Bio-based Polymers: A Mini Review

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Abstract

Most synthetic polymers are derived from fossil fuel resources, whose scarcity and imbalanced global distribution can affect plastics producers. Bio-based polymers, obtained from renewable biomass resources, have received wide attention in the past two decades. Bioplastics formulated using bio-based polymers are a promising sustainable alternative to oil-based plastics, and may particularly benefit countries that are heavily dependent on foreign oil. This paper provides a brief overview of the three types of bio-based polymers, discusses the strengths and limitations of each type, highlights the latest research progresses, and evaluates recent trends in related scientific publications. The annual publication volumes of most bio-based polymers analyzed share the common pattern of steady growths, followed by stabilization or declines starting from the mid-2010s. The trends may be ascribed to changes in the prices of fossil fuel-based plastics, which in turn reflect the fluctuations in crude oil prices. Without strong financial support or technological breakthroughs, the manufacture of bioplastics is still too costly to compete against oil-based materials. Aside from economic challenges, bio-based polymers often face skepticism from the public, likely a result of misconceptions. This review also aims at clarifying some of the confusions and helping raise public awareness of bio-based polymers' importance to sustainability.

1. Introduction

Plastics, the macromolecular materials found in a wide variety of products ranging from grocery bags to car bumpers, are composed predominantly of synthetic polymers such as polyethylene, polyesters and polyamides, along with small amounts of additives including plasticizers, antioxidants, UV stabilizers, etc. An estimated 368 million tons of plastics were produced in 2020.[1] Most synthetic polymers in use today are derived from petroleum. Monomers, the building blocks of polymers, are currently obtained directly from crude oil refining or synthesized from refining products. It is estimated that plastic-manufacturing processes consume 8-10% of the global oil supply,[2] and the number is forecast to double by 2040.[3] Petroleum is non-renewable, and the oil resources are rapidly being depleted from planet earth. Furthermore, world reserves of fossil fuels are unevenly distributed, and most countries depend on foreign

oil sources which are constantly affected by economic and political fluctuations. In the United States, for example, about 35% of crude oil are imported, with Canada, Mexico, Russia, Saudi Arabia and Colombia being the leading suppliers. [4] While energy is increasingly being produced from alternate sources, petrochemicals and plastics are still largely reliant on oil. Unless alternative sources become well established, sustainability concerns will negatively impact plastic production. The answer is bioplastics – plastics formulated using polymers that are prepared from biomass.

In 2009, the Coca-Cola Company introduced PlantBottle[TM],[5] a technology for manufacturing poly(ethylene terephthalate) (PET) plastic bottles with partially plant-based materials. In 2015, the company made further progress by announcing their capability of producing bottles entirely from renewable resources.[6] This is just one example of numerous efforts devoted to developing bio-based polymers in recent years. PET, the most common polyester, can be manufactured by polymerizing ethylene glycol (EG) with terephthalic acid (TPA) via esterification (Scheme 1).

Scheme 1. Synthesis of PET

EG and TPA are primarily produced from fossil feedstocks. Coca-Cola's initial PlantBottle™ product featured up to 30% bio-based PET by utilizing EG produced from carbohydrates in sugarcane. TPA, the other building block, was subsequently produced from biomass, enabling 100% biobased products.

Bioplastics have multiple advantages over fossil resource-derived plastics. They are generated from renewable sources which also fix CO_2 from the atmosphere. If bio-based plastics are prepared using similar amounts of energy to plastics from nonrenewable sources, their fixation of CO_2 will decrease greenhouse gas emissions at the same output. In addition, many biobased plastics are biodegradable, providing more flexibility in disposing products made with them. The one disadvantage of bioplastics is the cost and time necessary to develop these new polymers to meet market technical needs in barrier, strength, temperature and other polymer properties already met by established plastics.

Bioplastics research has been trending in recent years and was chosen as one of the top ten emerging technologies for the year 2019.[7] In this report, we review the various types of bio-based polymers, highlight recent progress in bioplastics research, and present an analysis of trends in research and inventions around bioplastics using data from CAS Content Collection. The paper will end with brief

discussions of challenges and opportunities of bio-based polymers. The terms "bio-based polymers" and "bioplastics" are synonymous and will be used interchangeably in the paper.

