* **1999**, *52*, 154–162. doi:10.1007/s002530051502.
93. Andreeßen B, Lange AB, Robenek H, Steinbüchel A. Conversion of Glycerol to Poly(3-Hydroxypropionate) in Recombinant *Escherichia coli. Appl. Environ. Microbiol.* **2010**, *76*, 622–626. doi:10.1128/AEM.02097-09.
94. Pollak B, Cerda A, Delmans M, Álamos S, Moyano T, West A, et al. Loop assembly: A simple and open system for recursive fabrication of DNA circuits. *New Phytol.* **2019**, *222*, 628–640.
95. El-Hadi A, Schnabel R, Straube E, Müller G, Riemschneider M. Effect of melt processing on crystallization behavior and rheology of poly (3-hydroxybutyrate)(PHB) and its blends. *Macromol. Mater. Eng.* **2002**, *287*, 363–372.
96. Owen A, Heinzel J, Škrbić Ž, Divjaković V. Crystallization and melting behaviour of PHB and PHB/HV copolymer. *Polymer* **1992**, *33*, 1563–1567.
97. Miu D-M, Eremia MC, Moscovici M. Polyhydroxyalkanoates (PHAs) as biomaterials in tissue engineering: Production, isolation, characterization. *Materials* **2022**, *15*, 1410.
98. Aragão G, Lindley N, Uribelarrea J, Pareilleux A. Maintaining a controlled residual growth capacity increases the production of polyhydroxyalkanoate copolymers by Alcaligenes eutrophus. *Biotechnol. Lett.* **1996**, *18*, 937–942.
99. Raza ZA, Riaz S, Banat IM. Polyhydroxyalkanoates: Properties and chemical modification approaches for their functionalization. *Biotechnol. Prog.* **2018**, *34*, 29–41.
100. Sharma V, Sehgal R, Gupta R. Polyhydroxyalkanoate (PHA): Properties and modifications. *Polymer* **2021**, *212*, 123161.
101. Volova TG. *Polyhydroxyalkanoates—Plastic Materials of the 21st Century: Production, Properties, Applications*; Nova Publishers: Hauppauge, NY, USA, 2004.
102. Veronese FM, Mero A. The impact of PEGylation on biological therapies. *BioDrugs* **2008**, *22*, 315–329.
103. Zhao S, Lee J, Xu W. Supramolecular hydrogels formed from biodegradable ternary COS-g-PCL-b-MPEG copolymer with α-cyclodextrin and their drug release. *Carbohydr. Res.* **2009**, *344*, 2201–2208.
104. Li Z, Lim J. Biodegradable polyhydroxyalkanoates nanocarriers for drug delivery applications. In *Stimuli Responsive Polymeric Nanocarriers for Drug Delivery Applications, Volume 1*, Elsevier: Amsterdam, The Netherlands, 2018; pp. 607–634.
105. Renard E, Rios A, Versace D-L, Langlois V. The design of functionalized PHA-based polymeric materials by chemical modifications. In *The Handbook of Polyhydroxyalkanoates*; CRC Press: Boca Raton, FL, USA, 2020; pp. 17–42.
106. Chaturvedi K, Ganguly K, Kulkarni AR, Nadagouda MN, Stowbridge J, Rudzinski WE, et al. Ultra-small fluorescent bile acid conjugated PHB–PEG block copolymeric nanoparticles: Synthesis, characterization and cellular uptake. *Rsc Adv.* **2013**, *3*, 7064–7070.
107. Garg A, Rai G, Lodhi S, Jain AP, Yadav AK. *In-vitro* and *in-vivo* assessment of dextran-appended cellulose acetate phthalate nanoparticles for transdermal delivery of 5-fluorouracil. *Drug Deliv.* **2016**, *23*, 1525–1535.
108. Tan D, Wang Y, Tong Y, Chen G-Q. Grand challenges for industrializing polyhydroxyalkanoates (PHAs). *Trends Biotechnol.* **2021**, *39*, 953–963.
109. Kumar M, Rathour R, Singh R, Sun Y, Pandey A, Gnansounou E, et al. Bacterial polyhydroxyalkanoates: Opportunities, challenges, and prospects. *J. Clean. Prod.* **2020**, *263*, 121500.
