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Polyhydroxyalkanoates (PHAs): Mechanistic Insights and Contributions to Sustainable Practices

Sushobhan Pradhan [1,*], Mohd Tauhid Khan [1] and Vijayanand S. Moholkar [2,*]

[1] School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078, USA
[2] Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India
* Correspondence: sushobhan.pradhan@okstate.edu (S.P.); vmoholkar@iitg.ac.in (V.S.M.); Tel.: +1-405-762-3246 (S.P.); +91-99547-09058 (V.S.M.)

Definition: A polymer is a long-chain molecule formed by linking numerous simpler repeating chemical units, known as monomers, with identical structures. Over the past two centuries, there has been a significant increase in the global production and use of petrochemical-based plastics. This surge has led to widespread ecological imbalances, affecting air quality, terrestrial and marine ecosystems, food chains, and plant life. Consequently, the excessive use of such polymers has created challenges in solid waste management, with methods like bio- or photo-degradation, incineration, landfilling, and recycling proving to be time-consuming and laborious. Therefore, there is a growing urgency for biodegradable polymers due to increasing demand. Biodegradable polymers consist of interconnected monomers with unstable links in the backbone, facilitated by various functional groups. Throughout the degradation process of these polymers, numerous biologically acceptable molecules are produced. This study examines the significance of biopolymers over petroleum-based counterparts, offering a detailed analysis. It is noteworthy that within the spectrum of biodegradable polymers, polyhydroxyalkanoates (PHAs) emerge as exceptionally promising candidates for substituting petroleum-derived polymers, owing to their remarkable physical attributes. Therefore, this study provides a systematic overview of PHAs, including their classification, historical background, methods of production, potential challenges to commercialization, and diverse applications.

Keywords: biopolymer; polyhydroxyalkanoate; microorganism; biodegradation

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1. Introduction

1.1. Overview to Petroleum-Derived Polymers

A polymer is a long-chain macromolecule composed of the interlinking of a large number of simpler repeating chemical units, also referred to as monomers, with identical structures. The term “polymer” originates from classical Greek, where “poly” signifies “many” and “meres” denotes “parts”. This etymological foundation reflects the fundamental characteristic of polymers. Natural polymers, such as proteins, cellulose, resin, wool, and silk, occur in nature. Synthetic polymers, including polyethylene, polypropylene, polystyrene, polyvinyl chloride, and nylon, are produced through chemical synthesis. Some natural polymers, like natural rubber (polyisoprene) derived from the Hevea tree, can also be synthesized artificially [1,2].

Over the past two centuries, global production and utilization of petrochemical-based plastics have surged significantly, causing ecological imbalances across air quality, ecosystems, food chains, and plant life [3]. For instance, global plastic production rose from two million tons in 1950 to over 400 million tons by 2022 [4]. Figure 1a illustrates the growth of petroleum-derived plastics over this period.

Initially, the adoption of petroleum-based plastics, such as polyethylene and polypropylene, aimed to enhance quality of life and comfort. This was due to their superior thermal, mechanical, electrical, and optical properties compared to conventional materials, as well as their cost-effectiveness. However, their pervasive use has led to challenges in solid waste management, incineration, landfilling, and recycling, which are labor-intensive and time-consuming [5,6]. Hence, the necessity for biodegradable polymers has become increasingly pressing. According to European Bioplastics e.V. (Berlin, Germany), as of 2022, bioplastics account for approximately 0.5 percent of the more than 400 million tons of plastic produced annually [7].

Based on data sourced from Statista, it has been revealed that the worldwide production capacity of bioplastics (biodegradable and bio-based/non-biodegradable) stood at 1.8 million tons in 2022. Current projections indicate an extraordinary trajectory for the industry, with anticipated growth leading to a production capacity of 7.5 million tons by 2028. This surge in bioplastic production capacity not only reflects a shift towards environmentally conscious practices but also signals a promising future for the bioplastics sector, poised to play a pivotal role in mitigating the environmental impacts associated with traditional plastics. Figure 1b encapsulates the production capacity of bioplastics in the year 2022 and the projections extending from 2023 to 2028 provide a glimpse into the anticipated growth trajectory of the bioplastics industry, highlighting its potential to meet the increasing demand for eco-friendly materials in a world increasingly focused on environmental sustainability [8].