2. Classification of bio-based polymers

2.1. Types of bio-based polymers

Depending on their sources and production methods, there are three major types of bio-based polymers:

A. Polymers obtained directly from biomass, such as starch, cellulose, chitosan, and alginates.
B. Polymers bio-synthesized using microorganisms and plants, or prepared directly from monomers that are predominantly bio-synthesized, such as polyhydroxyalkanoates (PHAs) and polylactic acid (PLA).
C. Polymers structurally same as oil-based polymers but prepared from bio-sourced monomers. Some of the most produced type C polymers and corresponding monomers are listed in Table 1.

Table 1: Some commonly reported Class C bio-based polymers and their building blocks. EG, ethylene glycol; TPA, terephthalic acid; BD, 1,4-butanediol; SA, succinic acid; FDCA: 2,5-furandicarboxylic acid.

Polymers	Monomers
Polyethylene	Ethylene
Polyethylene terephthalate (PET)	EG + TPA
Polybutylene succinate (PBS)	BD + SA
polybutylene adipate terephthalate (PBAT)	BD + adipic acid + TPA
Polyhexamethylene adipamide (Nylon 66)	Adipic acid + hexanediamine
Polyethylene furanoate (PEF)	EG + FDCA
Butadiene rubber	Butadiene

Some general paths to the production of bio-based polymers are schematically shown in Figure 1. A more comprehensive visual illustration of bio-based polymer production routes can be found in another report.[8]

Figure 1. Illustration of production routes to bio-based polymers. *Less popular routes leading to only partially bio-based polymers.

2.2. Bio-based vs. biodegradable

Bio-based polymers and biodegradable polymers are easily confused with each other. Although they were both developed to tackle global environmental issues, the former emphasizes reducing reliance on fossil resources, whereas the latter focuses on reducing plastics waste. Biodegradability depends eventually on the polymer's structure. While many bio-based polymers happen to be biodegradable, a lot of them are designed to be structurally identical to fossil fuel-derived polymers and are thus not biodegradable, as we shall see in the following sections. Some examples of polymers in each category are listed in Table 2.

Table 2. Examples of bio-based and fossil fuel-based polymers that are biodegradable and non-biodegradable

	Biodegradable	**Non-biodegradable**
Bio-based Polymers	Polylactic acid Starch	Polyethylene PET
	Biodegradable	**Non-biodegradable**
Fossil-based polymers	polybutylene succinate (PBS)	Polyethylene PET

3. Publication trends of important bio-based polymers

Utilizing publication volume data from CAS Content Collection, we have studied the trends over time of journal and patent publications pertinent to various classes of bio-based polymers in the past two decades.

To illustrate R&D interest in bio-based polymers in general, the annual journal and patent publication numbers for the years 2001-2021 are shown in Figure 2. It can be observed that the volumes of both journal publications and patents grew slowly in the first few years, then both started accelerating. The trend reflects the increased focus on sustainability in the world, pushing a huge desire to produce bioplastics. However, beginning around 2014, the growth in patent publication volume slowed down considerably, whereas the strong increase in journal publication numbers continued up to 2021.

Figure 2. Numbers of publications related to bio-based polymers in general from 2001 to 2021.

Since bio-based polymers are mainly developed as renewable alternatives to fossil-based plastics, substantial rises in the latter's prices would increase bioplastics' competitiveness, and significantly boost enthusiasm and confidence among researchers and inventors. Plastic prices are known to be tightly linked to oil price, which experienced substantial growth since the mid-2000s and an unprecedented sharp peak in 2008;[9] this may thus potentially explain the inflection point, particularly visible in the patent publication number curve at around 2008. Then, oil prices plummeted after 2014, making bioplastics relatively much more costly again, thus presumably discouraging inventors and causing the patent publication volume to level off at the exact same year. The impact on journal publications can also be seen, although not as severe as that on patents. The differences can naturally be attributed to patent inventions being more pragmatic and industrial application-driven than academic work, and thus more sensitive to the economy.