110. Singh M, Kumar P, Ray S, Kalia VC. Challenges and opportunities for customizing polyhydroxyalkanoates. *Indian J. Microbiol.* **2015**, *55*, 235–249.

111. Finch C. Anionic polymerisation to cationic polymerisation, volume 2. In *Encyclopedia of Polymer Science and Engineering*; Mark HF, Bikales NM, Overberger CG, Menges G, Eds.; Wiley-Interscience, New York, NY, USA, 1985.
112. Nair LS, Laurencin CT. Biodegradable polymers as biomaterials. *Prog. Polym. Sci.* **2007**, *32*, 762–798.
113. Woodruff MA, Hutmacher DW. The return of a forgotten polymer—Polycaprolactone in the 21st century. *Prog. Polym. Sci.* **2010**, *35*, 1217–1256.
114. Luciani A, Coccoli V, Orsi S, Ambrosio L, Netti PA. PCL microspheres based functional scaffolds by bottom-up approach with predefined microstructural properties and release profiles. *Biomaterials* **2008**, *29*, 4800–4807.
115. Pyo S-H, Park JH, Srebny V, Hatti-Kaul R. A sustainable synthetic route for biobased 6-hydroxyhexanoic acid, adipic acid and ε-caprolactone by integrating bio-and chemical catalysis. *Green Chem.* **2020**, *22*, 4450–4455.
116. Labet M, Thielemans W. Synthesis of polycaprolactone: A review. *Chem. Soc. Rev.* **2009**, *38*, 3484–3504.
117. Braud C, Devarieux R, Atlan A, Ducos C, Vert M. Capillary zone electrophoresis in normal or reverse polarity separation modes for the analysis of hydroxy acid oligomers in neutral phosphate buffer. *J. Chromatogr. B Biomed. Sci. Appl.* **1998**, *706*, 73–82.
118. Dong H, Wang H-d, Cao S-g, Shen J-c. Lipase-catalyzed polymerization of lactones and linear hydroxyesters. *Biotechnol. Lett.* **1998**, *20*, 905–908.
119. Yuan M, Xiong C, Deng X. Ring-opening polymerization of ε-caprolactone initiated by cyclopentadienyl sodium. *J. Appl. Polym. Sci.* **1998**, *67*, 1273–1276.
120. Stridsberg KM, Ryner M, Albertsson A-C. *Controlled Ring-Opening Polymerization: Polymers with Designed Macromolecular Architecture*; Springer: Berlin, Germany, 2002.
121. Riva R, Schmeits S, Jérôme C, Jérôme R, Lecomte P. Combination of ring-opening polymerization and "click chemistry": Toward functionalization and grafting of poly (ε-caprolactone). *Macromolecules* **2007**, *40*, 796–803.
122. Detrembleur C, Mazza M, Lou X, Halleux O, Lecomte P, Mecerreyes D, et al. New Functional Aliphatic Polyesters by Chemical Modification of Copolymers of ε-Caprolactone with γ-(2-Bromo-2-methylpropionate)-ε-caprolactone, γ-Bromo-ε-caprolactone, and a Mixture of β-and γ-Ene-ε-caprolactone. *Macromolecules* **2000**, *33*, 7751–7760.
123. Platel RH, Hodgson LM, Williams CK. Biocompatible initiators for lactide polymerization. *Polym. Rev.* **2008**, *48*, 11–63.
124. Bhaw-Luximon A, Jhurry D, Motala-Timol S, Lochee Y. Polymerization of ε-Caprolactone and its Copolymerization with γ-Butyrolactone using Metal Complexes. *Macromol. Symp.* **2005**, *231*, 60–68.
125. Mingotaud AF, Dargelas F, Cansell F. Cationic and anionic ring-opening polymerization in supercritical CO_2. *Macromol. Symp.* **2000**, *153*, 77–86.
126. Wang Y, Kunioka M. Ring-opening polymerization of cyclic monomers with aluminum triflate. *Macromol. Symp.* **2005**, *224*, 193–206.
127. Degée P, Dubois P, Jérôme R, Teyssie P. Macromolecular engineering of polylactones and polylactides. 9. Synthesis, characterization, and application of ι-primary amine poly (iε-caprolactone). *Macromolecules* **1992**, *25*, 4242–4248.