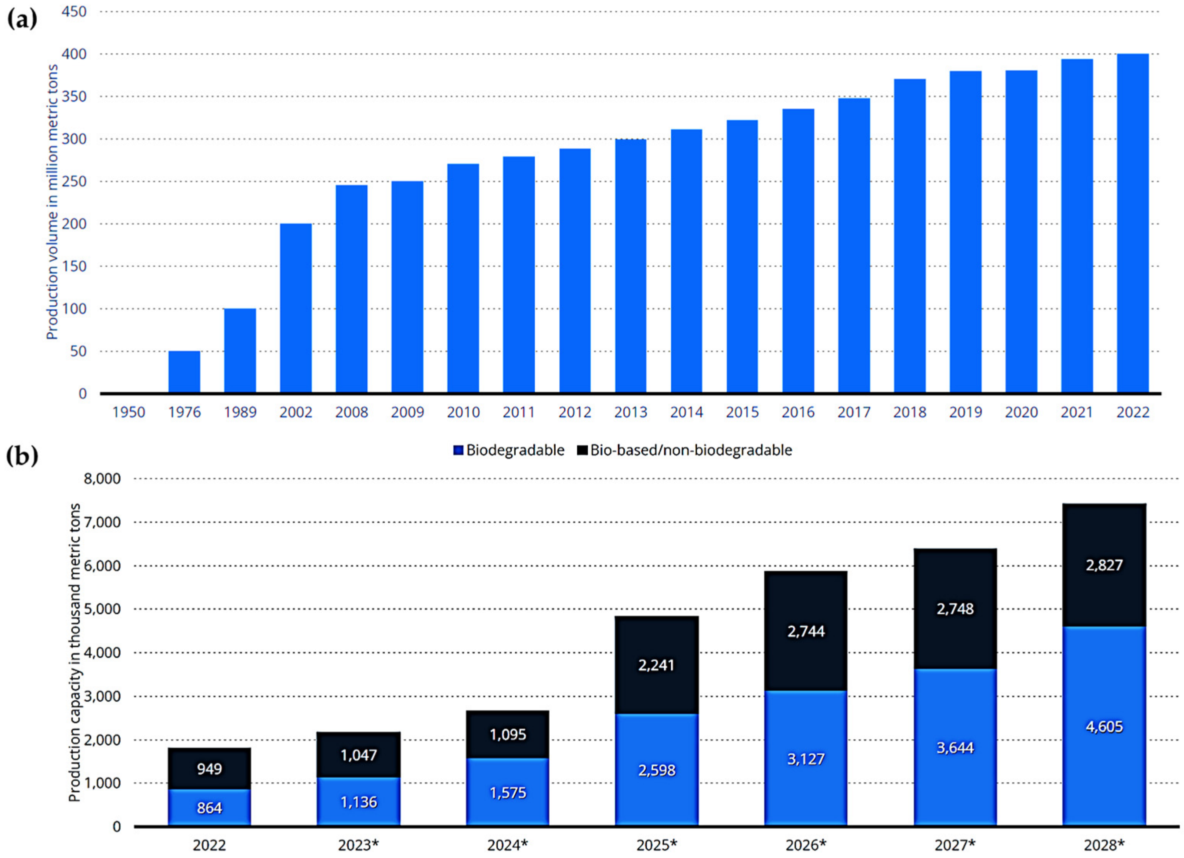

Figure 1. (**a**) Annual worldwide production of plastics from 1950 to 2022 (in million metric tons) and (**b**) production capacity of bioplastics globally from 2022 to 2028, categorized by type (in 1000 metric tons). * Figures from 2023 to 2028 are projections. Source: Statista—Bioplastic industry worldwide (2024) [8].

1.2. Overview to Bio-Based Polymers

According to ASTM standard D-5488-94d [9], "biodegradable" refers to the capability of a substance to breakdown into biomass, carbon dioxide (CO_2), inorganic substances, methane (CH_4), water, or primarily through the enzymatic action of microorganisms. This process can be measured by standardized tests within a specified period, reflecting typical disposal conditions [9]. Biodegradable polymers are composed of monomers interconnected via unstable links in the backbone, facilitated by various functional groups. During the degradation process of these polymers, various biologically accepted molecules are formed [5]. Based on the synthesis process, biodegradable polymers can be categorized into four main types: those derived from biomass, polymers produced through microbial processes, polymers originating from monomers sourced from agricultural resources, and polymers synthesized through chemical methods [10,11]. A diagram depicting diverse categories of biodegradable polymers has been presented, accompanied by specific examples, as shown in Figure 2.

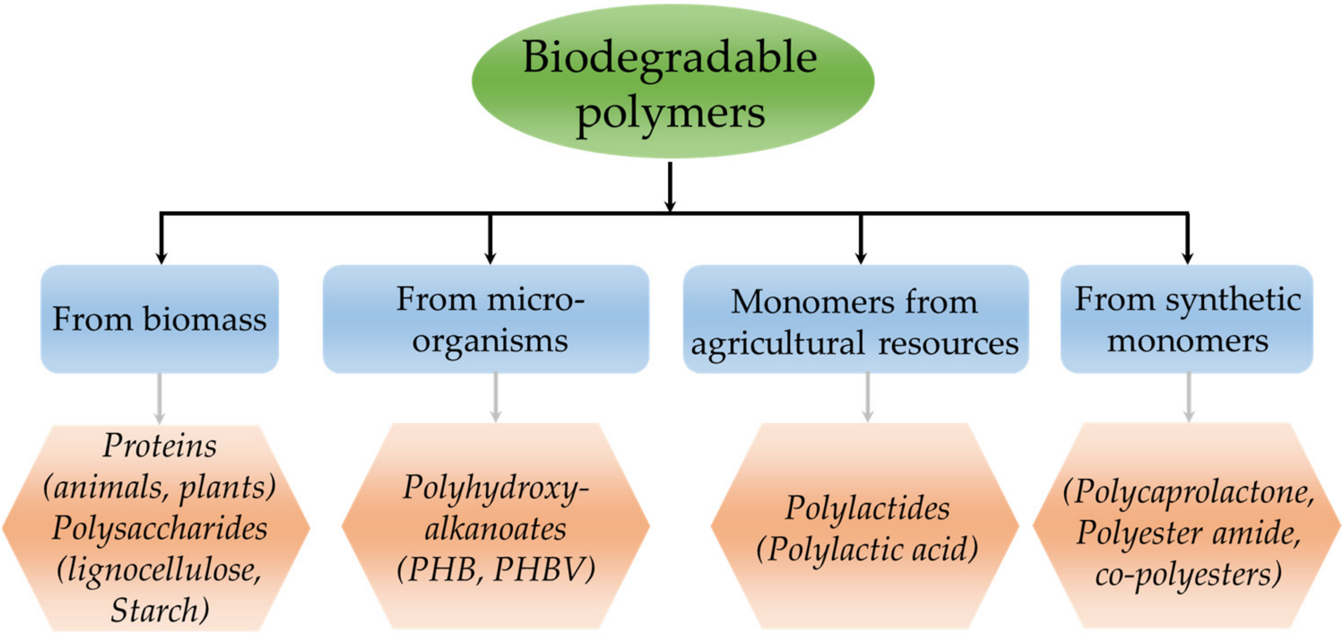

Figure 2. Classification of biodegradable polymers based on the synthesis process. Adapted with permission from ref. [12]. 2012 Springer Nature.