The publication trends relating to the different classes of bio-based polymers are then each analyzed individually. Figure 3 shows the publication trends of the most important Class A polymers. Both journal and patent publications related to starch dominated the other polymers in the class. Despite fluctuations, a patent publication trend consistent with that observed in Figure 2 can still be identified for starch, with

accelerated growth after 2008 and stabilization after 2014, although greater fluctuations occurred afterwards. No clear trends, however, can be found in patent publications for cellulose, chitosan, and alginates. It is worth mentioning that Class A polymers offer much inferior overall performance than the other two classes, and have so far been developed for specific undemanding applications rather than for replacement of oil-based plastics. Furthermore, they have always been widely used as reinforcing fillers for other plastics, and it is impossible to completely exclude the related "false positive" publications (where the polymers were studied as additives rather than plastic matrices) from the search results. These may well explain the lack of identifiable patterns in patents for most Class A polymers, as well as the high starting publication numbers for starch and cellulose. The journal publications, on the other hand, do show continuous increases for starch and cellulose albeit the bumps around 2011-2014. Chitosan and alginates had much fewer journal publications, but the increases since around 2009 are still evident.

Figure 3. Numbers of journal (left) and patent (right) publications on Class A bio-based polymers for the years 2001-2021.

Publication volumes for PHA and PLA, the most representative Class B bio-based polymers, are shown in Figure 4. Here, both polymers display clear trends of increasing publication numbers up to 2013-2014, levelling off or going down afterwards (except patent publications for PLA which peaked in 2008). Particularly, journal publication volumes for both polymers follow almost the same pattern. Again, the decreases after 2013-2014 can likely be attributed to dropping prices of oil-based plastics and the resulting fading interest in bio-based polymer development.

Figure 4. Numbers of journal (left) and patent (right) publications on Class B bio-based polymers for the years 2001-2021.

Publication volumes for some the most studied and commercialized Class C bio-based polymers are shown in Figure 5. Publications on all four polymers were largely non-existent up until 2008; the patent volumes for PE and PET then increased strongly afterwards and, again, somewhat levelled off after 2013-2014, while the patterns for PBS and PBAT are not quite as obvious, partially due to their low publication volumes. Journal publication numbers are low for all four polymers, but significant rises after 2008 can be clearly observed.

Figure 5. Numbers of journal (left) and patent (right) publications on Class C bio-based polymers for the years 2001-2021.

It should be noted that, since Class C polymers have structures identical to their oil-based counterparts, except they are manufactured from bio-based monomers, most of the research and inventions are expected to focus on the monomers, rather than the polymers. Data from Figure 5, obtained using the polymers as search terms, should therefore be considered merely as a general indication of research interest, and not necessarily as accurate reflections of research trends in the area. To gain better insights

into the development status of Classes B and C bio-based polymers, publication trends in the production of some representative bio-based monomers have been studied.

Figure 6 shows the publication numbers related to the preparation of some of the most developed monomers: ethylene, succinic acid (SA), and lactic acid (LA). Data for PHAs are also shown, since their preparation via fermentation is the bottleneck in their development, and related publication volumes would be a major indicator of their popularity with researchers and inventors. Here, unmistakable trends of patent volumes growing first then decreasing since 2013-2014 are observed for all four substances. The similarity in shapes among all the curves is striking considering that different search queues were used and tailored to fit each material. The trends are, again, less pronounced for journal publications, where a significant reduction in publication volume in the late 2010s is only observed for PHA.

Figure 6. Numbers of journal (left) and patent (right) publications on the preparation of leading bio-based monomers and PHAs for the years 2001-2021.

The results for newer, less established bio-based building blocks are shown in Figure 7. It can be seen that these monomers received research and innovation interest later compared to those in Figure 6: there are very limited numbers of publications prior to around 2009 for both journal articles and patents. Patent and journal publications of these less-established bio-based monomers behave similarly to their more-established siblings otherwise, with publication volumes for most monomers peaking in the early 2010s and decreasing afterwards.

Figure 7. Numbers of journal (left) and patent (right) publications on the preparation of some less studied bio-based monomers for the years 2001-2021.

