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Review

Bacteria for Bioplastics: Progress, Applications, and Challenges

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Cite This: *ACS Omega* 2024, 9, 8666−8686

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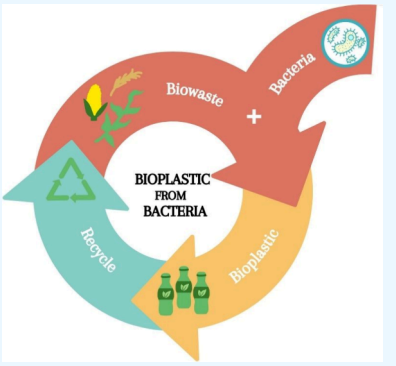
ABSTRACT: Bioplastics are one of the answers that can point society toward a sustainable future. Under this premise, the synthesis of polymers with competitive properties using low-cost starting materials is a highly desired factor in the industry. Also, tackling environmental issues such as nonbiodegradable waste generation, high carbon footprint, and consumption of nonrenewable resources are some of the current concerns worldwide. The scientific community has been placing efforts into the biosynthesis of polymers using bacteria and other microbes. These microorganisms can be convenient reactors to consume food and agricultural wastes and convert them into biopolymers with inherently attractive properties such as biodegradability, biocompatibility, and appreciable mechanical and chemical properties. Such biopolymers can be applied to several fields such as packing, cosmetics, pharmaceutical, medical, biomedical, and agricultural. Thus, intending to elucidate the science of microbes to produce polymers, this review starts with a brief introduction to bioplastics by describing their importance and the methods for their production. The second section dives into the importance of bacteria regarding the biochemical routes for the synthesis of polymers along with their advantages and disadvantages. The third section covers some of the main parameters that influence biopolymers' production. Some of the main applications of biopolymers along with a comparison between the polymers obtained from microorganisms and the petrochemical-based ones are presented. Finally, some discussion about the future aspects and main challenges in this field is provided to elucidate the main issues that should be tackled for the wide application of microorganisms for the preparation of bioplastics.



1. INTRODUCTION

Over the years there has been a continuous increase in the consumption of plastics mostly derived from nonrenewable sources as its production reached around 338 million tons in 2019 which was almost 6.5 times higher than that from 1975.[1] Even though there has been an effort to recycle plastics, in the United States, it only accounts for 10% of the amount wasted.[2] Such conditions lead to a considerable strain on the manufacturing and nonrecycling of plastics resulting in ending up in ecosystems and landfills.[3] Some of the major issues with these plastics are their long degradation time (over a century for most of the plastics) and the formation of harmful macro and microplastics during decomposition which discharge into the ecosystems. Continuing with a linear economy for plastic production can culminate in the exhaustion of nonrenewable resources along with environmental and economic issues. There has been an effort to increase the production of biobased and biodegradable materials which is expected to grow in the next few years (Figure 1).[4] Based on that, it is worth discussing the difference between biopolymers and bioplastics. In this sense, biopolymers can be considered as a broader range of materials that originate from natural sources or can be synthesized by living organisms, hence it includes carbohydrates (i.e., cellulose, chitin), proteins (i.e., silk, collagen), nucleic acids (i.e., DNAs and RNAs), among others.

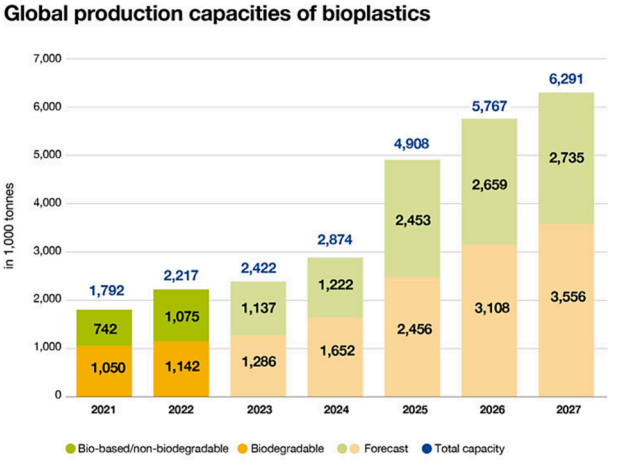


Figure 1. Worldwide production of bioplastics from 2021 to 2022 along with the forecast up to 2027. Adapted with permission.[4] Copyright 2022, European Bioplastics.

Received: October 7, 2023
Revised: January 17, 2024
Accepted: January 24, 2024
Published: February 12, 2024

These materials can be found in living organisms or obtained from biomass. The term Bioplastic can be defined as a more specific class of biopolymers that are plastics obtained from renewable resources or through the biosynthesis of microorganisms. Several renewable carbon sources can be used for the synthesis of bioplastics such as starch from corn, potatoes, cassava, sugar cane, cellulose, vegetable oils, algae, and agricultural biowaste. In this sense, some of the most known examples of bioplastics obtained from bacterial metabolic processes are polyhydroxyalkanoates (PHAs) which is a group of polymers that includes polyhydroxybutyrate (PHB),[5] polyhydroxyvalerate (PHV),[6] polyhydroxyhexanoate (PHH),[7] polyhydroxyoctanoate (PHO),[8] poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH),[9] among others. The previous examples of bioplastics are biodegradable; however, there are also nonbiodegradable bioplastics, such as bio polyethylene (PE), bio polypropylene (PP), and bio polyethylene terephthalate (PET), which can be obtained either from renewable or petrochemical sources.

Under this premise, one feasible option to work around this situation is based on the preparation of biodegradable polymers derived from renewable sources or biowaste as it can ease the burden on their petrochemical-based counterparts while promoting a circular and sustainable economy. That process can be performed through the use of bacteria which are capable of synthesizing a plethora of polymers such as polysaccharides, polyesters, polyamides, and even polyphosphates.[10] Bacteria can produce polymers mainly in two ways. First, it can break down larger molecules of biowaste into a monomer that can be further used for polymerization. Second, bacteria can be inserted into a type of environment that promotes the synthesis of a polymer that can be extracted. Usually, both processes take place through fermentation. Some examples of the first case, in which bacteria perform a fermentation process to obtain a monomer that can be later chemically polymerized are poly(lactic acid) (PLA), some starch-based polymers (TPS), and polybutylene succinate (PBS) which consist, in its majority, of biodegradable aliphatic thermoplastic polyesters. It is worth noting that, even though the PLA is mostly produced through a chemical polymerization process based on the ring-opening reaction of lactide, there have been some recent approaches that proposed a one-step fermentation process for the biosynthesis of PLA through metabolically engineered microorganisms.[11] For that, two main enzymes must be present which are the propionyl-CoA transferase and PHA synthase. The process consists of the conversion of lactic acid into lactyl-CoA through the enzymatic activity of propionyl-CoA transferase. Then, lactyl-CoA is polymerized by the PHA synthase. Some of the polymers that can be synthesized by bacteria are dextran, xanthan, and polyhydroxyalkanoates (PHAs), which include a vast number of polymers, such as polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), polyhydroxyalkanoate (PHO), among others.

PLA is commonly obtained from the fermentation of sugars or starch derived from carbohydrates from plants. Several sources which include corn starch, sugar cane, wheat, and rice straws can be used as starting materials to produce PLA. Such components are based on polysaccharides which contain cellulose and hemicellulose that can be depolymerized into sugars either through chemical or enzymatic routes. The obtained sugars can be fermented into lactic acid to be polymerized into PLA. Another attractive biodegradable polymer is PBS which is also a thermoplastic polyester that can be manufactured from food waste.[12] It can also be obtained from the same sources as PLA, as well as feedstock from algal, plant, or vegetable oils. It is most synthesized from the polycondensation reaction between succinic acid and 1,4-butanediol. It is worth noting that, even though 1,4-butanediol can be derived from petrochemicals it can also be obtained from the fermentation of sugars and molasses from beet, sugar cane, corn starch, corn stover, and wheat straw. The PHAs are another widely studied class of biodegradable polyesters that are produced by bacteria usually when there is a nutrient limitation related to the lack of P, N, and O. This polymer displays great versatility in terms of the substrate and bacteria that can be used for its synthesis. In this sense, some of the substrates are agricultural waste, fatty acids,[13] olive oil pomace, fermented molasses,[14] and paper and palm mill waste.[15,16] There is a plethora of microorganisms that can synthesize PHAs from the mentioned substrates which include *Pseudomonas sp.*,[17] *Rhodobacter sphaeroides*,[18] *Rhizobium sp.*,[19] *Ralstonia eutropha*,[20] *Enterobacter sp.*,[21] among many others. Such versatility in substrate and microorganisms available has led to well-established manufacturing processes biodegradable and biobased polymers such as PLA, PHAs, PBS, and starch blends. In addition, there are also some biodegradable polymers derived from nonrenewable sources such as polyethylene glycol (PEG), polycaprolactone (PCL), poly(trimethylene carbonate) (PTMC), and polybutylene adipate coterephthalate (PBAT) which have also gained some space in the market. These biodegradable polymers present several attractive properties such as a broad range of mechanical properties, processability through different techniques, biocompatibility, and structural versatility that allow their introduction into the market. Such features led to the production of around 2.22 million tons of biodegradable polymers worldwide in 2022 which are composed of several industries including food packing, cell scaffolds for tissue engineering, drug delivery systems, face masks, cosmetics, agricultural products, and many others (Figure 2).[4,22]

2. BACTERIA FOR BIOPLASTICS

Bacteria are versatile microorganisms capable of synthesizing many polymers through different mechanisms based on the type of material and enzymes. Some of the main polymers are polysaccharides, polyesters, proteins, peptidoglycans, among others. In the case of polysaccharides, there are subdivisions into exopolysaccharides or capsular polysaccharides. Exopolysaccharides can be either secreted or synthesized on the bacterial cell wall surface through the aid of enzymes, some examples include xanthan gum, dextran, PHAs, cellulose, and alginate. The capsular polysaccharides include K30 and glycogen, for instance. The synthesis of such polymers is a complex process that involves specific enzymes such as pyrophosphorylases and dehydrogenases along with several types of nucleoside diphosphate sugars that include adenosine diphosphate-glucose (ADP−glucose), guanosine diphosphate−mannuronic acid (GDP−mannuronic acid), and uridine diphosphate−N-acetyl glucosamine (UDP−N-acetyl glucosamine). The enzymes are proteins that act as natural catalysts to promote the reaction process meanwhile the different types of sugar may act as an energy source or substrate to promote the formation of a polymer. Furthermore, the formation process of exopolysaccharides and capsular polysaccharides are usually the limiting rate steps that can influence the flux of carbon to generate high molecular weight