2. Overview of Polyhydroxyalkanoates (PHAs)

PHAs have garnered significant interest as environmentally friendly biodegradable plastics [5,13,14]. Several advantages of PHAs over other biodegradable polymers are outlined below:

a. Numerous bacteria, including over 90 species spanning more than 300 classes of both Gram-positive and Gram-negative strains, synthesize PHA polymers as reserves for carbon and energy storage under nutrient-limited conditions, thriving in diverse environments ranging from aerobic to anaerobic settings.
b. PHAs stand out as a highly promising substitute for petroleum-based polymers, owing to their exceptional physical properties. A comparative study showing physical properties of selected petroleum-derived and bio-based polymers (PLA, PHA, and starch) is summarized in Table 1.

c. PHAs can degrade under both aerobic conditions (as well as in the presence of water) and anaerobic conditions (as well as in the presence of methane and water).
d. The attributes of biodegradability and biocompatibility exhibited by PHAs are of significant interest for both research endeavors and commercialization endeavors.
e. Over 150 varieties of (R)-3-hydroxy fatty acids are recognized as constituents within the PHA group.

Table 1. List of physical properties of selected petroleum-derived and bio-based polymers [adapted from Berezina and Martelli (2014), Chan et al. (2018), Dome et al. (2020), Lourdin et al. (2015)] [15–18].

Physical Properties	**Bio-Based Polymers**				**Petroleum-Derived Polymers**		
	PHB	**P(3HB-co-3HV)**	**PLA**	**Starch**	**PP**	**HDPE**	**LDPE**
T_m (°C)	162–181	64–171	150–162	Amorphous	160–169	130–137	105–125
T_g (°C)	−4–18	−13–10	45–60	31–98	−14–−6	−125–−90	−125–−90
E (GPa)	1.2–4	0.14–8.7	0.35–3.5, 3.6	0.17–1.5	1.1–2	0.7–1.4	0.14–0.3
Elongation at break (%)	0.8–4.5	1–970	3.6	0.8–60	20–75	100–1000	200–900
ρ (g/cc)	1.18–1.26	1.18–1.26	1.21–1.25	1.26–1.28	0.90–0.91	0.95–0.97	0.92–0.93
X (%)	50–80	53–56	2.5–6	15–45	50	79.8–81	43

T_m: melting point; **T_g**: glass transition temperature; **E**: tensile Young's modulus; **X**: crystallinity; **ρ**: density; **PP**: polypropylene; **LDPE**: low-density polyethylene; **HDPE**: high-density polyethylene (mechanical properties are measured at room temperature).

2.1. Sustainability of PHAs

The sustainability of PHAs stems from several key factors, which are discussed below:

- **Biodegradability**: PHAs can be broken down by microorganisms present in various environments, including soil and water. Unlike traditional plastics, PHAs degrade naturally in diverse settings such as soil, water, and marine environments, minimizing environmental pollution and supporting ecological balance [19]. This reduces the environmental impact of plastic waste and prevents the accumulation of non-degradable materials [20,21].
- **Renewable Resources**: PHAs are synthesized by bacteria using renewable resources like sugars and waste materials, reducing the reliance on fossil fuels [21,22].
- **Contribution to a Circular Economy**: PHAs align with the principles of a circular economy by integrating waste materials into their production and breaking down naturally at the end of their life cycle. This reduces resource consumption and closes material loops [19,23].
- **Reduced Carbon Footprint**: The production of PHAs has a lower carbon footprint compared to traditional petroleum-based plastics, contributing to a more sustainable production process [24].
- **Versatile Properties**: PHAs exhibit a wide range of properties, including flexibility, strength, and thermal resistance, making them suitable for various applications such as packaging, biomedical devices, and agriculture [25,26].

2.2. Classification and Structures of PHAs

A PHA molecule typically comprises 600 to 35,000 units of (R)-hydroxy fatty acids, making them polyesters of hydroxyalkanoates (HAs) [27]. PHAs can be categorized into two types based on the type of monomer present: homo-polymer PHA and hetero-polymer PHA. In the case of the homo-polymer PHA, the monomer unit comprises a single type of 3-hydroxy fatty acid. Conversely, the hetero-polymer PHA is characterized by the presence of multiple types of fatty acids with varying chain lengths. Figure 3 illustrates the general structures of both homo-polymer and hetero-polymer PHAs. Similarly, PHAs are classified into three different categories based on the number of monomer units: short-chain-length (*scl*), medium-chain-length (*mcl*), and long-chain-length (*lcl*) PHAs [28–30]. Table 2 presents the IUPAC nomenclature of PHAs, indicating the carbon numbers and type of alkyl group. Additionally, Table 3 provides a detailed study summarizing the classifications of PHAs based on the number of carbon units and the type of monomer units, accompanied by examples.

Table 2. Classification of PHAs based on number of carbon atoms and type of monomer unit.

<table>
<tr><th colspan="4">Classifications of PHAs</th></tr>
<tr><th colspan="2">Basis: No. of Carbon Atoms</th><th colspan="2" rowspan="2">Basis: Type of Monomer</th></tr>
<tr><th>No. of Carbon Atoms</th><th>PHA Name</th></tr>
<tr><td>3 to 5</td><td>short-chain length (<i>scl</i>) PHA</td><td rowspan="2">homo-polymer</td><td rowspan="2">hetero-polymer</td></tr>
<tr><td colspan="2">Example: Poly(3-hydroxybutyrate)</td></tr>
<tr><td>6 to 14</td><td>medium-chain length (<i>mcl</i>) PHA</td><td rowspan="4">Example: Poly(3-hydroxybutyrate)</td><td rowspan="4">Example: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)</td></tr>
<tr><td colspan="2">Example: Poly(3-hydroxyoctanoate)</td></tr>
<tr><td>15 and above</td><td>long-chain length (<i>lcl</i>) PHA</td></tr>
<tr><td colspan="2">Example: Poly(3-hydroxyhexadecanoate)</td></tr>
</table>

The first PHA to be discovered and consequently the most extensively studied is Poly-(3-hydroxybutyrate) (PHB). Polyhydroxybutyrate (PHB) is a homo-polymer composed of repeating units of 3-hydroxybutyrate (3HB), each containing four carbon subunits. It stands as the most prevalent and extensively studied member within the PHA family, offering a well-understood model for exploring the properties and applications of this biopolymer class [31]. PHB is a natural polymer that can be extracted through solvent extraction. It is a highly crystalline polyester (80%) and possesses a notably high melting point ranging from 173 to 180 °C. This distinguishes PHB from other biodegradable polyesters [10]. PHB is synthesized through metabolic pathways, wherein acetyl-coenzyme-A (acetyl-CoA) is first generated. Subsequently, this acetyl-CoA is transformed into PHB through the enzymatic actions of three key biosynthetic enzymes: 3-ketothiolase (PhaA), acetoacetyl-CoA reductase (PhaB), and PHB synthase (PhaC). A simplified schematic of the metabolic pathway for PHB synthesis is depicted in Figure 4.

