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Navigating the Future of PHA Composites: A Review of Challenges and Opportunities

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Abstract: The article offers a comprehensive overview of recent breakthroughs in eco-friendly polymers and polymer composites, underscoring their pivotal role in addressing sustainability challenges across diverse industrial sectors. Despite encountering obstacles related to performance and processability, biopolymers sourced from renewable materials emerge as promising alternatives for the plastics that are currently used by human beings. Natural fillers are highlighted as a strategic avenue for crafting sustainable composites, with residual natural fillers being particularly explored. Heightened environmental concerns propel discussions on the criticality of integrating biodegradable materials with natural fillers, underlining the urgency for clear frameworks and financial incentives to support adoption of these materials. Additionally, the article examines the potential of biodegradable polymers and polymer composites, with a specific emphasis on the utilization of polyhydroxyalkanoate (PHA) in composite materials and its market prospects. Moreover, it emphasizes the indispensable need for ongoing research and development endeavors to address environmental challenges within the polymer sector, reflecting a mounting interest in sustainable materials across industries.

Keywords: polyhydroxyalkanoate (PHA); polymer composites; biocomposites; waste natural fillers

1. Introduction

Since the introduction of different petrochemical-based polymer manufacturing processes, the plastic industry has grown significantly. Plastics have several advantages, including durability, lightweight, and affordability, with approximately half of all plastic materials utilized for single-use throwaway applications ranging from packaging to infrastructure components. Over 400 million plastic tons are produced worldwide each year, with little recycling and considerable environmental damage, necessitating immediate action. The EU and the High Ambition Coalition are leading the discussions for a legally enforceable instrument to reduce plastic pollution, which is a critical first step toward long-term solutions [1]. Plastic's environmental lifespan is still unknown due to its recent mass manufacture, with most varieties needing thousands of years to decompose depending on local environmental variables [2]. As a result, solid waste has emerged as a major global concern, leading to a shift in attention towards environmentally friendly materials made from natural fillers and polymers. Polymers are made up of long, repeating chains of molecules with varying bonding and structural features. Polymer composites are created by infusing polymers with nanomaterials and other substances, with the goal of outperforming and costing less than traditional materials such as metal, wood, and leather. With improved qualities such as increased strength, durability, and lightweight design, these composites have emerged as strong contenders for a variety of technical applications. Biocomposites made from biological materials are nontoxic, biodegradable, and safer to work with, providing benefits such as increased toughness, lower density, and lower pollutant emissions while reducing reliance on nonrenewable sources [3]. Composites find uses in electronics, medical equipment, construction, packaging, and aerospace, and are classified as laminate, fibrous, or particle composites based on their reinforcing type. Polyhydroxyalkanoates (PHAs) are microbial polyesters produced by several bacteria under nutritional stress circumstances that have thermoplastic characteristics similar to conventional polymers [4]. However, their relatively high cost limits their employment in single-use goods, mostly restricted to high-value applications such as the

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medical and pharmaceutical industries [5]. Increasing the use of PHA composites requires a reduction in the production costs of virgin PHA combined with the use of cheap natural and inorganic fillers. Composite materials are highly valued in industries due to their strength, lightweight nature, and capacity to survive challenging circumstances. Their popularity is further highlighted by their cost-effectiveness, which results from lower fuel and material utilization, especially in industries where weight is a concern. Furthermore, in situations where safety and performance have priority, their insulating abilities offer extra value. For instance, composite materials, which contain lignocellulosic fibers and natural fillers from agricultural and industrial crops such as maize, wheat, bagasse, and others, have been shown to have advantages such as low density and valuable mechanical properties and are used in packaging, automotive and construction industries [6]. Fiber-based composites, whether synthetic or plant-derived, are termed bio-based if utilizing biodegradable polymers offering benefits like enhanced toughness and lower cost. Plant fibers like pineapple, coir, and jute are increasingly favored over synthetic materials for their biodegradability, renewability, and higher resistance in load-bearing applications [7]. Although natural and synthetic biodegradable polymers are highly publicized, they often do not meet the technical criteria and their high cost hinders their wide use. However, upgrades through chemical or physical changes, reactive processing and polymer blends have the ability to overcome these limitations and improve performance in a variety of applications [8]. The plastic business has expanded significantly, with several petrochemical-based manufacturing technologies that provide durability, low weight, and economic benefits. However, the emphasis is increasingly on eco-friendly bio-composites, which use natural fillers like hemp or flax for biodegradability, lower density, cost efficiency, and reduced reliance on non-renewable sources [9]. The projected increase in primary plastic waste output by 2050, reaching 25 billion metric tons, has prompted a significant movement toward sustainability. By 2025, leading plastic packaging companies intend to include 100% recycled, biodegradable, or reusable plastics into their goods [10]. The market use of the natural fibers has also increased in the recent times. Companies are looking for alternatives that can replace their current products and lead the world toward sustainable and eco-friendly environment. Natural fiber composites (NFC) like wood, flax, hemp, kenaf, coir, sisal, and others serve diverse applications. Wood fibers are prized for construction and furniture, while flax offers lightweight strength for automotive and packaging. Hemp gains popularity in automotive and textiles for sustainability. Kenaf suits automotive interiors and construction. Coir aids erosion control and interiors. Sisal excels in industrial uses. Other fibers like jute, abaca, and banana find varied applications, contributing to sustainability across sectors [11]. Below Figure 1(A) illustrates the use of the natural fibers usages in percentage (based on [12]) And Figure 1(B) shows the consumption of natural and man-made fibers by region (based on [13]).