To summarize, the volumes of patent publications involving most bio-based polymers, with the exception of some Class B polymers, share the common trend of an initial rapid increase, mainly starting at late 2000s, peaking before mid-2010s, and stabilizing or declining afterwards. The journal publication volumes do not present as distinct trends; the same general patterns can still be identified for the majority of polymers studied, while the initial rise and final decline are not as pronounced. It is clear that research and development interest and activities in bio-based polymers have generally faded in the past few years, which, as alluded earlier, is presumably a result of low oil prices since the mid-2010s, significantly affecting bioplastics' potential profitability. The observation is probably not a reflection of stages of maturity and decline in the technology life cycle; production techniques of bio-based polymers or building blocks likely have not matured, since even the newly developed bio-based monomers invariably experienced stabilizing or falling patent publication numbers (Figure 7) in the most recent years.

4. Recent research and development progress in bio-based polymers

4.1. Class A bio-based polymers

This first type of biobased polymers are mainly polysaccharides, including starch, cellulose, chitosan, and alginates. These bioplastics are most widely used as packaging films.[10]

Starch, a white powder consisting of numerous α-glucose units joined by glycosidic bonds, is produced by plants for energy storage. Due to its low cost, wide availability and biodegradability, starch has been among the most widely produced bioplastics with over 400,000 metric tons produced annually today.[11] However, starch in its pure form is difficult to process, requiring water or plasticizers to enable it to be processed into thermoplastic starch (TPS).[12] In addition, TPS is hydrophilic and has inferior mechanical

and barrier properties. As a result, starch is mainly used in blends with other polymers or reinforced with fibers.[13-15] Most recent studies have focused on improving the mechanical strength of starch or its blends using various reinforcing fillers or fibers and other additives. Zhou et al.[16] studied sisal fiber-reinforced thermoplastic starch and found that the interfacial adhesion between the fibers and starch matrix was improved by the addition of glutaraldehyde and starch nanocrystals. Suan et al.[17] added beeswax to starch to achieve improved mechanical properties, moisture barrier and water resistance. Bakar et. al.[18] used photo-crosslinking to enhance the strength of starch films filled with microcrystalline cellulose. Schreurs et al.[19] reported the use of biochar particles as filler for starch/PLA blends.

Cellulose, a polysaccharide consisting of numerous β-glucose units joined by glycosidic bonds, is the main constituent of plant cell walls and is the most abundant organic polymer on earth.[20] It is insoluble in water or common organic solvents since it is highly crystalline and aggregates strongly via hydrogen bonding. It is thus difficult to separate from plants, and cannot be melt-processed. However, cellulose may be derivatized into esters or ethers, the most widely reported being cellulose acetate (CA), cellulose propionate (CP), and cellulose acetobutyrate (CAB), then isolated and processed into various forms of plastics.[21] For instance, cellulose acetate,[22] with its good clarity, toughness and processability, had been used as a film stock since 1934 before being replaced by polyester films in the 1980s. It still has wide applications today including optical films and food or drug packaging.[23] A recent study shed a new light on cellulose acetate's biodegradability and revealed that it disintegrates in seawater in just months, much faster than previously believed.[24] An alternative method to isolate cellulose is by dissolving it with some uncommonly used solvents containing various bases or salts, then casting into films or spinning into fibers, resulting in what is known as regenerated cellulose.[25] Research on various solvents, such as carbon disulfide, N-methylmorpholine-N-oxide, dimethylsulfoxide, and urea, have been reported; green solvents such as ionic liquids have recently been proposed to address environmental concerns.[26-28] Like starch, cellulose and derivatives are used more often as fillers or reinforcing fibers for other polymers, rather than as plastics themselves.

Chitosan is a carbohydrate obtained by treating shells of shrimp and other shellfish with an alkaline solution. It is being increasingly used as an alternative material for packaging films.[29] **Alginates** are salts (mostly sodium) of alginic acid, a polysaccharide consisting of glycosidic linkages of mannuronic acid and guluronic acid found in brown algae. While traditionally used as food additives and edible films, alginates recently found applications as plastics, mostly bags, although their potential in biomaterials and flexible electronics have also been reported.[30]

The above discussed naturally occurring polysaccharides have inadequate mechanical strength compared to most fossil-based plastics. Even when formulated with reinforcing fillers, impact modifiers, and/or other polymers, as they typically are, their applications as bioplastics have largely been limited to packaging materials. Other naturally occurring plant-based polymers, such as chitin and lignin, are used predominantly as fillers rather than as plastic matrices.[31, 32]