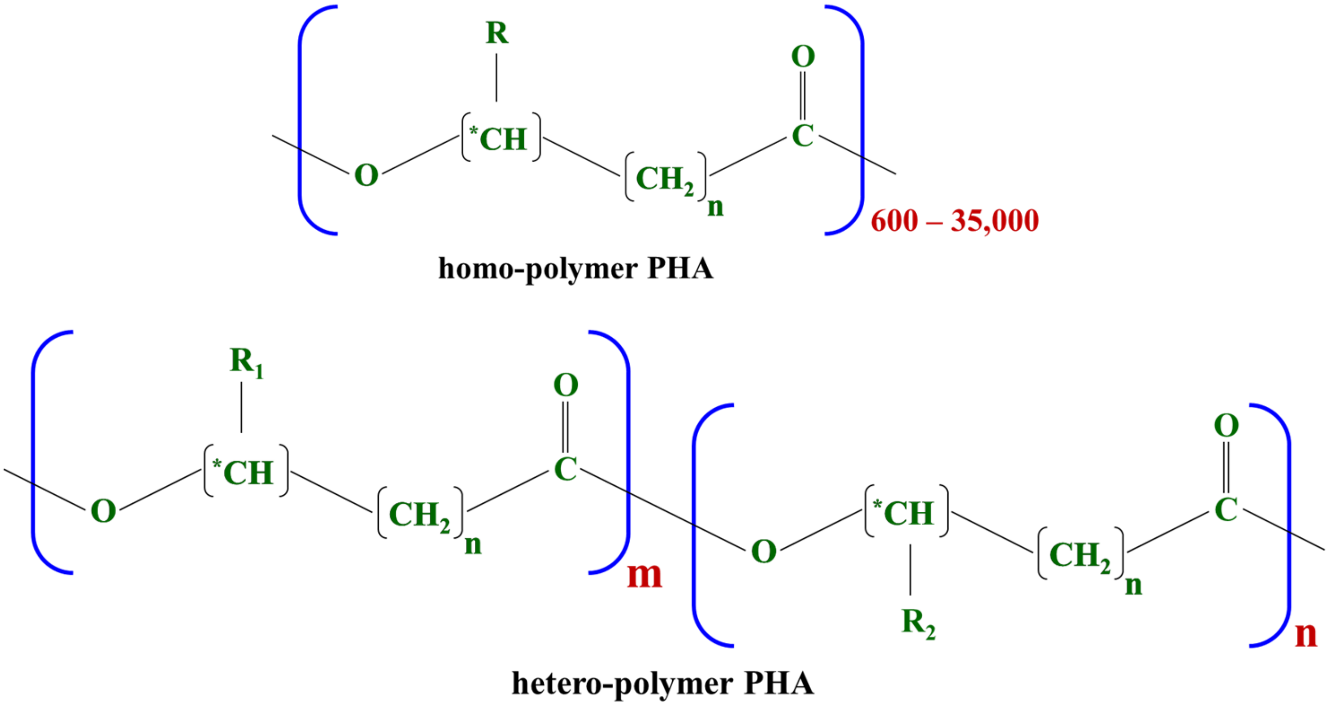

Figure 3. Structures of homo-polymer and hetero-polymer PHAs.

Table 3. IUPAC nomenclature of PHAs on basis of carbon numbers, type of alkyl group.

n	*R* Group	Carbon No.	IUPAC Nomenclature	Type of PHA
1	hydrogen	C_3	poly(3-hydroxypropionate)	*scl*-PHA
1	methyl	C_4	poly(3-hydroxybutyrate)	
1	ethyl	C_5	poly(3-hydroxyvalerate)	
1	Propyl	C_6	poly(3-hydroxyhexanoate)	*mcl*-PHA
1	Butyl	C_7	poly(3-hydroxyheptanoate)	
1	Pentyl	C_8	poly(3-hydroxyoctanoate)	
1	Hexyl	C_9	poly(3-hydroxynonanoate)	
1	Heptyl	C_{10}	poly(3-hydroxydecanoate)	
1	Octyl	C_{11}	poly(3-hydroxyundecanoate)	
1	Nonyl	C_{12}	poly(3-hydroxydodecanoate)	
1	Decyl	C_{13}	poly(3-hydroxytridecanoate)	
1	Undecyl	C_{14}	poly(3-hydroxytetradecanoate)	
1	Dodecyl	C_{15}	poly(3-hydroxypentadecanoate)	*lcl*-PHA
1	Tridecyl	C_{16}	poly(3-hydroxyhexadecanoate)	
1	Tetradecyl	C_{17}	poly(3-hydroxyheptadecanoate)	
1	Pentadecyl	C_{18}	poly(3-hydroxyoctadecanoate)	
2	hydrogen	C_4	poly(4-hydroxybutyrate)	*scl*-PHA
2	methyl	C_5	poly(4-hydroxyvalerate)	
2	ethyl	C_6	poly(4-hydroxyhexanoate)	*mcl*-PHA
3	hydrogen	C_5	poly(5-hydroxyvalerate)	*scl*-PHA
3	methyl	C_6	poly(5-hydroxyhexanoate)	*mcl*-PHA
3	ethyl	C_7	poly(5-hydroxyheptanoate)	

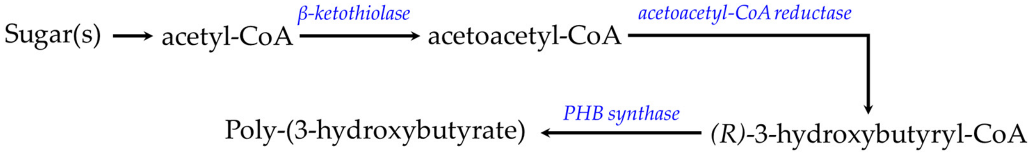

Figure 4. Simplified metabolic pathway of PHB synthesis (adopted from Verlinden et al. (2007)) [32].