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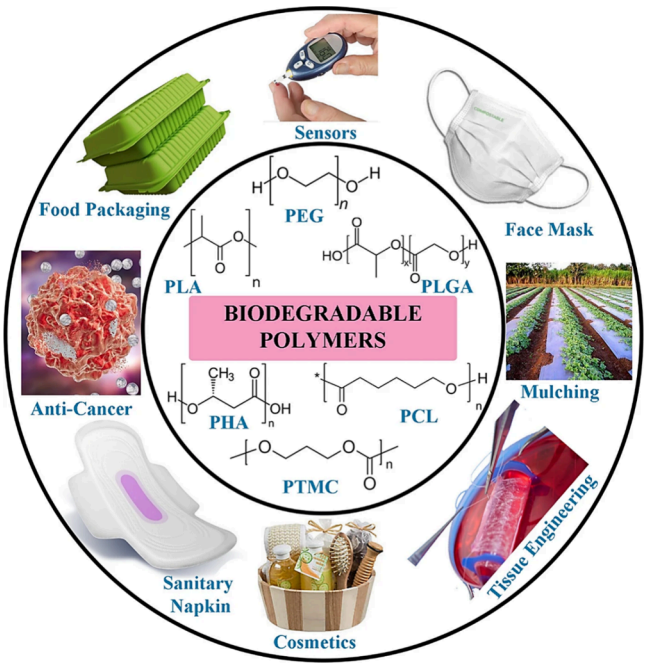

Figure 2. Biodegradable polymers and their main applications. Adapted with permission.[22] Copyright 2022, Springer Nature.

exopolymers. The bacterial polymer biosynthesis involves several other steps as its schematics are shown in Figure 3.

The complexity of such processes has been studied over the years with the aid of genome sequencing, cloning, functional genomics along other characterizations as a way to provide more information regarding the synthetic pathways of biopolymers produced by bacteria.[23−26] In this sense, the production of biopolymers such as PHA, poly-γ-glutamate (PγGA), and cyanophycin granule peptide (CGP) had its processes optimized.[27−30] PHAs are one of the most produced biopolymers through fermentation by recombinant *E. coli* which can undergo an *in vivo* tailoring process.[31] Based on that, the *in vivo* process for the manufacturing of PHA can follow different pathways which can be either as exopolymer or capsular polymer. In the case of exopolymer, the precursor substrate is absorbed by the bacteria which is converted to the activated precursor. Following that, the activated precursor can undergo the action of a polymerizing enzyme that leads to the formation of a polymer on the outer cell wall of the bacteria. On the other hand, the activated precursor can be in contact with polymer-modifying enzymes that lead to the formation of different polymers that can be obtained in capsular form. This process is schematized in Figure 4a. Furthermore, the synthesis of biopolymers can also be performed *in vitro*. The type of biopolymer can be tailored based on the substrate used as when it enters in contact with the polymerizing enzyme it can lead to the formation of a specific type of biopolymer. In addition to that, an isolated biopolymer can be further modified by either introducing an enzyme capable of functionalizing the biopolymer or by performing a chemical modification. The schematic for this process is presented in Figure 4b.

Notably, the substrate can influence the type of biopolymer. The bacteria can also produce different biopolymers along with promoting modifications to its chemical structure. Under this line, there are several types of bacteria used for the synthesis of biopolymers for example *Cupriavidus necator* which was also known as *Ralstonia eutropha* as well as *Pseudomonas sp.* are

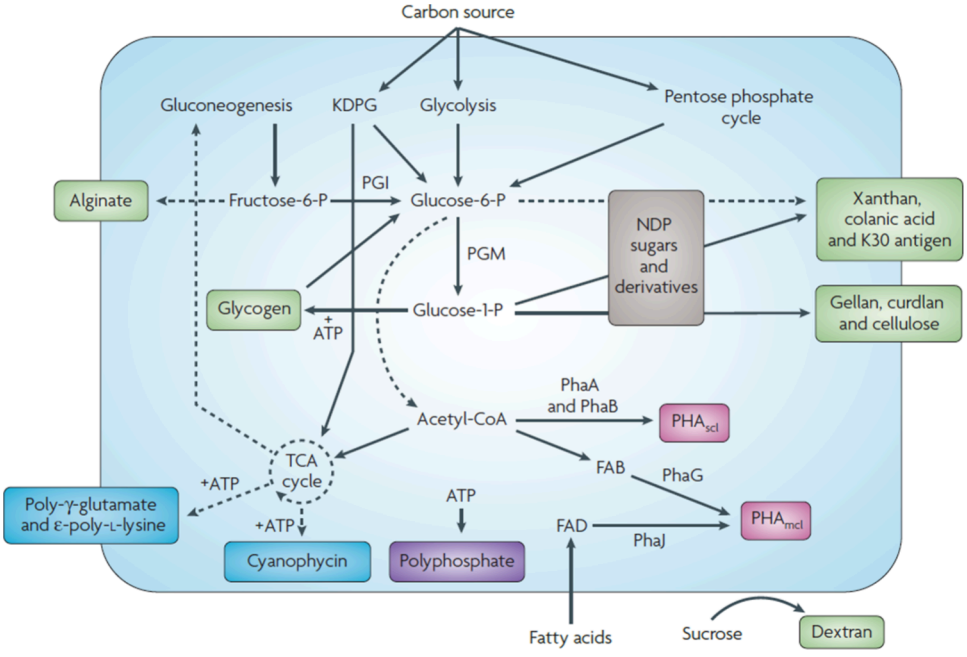

Figure 3. Main bacterial metabolic routes for the synthesis of different polymers. Solid lines represent the pathways for the primary metabolic with intermediates of the biopolymers or processes catalyzed by enzymes to form the polymer precursor. The dashed lines describe secondary enzymatic steps. The color of the boxes represents different types of polymers such as polysaccharides (green), polyesters (pink), polyamides (blue), and inorganic polyphosphate (purple). Furthermore, the terms described are tricarboxylic acid (TCA) cycle, medium chain length PHAs (PHA_{mcl}), short chain length PHAs (PHA_{scl}), PHA synthesis enzyme (Pha), phosphoglucomutase (PGM), phosphoglucoisomerase (PGI), phosphate (P), nucleoside 5′-diphosphate (NDP), 2-keto-3-deoxy-6-phosphogluconate (KDPG), fatty acid β-oxidation (FAD), and fatty acid *de novo* biosynthesis (FAB). Adapted with permission.[10] Copyright 2010, Springer Nature.

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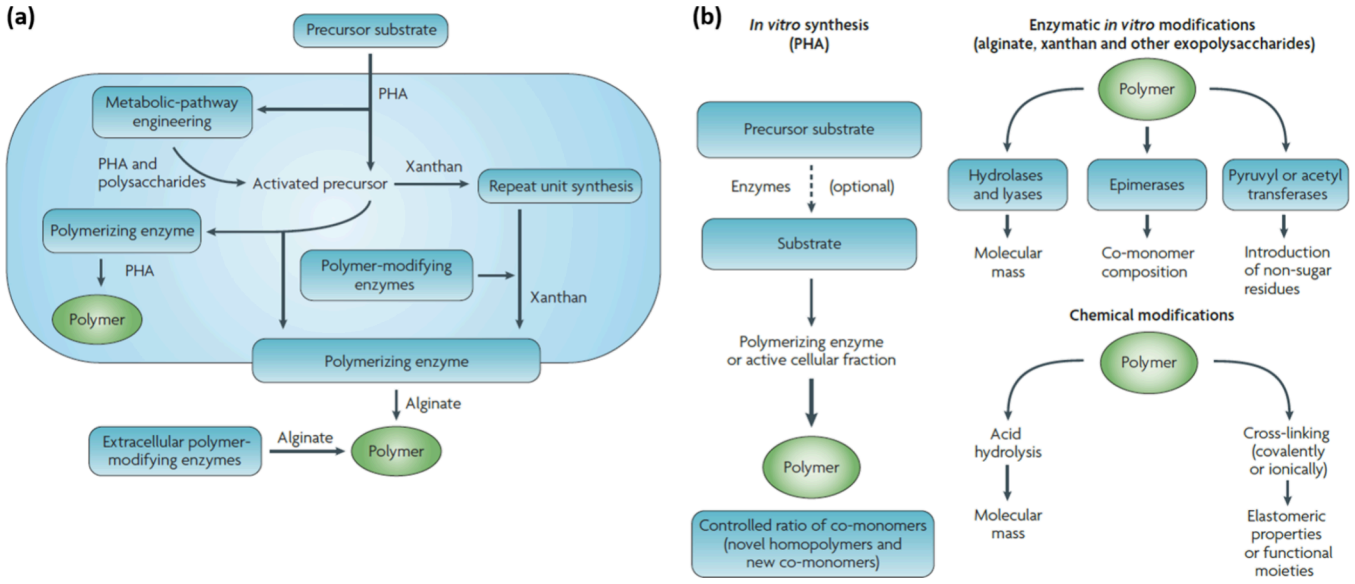

Figure 4. Schematic displaying some of the strategies to produce biopolymers. (a) *In-vivo* process to obtain either an exopolymer or capsulate polymer with optimized yield or tailored properties based on the type of enzyme and precursor utilized. (b) *In-vitro* process for the fabrication of biopolymers which can be obtained using specific substrates exposed to polymerizing enzymes or chemical modifications. Adapted with permission.[10] Copyright 2010, Springer Nature.