4.2. Class B bio-based polymers

Polylactic acid (PLA, Scheme 2), also known as polylactide, is produced from lactic acid, a naturally occurring α-hydroxycarboxylic acid constantly produced in living organisms. The market for PLA has grown significantly over the last 10 years so that over 400,000 metric tons are produced annually today.[11] Lactic acid is manufactured by microbial fermentation of C5 or C6 sugars, typically glucose and sucrose, obtained from enzymatic hydrolysis (saccharification) of biomass such as sugar cane, corn, and beet.[33, 34] The method generates optically pure isomers (L-lactic acid in most cases) and the products account for approximately 90% of all lactic acid industrially produced. However, preparing bio-based lactic acid economically is challenging. Improvements in the yield and optical purity of lactic acid as well as maximizing the utilization of biomass have long been the goals of most research efforts.[35] More recent research has focused on increasing fermentation efficiency by strain selection and mutagenesis of lactic acid bacteria, by optimization of biomass hydrolysate composition, and by finding sustainable fermentation substrates, such as food wastes, milk whey, and paper mill sludge.[36, 37]

Scheme 2. Polylactic acid

Polylactic acid prepared from bio-based optically pure lactic acid is highly crystalline and thus has good mechanical strength comparable to some fossil-based plastics. It is therefore considered one of the most promising bioplastics. PLA has also been the most widely used material for 3D printing, primarily due to the low printing temperature enabled by its low melting point.[38] However, PLA's high crystallinity also results in poor impact resistance; its potential for high temperature applications is also limited by the low melting point. As with starch, PLA is frequently formulated with toughening additives or used in blends with other polymers.[39, 40]

Polyhydroxyalkanoates (PHAs) are bio-based polyesters that can be produced directly from biomass via fermentation. They have a general structure shown in Scheme 3, where x typically ranges from 1 to 8 and

R represents alkyl groups of various sizes. PHAs can be homopolymers or copolymers. Among the most studied are poly(3-hydroxybutyrate) (PHB, x = 1, R = methyl), poly(3-hydroxyvalerate) (PHV, x = 1, R = ethyl), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV, x = 1, R = methyl, ethyl), and poly(4-hydroxybutyrate) (x = 2, R = H).[41]

Scheme 3. Polyhydroxyalkanoates

PHAs are obtained by fermentation of bacteria under nitrogen- or phosphorus-limiting conditions, forcing them to produce copious amounts of PHA as an energy reserve.[42] The polymer beads are then isolated from the cells typically by extraction and precipitation. The composition of the obtained polymer is dependent on the bacterial strain and carbon substrate used, as well as on the fermentation conditions.[43, 44] Besides packaging, PHAs have been used in medical and surgical applications due to their biocompatibility.[45] Further expansion of their applications, however, has been limited due to their nonoptimal thermal and mechanical properties, and high cost of production. Although thermal and mechanical properties can be tailored by modifying the monomer composition and side chain lengths, an optimum balance between mechanical hardness, toughness and thermal processability is difficult to attain.[41] Again, blending with other bio-based or fossil-based polymers is considered necessary for PHAs' adoption as structural plastics.[46]

Still, high manufacturing cost due to low yields and/or cost of separation from fermentation broth is the major obstacle to the replacement of oil-based plastics by PHA which are produced today at about 40,000 metric tons per year.[11] While continuous progress has been achieved in improving fermentation yield and efficiency using biological tools, PHAs differ from other fermentation-derived chemicals in that the polymers' structures and molecular weights are sensitive to the fermentation substrate. Manufacturers thus depend on stable supplies of feedstocks to maintain consistent product quality, making the utilization of biowaste substrates with varying compositions a challenge. Efforts to solve the problem by integrating PHA production facilities into food manufacturing plants or wastewater treatment facilities, to take advantage of their continuous access to consistent organic waste streams, have been reported.[47, 48]

4.3. Class C bio-based polymers

Although Class A and B polymers are all biodegradable and are nearly all bio-based, they have inferior properties compared to oil-based plastics. In addition, the lack of structural diversity and available

modifications to Class A and B polymers limits the ability to tailor polymers for specific purposes, without having to blend with other polymers or fibers. The third class of polymer (Class C), on the other hand, are structurally same as fossil fuel-derived polymers but are manufactured from bio-based building blocks, thus offering a combination of performance and renewability. Bio-based ethylene, ethylene glycol and terephthalic acid (building blocks for CocaCola's PlantBottle™) are typical examples. The conversion of renewable feedstocks to synthetic monomers, however, is nontrivial. The monomers are typically produced via biomass fermentation followed by chemical reactions, and major advancements in fermentation efficiency, biowaste utilization, catalysis and/or purification techniques are still needed to make their manufacturing more economically viable. In addition, bio-based versions of oil-derived polymers are in most cases not biodegradable and thus share the disposal and recycling issues of the oil-based polymers.