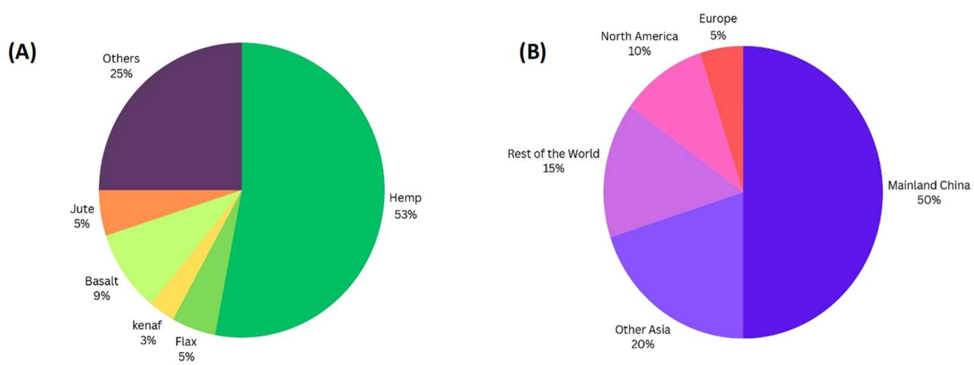

Figure 1. (A)Market use of natural fibres in percentage [12]; (B) world consumption of natural and man-made fibers by region [13].

2. PHA Composites

PHAs are biodegradable polymers generated by microorganisms under nutrient-limiting circumstances, providing a sustainable alternative to typical petroleum-based plastics **[14]**. PHAs,

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thermoplastic materials similar to petrochemical plastics, are produced from hydroxyalkanoic acids. The characteristics of a monomer are determined by the length of its carbon chain; medium-chain PHAs exhibit elastomeric properties, while short-chain PHAs resemble conventional polymers like polypropylene **[15**]. Bio-composites, blending natural fibers from renewable byproducts with PHAs, drive sustainable material innovation. PHAs, biodegradable polymers produced by microorganisms under nutrient-restricted circumstances, offer environmentally beneficial alternatives for conventional plastics derived from petroleum. Natural fibers from sources like wood and agricultural wastes are perfect for use as reinforcing materials in composites because of their favorable qualities like high strength, low density, and renewability **[16]**. Bio-composites, which combine natural fibers and PHAs, are used in a variety of packaging and automotive applications. They improve mechanical properties, accelerate biodegradation, and reduce environmental impact **[17]**. These bio-composites hold promise as long-term replacements. Researchers are also looking at the production of PHA in transgenic **[18]**. Common PHA polymers like PHB and PHBV serve as substrates for bacterial energy storage, just like plant starches and animal fats do. Energy-rich feedstocks are transformed into fatty acid feedstocks throughout the industrial PHA manufacturing process. Purified polymer powders or particles are produced by the separation, dissolution, and extraction cycles that cells go through **[19]**. Poly-3-hydroxybutyrate (P3HB or PHB) is likely the most common and researched polyhydroxyalkanoate, derived from the fermentation of sugars or fats by bacteria, characterized by its high crystallinity and brittleness. The increasing usage of PHA-based materials in common applications can be attributed to their biodegradability and biocompatibility. Copolymerization with copolymer, such as poly (ethylene glycol) (PEG), can modify the mechanical and thermal characteristics of PHA **[20]**. The mechanical properties of bio-composites containing fibers like hemp, abaca, flax, and kenaf surpass those of pure polymers. PHA composite properties are influenced by factors such as fiber modulus, aspect ratio, morphology, and interfacial adhesion. Efforts to enhance PHAs' biodegradation focus on natural fillers and fibers, which introduce channels for water and enzymes into the polymer matrix, accelerating degradation **[21]**. PHA is a useful biomaterial with promise for a wide range of applications across numerous sectors due to its structural variety and adaptable qualities. Despite the aforementioned obstacles like elevated production expenses and molecular instability, there is a continuous research effort to curtail costs and broaden PHA's commercial acknowledgment, projecting it as a multifaceted and eco-friendly substance with auspicious uses. Biopolymers are now an integral part of our lives and are used in every industry today, as shown in Figure 2 **[22]**.

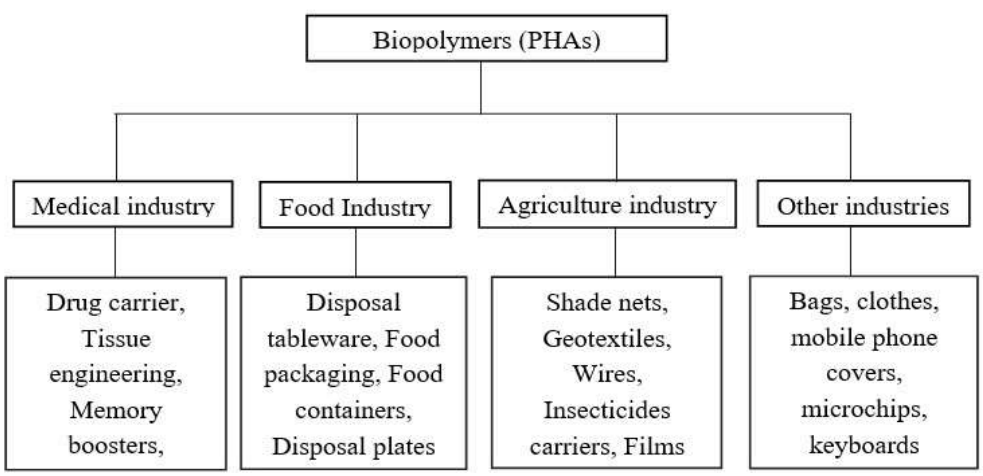

Figure 2. Biopolymer (PHAs) usage in different industries [22].