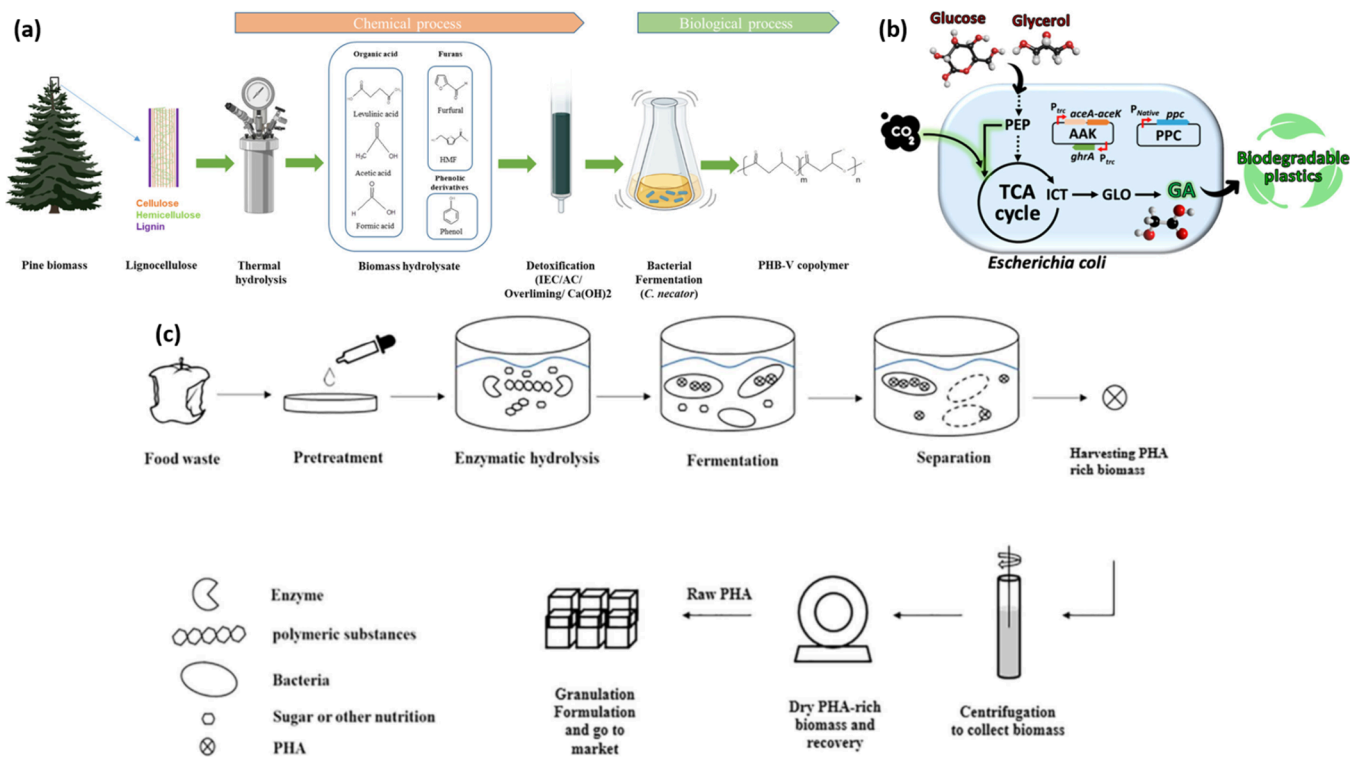

Figure 5. (a) Schematics for the biosynthesis of PHB-V copolymer through levunilic acid as substrate performed by *Cupriavidus necator*. Adapted with permission.[51] Copyright 2021, American Chemical Society. (b) Scheme displaying the biosynthetic route of genetically engineered *Escherichia coli* strains to obtain glutamic acid with lower CO_2 consumption while using glucose and glycerol as substrate. The glutamic acid could be further polymerized into PGA. Adapted with permission.[52] Copyright 2023, American Chemical Society. (c) Step process for the biosynthesis of PHA. Adapted with permission.[53] Copyright 2019, The Authors. Published by Elsevier Ltd. This is an open-access article under the Creative Commons CC-BY license.

bacteria capable of synthesizing different types of PHAs.[32−36] Also, *Xanthomonas campestris* are widely used bacteria for the manufacturing of xanthan gum which is used as a thickening and stabilizing agent in food and cosmetics.[37,38] *Bacillus subtilis* is another bacteria able to produce polyglutamic acid (PGA) which is used in biomedical, pharmaceutical, and food industries.[39] Similarly, *Azobacter vinelandii* can produce alginate and *Streptomyces sp.* can synthesize several polymers such as cellulose, chitin, and pullulan which can also be employed in the biomedical, pharmaceutical, and food

https://doi.org/10.1021/acsomega.3c07372
ACS Omega 2024, 9, 8666−8686

industries.[40−45] The broad number of polymers that can be obtained from bacteria makes it an attractive asset for industry. It is worth noting that the polymer's yield is influenced by the relative amount and type of substrate and by the processing techniques employed. For instance, capsular polymers such as PHAs require the disruption of the bacterial cells for their extraction which leads to an increase in cost due to the separation steps needed. The approaches for that can be performed through micro- or nanofiltration, chromatography, precipitation, crystallization, or solvent extraction, for instance. It is also worth noting that, that biopolymers present some advantages in comparison to synthetical ones as toxic metal-based catalysts are not used and there is usually a lower cost on the disposal. Meanwhile, synthetical polymers have their price influenced by crude oil, and biopolymers have their price influenced by starch, sugars, vegetable oils, and glycerol, which tend to present fewer fluctuations in terms of price.

Alongside the convenient source of substrates, biopolymers can be synthesized by microorganisms through several routes such as biosynthesis, fermentation, excretion, or through genetic engineering. In the case of biosynthesis, microorganisms can synthesize proteins using ribosomes which can polymerize amino acids into proteins or by bonding sugar molecules to form polysaccharides. Another example of biosynthesis consists of some bacteria that can convert CO_2 into PHBs through a photosynthetic or autotrophic process.[46] Fermentation is a widely used process by which the bacteria convert a substrate, in the absence or lack of oxygen, into monomers such as lactic acid or polymers such as PHAs.[47] Microorganisms can also produce extracellular polymeric substances (EPS) through the excretion process some examples include cellulose, PGA, Curdlan, and alginate, for instance.[48−50] Based on the several ways that microorganisms can synthesize biopolymers, Mohan et al.[51] investigated the use of *Cupriavidus necator* for the synthesis of PHAs, i.e., PHB-V copolymer, through consumption of levunilic acid obtained from acid treatment of pine sawdust which was followed by extensive detoxification processes to diminish the presence of compounds that could act as inhibitors for the bacterial biosynthesis such as phenolic compounds (phenol), organic acids (acetic acid and formic acid), furanics (furfural and 5-hydroxymethylfurfural (HMF)), and Ni. The optimal conditions for the fermentation of the lignocellulosic biowaste were obtained through detoxification methods based on ion-exchange purification (IEP) followed by activated carbon (AC), and pH control through $Ca(OH)_2$. Based on that, *Cupriavidus necator* presented an optimized fermentation process for the biosynthesis of PHAs after the detoxification process. Also, the presence of Ni was the most influential inhibitor for biosynthesis. The schematic for the chemical and biological processes for the conversion of biomass into PHAs is presented in Figure 5a. In another study, Yi et al.[52] used a genetically engineered *Escherichia coli* that could synthesize glutamic acid while reducing around 72.6% of CO_2 consumption, in comparison to the nonmodified strains, while using glucose and glycerol as carbon sources. The CO_2 uptake of the bacteria was optimized into the Krebs cycle through the addition of the enzymes such as pyruvate carboxylase (*pyc*) and phosphoenolpyruvate carboxylase (*ppc*) which led to a glutamic acid productivity and titer of 0.23 g/L/h and 11.9 g/L. Glutamic acid could be extracted and polymerized into PGA. Despite the specific requirements and techniques required to produce the monomer, this example described a way to optimize the biosynthesis of materials that could provide an eco-friendlier approach. The schematic for the biosynthesis of glutamic acid from *Escherichia coli* is presented in Figure 5b. The fermentation performed by bacteria is a widely explored biochemical metabolism as it can yield a myriad of products that can be used in the food, packing, and pharmaceutical industries, among others. PHAs are among the most explored bioplastics synthesized by bacteria. Such polymers are produced when the microorganism is exposed to environmental stress such as lack of nutrients, pH and temperature variations, and limited presence of electron donors or acceptors, among other factors.[53] PHA is synthesized and stored in the form of granules in the cytoplasm which can be later extracted through cell lysis.[54] The properties of PHA are also influenced by the environment conditions as well as the type of bacteria and conditions for the fermentation process.[55] The main procedures involved in the biosynthetic process of PHA are illustrated in Figure 5c.

3. SYNTHESIS OF BIOPLASTICS USING BACTERIA

The overall manufacturing of bioplastics derived from bacteria passes through a multistep process based on strain selection, genetic engineering, substrate preparation, fermentation, synthesis, harvesting, recovery, purification, refinement, formulation, and processing. Strain selection is important to introduce the microbe with the most satisfactory enzymatic activity concerning substrate concentration and media at which is immersed to produce the polymer.[56] Genetic engineering usually consists of introducing a specific gene into the bacteria that enables it to improve polymer production as it can change some metabolic pathways to facilitate that process.[57] The substrate preparation and selection can greatly influence the polymer's properties and production efficiency. Some examples include sucrose, glucose, glycerol, lignocellulosic biomass among many others. Ideally, bacteria should consume a low-value bioproduct or waste as it leads to a more sustainable and economically convenient process.[58] Fermentation is one of the biochemical processes performed by bacteria to synthesize either the polymer or the monomer that is later used for polymerization. This step can be heavily influenced by several parameters such as pH, temperature, stirring, nutrients, oxygen concentrations, among others.[59,60] Hence, properly controlling the parameters is a crucial aspect of the synthesis. The metabolic pathway may change based on the substrate utilized which can lead to a different type of biopolymer. The harvesting, recovery, and purification processes are performed to separate and purify the biopolymer from the fermentation mixture and byproducts which can be performed through filtration, centrifugation, chromatography, or other purification techniques. After the biopolymer is obtained several techniques can be applied in terms of processing such as injection molding, melt extrusion, solvent casting, 3D printing, among others to obtain the polymer in the desired shape.[61−64]

Furthermore, varying certain parameters during bacterial polymer production can greatly influence the manufacturing rate and the polymer's properties. Based on that, some of the influential factors can be divided into physical or chemical. The former is related to osmotic pressure and temperature whereas the latter consists of oxygen and nutrient availability, pH variation, and microbial inhibitors. Osmotic pressure can be induced in a microbial media due to the presence of inorganic salts that can be on substrates such as molasses, a byproduct of sugar production, proteins derived from dairies, or glycerol