128. Florjańczyk Z, Plichta A, Sobczak M. Ring opening polymerization initiated by methylaluminoxane/AlMe3 complexes. *Polymer* **2006**, *47*, 1081–1090.
129. Duda A, Florjanczyk Z, Hofman A, Slomkowski S, Penczek S. Living pseudoanionic polymerization of iε-caprolactone. Poly (iε-caprolactone) free of cyclics and with controlled end groups. *Macromolecules* **1990**, *23*, 1640–1646.
130. Nobes GA, Kazlauskas RJ, Marchessault RH. Lipase-catalyzed ring-opening polymerization of lactones: A novel route to poly (hydroxyalkanoate) s. *Macromolecules* **1996**, *29*, 4829–4833.
131. MacDonald RT, Pulapura SK, Svirkin YY, Gross RA, Kaplan DL, Akkara J, et al. Enzyme-catalyzed. epsilon.-caprolactone ring-opening polymerization. *Macromolecules* **1995**, *28*, 73–78.
132. Kobayashi S. Enzymatic polymerization: A new method of polymer synthesis. *J. Polym. Sci. Part A Polym. Chem.* **1999**, *37*, 3041–3056.
133. Kobayashi S, Uyama H, Ohmae M. Enzymatic polymerization for precision polymer synthesis. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 613–635.
134. Wu C-S. Physical properties and biodegradability of maleated-polycaprolactone/starch composite. *Polym. Degrad. Stab.* **2003**, *80*, 127–134.
135. Sachan R, Warkar SG, Purwar R. An overview on synthesis, properties and applications of polycaprolactone copolymers, blends & composites. *Polym. -Plast. Technol. Mater.* **2023**, *62*, 327–358.
136. Asadpour S, Yeganeh H, Ai J, Kargozar S, Rashtbar M, Seifalian A, et al. Polyurethane-polycaprolactone blend patches: Scaffold characterization and cardiomyoblast adhesion, proliferation, and function. *ACS Biomater. Sci. Eng.* **2018**, *4*, 4299–4310.
137. Wan Y, Lu X, Dalai S, Zhang J. Thermophysical properties of polycaprolactone/chitosan blend membranes. *Thermochim. Acta* **2009**, *487*, 33–38.
138. Vert M, Li S, Spenlehauer G, Guérin P. Bioresorbability and biocompatibility of aliphatic polyesters. *J. Mater. Sci. Mater. Med.* **1992**, *3*, 432–446.
139. Middleton JC, Tipton AJ. Synthetic biodegradable polymers as orthopedic devices. *Biomaterials* **2000**, *21*, 2335–2346.

140. Gunatillake PA, Adhikari R, Gadegaard N. Biodegradable synthetic polymers for tissue engineering. *Eur. Cell Mater.* **2003**, *5*, 1–16.
141. Sun H, Mei L, Song C, Cui X, Wang P. The *in vivo* degradation, absorption and excretion of PCL-based implant. *Biomaterials* **2006**, *27*, 1735–1740.
142. Pitt C, Schindler A. Capronor: A biodegradable delivery system for levonorgestrel. *Long-Act. Contracept. Deliv. Syst.* **1984**, *3*, 48–63.
143. Pitt G, Gratzl M, Kimmel G, Surles J, Sohindler A. Aliphatic polyesters II. The degradation of poly (DL-lactide), poly (ε-caprolactone), and their copolymers *in vivo*. *Biomaterials* **1981**, *2*, 215–220.
144. Freed LE, Vunjak-Novakovic G, Biron RJ, Eagles DB, Lesnoy DC, Barlow SK, et al. Biodegradable polymer scaffolds for tissue engineering. *Bio/Technol.* **1994**, *12*, 689–693.
145. Hutmacher DW. Scaffolds in tissue engineering bone and cartilage. *Biomaterials* **2000**, *21*, 2529–2543.
146. Kurella A, Dahotre NB. Surface modification for bioimplants: The role of laser surface engineering. *J. Biomater. Appl.* **2005**, *20*, 5–50.