Global manufacturing limits restrict the development of goods based on PHA. The growth rate of bio-based polymer manufacturing capacity has decreased, from 10% per year between 2012 and 2014 to 4% per year between 2014 and 2016, which is consistent with the growth rate of global polymer production as a whole. Although PHA has the greatest growth rate, bio-based polymers as a whole expand at a slower pace than expected [23]. Low oil prices, adverse political environments

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in the majority of nations, a slower-than-anticipated pace of development in capacity utilization, and social reservations about embracing novel bio-products are some of the reasons behind this [24]. Moreover, recent developments in this field show that AI is causing a composite revolution by offering unprecedented opportunities for material modelling and design. AI can examine large datasets and find new composite formulations with exact properties by using techniques like machine learning and deep learning. This improves durability and performance through precise material behavior prediction, manufacturing process optimization, and complex microstructure design. Automation of material characterization expedites research, and multi-scale modeling offers a thorough comprehension of intricate ideas. AI-powered sustainability programs enhance formulations even more, cutting down on waste and resource use [25].

3. Polymer Composites with Natural Waste Fillers

Environmental concerns have driven countries to make significant investments in the use of renewable resources across a wide range of businesses. These materials include waste from wood flour, natural fibers, and agricultural byproducts such as corncob, rice husk, and rice straw **[26]**. However, efficient use of waste substrates has always been a major difficulty. While some substrates are now in use to some level, millions of tons of garbage go unutilized, enabling possibilities for a variety of everyday applications. The waste with its volume and applications is illustrated below in Table 1 **[27].**

Table 1. Application of waste with estimated volume [27].

Waste substrate	Commercial Volume (million Tonnes/year)	Applications
Food waste	931	Bio-gas
Animal waste	1400	Fertilizers, Bio-energy
Agriculture waste	2500	Recycling Materials
Municipal waste	2010	Energy resource
Industrial waste	3400	Coal Combustion products
Sewage waste	10.4	Fertilizer, Soil improver
Forest residue	4600	Bio-fuel production
Paper waste	67.4	Newspapers, Paper towels
Waste water	0.6-13.5	Treated waste water
Lignocellulosic waste	1300	Animal feed

High polymer research emphasizes the underutilized potential of organic waste by focusing on renewable resources and developing biodegradable aliphatic polymers. Nevertheless, research has shown that it is possible to use organic waste to create valuable biomaterials, providing a chance to substitute out the present waste management techniques for more environmentally friendly ones **[28]**. In a study of the biochar composites, it has been investigated that it could be used to make new materials. The mixing of biochar with PBAT/PLA reduces the surface resistivity. It showed increased elastic modulus with filler content, while thermal stability was minimally affected. Overall, biochar incorporation shows promise for specialized applications as an antistatic agent **[29]**. The application of biopolymers and alternative manufacturing methods presents several opportunities. Given the use of organic waste it can be used as fermented sugars. Many different kinds of organic waste that can be used as sustainable feedstocks for biopolymer synthesis are agricultural residues, garden waste, forest waste, livestock waste, paper waste, wastewater sludge, municipal solid waste, and kitchen garbage **[30]**. The cost and accessibility of feedstock in various parts of the world have a major impact on the production processes of biopolymers. Composite materials are being investigated as potential substitutes for conventional materials by scientists and researchers who are constantly looking for materials with high strength and low density. Composite materials, which are made up of two or more insoluble components, have special qualities that distinguish them from their component parts

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[31]. In particular, plant fiber-reinforced polymer composites are becoming more popular because of their prospective applications and biodegradability. With natural composites, which can be fully or partially biodegradable depending on the mix of biobased fibers and polymers, the emphasis is on sustainability. Because they are lightweight and environment friendly, these materials are becoming more and more in demand in the automotive and construction sector **[32]**, Plant fibers with varying mechanical and tribological capabilities include abaca, sisal, jute, rice husk and kenaf. Sisal and jute have better flexural properties **[33]**. A combination of fiber volume, orientation, and surface modification enables hybrid plant fiber-reinforced composites to perform better than glass fiber laminates. These composites are excellent in mechanical, acoustic, and thermal qualities, making them useful for a variety of uses **[34]**. Many waste products have been considered for PHA production, including as vegetable oils, molasses, animal fats high in carbon and nitrogen, and agricultural leftovers. Bacteria like Escherichia coli, Alcaligenes latus, and Pseudomonas species manufacture PHA from these substrates; yields are optimized by the use of methodologies like Design of Experiments (DOE) **[35]**. PHA synthesis has increased due to developments in fermentation techniques and the availability of cheap waste substrates, creating waste management solutions that are both economical and advantageous for the environment **[36]**. Taking advantage of biorefineries for sustainability is another idea, which involves using organic resources like food waste and specialty crops to turn biomass into marketable goods. Though cost-effective ways to use fermentable sugars from lignocellulose are still lacking, integrating PHA production within biorefineries employing waste streams like glycerol and lignocellulosic sugars shows promise **[37]**. Biorefinery becomes sustainable when organic waste acceptance is conditioned by charging waste management costs. Long-term survival requires overcoming logistical, technological, financial, moral, and legal challenges, especially given the pressing need to address waste issues and transition to a circular economy **[38]**. Engineered materials utilize polymer composites, which are composed of two or more insoluble components, combining a thermoplastic or thermoset matrix with organic or inorganic fillers like wood flour or fibers, to achieve desired **[39]**. Although natural fibers are mechanically strong and biodegradable, their hydrophilic nature can make them incompatible with conventional plastic materials **[40]**. Component composition, ambient factors, and surface properties all affect how quickly composite materials biodegrade; natural fillers may encourage microbial activity and accelerate breakdown **[41]**.

4. Applications and Properties

Natural fibers and PHAs have numerous applications that promote environmental preservation and sustainable development. Natural fibers, derived from plants or animals, are biodegradable, lightweight, and renewable, and have many day-today applications **[42]**, that are illustrated below.