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ACS Omega 2024, 9, 8666−8686

formed as a byproduct from biodiesel.[65−67] During the biochemical process, salts may be added to control the pH which leads to an increase in osmotic pressure against the bacterial cell wall. It has been observed that bacteria that could synthesize relatively larger PHA granules could withstand larger osmotic pressures as the PHA can function as an intracellular scaffold that can prevent the disruption of the bacteria's cell.[68] Under such conditions, halophile bacteria may be a suitable candidate for the synthesis of PHA since the high concentration of salt can make the environment more selective toward such type of microorganism.[69] Furthermore, halophiles can consume substrates such as lignocellulose hydrolysates which present an inherently high salt concentration.[70] Along with that, seawater can serve as a low-cost cultivation environment.[71] Some examples of halophilic bacteria that can synthesize PHAs are *Halomonas sp.*,[72,73] *Halobacterium genus*,[74−76] *Halobacterium halobium*,[77,78] and *Halobacterium noricense*.[79,80] Halophiles can be convenient for industrial applications since they can operate in an aggressive environment in comparison to other bacteria. Through that, the environment can be partially sterilized from other microorganisms that would act as a contaminant.[69] Furthermore, the isolation of PHA can be performed through low-cost hypotonic lysis. Other products that include ectoine, which are small amino acid molecules, and trehalose, a disaccharide, are also biosynthesized by the bacteria. Such compounds are used in the cosmetic, food, and pharmaceutical industries.[81] Aside from the specific case of halophiles, the addition of a controlled amount of salt such as NaCl can prompt the biosynthesis of PHA even for nonhalophilic bacteria strains. A previous report demonstrated an optimization of PHA accumulation in *Cupriavidus necator* in a media containing a salt concentration of 10 g/L.[82,83] However, there have been some cases at which concentrations of 50 g/L of salt could increase the PHA synthesis in *Spirulina subsalsa*, cyanobacteria, as well as in *Bacillus meagaterium*.[84,85] It has been observed that NaCl concentrations of around 10 to 15 g/L are more effective in inducing the synthesis of PHA in nonhalophilic bacteria as concentrations above this value can halt the synthesis of PHA and induce its hydrolysis. Such phenomena may occur as the microorganism may use the PHA's monomers as a source of energy to withstand the environmental conditions.[86]

Temperature plays a major role in the metabolism of bacteria as it can direct certain types of synthesis based on that condition. In this regard, both low and high temperatures can induce the synthesis of PHA in a microbial broth. In this sense bacteria such as *Pseudomonas extremaustralis* and *Cupriavidus necator* were able to synthesize PHA at cold temperatures as the latter is industrially employed for the synthesis of PHA at temperatures around 4 °C.[87−89] On the other hand, some microorganisms including *Aeromonas hydrophila*,[90] *Pseudomonas* spp.,[91,92] and *Azospirillum brasilense*[93,94] can synthesize PHA when exposed to heat stress. For that, the bacteria produce the biopolymer as a defense response to avoid the denaturation of enzymes. Furthermore, even though the accumulation of PHA is not as common for thermophiles when compared to halophiles there are still some cases that can be potentially employed in the industry. Some examples are *Caldimonas taiwanensis* which can synthesize PHA from starch and *Chelatococcus thermostellatus* which can function in temperatures around 50 °C. It is an advantageous condition to keep a monoseptic environment as it avoids the costs of sterilization.[95,96] Another attractive example of a thermophile is *Schlegelella thermodepolymerans* as these bacteria are more selective toward xylose instead of glucose which makes it more convenient for the consumption of lignocellulose-based resources for the synthesis of PHA.[97]

Pressurized environments are often employed for the cultivation of microorganisms as it increases the dissolution of O_2 which leads to an optimization of aerobic processes due to a higher oxygen transfer rate. However, it can also negatively affect the system as it may increase the dissolution of CO_2 which can be undesired in certain media. A previous work performed by Follonier et al.[98] demonstrated the effect of a relatively high pressurized environment on the production of PHA_{mcl} synthesized by *Pseudomonas putida*. It was observed that a pressure of 7 bar supported the synthesis of PHA but led to a decrease in bacterial growth rate. Furthermore, it has been shown that some microbes may produce PHA in response to the stress applied by high hydrodynamic pressurized environments.[99] However, low molecular PHA or monomers are obtained which are proposed to function as piezolytes to protect some of the internal compounds of the microbe from the effects of the hydrodynamic pressure. Some of the bacteria in that regard include *Salinimonas sediminis*,[100] *Photobacterium profundum*,[101] *Halomonas profundus*.[102] Hence, such a trend was observed in other studies suggesting that high pressure leads to some increase in PHA accumulation with relatively low molecular weight along with low bacterial proliferation.[98,103,104]

The presence of oxygen is a critical parameter for biochemical reactions performed by a microbe. It is worth noting that aerobic processes are predominant for the synthesis of PHA as the bacteria can utilize the dissolved O_2 as an electron acceptor.[105] Hence, it is usually advantageous for the microbial cells to be in an O_2-rich atmosphere as otherwise, it leads to a decrease in the culture's growth rate. Also, if NO_3^- is employed as a N source the lack of oxygen can promote the conversion of NO_3^- to NO_2^- which is an inhibitor of microbial growth. Such a condition is highly undesirable since PHA is synthesized within the cell and therefore the decrease in biomass concentration leads to lower volumetric production. On the other hand, in terms of cell metabolism, it has been observed that oxygen limitation can promote the cell to produce more PHA in some cases.[106] Under this line, it has been observed that applying a microaerophilic condition promoted the accumulation of PHA_{mcl} by *Pseudomonas putida*.[107] For this case, it was noted that 1 to 5% of dissolved oxygen (DO) at 30 °C promoted an increase in the production of PHA_{mcl}. Yet, upon further reduction of DO, there was yet another increment in the PHA_{mcl} biosynthesis. Furthermore, when a volumetric oxygen mass transfer coefficient (k_La) of 38 h^{-1} reached the DO was below the detection limit, and the PHA_{mcl} content as well as its yield reached the highest levels. In a follow-up study, the authors proposed that the inherent limitation of O_2 induced in a culture with high cell density could be used as a convenient approach to increase the biosynthesis of PHA_{mcl} from fatty acids as substrate.[108] A different strategy was performed by Faccin et al.[109] who utilized partial oxygen limitation during the cultivation time which led to the formation of PHA_{scl} by *Bacillus megaterium*. From that, it was notable that PHA biosynthesis was strongly influenced by the concentration of O_2 in the media. In this sense, oxygen limitation along with mild oxidative pressure can be employed to enhance the PHA production. However, optimization is required to prevent the environment from

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ACS Omega 2024, 9, 8666−8686

becoming too harsh on the cells as it is meant to stimulate them toward a positive metabolic effect associated with the applied stress. It is also worth noting that the applications of stresses such as oxygen or nutrient limitation can prevent microbial growth. Hence, it is more reasonable to introduce such conditions at the beginning of the stationary phase as beyond that point there is not a considerable reproduction of bacteria.

The pH is another core factor for the efficiency of the biosynthesis of polymers. A complex study was performed by Khosravi-Darani et al.[110] where *Microbacterium sp*. was used to produce PHA from CH_4. After selecting the proper media, several parameters were evaluated such as inoculum age, concentration of Na_2HPO_4 as N source, CH_4 to air ratio, and pH. From that, it was observed that pH was the most influential parameter in PHA biosynthesis. The pH can define some growth kinetics of the microbial system in a way that a pH close to the optimal condition can enhance cell density. Such a process is important as it relates to the amount of bioactive cells that are filled with PHA. Consequently, it also leads to high volumetric productivity for the biopolymer. Another important factor is that the pH can alter the kinetics of enzymes and therefore, finding the optimal pH conditions enables a higher synthase activity leading to a high specific productivity of the biopolymer. However, it has been shown that a lower synthase activity, in other words, a lower amount of enzymes active per cell, can result in the formation of biopolymers such as PHA with higher molecular weight.[111,112] Suzuki et al.[113] performed a study with *Rhodobacter sphaeroides* that showed better activity at alkaline pH values. In this sense, at pH = 7.5 optimal cell multiplication was observed whereas a pH between 8.0 to 8.5 led to an increase in mass fraction for PHA within the bacterial cells. Hence, it was concluded that to reach the maximum volumetric productivity there should be proper control of the pH in the cultivation phase and at the stationary phase. Such a trend has been observed in several studies which suggested that there is a difference between the pH that induces cell growth and the pH that induces volumetric productivity.[114−116]

Another parameter that should be considered when performing biosynthesis is microbial inhibitors. It is known that using low-cost waste components from agriculture or the food industry is highly desired as substrates to promote the feasible production of PHA. An example of that is waste glycerol from biodiesel which can be a promising substrate for the biosynthesis of PHA. However, impurities such as methanol, fatty acids, hydroxide residues, or salts can inhibit some microbial activity.[117,118] One of the goals is to find a strain that can either tolerate or metabolize the impurities that might be present in the substrate. One example is *Methylomonas extorquens* which has a preference for converting methanol before glycerol as a C source.[119] Such characteristics are important since methanol can be a strong inhibitor for some strains. Other microbial inhibitors are phenolic-based compounds, organic acids, i.e., formic, acetic, and levulinic acids, and furfurals which can be found in substrates based on lignocellulose. It has been proposed that phenolic compounds interact with the bacterial cell membrane and promote a change in the protein-to-lipid ratio. Such an effect can lead to protein denaturation and precipitation.[120,121] In addition to that, organic acids can also jeopardize cell activity as they can diffuse through the cell membrane and dissociate within it. Such a process leads to a decrease in the inner cell's pH which decreases the metabolic activity.[86] Furfurals are also toxic compounds as they can hinder the conversion of ATP into ADP, blocking a route for the cell to acquire energy. Some of the common approaches to removing the inhibitor from the system consists of overliming which is a process in which the inhibitors are precipitated and destabilized by lime. It can be used on hemicellulose hydrolysate for PHA biosynthesis.[122] Also, adsorbents such as lignite or activated carbon can be employed to remove inhibitors.[123]

Promoting an optimal increase in the molecular weight of a polymer is often desired to achieve certain properties. Under this line, directing the biopolymer's synthesis to obtain longer chains can be achieved by selecting the proper bacteria strain.[124] Yet, the final product can undergo considerable variation since several factors can impact its synthesis. First, certain bacteria strains can naturally synthesize biopolymers with higher molecular weight. In this sense, *Cupriavidus necator* is an example of a bacteria that can synthesize PHAs with relatively higher molecular weight.[125] Some strains of *Pseudomonas putida* can also do so with the advantage that they can consume a larger variety of carbon sources.[126] Other bacteria include *Cupriavidus taiwanensis*,[127] *Bacillus megaterium*,[128] *Aeromonas hydrophila*,[129] among others. Even though these microorganisms can synthesize PHAs, their properties would often be different not only due to the different bacteria strains but also due to other factors such as the genetic variations of the bacteria itself, carbon source utilized for the synthesis, parameters of the fermentation process, strain stability, among other factors. Because of such factors, obtaining a consistently precise molecular weight and properties for biopolymers obtained from bacteria can be a challenge. On the other hand, a broader range of materials can be obtained giving more room for research and optimization.