2.3. Discovery and Historical Overview of PHAs

The presence of polyhydroxyalkanoate (PHA) granules within bacterial cells was initially documented under microscopic observation in 1888. Lemoigne, a bacteriologist and analytical chemist, authored a series of papers spanning from 1923 to 1927. Notably, these papers showcase a remarkable breadth of research, particularly focusing on PHAs, specifically PHB. In 1927, Lemoigne achieved a significant breakthrough by determining the composition of a PHA for the first time, having the empirical formula $(C_4H_6O_2)_n$. This significant breakthrough stemmed from an investigation into a soil bacillus, exhibiting a close resemblance to *Bacillus megaterium*. Under anaerobic conditions, this bacterium facilitated the degradation of an unidentified substrate, yielding 3-hydroxybutyric acid as a metabolic byproduct. Lemoigne characterized this compound as a homo-polyester, derived from the hydroxyacid 3-hydroxybutyrate, introducing the term poly-3-hydroxybutyrate (PHB) to denote this novel polymer. Lemoigne categorized PHB as a reserve material, indicating its potential significance in biological systems [33–36].

Further research conducted by Lemoigne and colleagues in 1944 revealed a correlation between the quantity of this extractable polymer and the presence of refractile “fatty” cytoplasmic granules in the bacilli [37]. Later, in 1950, Lemoigne highlighted variations in the quantities of PHB produced when cultivating *B. megaterium* on different media [38]. In 1953, Weibull reported that PHB was a key component of the “lipid” granules isolated after the dissolution of the cell wall of *B. megaterium* by lysozyme [39]. In 1958, Williamson and Wilkinson demonstrated that an alkaline hypochlorite solution could release PHB granules, which upon recovery and analysis were found to predominantly comprise PHB. Furthermore, they observed that higher concentrations of glucose in the growth medium led to increased formation of PHB, and there exist an association of acetate and coenzyme A complexes in the pathway of PHB production [40].

The groundbreaking articles mentioned above sparked a surge of interest in polyhydroxybutyrate (PHB) that intensified over time. Following the 1960s, there was a notable increase in research publications, leading to significant advancements in our understanding of PHAs. These advancements include the synthesis of PHAs across various microorganisms beyond the Bacillus genus (including bacterial genera such as *Azotobacter*, *Chromatium*, *Pseudomonas*, etc.), the exploration of their physical and chemical properties, and the development of detection and extraction methods, among others [33,41–44].

A study conducted by Wallen and Rohwedder (1974) identified hydroxyalkanoates beyond poly-3-hydroxybutyrate (PHB), pinpointing 3-hydroxyvalerate (3HV) and 3-hydroxyhexanoate (3HH) as predominant constituents [45]. In 1983, Findlay and White (1983) documented the development of hetero-polymers, specifically highlighting 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) as major components among other hydroxyalkanoate units [46]. In 1982, Imperial Chemical Industries Ltd. (ICI), London, UK, produced a thermoplastic polyester that was completely biodegradable through a large-scale fermentation process. This process involved utilizing *Alcaligenes eutrophus* bacterium, which was later renamed as *Ralstonia eutropha*, to produce about 90 percent of the polymer [34].

To date, more than 90 bacterial species, encompassing up to 300 classes, have been identified as producers of PHAs. These organisms demonstrate adaptability to diverse environmental conditions, under both aerobic and anaerobic conditions [27]. Figure 5 presents a historical overview illustrating the evolution of PHA research and technological advancements in the twentieth century. This advancement paved the way for the near-future production of PHAs, offering high potential for eco-friendly applications.