- Active and intelligent food packaging;
- Bio-packaging;
- Biomedical applications;
- Wound healing;
- Bio-based composites as fertilizer delivery and their applications as agricultural inputs;
- Applications for Wood-PHA Composites (Rigid tableware, Disposable tableware);
- Other innovative bio-based composites applications

Natural fibers have different qualities depending on things like crop location, processing techniques, and chemical composition. PHAs are utilized in waste management, biomedical engineering, and packaging because of their reputation for biodegradability and biocompatibility **[42]**. Recent years have seen a surge in interest in natural Fiber reinforcement in composite materials because of its exceptional mechanical properties. The complete biodegradability, renewable nature, eco-friendliness, affordability, availability, and low density of these fibers are widely recognized **[43]**. Because plant fibers are biological and strongly biodegradable, they contribute to ecological balance while being heavier than mineral fibers. Natural fiber-reinforced polymers are widely utilized in industry due to their great performance when their life cycle comes to a conclusion, the CO_2 they absorb during growing balances the CO_2 they release while burning. Furthermore, the recycling of composite materials is made easier by the low friction potential of plant fibers **[44]**. Natural fibers are more lightweight than fibers made of minerals, but they nevertheless perform well and support ecological balance. Transparent fillers, such as silica particles or fibers, can be used in place of glass

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in polymer matrices to provide optical clarity and impact resistance in applications such as automotive glazing and optical lenses. While not entirely replacing glass, they provide an appropriate choice when the benefits of composites are needed, such as lower weight and greater impact resistance, yet maintain optical qualities **[45]**. Natural Fibers, despite potentially lower mechanical properties compared to glass or mineral-based Fibers, offer similar stiffness and tensile strength, making them valuable reinforcements in composite applications **[46]**. New applications for biobased composites and nanocomposites have evolved through the utilization of green generated nanoparticles and agri-food industry byproducts. In addition, with applications ranging from dye removal to water desalination, research into biobased composites and nanocomposites for water treatment and pollutant removal is critical for clean water sustainability. They also have potential in rigid electronics and energy storage systems, as demonstrated by biocomposite membranes that include microcrystalline cellulose into polymer matrices **[47]**. Furthermore, research on wood panels created from industry residues and ecologically friendly adhesives as substitutes for synthetic counterparts indicates that biobased materials have promise for usage in the construction industry. Polyester systems offer promise as paper covers for multilayer packaging materials **[48]**, whereas jute fibers, observed for their biodegradability and compatibility with biodegradable polymers, are used in eco-friendly packaging solutions **[49]**.

5. Current Developments

On the global market, there has been a discernible rise in demand for natural and bio-based fillers. Filler usage increased in the United States over the preceding few decades, rising from 525000 tons to 1925000 tons **[3]**. The addition of natural fillers to biodegradable polymer matrices enhances the versatility and application potential of eco-friendly products. Economic considerations are crucial for manufacturers, but the ability to alter product properties through varying filler amounts opens up new application avenues **[50]**. The addition of cork as a natural filler to P(3HB-co-4HB) composites has shown enhanced thermal stability, resulting in slower degradation rates compared to the pure matrix in various environments **[51]**. In other findings, composites comprising P(3HB-co-4HB) and wood flour exhibited accelerated degradation processes under both laboratory and industrial composting conditions, with the inclusion of wood flour significantly altering the thermal and mechanical properties of the composites. The presence of acidic by-products from hydrolytic degradation and compounds derived from the filler contributes to enhanced thermal stability. This gives great promise in food packaging applications **[52]**. By carefully choosing the types of polymer matrix and filler, content ratios, and size distributions, manufacturers can customize the final qualities of these materials to fit a variety of applications. Research into substitute biomass-based polymeric materials and composites has been spurred by worries about the depletion of fossil fuels and their potential environmental effects on composites **[53]**. This change is reflected in the sharp rise in research publications on bio-composites that emphasize the inventiveness and potential of these materials. The main objective is to move toward a circular or sustainable economy that focus attention on the use of bio sourced and biodegradable products. Reusability, recycling, and biodegradability have been prioritized in end-of-life cycle optimization through recent programs. However, creating fully sustainable goods and procedures calls for upgrades to production techniques, waste management systems, and retail distribution networks **[54]**. This has led to a rise in interest in fully integrated production systems, such biorefineries, which integrate several manufacturing phases in an effort to minimize emissions, transportation expenses, and waste formation. To realize bioplastics and biocomposites full potential in advancing global sustainability, however, comprehensive and reliable information about their sustainability is necessary **[55]**. For these resources to be sustainable, just agricultural systems that respect both the environment and society must be developed. To do this, methods for producing biomass must be made sure to advance the welfare of farmers, communities, and the environment. Although biopolymers possess inherent benefits for eco-friendly uses such as PHAs, cost remains an issue. PHAs, or naturally occurring polyesters made by bacteria under harsh circumstances when fermenting fat or sugar, have enormous promise for the development of sustainable materials. Reusing a lot of leftovers can save expenses and increase sustainability by using biomass from food production byproducts and Agrofood wastes **[56]**. When natural fillers are added to biopolymers to enhance their properties, green composites are produced. For instance, rice husk flour (RHF), compatibilizers, and initiators have been combined with commercial poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) made from fruit pulp waste to successfully construct green composites **[57]**. The increasing demand for these fillers reflects the evolving dynamics of material design, prioritizing solutions driven by specific application demands. Composite materials have emerged as market leaders due to their adaptability in this ever-changing environment **[58]**. Using this unique method, films with better thermal stability, balanced strength and ductility, and robust barrier qualities have been created, making them appropriate for rigid packaging applications. Partnerships among scientists, producers, and other interested parties displays a commitment to developing environmentally friendly and financially successful sustainable materials **[59]**.