4. APPLICATIONS OF BIOPLASTICS

The sustainable and ecofriendly credentials of materials are becoming more notable features given the current concern with the environment. Yet, presenting competitive properties to enable their use in industrial sectors is a core aspect of the incorporation in the market. For that, bioplastics currently find some applications in packing, agricultural films, and medical devices. The most used biobased plastics for the packing industry are PLA, cellulose- and starch-based materials along with others such as PHAs, PHB, and PBS.[130] This is an important industrial segment for bioplastics as more than half of the worldwide manufacturing is used in the packing industry.[131] In this sense, PLA is being explored as a material suitable for packing as it can be processed through several techniques such as injection molding, blow molding, extrusion over cast film extrusion, and thermoforming.[132−136]

The application of bioplastics in the packing industry is highly sought after as the biodegradability of such materials greatly diminishes the environmental impact caused by nondegradable materials. Alongside that, bioplastics can be processed through several techniques which make them convenient for industrial processes. Because of that, bioplastics can potentially cover most of the applications currently filled by conventional plastics. Yet, it is still required to decrease the overall cost and availability of these bioplastics to make them more competitive with the already established nondegradable and petrochemical counterparts. A schematic of the application of bioplastics in the packing industry in comparison to some conventional plastics is presented in Figure 6.

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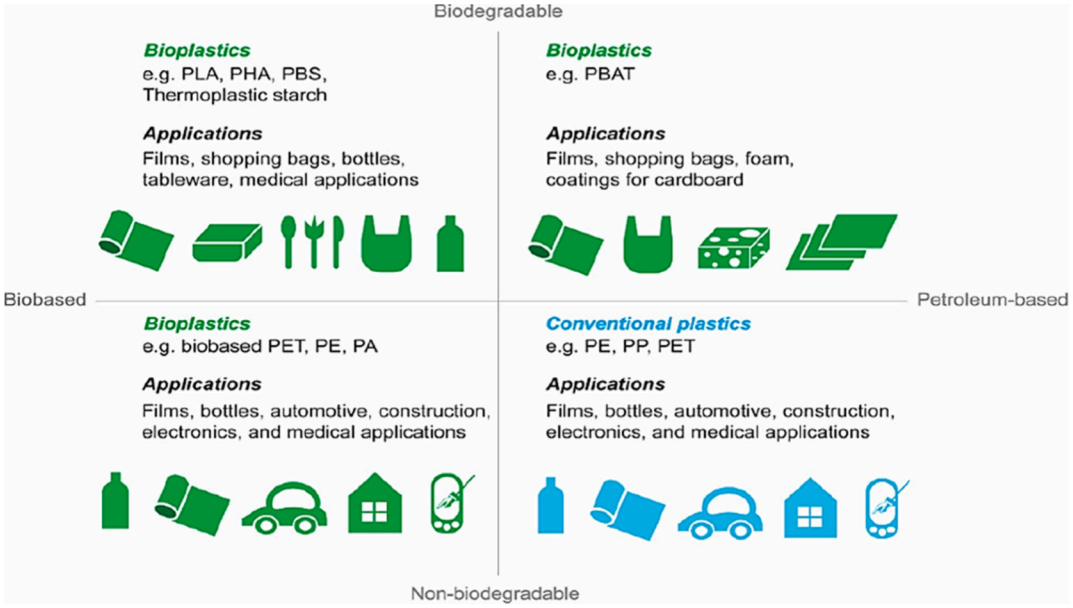

Figure 6. Schematic of some bioplastics and their application in the packing industry along with conventional plastics. Adapted with permission.[137] Copyright 2020, American Chemical Society.

Despite being a common widespread application, packing requires materials that can cover a broad range of properties in practical terms such as proper water and vapor permeability, varied mechanical properties, transparency, printability, anti-fogging, and satisfactory shelf life. It is known that non-degradable biobased PE, PET, or PP display the same properties when compared to polymers originating from petrochemical sources. However, most of the biodegradable bioplastics display relatively lower mechanical properties when compared to those such as lower elongation, impact strength, and higher flexural modes which refer to lower ductility, toughness, and flexibility, respectively. Despite that, some bioplastics such as PBAT are comparable to low-density polyethylene (LDPE). Another case is a PHA named poly-3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHBV) which displays a similar heat deflection temperature (HDT) when compared to polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS). In this sense, HDT is defined as the temperature that causes a material to deform when a specific load is applied which is a crucial aspect in the food packing industry. Furthermore, both PLA and PBAT can present thermal degradations around 350 to 400 °C which are similar to PP, PET, and PS.[138] It is also worth noting that, most biodegradable bioplastics present oxygenated chemical groups in their structure which leads to a more hydrophilic character and therefore lower moisture barriers when compared to conventional plastics.[139] Because of that, the application of such bioplastics should be directed toward short shelf life products. Another important aspect that surrounds bioplastics is that their chemical structure is mostly linear with a low cross-linking degree. Because of that, some of its rheological properties such as melt strength, and viscosity are usually lower when compared to conventional plastics. Such aspects can hinder their use of processing techniques such as vacuum thermoforming or film blowing since high melt strength is required. Despite such disadvantages biodegradable bioplastics are manufactured into consumable goods from several companies.

Even though there are some disparities in terms of properties when comparing bioplastics and conventional plastics there are some approaches that can reduce these differences. In terms of mechanical properties bioplastics tend to be relatively more brittle and rigid. There are several approaches available that can counter such drawbacks, the most common being polymeric blending. Such a process consists of mixing different polymeric materials in specific ratios to modulate their properties to reach a desired value. External plasticization can be performed to improve the chain mobility and therefore flexibility. One example was performed by Zhang et al.[140] who improved the flexibility and ductility of maize starch through external plasticization with an addition of 10 to 25 wt % of a hyperbranched polyester. Yet, it could still lead to phase separation due to low mixability, hence further adjustments such as the addition of surfactants or other components could further optimize the properties.[141] Also, simple blending between biopolymers such as PHAs with PLA, PCL, starch, and cellulosic-based compounds, among others has been performed as a cost-effective approach to tune the mechanical properties.[142,143]

Internal plasticization can also be performed as it consists of chemically grafting a monomeric unit to the polymer which can lead to a less ordered structure and therefore more flexible.[144] An example from the literature was based on the internal plasticization of hemicellulose through vinyl laurate which led to an improvement in tensile elongation of 200%.[145] In their work, hemicellulose laurate (LH) was synthesized through a transesterification reaction between hemicelluloses and vinyl laurate (VL) in ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim]OAc) which acted simultaneously as a solvent and activating agent. The chemical attachment of VL into the structure of hemicellulose increased the hydrophobicity of the LH as the hydroxyls were converted into ester groups with a long aliphatic chain from the VL. Such a factor was important to make the biopolymer more processable in organic solvents to obtain films through solvent casting method. Through that, the organic solvent could be easily evaporated to form the LHs packing films. The evaporation of

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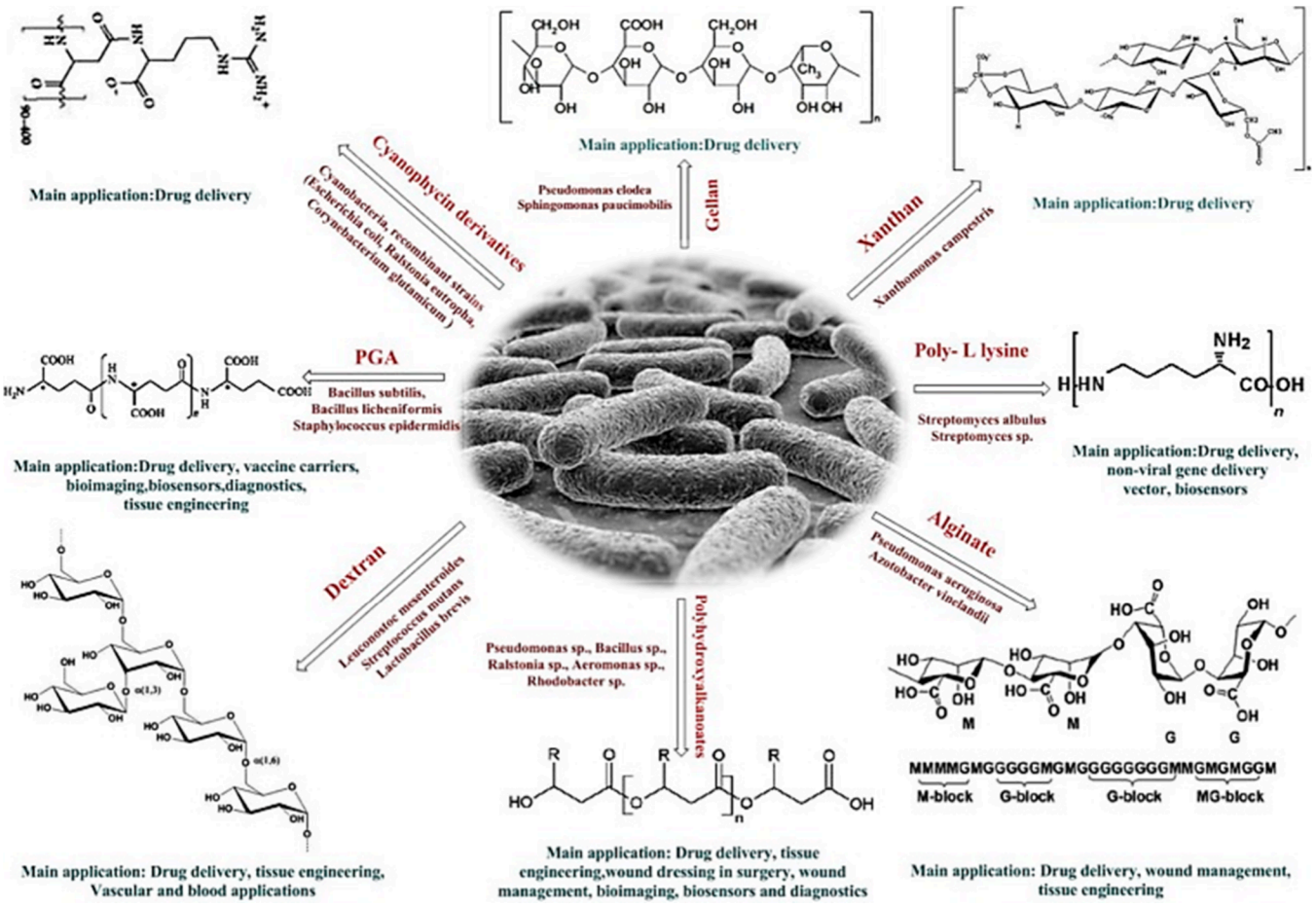

Figure 7. Different types of biopolymers derived from bacteria can be applied in the biomedical field for various uses. Adapted with permission.[174] Copyright 2016, Elsevier.

solvent was an important step to introduce micropores into the film formation as a higher solubility of the LH films led to the formation of higher number of pores with more regular size. Furthermore, the presence of long aliphatic chains from VL promoted a densely cross section networked structure that provided good oxygen and water barrier for the LH films. On top of that, the presence of laurate chains introduced some degree of antioxidant behavior which is an important factor to increase the shelf life of food in the packing. Throughout that, the authors could obtain a film that preserved green chili peppers from longer when compared to a commercial clipping wrap.