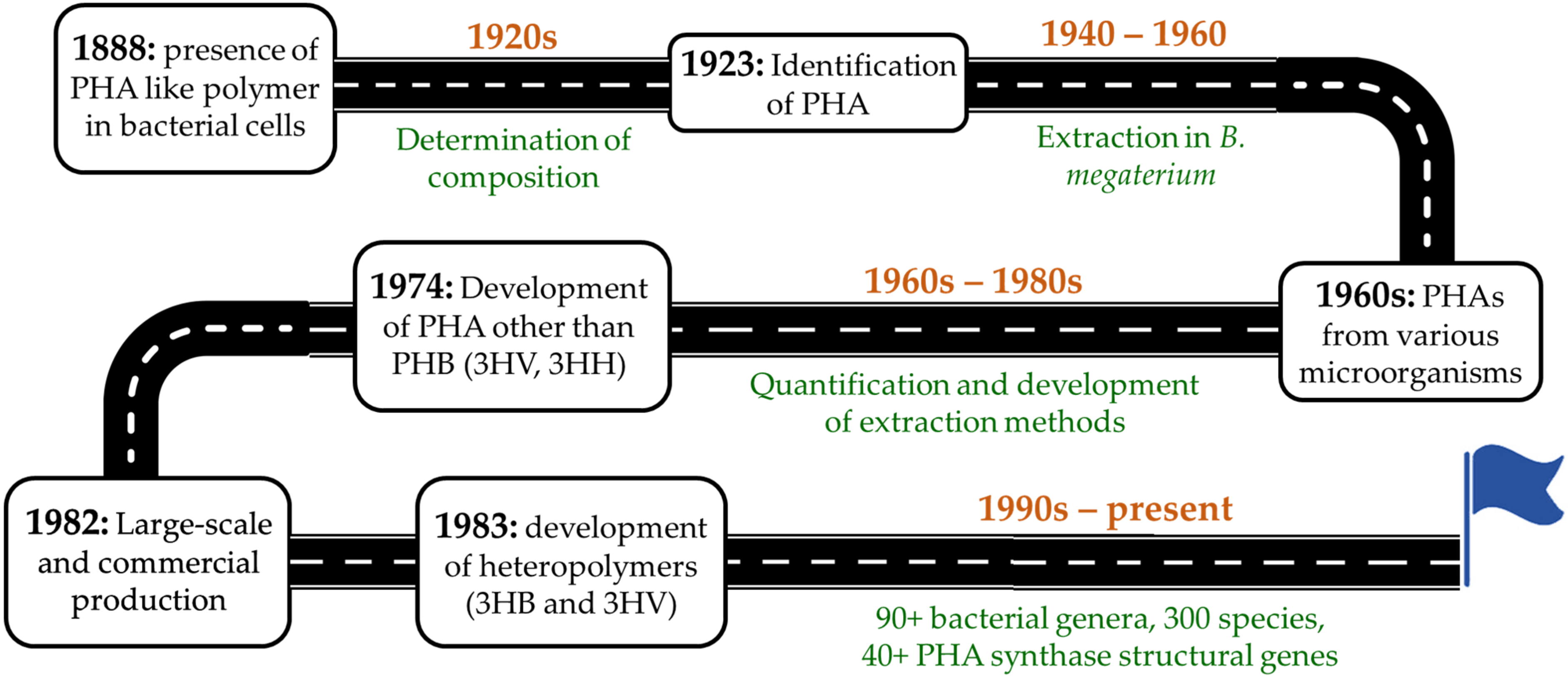

Figure 5. Development/evolution of PHA research and technological advancements.

3. Overview of PHA Production

As previously outlined, biologically derived polymers have had a profound impact on petroleum-based polymers, particularly in terms of green synthesis methodologies and environmentally sustainable applications. A standard production pathway for polyhydroxyalkanoates (PHAs) involves the cultivation of microorganisms in a nutrient-rich broth, followed by fermentation. After fermentation, PHA granules are extracted and subsequently dried for further use. A schematic representation of the biotechnological process for PHA production is provided in Figure 6.

In Figure 7, the biosynthesis pathway of PHA is illustrated briefly to enhance comprehension of its molecular mechanisms through three different pathways [47]. The pathway in *Cupriavidus necator* (*Ralstonia eutropha*) is one of the most thoroughly studied routes for PHA production. In this process (Pathway I), 3-hydroxybutyrate (3HB) monomers are synthesized through the condensation of two acetyl-CoA molecules derived from the tricarboxylic acid (TCA) cycle. This reaction is catalyzed by the enzyme β-ketothiolase, producing acetoacetyl-CoA, which is subsequently reduced to 3-hydroxybutyryl-CoA by acetoacetyl-CoA reductase. Finally, PHA synthase catalyzes the polymerization of 3-hydroxybutyryl-CoA via esterification to produce poly(3-hydroxybutyrate).

In addition to PHA synthesis from acetyl-CoA, fatty acid metabolism also contributes to the formation of various hydroxyalkanoate monomers. For instance, the β-oxidation pathway (Pathway II) in *Pseudomonas* species, such as *Pseudomonas aeruginosa*, generates substrates that PHA synthases convert into medium-chain-length PHAs, utilizing carbon sources like alkanes, alkenes, and alkanols. The composition of the resulting monomers is influenced by specific intermediates formed during the β-oxidation process in *Pseudomonas aeruginosa*.

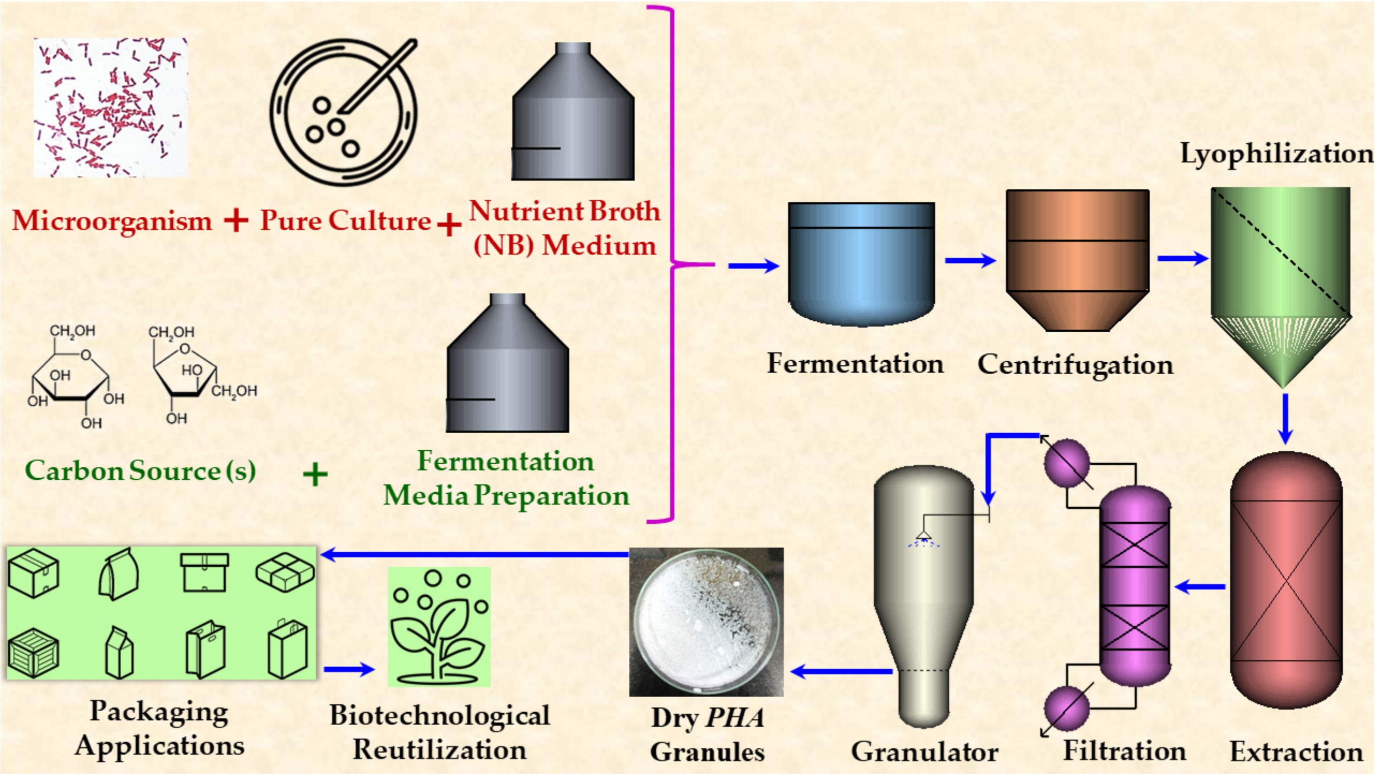

Figure 6. Schematic showing overview of PHA production and extraction process.