6. Challenges and Future Aspects

Commercializing PHAs offers significant obstacles due to their higher production costs as compared to petroleum-based polymers, as well as market acceptance concerns got worse by competition from established brands. Despite their competitiveness in specific applications, PHAs face price parity difficulties with petroleum-based polymers **[60]**. For instance, utilizing lignocellulosic waste presents challenges due to incompatibilities between the hydrophilic nature of natural fillers and the hydrophobicity of the thermoplastic matrix, affecting mechanical properties dependent on interfacial adhesion **[61]**. While water-based polymer composites have some advantages, they also face issues such as lower mechanical qualities, difficulties in optimizing filler-matrix interaction, restricted recyclability, and high energy requirements at the end of life. However, green synthesis methods and the use of recycled or biodegradable polymers show promise for improving waste management practices, exploring new markets, and tackling issues in polymer composites **[62]**.

Future research aims to optimize PHA production, reduce costs, enhance stability, and explore high-value applications, leveraging their diverse structures and adaptive features **[63]**. The creative use of waste materials, focus on improving material compositions and processing techniques, and development of hybrid materials for construction (for example use of bamboo in south Asia for different constructions **[64]**, and automotive industries show promise, along with the creation of affordable and biodegradable resins and adhesives using waste-derived resources **[65]**. Achieving superior mechanical characteristics and filler-matrix interactions through chemical changes is the main goal of research on biofiber reinforced polymer composites. Developments in waste-based polymer composites are being driven by continuous efforts in ecologically friendly synthesis techniques and the use of waste-derived components **[66]**. Variability in waste composition, limited bacterial strains, metabolic engineering, and PHA extraction are some challenges which require ongoing research and development to realize the full potential of PHAs as sustainable biopolymers **[67]**. To promote widespread usage of sustainable materials across industries, future efforts should concentrate on optimization, technological advancements, and environmentally responsible solutions **[68]**.

7. Conclusions

In brief, PHAs are unique in that they biodegrade easily in both aerobic and anaerobic circumstances, while mixing with other polymers and specific chemicals can affect how quickly they break down. Further study is required to address scalability, affordability, mechanical qualities, and regulatory challenges. However, improving PHAs' properties and broadening their applications by functionalization appears promising **[69]**. Studies on vegetal inclusions and biodegradable polymers have increased, with possible applications ranging from packaging to tissue regeneration. Usability testing and the inclusion of antimicrobial chemicals are suggested to increase their performance in a variety of applications. Waste-based polymer composites show promises as low-cost, renewable, and environment friendly engineering materials **[70]**. These composites, which incorporate waste materials as reinforcement, have better physical and mechanical properties, making them appropriate for structural applications **[71]**. While most plastics originate from fossil fuels, there is a growing interest in biodegradable polymers such as PHA and PLA, driven by rising consumer awareness and demand for sustainable packaging products. Many countries continue to face the difficulty of limited production capacities for biodegradable products **[72]**. Ongoing research and development in waste-derived composite materials and biodegradable polymers show promises in addressing environmental problems and meeting the diverse needs of modern industries. Additionally, there is increasing interest in labeling biodegradable polymers to track their environmental fate, especially for specific applications **[73]**.

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References

1. European Union. https://environment.ec.europa.eu/news/eu-calls-global-ban-some-plastic-products-fight-pollution-2024-04-19_en.
2. Andrady, A.L. Assessment of Environmental Biodegradation of Synthetic Polymers. *Journal of Macromolecular Science, Part C: Polymer Reviews* **1994**, *34*, 25–76.
3. Zaaba, N.F.; Ismail, H. Thermoplastic/Natural Filler Composites: A Short Review. *Journal of Physical Science* **2019**, *30*.
4. Philip, S.; Keshavarz, T.; Roy, I. Polyhydroxyalkanoates: Biodegradable Polymers with a Range of Applications. *Journal of chemical technology & biotechnology: International research in process, Environmental & clean technology* **2007**, *82*, 233–247.
5. Mukherjee, A.; Koller, M. Microbial polyHydroxyAlkanoate (PHA) Biopolymers—Intrinsically Natural. *Bioengineering* **2023**, *10*, 855.
6. Cinelli, P.; Mallegni, N.; Gigante, V.; Montanari, A.; Seggiani, M.; Coltelli, M.B.; Bronco, S.; Lazzeri, A. Biocomposites Based on Polyhydroxyalkanoates and Natural Fibres from Renewable Byproducts. *Applied Food Biotechnology* **2019**, *6*, 35–43.
7. Mohit, H.; Mavinkere Rangappa, S.; Siengchin, S.; Gorbatyuk, S.; Manimaran, P.; Alka Kumari, C.; Khan, A.; Doddamani, M. A Comprehensive Review on Performance and Machinability of Plant Fiber Polymer Composites. *Polymer Composites* **2022**, *43*, 608–623.
8. Dacko, P.; Kowalczuk, M.; Janeczek, H.; Sobota, M. Physical Properties of the Biodegradable Polymer Compositions Containing Natural Polyesters and Their Synthetic Analogues. In Proceedings of the Macromolecular symposia; Wiley Online Library, 2006; Vol. 239, pp. 209–216.
9. Das, P.P.; Chaudhary, V. Moving towards the Era of Bio Fibre Based Polymer Composites. *Cleaner engineering and technology* **2021**, *4*, 100182.
10. Tumu, K.; Vorst, K.; Curtzwiler, G. Global Plastic Waste Recycling and Extended Producer Responsibility Laws. *Journal of Environmental Management* **2023**, *348*, 119242.
11. Thapliyal, D.; Verma, S.; Sen, P.; Kumar, R.; Thakur, A.; Tiwari, A.K.; Singh, D.; Verros, G.D.; Arya, R.K. Natural Fibers Composites: Origin, Importance, Consumption Pattern, and Challenges. *Journal of Composites Science* **2023**, *7*, 506.
12. Ramu, S.; Senthilkumar, N. Approaches of Material Selection, Alignment and Methods of Fabrication for Natural Fiber Polymer Composites: A Review. *Journal of Applied and Natural Science* **2022**, *14*, 490–499.
13. Townsend, T. 1B - World Natural Fibre Production and Employment. In *Handbook of Natural Fibres (Second Edition)*; Kozłowski, R.M., Mackiewicz-Talarczyk, M., Eds.; Woodhead Publishing Series in Textiles; Woodhead Publishing, 2020; pp. 15–36 ISBN 978-0-12-818398-4.
14. Akinmulewo, A.B.; Nwinyi, O.C. Polyhydroxyalkanoate: A Biodegradable Polymer (a Mini Review). In Proceedings of the Journal of physics: Conference series; IOP Publishing, 2019; Vol. 1378, p. 042007.
15. Vannini, M.; Marchese, P.; Sisti, L.; Saccani, A.; Mu, T.; Sun, H.; Celli, A. Integrated Efforts for the Valorization of Sweet Potato By-Products within a Circular Economy Concept: Biocomposites for Packaging Applications Close the Loop. *Polymers* **2021**, *13*, 1048.
16. Thyavihalli Girijappa, Y.G.; Mavinkere Rangappa, S.; Parameswaranpillai, J.; Siengchin, S. Natural Fibers as Sustainable and Renewable Resource for Development of Eco-Friendly Composites: A Comprehensive Review. *Frontiers in Materials* **2019**, *6*, 226.
17. Raj, H.; Tripathi, S.; Bauri, S.; Choudhary, A.; Mandal, S.; Maiti, P. Green Composites Using Naturally Occurring Fibers: A Comprehensive Review. *Sustainable Polymer & Energy* **2023**, *1*, 10010.
18. Dobrogojski, J.; Spychalski, M.; Luciński, R.; Borek, S. Transgenic Plants as a Source of Polyhydroxyalkanoates. *Acta Physiologiae Plantarum* **2018**, *40*, 1–17.
19. Sun, J.; Shen, J.; Chen, S.; Cooper, M.A.; Fu, H.; Wu, D.; Yang, Z. Nanofiller Reinforced Biodegradable PLA/PHA Composites: Current Status and Future Trends. *Polymers* **2018**, *10*, 505.