147. Kim E, Yang J, Choi J, Suh J-S, Huh Y-M, Haam S. Synthesis of gold nanorod-embedded polymeric nanoparticles by a nanoprecipitation method for use as photothermal agents. *Nanotechnology* **2009**, *20*, 365602.
148. Lu X, Sun Z, Cai W, Gao Z. Study on the shape memory effects of poly (l-lactide-co-ε-caprolactone) biodegradable polymers. *J. Mater. Sci. Mater. Med.* **2008**, *19*, 395–399.
149. Thomas V, Jose MV, Chowdhury S, Sullivan JF, Dean DR, Vohra YK. Mechano-morphological studies of aligned nanofibrous scaffolds of polycaprolactone fabricated by electrospinning. *J. Biomater. Sci. Polym. Ed.* **2006**, *17*, 969–984.
150. Arif ZU, Khalid MY, Noroozi R, Sadeghianmaryan A, Jalalvand M, Hossain M. Recent advances in 3D-printed polylactide and polycaprolactone-based biomaterials for tissue engineering applications. *Int. J. Biol. Macromol.* **2022**, *218*, 930–968.
151. Abrisham M, Noroozi M, Panahi-Sarmad M, Arjmand M, Goodarzi V, Shakeri Y, et al. The role of polycaprolactone-triol (PCL-T) in biomedical applications: A state-of-the-art review. *Eur. Polym. J.* **2020**, *131*, 109701.
152. Mahata D, Karthikeyan S, Godse R, Gupta VK. Poly (butylene adipate-co-terephthalate) polyester synthesis process and product development. *Polym. Sci. Ser. C* **2021**, *63*, 102–111.
153. Li G, Shankar S, Rhim J-W, Oh B-Y. Effects of preparation method on properties of poly (butylene adipate-co-terephthalate) films. *Food Sci. Biotechnol.* **2015**, *24*, 1679–1685.
154. Herrera R, Franco L, Rodríguez-Galán A, Puiggalí J. Characterization and degradation behavior of poly (butylene adipate-co-terephthalate) s. *J. Polym. Sci. Part A Polym. Chem.* **2002**, *40*, 4141–4157.
155. Boonprasertpoh A, Pentrakoon D, Junkasem J. Effect of PBAT on physical, morphological, and mechanical properties of PBS/PBAT foam. *Cell. Polym.* **2020**, *39*, 31–41.
156. Sritham E, Phunsombat P, Chaishome J. Tensile properties of PLA/PBAT blends and PLA fibre-reinforced PBAT composite. *MATEC Web Conf.* **2018**, *192*, 03014.
157. Çoban O, Bora MÖ, Kutluk T, Özkoç G. Mechanical and thermal properties of volcanic particle filled PLA/PBAT composites. *Polym. Compos.* **2018**, *39*, E1500–E1511.
158. Liu Y, Liu S, Liu Z, Lei Y, Jiang S, Zhang K, et al. Enhanced mechanical and biodegradable properties of PBAT/lignin composites via silane grafting and reactive extrusion. *Compos. Part B Eng.* **2021**, *220*, 108980.
159. Fukushima K, Wu M-H, Bocchini S, Rasyida A, Yang M-C. PBAT based nanocomposites for medical and industrial applications. *Mater. Sci. Eng. C* **2012**, *32*, 1331–1351.
160. Roy S, Ghosh T, Zhang W, Rhim J-W. Recent progress in PBAT-based films and food packaging applications: A mini-review. *Food Chem.* **2024**, *437*, 137822.
161. Bheemaneni G, Saravana S, Kandaswamy R. Processing and characterization of poly (butylene adipate-co-terephthalate)/wollastonite biocomposites for medical applications. *Mater. Today Proc.* **2018**, *5*, 1807–1816.
162. Xu Y, Xu J, Liu D, Guo B, Xie X. Synthesis and characterization of biodegradable poly (butylene succinate-co-propylene succinate) s. *J. Appl. Polym. Sci.* **2008**, *109*, 1881–1889.
163. Rajgond V, Mohite A, More N, More A. Biodegradable polyester-polybutylene succinate (PBS): A review. *Polym. Bull.* **2024**, *81*, 5703–5752.