Once obtained, the monomers can fit seamlessly into existing production lines of traditional plastics manufacturing facilities. While it is beyond the scope of this paper to provide an exhaustive list of all bio-derived monomers, representative production routes to some of the most studied monomers are schematically shown in Scheme 4.

Scheme 4. Manufacturing routes to common bio-based monomers (in red). (a) ethylene; (b) ethylene glycol (EG); (c) butadiene; (d) adipic acid; (e) succinic acid (SA); (f) 1,4-butanediol (BD); (g) hexanediamine; (h) 1,6-hexanediol; (i) 2,5-furandicarboxylic acid (FDCA); (j) terephthalic acid (TPA);

(k) muconic acid; (l) glucaric acid; (m) 5-hydroxymethylfurfural (HMF); (n) 2,5-dimethylfuran; (o) *p*-xylene; (p) isobutanol.

2,5-Furandicarboxylic acid (FDCA) is an exception to monomers for Class C polymers in that it is predominantly produced from bioresources, rather than as a replacement of its oil-derived counterpart. Polyethylene furanoate (PEF), obtained by polymerization of FDCA with EG, while not yet commercialized, is considered a potential alternative to PET for packaging applications.[49] PEF has the advantage of being fully bio-based and better barrier properties than PET while having similar mechanical properties. The most studied production route to FDCA is the oxidation of 5-hydroxymethylfurfural (HMF), a versatile platform chemical for production of renewable materials.[50, 51] HMF is typically obtained via dehydration of furanoses, although efforts on one-pot preparation from waste biomass, combining cellulose depolymerization and monosaccharide dehydration, have been reported.[52] Research on FDCA synthesis has been focused on the development of efficient, inexpensive, and greener catalysts for the oxidation of HMF.[53] Thus, while noble metal catalysts such as platinum have proven more effective,[54] enzymes and electrocatalysis have drawn considerable interest.[55, 56]

Ethylene is the most produced industrial organic compound.[57] Bio-based ethylene is primarily prepared from the commercially established bioethanol, which is obtained most often by fermentation of sugarcane or other biomass feedstocks.[58] Ethanol is converted into ethylene via intramolecular dehydration at elevated temperatures in the presence of catalysts.[59] Aluminum oxide, silica and zeolites are among the commonly studied catalysts.[60-63] In most cases, high ethylene selectivity and quantitative ethanol conversion have only been achieved at temperatures above 400°C or by using expensive lanthanum dopants; however, Sheng et al.[61] reported bioethylene production at 98.8% selectivity and 99% ethanol conversion at 250°C using HZSM-5 zeolite catalyst. The 2019 global bioethylene market was $414 million,[64] compared to $166 billion[65] for the total ethylene market.

Bio-based **ethylene glycol** (EG) has typically been produced from bioethanol via petrochemical routes, i.e. by dehydration and epoxidation, followed by hydrolysis (Scheme 4).[66] An alternative, simpler approach to preparing EG via hydrogenolysis of carbohydrates has also been investigated:[67, 68] cellulose is hydrolyzed into glucose, which undergoes pyrolysis to form C2 species, particularly glycolaldehyde. The latter is then hydrogenated to give EG (Scheme 5). Production of high purify EG via this route is challenging due to complex mixtures formed during the cleavage of glucose. Enhancements in EG selectivity have been achieved by using a variety of tungstate catalysts.[69-71] It is more economically viable to utilize wood or biomass wastes directly, rather than neat cellulose; however, lignocellulose present in these raw materials have been found to impact the activity of catalysts.[72] Pretreatments of biomass feedstocks, leading to improved EG yields, have been reported.[73, 74]

Scheme 5. Preparation of EG from glucose.