Furthermore, research by Huijberts et al. demonstrated that *Pseudomonas putida*, commonly involved in PHA synthesis from fatty acids, can also produce PHA from glucose [48]. This process occurs through the de novo fatty acid biosynthesis pathway (Pathway III), which is particularly important for generating PHA from cost-effective carbon sources such as glucose, sucrose, and fructose. In this pathway, (R)-3-hydroxyacyl intermediates from fatty acid biosynthesis are converted from their acyl-carrier protein (ACP) form to their CoA form by the enzyme acyl-ACP transacylase, encoded by the *phaG* gene. This enzyme acts as a crucial link between fatty acid synthesis and PHA production.

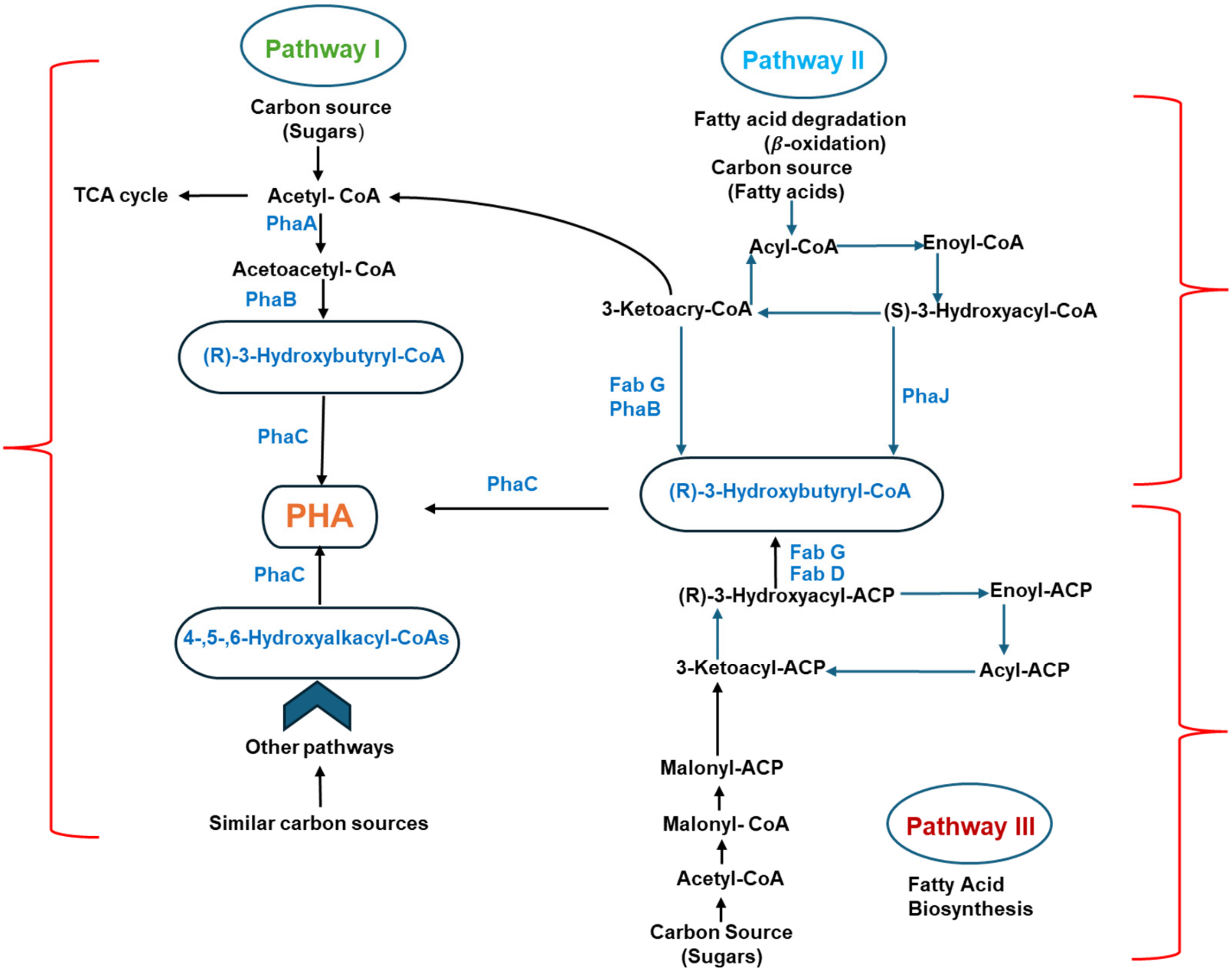

Figure 7. Various biosynthesis pathways of PHA production (adapted with permission from ref. [47]. 2007 John Wiley and Sons).

4. Challenges and Potential Solutions with PHA Production

4.1. Practical Limitations with Commercial PHA Production

As mentioned in the earlier sections, PHA has proven to be a valuable biomaterial due to its natural biodegradability and biocompatibility. Despite the numerous advantages of PHAs, their commercialization remains challenging owing to the elevated production costs when compared to polymers derived from the conventional petroleum feedstock. For instance, the price of conventional petroleum-derived polymers, such as polyethylene and polypropylene, is approximately 1–2.5 USD per kg. However, the price for PHAs has been reported to be up to 6–16 times higher (starting from 7.6 USD per kg) than that of petroleum-derived polymers [27,49–51]. Some of the primary reasons regarding the elevated cost of PHA production are listed below [5,27,51,52].