Biodegradable bioplastics have been widely employed in the agricultural sector as mulch films. Some of the polymers used for that application include starch-based polymers derived from corn or potato, cellulose, cellulosic fibers, and blends of PLA with PBAT, among many others.[146−149] Aside from its inherently ecofriendly aspects, the use of such materials can improve the overall quality of soil in terms of chemical, physical, and biological properties. In this sense, mulches can maintain the soil's moisture constant, reduce erosive processes, control the microenvironment temperature, and improve plant rooting and growth.[150,151] Associated with those factors, biodegradable plastic mulches can improve the microenvironmental rhizosphere as they can maintain a controlled temperature and moisture near the rooting zone of plants. Such conditions enhance the population of microbes that are beneficial for plant growth such as N-fixing bacteria. Another important feature of biodegradable film mulches is their capability to suppress the growth of weed, which competes for nutrients against the crops. It has been observed that biodegradable bioplastics that present a darker color are more effective in preventing the growth of weeds as it prevents light transmittance. Based on that, a study performed by Cowan et al.[152] showed that both biodegradable bioplastics and petrochemical-based PE had similar results in preventing weed growth when obtained in brown or black colors. In this sense, the use of biodegradable mulch films can optimize the growth of plants as well as decrease the maintenance cost of a crop as it can reduce the amount of water, control the growth weed, and promote the proliferation of microbes that support the development of the plant by providing important nutrients.

The use of biodegradable mulch films can also improve the soil's properties. It has been observed that even though rain is a crucial element for the soil it can, in some cases, cause the breakdown of aggregates which is also influenced by the drying and wetting cycles as well as the raindrop's kinetic energy.[153,154] Based on that, a study performed by Domagała-Swiatkiewicz et al.[155] analyzed the effect of water on bare soil treatment and PBS-based mulch films in an onion crop. It was observed that the soil presenting the PBS-based mulch film could maintain stable aggregates that had relatively larger diameters between 2.5 and 4.0 mm whereas the bare soil had aggregates of around 0.25 and 1.0 mm. Such variation in size led to a decrease in bulk density and therefore a decrease in soil's compaction.[156] Relatively larger particulates could

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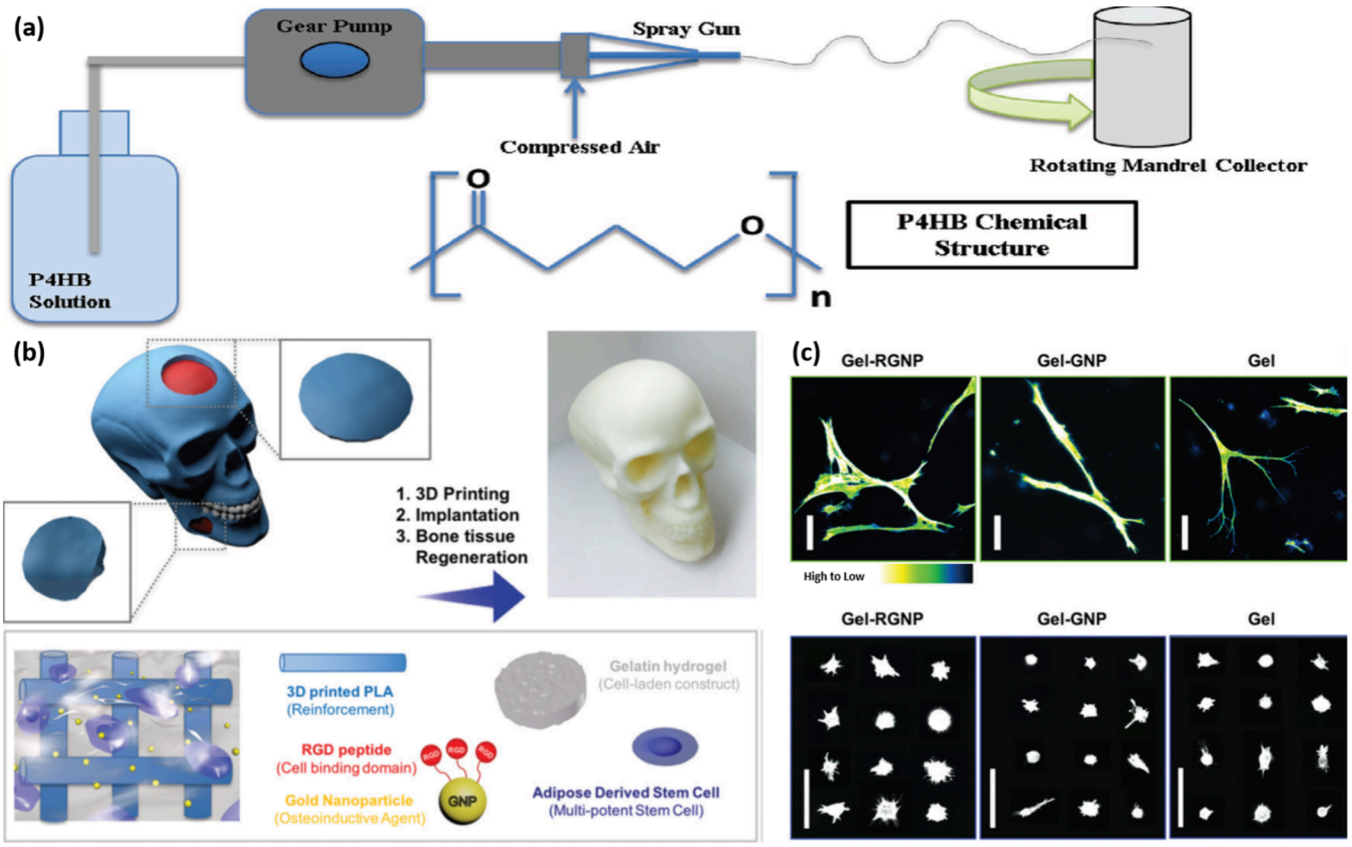

Figure 8. (a) Schematics to produce P4HB-based scaffold through dry spinning technique. Adapted with permission.[179] Copyright 2017, John Wiley and Sons. (b) Schematics for the hydrogel composite based on 3D printed PLA incorporated with gelatin containing Au nanoparticles conjugated with RGD suitable for ADSC adhesion and growth. (c) Upper: Organization of actin cytoskeletal for the ADSCs after seeding of 24 h (scale bar: 100 μm). Lower: ADSCs outlines after seeding of 24 h. Adapted with permission.[180] Copyright 2017, Royal Society of Chemistry.

likely allow more space between the particles. Such conditions may facilitate water diffusion and air permeation into the soil. On the other hand, small particulates may become more compact as the rain hits its surface which may prevent the aeration and wetting of soil, therefore causing the crop to decrease its nutrient absorption and breathability.[157,158] Under this effect, it is worth noting that soil aeration is an important aspect of crop growth. For that, the biodegradable mulch films can maintain the soil's porosity by avoiding its compaction from the rain. Through that, better control between the water and air ratio can be promoted. Also, several parameters should be considered such as soil type, pH, weather, and organic matter content, among many others that can influence crop growth. Furthermore, other studies showed the positive influence of biodegradable mulch films on moisture retention as well as a decrease in temperature variation.[159,160] Such factors play an important role in plant development as they can create a more stable environment along with saving the costs of irrigation and the use of fertilizers, which is a core aspect of drier soils.[161] Lastly, the use of biodegradable mulch films instead of nonbiodegradable ones is a highly desired factor for more sustainable and effective plant growth since the latter often presents a laborious recycling process along with the formation of residues that form macro and microplastics, which are harmful to the environment. Oppositely, the biodegradable mulch films are a sustainable alternative as it can be naturally incorporated into the soil to serve as nutrients for the crop at the end of its service meanwhile presenting comparable properties to nonbiodegradable mulch films. Hence, finding ways to decrease the manufacturing cost of biodegradable mulch films is an important factor to facilitate their access in the agricultural fields. Alongside that, these biodegradable polymers can lead to several advantages in the long term, which can make them more convenient than nonbiodegradable ones.

One of the most researched applications of biodegradable polymers is within the medical and biomedical fields as these materials are sought as drug delivery systems,[162−164] therapeutic devices,[162,163,165] 3D implants, and scaffolds for tissue regeneration.[166−169] Such applications are inherently demanding since a drug delivery system must satisfy some requirements such as having a high drug encapsulation efficiency, good drug release rate to promote optimum therapeutic effect, increased residence time in the targeted region, biodegradation within a time that matches with the healing of the targeted tissue, and the polymer should degrade into fragments that do not trigger an allergic reaction of an inflammatory response from the immunological system.[170−172] To satisfy such requirements some of the parameters taken into consideration are polymeric composition, molecular weight, surface charge, tacticity, nanoparticle size distribution, colloidal stability, and proper hydrophilic/hydrophobic ratio.[173] There is a myriad of bioplastics with properties that can make them suitable for applications in the biomedical and medical fields some of the most known examples are provided in Figure 7.