The development of bio-based **terephthalic acid** (TPA), critical to the production of 100% renewable PET, has been slower compared to the much less expensive EG. Like its oil-based counterpart, bio-based TPA is typically prepared via oxidation of *p*-xylene. As shown in Scheme 4, isobutanol and 5-hydroxymethylfurfural (HMF) have been the precursors used in representative pathways to bio-based *p*-xylene production.[75, 76] The critical step in the HMF route is the Diels-Alder cycloaddition between 2,5-dimethylfuran and ethylene. Various catalysts including zeolites, carbon, silica, titania and alumina have been studied.[75, 77, 78] Feng et al. used mesoporous tin phosphates with controllable acid sites and improved mass transfer, resulting in the inhibition of 2,5-hexanedione byproduct formation and production of *p*-xylene with 93% yield, and at a high productivity of 173 mol/mol acid sites.[79] Zhao et al. obtained *p*-xylene with 97% yield and quantitative conversion of dimethylfuran, using alumina-doped H-Beta zeolite catalyst.[80] One drawback of the HMF route is the high temperature and high ethylene pressure required for the cycloaddition. Also, the PTA produced is only bio-based if the ethylene used is bio-derived, which further adds to the cost. The isobutanol route was developed by Gevo Inc.,[81, 82] where isobutanol is obtained by fermentation of glucose using proprietary bacteria, then dehydrated into isobutylene, which then forms *p*-xylene at modest conversion but high selectivity (75-85%) via dimerization and subsequently dehydrocyclization.

An alternative method to produce PTA directly via oxidation of *p*-cymene, a compound that can be easily prepared from limonene or terpenes, has been studied more recently (Scheme 6).[83, 84] The oxidation produces various intermediates including *p*-cymenol, *p*-methylacetophenone, and *p*-toluic acid, all of which are eventually further oxidized into PTA. Quantitative conversion with 38% PTA selectivity has been reported.[83, 85] Life cycle assessment analyses revealed that this method is greener compared to the isobutanol route or the HMF route, largely due to *p*-cymene being readily available from biomass waste.[86]

Scheme 6. Preparation of PTA from *p*-cymene.

Adipic acid is an important building block for the polyester and nylon industries. Representative routes for producing bio-based adipic acid are through hydrodeoxygenation or hydrogenation of glucaric acid or

muconic acid, respectively (Scheme 4). Glucaric acid is typically prepared from glucose via oxidation. Noble metal catalysts have been recently studied for optimum oxidation efficiency and selectivity;[87-89] Shi et al. reported less expensive Pt-Cu catalyst with 92% yield and 60% selectivity.[90] Muconic acid, on the other hand, can be either biosynthesized from glucose or prepared from lignin through depolymerization and fermentation. The latter method is promising in that abundant lignocellulosic biomass waste can be used without depleting food supplies; however, feasibility analyses performed by Unlu et al.[91] suggested that the lignin pathway is overall less sustainable and economical than the glucose-glutaric acid route. This was attributed to low efficiencies of lignin conversion and the large number of unit operations. Alternative renewable production routes to adipic acid have been reported, including synthesis from HMF, where FDCA was obtained via the oxidation of HMF and subsequently deoxygenated to form adipic acid (Scheme 7);[92] and from succinic acid, which was hydrogenated into 1,4-butanediol and then converted into adipic acid through carboxylation with carbon monoxide (Scheme 8).[93, 94] Adipic acid have also been produced directly from glucose by a variety of metabolic pathways.[95] The various preparation methods were summarized and compared for sustainability and cost competitiveness in a review by Rios et al.[96]

Scheme 7. Preparation of adipic acid from FDCA.

Scheme 8. Preparation of adipic acid from SA.

Unlike the above-mentioned monomers, bio-based **succinic acid** (SA) has only been produced directly via fermentation of carbohydrates or biomass feedstocks. Wild bacteria and fungi [97, 98] as well as metabolically engineered strains [99, 100] have been employed, and the fermentation of a great variety of substrates, including glucose, glycerol, bagasse, wood hydrolysates, food wastes, etc., has been studied.[101-104] Again, crop residues and food wastes are environmentally preferable but their sustainability advantages are undermined by challenges in the efficient utilization of their carbohydrate components. Dickson et al. conducted a multi-criteria analysis and found glycerol to be the better carbon source compared to glucose, corn stover, and seaweed, considering overall economic and environmental factors.[105] Product purification has long been the subject of numerous studies,[106, 107] as the production of SA by fermentation is prone to byproduct formation such as formic acid and acetic acid. The advantages and limitations of various purification techniques are summarized in Dickson et al.'s review.[105] The 2020

global market for bio-based SA was approximately $17 million,[108] compared to $147 million [109] for the total SA market.