20. Chodak, I. Polyhydroxyalkanoates: Origin, Properties and Applications. In *Monomers, polymers and composites from renewable resources*; Elsevier, 2008; pp. 451–477.
21. Maiti, S.; Islam, M.R.; Uddin, M.A.; Afroj, S.; Eichhorn, S.J.; Karim, N. Sustainable Fiber-reinforced Composites: A Review. *Advanced Sustainable Systems* **2022**, *6*, 2200258.
22. Abd El-malek, F.; Khairy, H.; Farag, A.; Omar, S. The Sustainability of Microbial Bioplastics, Production and Applications. *International journal of biological macromolecules* **2020**, *157*, 319–328.
23. Aeschelmann, F.; Carus, M. Bio-Based Building Blocks and Polymers in the World. *Capacities, production and applications: Status quo and trends towards 2020* **2015**.
24. Vandi, L.-J.; Chan, C.M.; Werker, A.; Richardson, D.; Laycock, B.; Pratt, S. Wood-PHA Composites: Mapping Opportunities. *Polymers* **2018**, *10*, 751.
25. Huang, J.S.; Liew, J.X.; Ademiloye, A.S.; Liew, K.M. Artificial Intelligence in Materials Modeling and Design. *Archives of Computational Methods in Engineering* **2021**, *28*, 3399–3413.
26. Kalak, T. Potential Use of Industrial Biomass Waste as a Sustainable Energy Source in the Future. *Energies* **2023**, *16*, 1783.
27. Jaffur, N.; Kumar, G.; Jeetah, P.; Ramakrishna, S.; Bhatia, S.K. Current Advances and Emerging Trends in Sustainable Polyhydroxyalkanoate Modification from Organic Waste Streams for Material Applications. *International Journal of Biological Macromolecules* **2023**, 126781.
28. Acharjee, S.A.; Bharali, P.; Gogoi, B.; Sorhie, V.; Walling, B.; Alemtoshi PHA-Based Bioplastic: A Potential Alternative to Address Microplastic Pollution. *Water, Air, & Soil Pollution* **2023**, *234*, 21.
29. Musioł, M.; Rydz, J.; Janeczek, H.; Kordyka, A.; Andrzejewski, J.; Sterzyński, T.; Jurczyk, S.; Cristea, M.; Musioł, K.; Kampik, M. (Bio) Degradable Biochar Composites–Studies on Degradation and Electrostatic Properties. *Materials Science and Engineering: B* **2022**, *275*, 115515.
30. Battista, F.; Frison, N.; Pavan, P.; Cavinato, C.; Gottardo, M.; Fatone, F.; Eusebi, A.L.; Majone, M.; Zeppilli, M.; Valentino, F. Food Wastes and Sewage Sludge as Feedstock for an Urban Biorefinery Producing Biofuels and Added-value Bioproducts. *Journal of Chemical Technology & Biotechnology* **2020**, *95*, 328–338.
31. Khan, A.; Saxena, K.K. A Review on Enhancement of Mechanical Properties of Fiber Reinforcement Polymer Composite under Different Loading Rates. *Materials Today: Proceedings* **2022**, *56*, 2316–2322.
32. Kordi, M.; Farrokhi, N.; Pech-Canul, M.I.; Ahmadikhah, A. Rice Husk at a Glance: From Agro-Industrial to Modern Applications. *Rice Science* **2023**.
33. Jabu, M.A.; Alugongo, A.A.; Nkomo, N.Z. Application of Natural Fibre Composites in Interior Panels in the Automotive Industry: A Review.
34. Mohammed, L.; Ansari, M.N.; Pua, G.; Jawaid, M.; Islam, M.S. A Review on Natural Fiber Reinforced Polymer Composite and Its Applications. *International journal of polymer science* **2015**, *2015*.
35. Nikodinovic-Runic, J.; Guzik, M.; Kenny, S.T.; Babu, R.; Werker, A.; Connor, K.E. Carbon-Rich Wastes as Feedstocks for Biodegradable Polymer (Polyhydroxyalkanoate) Production Using Bacteria. *Advances in applied microbiology* **2013**, *84*, 139–200.
36. Coats, E.R.; Loge, F.J.; Wolcott, M.P.; Englund, K.; McDonald, A.G. Synthesis of Polyhydroxyalkanoates in Municipal Wastewater Treatment. *Water Environment Research* **2007**, *79*, 2396–2403.
37. Jiang, G.; Hill, D.J.; Kowalczuk, M.; Johnston, B.; Adamus, G.; Irorere, V.; Radecka, I. Carbon Sources for Polyhydroxyalkanoates and an Integrated Biorefinery. *International Journal of Molecular Sciences* **2016**, *17*, 1157.
38. Chirdon, W.M. Utilization of Biorefinery Waste Proteins as Feed, Glues, Composites, and Other Co-Products. *Algal Biorefineries: Volume 2: Products and Refinery Design* **2015**, 367–392.
39. Brebu, M. Environmental Degradation of Plastic Composites with Natural Fillers—a Review. *Polymers* **2020**, *12*, 166.
40. La Mantia, F.P.; Morreale, M. Green Composites: A Brief Review. *Composites Part A: Applied Science and Manufacturing* **2011**, *42*, 579–588.
41. Dina, I.A.; Gimba, C.E.; Hamza, A.; Ekwumemgbo, P. THE STUDY OF USING NATURAL FILLERS ON THE BIODEGRADATION PROPERTIES OF VIRGIN/WASTE LOW DENSITY POLYETHYLENE AND VIRGIN/WASTE HIGH DENSITY POLYETHYLENE COMPOSITES. *Journal of Chemical Society of Nigeria* **2023**, *48*.
42. Kaniuk, Ł.; Stachewicz, U. Development and Advantages of Biodegradable PHA Polymers Based on Electrospun PHBV Fibers for Tissue Engineering and Other Biomedical Applications. *ACS biomaterials science & engineering* **2021**, *7*, 5339–5362.
43. Saber, D.; Abdelnaby, A.H. Recent Developments in Natural Fiber as Reinforcement in Polymeric Composites: A Review. *Recent Developments in Natural Fiber as Reinforcement in Polymeric Composites: A Review (October 19, 2022). D. Saber & AH Abdelnaby" Recent Developments in Natural Fiber as Reinforcement in Polymeric Composites: A Review" Asian Journal of Applied Science and Technology (AJAST) Volume* **2022**, *6*, 56–75.