164. Cury B, Klein S, Evangelista RC. Modeling a system of phosphated cross-linked high amylose for controlled drug release. Part 1: Synthesis and polymer characterization. *React. Funct. Polym.* **2008**, *68*, 1200–1206.
165. Ferreira LP, Moreira AN, Pinto JC, de Souza FG, Jr. Synthesis of poly (butylene succinate) using metal catalysts. *Polym. Eng. Sci.* **2015**, *55*, 1889–1896.
166. Zhang Y, Lu B, Lv F, Guo W, Ji J, Chu PK, et al. Effect of processing conditions on poly (butylene succinate) foam materials. *J. Appl. Polym. Sci.* **2012**, *126*, 756–761.
167. Xu J, Manepalli PH, Zhu L, Narayan-Sarathy S, Alavi S. Morphological, barrier and mechanical properties of films from poly (butylene succinate) reinforced with nanocrystalline cellulose and chitin whiskers using melt extrusion. *J. Polym. Res.* **2019**, *26*, 1–10.

168. Shen S, Kopitzky R, Tolga S, Kabasci S. Polylactide (PLA) and its blends with poly (butylene succinate)(PBS): A brief review. *Polymers* **2019**, *11*, 1193.
169. Gan Z, Abe H, Kurokawa H, Doi Y. Solid-state microstructures, thermal properties, and crystallization of biodegradable poly (butylene succinate)(PBS) and its copolyesters. *Biomacromolecules* **2001**, *2*, 605–613.
170. Liu L, Yu J, Cheng L, Qu W. Mechanical properties of poly (butylene succinate)(PBS) biocomposites reinforced with surface modified jute fibre. *Compos. Part A Appl. Sci. Manuf.* **2009**, *40*, 669–674.
171. Mochane MJ, Magagula SI, Sefadi JS, Mokhena TC. A review on green composites based on natural fiber-reinforced polybutylene succinate (PBS). *Polymers* **2021**, *13*, 1200.
172. Chinnasamy S, Ramachandran M, Soundharaj S. Mechanical and Thermal Properties of poly butylene succinate (PBS) Nano Composites. *REST J. Emerg. Trends Model. Manuf.* **2022**, *8*, 58–67.
173. Lin C, Liu L, Liu Y, Leng J. 4D printing of shape memory polybutylene succinate/polylactic acid (PBS/PLA) and its potential applications. *Compos. Struct.* **2022**, *279*, 114729.
174. Tecchio P, Freni P, De Benedetti B, Fenouillot F. Ex-ante Life Cycle Assessment approach developed for a case study on bio-based polybutylene succinate. *J. Clean. Prod.* **2016**, *112*, 316–325.
175. Vashisht A. Poly Butylene Succinate: Synthesis of an Issue. 2024. Available online: https://www.researchgate.net/publication/384661259_POLY_BUTYLENE_SUCCINATE_SYNTHESIS_OF_AN_ISSUE (accessed on 9 November 2024).
176. Domínguez-Robles J, Larrañeta E, Fong ML, Martin NK, Irwin NJ, Mutjé P, et al. Lignin/poly (butylene succinate) composites with antioxidant and antibacterial properties for potential biomedical applications. *Int. J. Biol. Macromol.* **2020**, *145*, 92–99.
177. US Food and Drug Administration. Tepha, Inc-SurgiLattice Scaffold. 2021, Available online : https://www.accessdata.fda.gov/cdrh_docs/pdf20/K202425.pdf (accessed on 9 November 2024).
178. Swift G. Biodegradability of polymers in the environment: Complexities and significance of definitions and measurements. *FEMS Microbiol. Rev.* **1992**, *9*, 339–345.
179. Raclavská H, Růžičková J, Kucbel M, Švédová B, Raclavský K. Definitions and Procedures for Characterization of Biodegradable Waste. *Biodegrad. Waste Manag. Circ. Econ. Chall. Oppor.* **2022**, 55–67. doi:10.1002/9781119679523.ch4.
180. Liu Y, Zheng Y, Chen XH, Yang JA, Pan H, Chen D, et al. Fundamental theory of biodegradable metals—Definition, criteria, and design. *Adv. Funct. Mater.* **2019**, *29*, 1805402.