From that is worth noting that, the importance of such technology ultimately lies in improving drug efficiency while

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ACS Omega 2024, 9, 8666−8686

simultaneously diminishing the side effects due to a lack of therapeutic potential when the drug is used in its free form. One example from the literature was based on a nanoparticle composed of a PLA core and an outer layer of PEG that was decorated with a prostate-specific membrane antigen.[175] The nanoparticle polymeric composite was highly specific toward the solid tumor cells. In this sense, PLA was used as a core due to its better interaction with the docetaxel drug, which improved the overall drug encapsulation efficiency. On the other hand, the outer layer of PEG could be decorated with the prostate-specific antigen which functioned as the probe to recognize the tumor cells. Bioplastic polymers are viable candidates for *in vivo* implants as some of the most employed include collagen-based polymers and hyaluronic acid due to their inherent biocompatibility.[176] Yet, other bioplastics such as PLGA present relatively lower biocompatibility. Such an issue can be addressed by compositing the biopolymer with an extracellular matrix (ECM). Such a strategy was employed by Lih et al.[177] who introduced ECM into a PLGA-based scaffold as a means to proliferate renal cortical epithelial cells that were implanted in mice. The scaffold promoted the recovery of blood vessels along with the regeneration of glomeruli. The results obtained from this research could serve to reduce the need for dialysis for kidneys. In another work, Somekawa et al.[178] obtained a gel based on two copolymers: poly(L-lactic acid) and PEG (PLLA−PEG), and another copolymer based on poly(D-lactic acid) and PEG (PDLA−PEG). Then, both copolymers were dispersed in an aqueous solution to obtain a PLLA−PEG/PDLA−PEG suspension. The copolymeric composite displayed a sol-to-gel transition which occurred close in the range of body temperature. PLLA−PEG/PDLA−PEG gel was used as a potential compound that could promote the cavity reduction of left ventricular remodeling in myocardial infarction which made it a potential candidate for myocardial infarction application. Another example of tissue engineering and regeneration was studied by Masoumi et al.[179] who obtained poly-4-hydroxybutyrate (P4HB) biosynthesized by a strain of *Escherichia coli* K12. Furthermore, P4HB nonwoven scaffolds with high porosity were obtained through a dry spinning process as presented in Figure 8a.

Furthermore, a methacrylated gelatin (GelMa) was photo-cross-linked and employed as a scaffold for the mesenchymal stem cells to allow tissue ingrowth. Through that, the composited fibrous scaffold enabled the proper growth and elongation of cells. Also, the introduction of GelMa was advantageous to properly encapsulate the cells which led to the formation of a 3D tissue that spread throughout the scaffold. The combination of both materials provided satisfactory mechanical support as well as an anisotropic structure that could mimic some of the features of cardiovascular tissue. The hybrid scaffold displayed satisfactory properties in terms of biocompatibility, activity of myofibroblasts, and growth of aligned tissue with the scaffold's anisotropic structure. The development of 3D tissue regeneration materials can make use of hydrogels due to their high surface area which allows the cells to properly grow. However, this type of material may not be desired for the regeneration of musculoskeletal cells due to its lack of mechanical properties that differ from the actual tissue. Such hindrances can be countered by compositing different biopolymers to optimize their mechanical properties. Heo et al.[180] fabricated a composite based on PLA as reinforcement and (GelMa) hydrogel that was embedded with Au nanoparticles conjugated with argigine−glycine−aspartate (RGD), named RGNP, to improve the adhesion of adipose-derived stem cells (ADSC). The scheme for the hydrogel fabrication is presented in Figure 8b. The mechanical properties of the hydrogel could be controlled based on the PLA fiber spacing during the 3D printing process as shorter spacing led to higher compressive modulus. In this sense, the hydrogel composite's stiffness could be adjusted to a similar value of a mandibular bone. Furthermore, the proliferation, spreading, and organization of ADSCs were also analyzed. The hydrogel composite containing the RGNP (Gel-RGNP) enabled proper cell growth which presented the highest spreading and large lamellar morphology, suggesting a more satisfactory interaction with the hydrogel when compared to the composites based on the neat gel and gel containing only RGD (Gel-GNP). The cell growth process on the hydrogel composites is presented in Figure 8c. Such difference in cell interaction was attributed to the better affinity of Au nanoparticles which improved the cell adhesion, therefore facilitating their spreading and organization on the hydrogel's structure.[181,182] In another example, Czechowska et al.[183] fabricated a scaffold for bone tissue engineering that was based on β tricalcium phosphate (βTCP) coated with poly(3-hydroxybutyrate) (P3HB) a bacteria-derived polymer that was doped with Ag. The composite presented a compressive strength of around 3.8 MPa which is within the range for surgical processes for implantation. Alongside that, its hydrolytic degradation leads to the formation of (R)-3-hydroxybutyric acid along with other oligomers that can serve as nourishment for the surrounding tissues. Lastly, the presence of Ag provides antibacterial properties without inducing microbial resistance. Furthermore, PHAs are another versatile group of polymers derived from bacteria that can present a wide range of applications not only due to the different structured which they can be obtained but also through some composite approaches that can allow them to be used in several application fields.[184]

Materials that display piezoelectric properties are highly desirable in the biomedical field as the conversion of mechanical energy into electricity can have several applications. For example, monitoring of physiological parameters of the body, drug delivery systems,[185,186] dental applications,[29,187] and tissue engineering.[188,189] Based on the latter and the use of biopolymers in tissue engineering applications, Chernozem et al.[190] performed a critical study on the piezoelectric properties of PHB and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) films by controlling of thickness, molecular weight, and content of 3-hydroxyvalerate (3-HV). They observed that an increase in the film's thickness from 30 to 100 μm led to a decrease in crystallite sizes and induced a higher degree of crystallinity with negligible change in the thermal behavior. Yet, they found that a decrease in PHB molecular weight from 803 to 102 kDa led to a decrease in the piezoelectric domains, even though the degree of crystallinity and roughness remained unaltered. Further on their studies, they found that a PHB-HV molecular weight of 756 kDa led to the highest degree of crystallinity of 32% which was favorable for the piezo electronic properties and tissue engineering applications.

Another widely used biopolymer produced by bacteria is xanthan gum which is a water-soluble anionic polysaccharide usually employed for rheological control in the food, cosmetic, and pharmaceutical industries. Based on that, Izawa et al.[191] explored the uses of xanthan gum by preparing a hydrogel. It consisted of a heating−cooling process of the xanthan gum in

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ACS Omega 2024, 9, 8666−8686

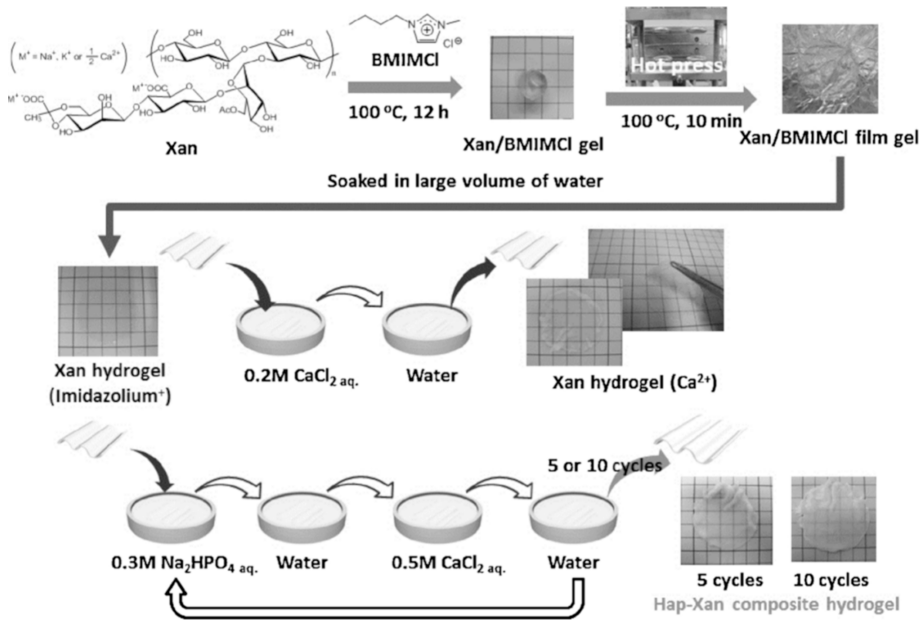

Figure 9. Fabrication process of the Hap-Xan hydrogel composite followed by a soaking approach utilized for the growth of hydroxyapatite over the hydrogel's surface. Adapted with permission.[191] Copyright 2014, Elsevier.

1-butyl-3-methylimidazolium chloride (BMIMCl) to form the Xan/BMIMCl gel. After drying it was soaked in water to form a Xan hydrogel which presented appreciable elastic behavior. Yet, as mentioned, xanthan gum has an anionic charge surface due to the presence of carboxyl groups. Such moieties can serve as a natural template for the complexation of Ca^{2+}. Based on these aspects, hydroxyapatite, a calcium phosphate mineral commonly found on bones, could be mineralized over at the Xan hydrogel through a cyclic soaking process in different solutions containing Ca^{2+} and PO_4^{3-} which enabled the mineralization of hydroxyapatite in the hydrogel's surface. The increased number of soaking cycles led to a more brittle hydrogel due to the formation of hydroxyapatite which could disrupt the double helix structure of the Xan hydrogel while increasing the rigidity of the composite due to the mineralization. From that, the Xan hydrogel with mineralized hydroxyapatite could serve as a potential scaffold for bone regeneration as proposed by the authors.[192] The complete schematic process for the fabrication of the Xan hydrogel mineralized with hydroxyapatite (Hap-Xan) is presented in Figure 9. Regenerative medicine and tissue engineering make use of several processing techniques to obtain scaffolds or carriers with a desired architecture. Bioprinting is a technique that consists of accurately depositing biomaterials, cells, or other biomolecules on a surface to fabricate a tissue. For that, bioinks, which are materials containing high concentrations of cells can be utilized to print complex biological structures. Under this line, bioinks usually present microcarriers in their composition which are particles made of biodegradable and/or biocompatible materials that function as drug carriers or scaffolds for cell growth. Through that, microcarriers can offer better cell attachment, enhance viability, and promote a homogeneous cell distribution throughout the structure. Based on this technology and its nuances, Levato et al.[193] utilized bioprinting combined with microcarrier technology to construct a hydrogel composite based on PLA microcarrier loaded with mesenchymal stromal cells (MSC) which were encapsulated in gelatin methacryalmide-gellan gum bioinks. Through that, a hydrogel construct with high cell concentration as well as viability was obtained. Such aspects were attributed to the PLA microcarrier that could promote better cell adhesion, improve the hydrogel's compressive modulus, and facilitate osteogenic differentiation for the bone compartment.