 doi:10.20944/preprints202405.1308.v1

44. Elfaleh, I.; Abbassi, F.; Habibi, M.; Ahmad, F.; Guedri, M.; Nasri, M.; Garnier, C. A Comprehensive Review of Natural Fibers and Their Composites: An Eco-Friendly Alternative to Conventional Materials. *Results in Engineering* **2023**, 101271.
45. Andrew, J.J.; Dhakal, H.N. Sustainable Biobased Composites for Advanced Applications: Recent Trends and Future Opportunities–A Critical Review. *Composites Part C: Open Access* **2022**, *7*, 100220.
46. Koohestani, B.; Darban, A.K.; Mokhtari, P.; Yilmaz, E.; Darezereshki, E. Comparison of Different Natural Fiber Treatments: A Literature Review. *International Journal of Environmental Science and Technology* **2019**, *16*, 629–642.
47. Ortega, F.; Versino, F.; López, O.V.; García, M.A. Biobased Composites from Agro-Industrial Wastes and by-Products. *Emergent Materials* **2022**, *5*, 873–921.
48. Sikorska, W.; Dacko, P.; Sobota, M.; Rydz, J.; Musioł, M.; Kowalczuk, M. Degradation Study of Polymers from Renewable Resources and Their Compositions in Industrial Composting Pile. In Proceedings of the Macromolecular symposia; Wiley Online Library, 2008; Vol. 272, pp. 132–135.
49. Musioł, M.; Janeczek, H.; Jurczyk, S.; Kwiecień, I.; Sobota, M.; Marcinkowski, A.; Rydz, J. (Bio) Degradation Studies of Degradable Polymer Composites with Jute in Different Environments. *Fibers and Polymers* **2015**, *16*, 1362–1369.
50. Anwajler, B.; Zdybel, E.; Tomaszewska-Ciosk, E. Innovative Polymer Composites with Natural Fillers Produced by Additive Manufacturing (3D Printing)—A Literature Review. *Polymers* **2023**, *15*, 3534.
51. Jurczyk, S.; Musioł, M.; Sobota, M.; Klim, M.; Hercog, A.; Kurcok, P.; Janeczek, H.; Rydz, J. (Bio) Degradable Polymeric Materials for Sustainable Future—Part 2: Degradation Studies of P (3HB-Co-4HB)/Cork Composites in Different Environments. *Polymers* **2019**, *11*, 547.
52. Musioł, M.; Jurczyk, S.; Sobota, M.; Klim, M.; Sikorska, W.; Zięba, M.; Janeczek, H.; Rydz, J.; Kurcok, P.; Johnston, B. (Bio) Degradable Polymeric Materials for Sustainable Future—Part 3: Degradation Studies of the PHA/Wood Flour-Based Composites and Preliminary Tests of Antimicrobial Activity. *Materials* **2020**, *13*, 2200.
53. Kamarudin, S.H.; Mohd Basri, M.S.; Rayung, M.; Abu, F.; Ahmad, S.; Norizan, M.N.; Osman, S.; Sarifuddin, N.; Desa, M.S.Z.M.; Abdullah, U.H. A Review on Natural Fiber Reinforced Polymer Composites (NFRPC) for Sustainable Industrial Applications. *Polymers* **2022**, *14*, 3698.
54. Markevičiūtė, Z.; Varžinskas, V. Smart Material Choice: The Importance of Circular Design Strategy Applications for Bio-Based Food Packaging Preproduction and End-of-Life Life Cycle Stages. *Sustainability* **2022**, *14*, 6366.
55. Jan-Georg, R.; Langer, R.; Giovanni, T. Bioplastics for a Circular Economy. *Nature Reviews. Materials* **2022**, *7*, 117–137.
56. Naser, A.Z.; Deiab, I.; Darras, B.M. Poly (Lactic Acid)(PLA) and Polyhydroxyalkanoates (PHAs), Green Alternatives to Petroleum-Based Plastics: A Review. *RSC advances* **2021**, *11*, 17151–17196.
57. Melendez-Rodriguez, B.; Torres-Giner, S.; Aldureid, A.; Cabedo, L.; Lagaron, J.M. Reactive Melt Mixing of Poly (3-Hydroxybutyrate)/Rice Husk Flour Composites with Purified Biosustainably Produced Poly (3-Hydroxybutyrate-Co-3-Hydroxyvalerate). *Materials* **2019**, *12*, 2152.