- **Procurement of carbon sources:** The high production cost of PHAs is primarily due to the use of standard carbon sources as substrates, such as glucose, xylose, fructose, and γ-butyrolactone in the biosynthesis of PHA, which has hampered its commercial production. Carbon sources employed in microbial fermentations conducted in pure culture substantially impact both environmental footprint and production expenses. Hence, substantial effort is being put in to develop simple, cheap, and renewable resources to reduce the production cost [53–58].
- **Variation in optimized growth conditions:** In addition to the previously mentioned basic challenges, numerous technical hurdles are associated with the production process. The principal challenge involves identifying the optimal growth parameters for bacterial cultures and microbial cell yield [54,59–61]. The whole synthesis procedure is characterized by its labor-intensive nature and significant time requirements, often spanning several weeks for completion.
- **Variation in PHA conversion:** Under specific stringent conditions, the conversion of substrates to PHA can attain a maximum yield of up to 89%, contingent upon the particular strain types and carbon sources utilized. However, this high conversion rate is limited to specific types of PHA [62–64]. In contrast, the conversion of petroleum-derived polymers such as polyethylene and polypropylene can approach nearly 100% yield from their respective monomers.
- **Expensive extraction methods:** The intracellular nature of PHA necessitates an extraction process that notably impacts overall production costs. Solvent-based extraction methods lead to the accumulation of hazardous waste in the environment, presenting challenges for disposal and recycling. Alternatively, techniques such as the digestion method are observed to be costly, while mechanical approaches demand significant energy inputs to break down cell walls and release the PHA polymer [65,66].

4.2. Potential Solutions for Commercialization of PHA Production

Incorporating biopolymers into the global market necessitates a meticulous examination of costs and the implementation of strategies to mitigate them. This entails conducting a thorough cost analysis to identify areas where production expenses can be reduced effectively. Moreover, it involves the exploration and adoption of innovative technologies designed to streamline manufacturing processes while ensuring minimal environmental impact. By embracing such approaches, the seamless integration of biopolymers into various industries becomes not only feasible but also advantageous for both economic and ecological sustainability.

The utilization of mixed microbial cultures, utilizing low-cost sustainable feedstock (liquid and gaseous waste streams) such as agricultural wastes, glycerol, landfill gas, carbon dioxide, molasses, plant oils, starch, wastewater, waste cooking oil, and whey, could be considered a sustainable approach for bioplastics production [49,50,67]. However, these feedstocks may contain contaminants such as heavy metals, toxins, or inhibitory compounds, which can reduce conversion efficiency. Low-cost feedstocks may also lack the essential micronutrients required for microbial metabolism, potentially affecting PHA yield. Furthermore, variability in feedstock composition can result in inconsistencies in the physical properties of PHAs, such as crystallinity, tensile strength, and biodegradability.

Reducing the production cost of PHA could involve achieving the desired PHA content in a shorter fermentation time by utilizing high-PHA-producing strains. Furthermore, the successful commercialization of PHAs necessitates collaborative efforts among scientists, entrepreneurs, investors, and government organizations [68].

Additionally, a viable approach to mitigate the extraction cost of PHA involves integrating sophisticated mechanical techniques like ultra-sonication with reduced solvent consumption, such as chloroform. This strategy presents a promising avenue for achieving a more energy-efficient alternative in the extraction of intracellular polymers [69,70]. Ultrasound waves exhibit high efficacy in rupturing cell walls/membranes, emulsification, and homogenization due to their localized action within a specific volume. This process relies on the rapid sinusoidal motion of sound waves within a liquid medium. Sonication induces the formation of microbubbles, initiating cavitation phenomena. In the cavitation phenomenon, the conversion of sonic or vibrational energy into mechanical energy occurs through the principle of momentum conservation. This transformation generates high-pressure shockwaves, which subsequently disrupt cellular structures [71–75].

5. Biodegradation of PHAs

PHAs distinguish themselves from other biopolymers due to their remarkable biodegradability and biocompatibility attributes, which are achievable in both natural settings and isolated environments. The distinctive degradation processes of PHAs play a pivotal role in their environmental impact and are summarized below [32,47,76–80].

- **Degradation environments**: PHAs are susceptible to degradation in both aerobic and anaerobic environments. Other mechanisms of PHA degradation include thermal degradation, microbial depolymerase, as well as enzymatic and non-enzymatic hydrolysis.
- **Degradation process**: During the degradation process, conversion of the PHA molecules occurs into water-soluble monomers and oligomers, serving as a carbon source. Additionally, microorganisms capable of PHA production possess the ability to degrade PHAs intracellularly.
- **End products**: Upon the degradation of PHAs in aerobic environments, the resultant end products consist of carbon dioxide and water. However, during anaerobic degradation, the final byproducts comprise carbon dioxide, methane, and water.
- **Degradation time**: The degradation time of PHAs can range from a few months under anaerobic conditions to several years in saline water. Additionally, the degradation process can be accelerated by exposure to UV light.
- **Parameters affecting PHA degradation**: The physical and chemical properties of PHAs, such as melting point, molecular weight, stereo-regularity, and crystallinity, significantly influence their characteristics.
- **External factors affecting PHA degradation**: External factors in the disposal environment, such as microbial efficacy, moisture, pH, pressure temperature, and surface area, affect the degradation process of PHA.

6. Conclusions and Prospects

Petroleum-based plastics present significant environmental hazards, compounded by concerns regarding oil scarcity and price volatility. Bioplastics, notably PHAs, offer a promising avenue for mitigation. Despite the comparative expense of PHA production vis-à-vis conventional plastics, ongoing research endeavors focus on optimizing production methodologies leveraging cost-effective substrates and microbial strains. This optimization process requires the meticulous adjustment of parameters such as pH, microorganism, carbon source, and temperature. The utilization of agricultural residues, industrial byproducts, and waste oils as feedstock for PHA synthesis holds promise for enhancing environmental sustainability. PHAs are poised to emerge as pivotal players in the plastics industry due to their versatility and unique biodegradable characteristics. The application of advanced analytical techniques is expected to provide deeper insights into the physical properties and degradation mechanisms of PHAs in the foreseeable future.

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