The biosynthesis of copolymeric PHAs can yield compounds with appreciable properties that are also friendly to the environment. One of these materials is the copolymer obtained from the monomers 3-hydroxybutyrate (3-HB) and 3-hydroxyhexanoate (3HH), which can yield poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHH). This polymer presents appreciable flexibility as well as marine biodegradability, which makes it convenient to be used in certain types of packing and plastic bags as it can greatly decrease the volume of waste in the oceans. Based on that, Tanaka et al.[194] studied the biosynthesis of PHBHH from an engineered *Cupriavidus necator* through the use of a gas mixture containing CO_2 as a carbon source along with sucrose. Further on that, it was proposed the composition of the polymer could be regulated through the use of the enzyme (R)-enoyl-CoA hydratase (PhaJ). Through that, the composition of 3HH could be controlled to a level that enabled its use for practical applications. Another class of polymers that can be obtained from bacteria is polythioesters as it was presented in the work of Ceneviva et al.[195] who utilized a genetically engineered *Escherichia coli* to biosynthesize poly(3-mercapto-2-methylpropionate) [P(3M2MP)] using 3-mercapto-2-methylpropionic acid as a precursor. The P(3M2MP) presented a high molecular weight along with appreciable elastic properties as it presented around 2600% elongation at break. The authors could also promote a considerable degree of property tunability based on the concentration of precursors in the system. In this sense, 3-HB could also be introduced to obtain P(3HB-*co*-3M2MP) copolymer through the expression of 3-HB-supplying enzymes. Furthermore, it was observed that increasing the fraction of 3M2MP led to a decrease in molecular weight, making the polymer softer, and more

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ACS Omega 2024, 9, 8666−8686

amorphous, with a lower glass transition temperature and higher flexibility with quick recovery. Such a degree of tunability can yield versatile elastomeric materials that can potentially cover a wide range of mechanical properties. It was proposed by the authors that, the presence of S could be one of the factors that promoted elastomeric properties because S has a similar electronegativity when compared to C.[196,197]

It is noticeable that bioplastics present some inherent properties that divert from the nonrenewable or petrochemical-based polymers which makes them specific for certain types of applications. In this sense, bioplastics have some inherent advantages over petrochemical-based plastics such as environmental credentials based on origin from renewable sources, reduced carbon emission during its manufacturing, and biodegradability, in some cases. Alongside that, bioplastics have great versatility since PHAs for example can be biosynthesized through a plethora of microorganisms which leads to materials with a wide range of properties. Also, most of the techniques employed for the processing of petrochemical-based can be employed for bioplastics, which has facilitated its introduction in the market. Furthermore, the biocompatibility of most bioplastics is an important distinction from most petrochemical-based plastics, which has demonstrated many valuable possibilities for the development of technologies within the biomedical and medical fields. Lastly, Table 1 displays some of the main applications, properties, and manufacturers of the four most produced bioplastics.

5. CHALLENGES AND OUTLOOK

The use of bioplastics derived from bacteria is a promising technology as it can offer a sustainable and economically feasible approach to obtaining a variety of applicable polymers. Under this line, one of the attractive aspects is that the microorganisms perform the polymers' biosynthesis by consuming low-cost substrates derived from agricultural and food waste. However, there are some inherent challenges to the use of microbes. First, there is the need to find the optimal microbial strain that can operate in optimal conditions. On top of that, it must have high productivity and selectivity toward the product. For that, genetical engineering is often required to improve the yield or direct a microorganism to consume a specific substrate. Second, fermentation processes require meticulous control of the environment in terms of temperature, pH, substrate concentration, and oxygen availability to name a few. Because of that, it is inherently challenging to scale-up such a process since controlling the parameters can be a costly step in the industry. It is important that microbial media can consume the selected substrate as it produces the polymer at a satisfactory rate. For that, the optimal conditions regarding bacterial growth and polymer biosynthesis must be met. Microorganisms may not produce a single type of polymer or bioproducts. Hence, purification steps are often required to isolate a specific product. Based on such factors, at this point, bioplastics tend to be relatively costlier than their petrochemical counterparts as further optimization and scaling of their manufacturing processes are still relatively new. The properties of bioplastics can vary considerably when compared to their petrochemical-based counterparts. In this sense, bioplastics are more brittle and hydrophilic. Yet, they can present relatively similar mechanical properties in terms of flexural modulus and tensile strength at yield. The property comparison between some bioplastics and petrochemical plastics is presented in Table 2.

Table 1. Main Applications, Properties, and Manufacturers of the Most Produced Bioplastics

Polymer	Applications	Properties	Manufacturers	Ref
PLA	Packing, films, coatings, 3D printing, tissue engineering scaffolds, drug delivery systems, and agricultural films for plague control	High strength and modulus, brittleness, low thermal stability, hydrophobicity, low degradation rate, biocompatibility	Cargill, Galactic, Pyramid bioplastics, Corbion, NatureWorks LLC	198−200
PBS	Packing films, hygiene products, bags, coffee capsules, plastic, and wood composites	Similar mechanical properties to PP and PE, high thermal stability, slow degradation rate, high crystallinity	Showa Denko, Mitsubishi, Bio-Amber & Genomatica (Monomers)	142, 201−204
PHA	Packing (cosmetics and hygiene products), nanoparticles for drug delivery systems, biocompatible implants, and tissue engineering scaffolds	Fast degradation in several environments, good gas-barrier properties, biocompatibility, low thermal stability	GreenBio Materials, BioMatera, Danimer Scientific, Bio-on	205−207
Starch Blends	Food packing, bags, agricultural, textile, and automotive-related products	Low HDT, moisture sensitivity, brittleness	Biobag, Avebe, BIOTEC, CPR Corp., Cere-plast, Huhtamaki, EarthShell	208−212

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ACS Omega 2024, 9, 8666−8686

Table 2. Properties of Some Bioplastics and Petrochemical Plastics

Polymer	Tensile elongation at break (%)	Flexural modulus (GPa)	Tensile strength at yield (MPa)	Water absorbance (% in 24 h at 23 °C)	HDT (oF 66 psi/264 psi)	Ref
PLA	0.5−9.2	2.392−4.930	37−66	3.1	121−126/118−122	213−217
PBS	8.0−13.0	-	30−35	-	-	218, 219
PHA	1.4−5.5	1.28−3.668	20−40	0.7	239−293	220−223
Starch Blends	3	∼0.77	3−10	4−8	185	223−226
PET	15−165	0.138−73.8	55−79	0.1−0.2	158−240/149−175	227, 228
PP	100−600	∼1.5	21−27.5	0.01−0.1	210−210	229−231
HDPE	150−400	0.280−1.86	∼27.32	0.005−0.01	172−185/140	232−235
LDPE	600	0.152−2.21	12.41−15.16	0.005−0.015	122/120	230, 231, 235, 236

Despite the inherent challenges surrounding the synthesis and manufacturing of bioplastics, there has been a considerable increment in their production over the years which is expected to increase worldwide.[237] PLA has been sought as a viable polymer for applications in the packing industry due to its appreciable mechanical properties alongside inherent biodegradability which can greatly decrease the burden of plastic waste for packing from nondegradable polymers.[238,239] Hence, such competitive properties, feasible manufacturing processes, and a broad range of sources allowed PLA to reach the market. Alongside that, PHAs and their derivatives have also been employed for packing-related applications since they can be synthesized through a plethora of microorganisms and can present several variations in their chemical structures. Furthermore, biodegradable polymers such as PLA, PHAs, and PBS are convenient materials for agricultural applications such as mulch films. Such polymers can improve the soil's quality for the growth of plants by maintaining a constant moisture content, and temperature which allows for the proliferation of microbes that aid the plants to harvest nutrients for the soil. Also, mulch films can serve as a protection against aggressive environments such as heavy rain that can cause the soil to be compressed leading to a decrease in air and water circulation. Lastly, their biodegradability is highly convenient since after performing their role of soil optimization they can be naturally degraded and incorporated into the crop as a carbon source. Another important aspect that is specific to biodegradable polymers is related to the biocompatibility such as for the case of PLA and PHAs, for example. Such property is an important factor for biomedical applications. Through that, these materials can be obtained as porous structures that can serve as scaffolds for the growth of cells to repair a tissue. Also, they can serve as polymeric matrices for the encapsulation of a drug followed by functionalization with a probe. Such experimental design allows them to function as targeted drug delivery system or biosensors. Following on that, the biodegradability of these polymers also plays an important role in their application in this field since they can degrade into safe components that can be either absorbed or expelled from the body without triggering allergic reactions. Such applications show a more unique aspect of such biopolymers that can fill an important gap for the biomedical and medical applications that are not covered by their petrochemical counterparts.

6. CONCLUSION

Throughout this review, it could be observed that bioplastics can offer a convenient way to utilize food and agricultural waste as sources to biosynthesize polymers using microbes. Many microorganisms can be used for the synthesis of polymers or monomers to produce PLA, PHAs, PLGA, and PBS, among many others. These factors unlocked a broad range of possibilities for the synthesis of polymers that can serve as an alternative to petrochemical-based materials. Hence, the investment in such technology is an important step toward a more sustainable future as the manufacture of these bioplastics can simultaneously help with waste management as well as decrease the strain on the demand applied to petrochemical-based polymers. Bioplastics can be employed in many sectors such as packing, cosmetics, pharmaceutical, biomedical, medical, sanitary, and agricultural. On top of that, biopolymers such as PLA, PGA, chitin, and cellulose for instance are biodegradable which can promote a circular economy with a considerably reduced generation of waste and carbon footprint. It has been proposed that biopolymers should play a major role in the future as they have already been implemented in the market such as in the case of PLA and PHAs, for instance. Yet, these materials are still in their infant phase and further investment is still required to diminish their overall production cost as well as make their properties more competitive against petrochemical-based polymers. Even though this process is inherently challenging, as it requires optimization in every step of the production, several parameters can be varied such as type of microbe strain, substrate, polymerization techniques, compositing, processing, and manufacturing which can lead to polymers with a wide range of properties. Yet, these steps also have their challenges that may hinder the optimal manufacturing of biopolymers when compared to polymers obtained without the need for microorganisms. First, there is a need to improve the yield and productivity as it can be affected by the substrate, environment parameters, and the presence of different strains in the microbial system. Second, enhancing the polymer synthesis through genetic engineering can be a time-consuming process. Third, finding the optimal balance between a suitable feedstock for the bacteria as well as utilizing waste biomass to promote a more economically viable and sustainable process. Fourth, the processing and purification processes to extract the polymer from the bacteria can be energy-demanding and costly. Hence, optimizing these processes is also required to increase their competitivity.[240] Yet, despite these challenges the production of biopolymers such as PLA, PBS, PBAT, PHA, and starch-blend is expected to increase up to 2025.[241−243] However, even though the production of biopolymers is leaning upward is still challenging to confirm if

Thus, further research on bioplastics to make their properties more competitive against petrochemical-based polymers along with the decrease in cost can lead to a

https://doi.org/10.1021/acsomega.3c07372
ACS Omega 2024, 9, 8666−8686

considerable shift in the market as they can potentially solve issues related to the waste generation and aggressive consumption of nonrenewable resources.

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Authors acknowledge Pittsburgh State University for providing research and financial support.

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