58. Jaffur, N.; Kumar, G.; Jeetah, P.; Ramakrishna, S.; Bhatia, S.K. Current Advances and Emerging Trends in Sustainable Polyhydroxyalkanoate Modification from Organic Waste Streams for Material Applications. *International Journal of Biological Macromolecules* **2023**, 126781.
59. Zhang, K.; Misra, M.; Mohanty, A.K. Toughened Sustainable Green Composites from Poly (3-Hydroxybutyrate-Co-3-Hydroxyvalerate) Based Ternary Blends and Miscanthus Biofiber. *ACS Sustainable Chemistry & Engineering* **2014**, *2*, 2345–2354.
60. Oliver-Ortega, H.; Julian, F.; Espinach, F.X.; Tarrés, Q.; Ardanuy, M.; Mutjé, P. Research on the Use of Lignocellulosic Fibers Reinforced Bio-Polyamide 11 with Composites for Automotive Parts: Car Door Handle Case Study. *Journal of cleaner production* **2019**, *226*, 64–73.
61. Berzin, F.; Vergnes, B. Thermoplastic Natural Fiber Based Composites. In *Fiber Reinforced Composites*; Elsevier, 2021; pp. 113–139.
62. Halley, P.J.; Dorgan, J.R. Next-Generation Biopolymers: Advanced Functionality and Improved Sustainability. *MRS bulletin* **2011**, *36*, 687–691.
63. Khamkong, T.; Penkhrue, W.; Lumyong, S. Optimization of Production of Polyhydroxyalkanoates (PHAs) from Newly Isolated Ensifer Sp. Strain HD34 by Response Surface Methodology. *Processes* **2022**, *10*, 1632.
64. Suhaily, S.S.; Khalil, H.A.; Nadirah, W.W.; Jawaid, M. Bamboo Based Biocomposites Material, Design and Applications. In *Materials science-advanced topics*; IntechOpen, 2013 ISBN 953-51-1140-X.
65. Lange, J.-P. Managing Plastic Waste─ Sorting, Recycling, Disposal, and Product Redesign. *ACS Sustainable Chemistry & Engineering* **2021**, *9*, 15722–15738.
66. Mishra, T.; Mandal, P.; Rout, A.K.; Sahoo, D. A State-of-the-Art Review on Potential Applications of Natural Fiber-Reinforced Polymer Composite Filled with Inorganic Nanoparticle. *Composites Part C: Open Access* **2022**, *9*, 100298.

 doi:10.20944/preprints202405.1308.v1

67. Marciniak, P.; Możejko-Ciesielska, J. What Is New in the Field of Industrial Wastes Conversion into Polyhydroxyalkanoates by Bacteria? *Polymers* **2021**, *13*, 1731.
68. Mohanty, A.K.; Misra, M. and; Hinrichsen, G.I. Biofibres, Biodegradable Polymers and Biocomposites: An Overview. *Macromolecular materials and Engineering* **2000**, *276*, 1–24.
69. Boey, J.Y.; Mohamad, L.; Khok, Y.S.; Tay, G.S.; Baidurah, S. A Review of the Applications and Biodegradation of Polyhydroxyalkanoates and Poly (Lactic Acid) and Its Composites. *Polymers* **2021**, *13*, 1544.
70. Islam, M.Z.; Sarker, M.E.; Rahman, M.M.; Islam, M.R.; Ahmed, A.F.; Mahmud, M.S.; Syduzzaman, M. Green Composites from Natural Fibers and Biopolymers: A Review on Processing, Properties, and Applications. *Journal of Reinforced Plastics and Composites* **2022**, *41*, 526–557.
71. Dubey, S.C.; Mishra, V.; Sharma, A. A Review on Polymer Composite with Waste Material as Reinforcement. *Materials Today: Proceedings* **2021**, *47*, 2846–2851.
72. Rydz, J.; Duale, K.; Sikorska, W.; Musioł, M.; Janeczek, H.; Marcinkowski, A.; Siwy, M.; Adamus, G.; Mielczarek, P.; Silberring, J. Oligopeptide-Based Molecular Labelling of (Bio) Degradable Polyester Biomaterials. *International Journal of Biological Macromolecules* **2024**, 131561.
73. Rydz, J.; Musioł, M.; Zawidlak-Węgrzyńska, B.; Sikorska, W. Present and Future of Biodegradable Polymers for Food Packaging Applications. *Biopolymers for food design* **2018**, 431–467.