1,4-Butanediol (BDO) is a critical building block for polyesters and polyurethanes. Bio-based BDO is prepared commercially via fermentation, with a yield of 0.35 g BDO / g sugar reported for production from glucose.[110] Fermentation of xylose was achieved with a similar yield, and with the advantage of simplified enzymatic steps.[111] Alternatively, BDO may be obtained by catalytic reduction of bio-based SA (Scheme 4). Ruthenium-containing catalysts have been successfully employed due to their ability to completely hydrogenate carboxylic acids into alcohols.[112, 113] Baidya et al. reported cost effective production of BDO from a biorefinery, where waste glycerol generated from biodiesel production was fermented to give SA, which was subsequently hydrogenated into BDO.[113] Bio-based BDO had a global market of $191 million in 2020,[114] compared to $9.7 billion total BDO market.[115]

4.4. Production and market status of some bio-based polymers

The production volumes, leading suppliers, and main applications for some of the most important commercial bio-based polymers are summarized in Table 3. Starch and PLA are the most manufactured bioplastics, most likely due to their lower costs. PHAs, on the other hand, have high production costs and thus have been made in much lower quantities. Commercial bioplastics have been mainly used in packaging. It is also worth noting that polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT) are among the few Class C bio-based polymers that are biodegradable.

Table 3. Production and applications of top commercial bio-based polymers [11]

Bio-based polymer	2020 Global capacity (tons)	Major producers	Main applications	Biodegradable?
Starch and blends	435K	Futerro, Novamont, Biome	Flexible packaging, consumer goods, agriculture	Yes
Polylactic acid (PLA)	435K	NatureWorks, Evonik, Total Corbion PLA	Flexible packaging, Rigid packaging, consumer goods	Yes
Polyhydroxyalkanoates (PHA)	40K	Yield10 Bioscience, Tianjin GreenBio Materials, Bio-on	Flexible packaging, Rigid packaging	Yes
Polyethylene (PE)	244K	Neste, LyondellBasell	Flexible packaging, Rigid packaging	No

Polyethylene terephthalate (PET)	181K	Toray Industries, The Coca-Cola Company, M&G Chemicals	Rigid packaging	No
Polybutylene adipate terephthalate (PBAT)	314K	Algix, BASF	Flexible packaging, Rigid packaging, agriculture	Yes
Polybutylene succinate (PBS)	95K	Roquette, Mitsubishi Chem., Succinity	Flexible packaging, agriculture	Yes

5. Challenges of bio-based polymers

Despite the recent dwindling patent publication activities, industrial production volumes of bioplastics are increasing every year. However, conventional plastics production has been growing at a faster pace, and the global market of bioplastics has remained only about 1 percent of all plastics.[116] The obvious leading reason is cost. Bio-based polymers are not *that* expensive; it is more of fossil fuels' low prices that are making bioplastics struggle. The sinking oil prices since 2014, along with recent rapid developments in shale oil, have apparently exacerbated bioplastics' cost disadvantage, forcing a number of producers out of business.[117-121]

Although cost and pricing information for bioplastics are scarce, some estimated price ranges are shown in Table 4 along with those of some conventional plastics. Note that these price ranges are reported for 2010-2011, during which conventional plastics were expensive owing to surging oil prices. Even then, bioplastics offered hardly any cost advantage over oil-based polymers. Nevertheless, the differences may not be unmanageable, and the disparities in cost may not be as hefty as it appears, considering that conventional plastics enjoy economies of scale. Increasing oil prices, diversification of plastics supplies due to the COVID pandemic, and advancements in production may improve the commercial and financial prospects of bio-based polymers.

Table 4. Reported prices of some bioplastics and fossil fuel-derived plastics in 2010-2011

Bioplastics	Price ($/Kg)	Conventional plastics	Price ($/Kg)
Starch and blends	2.4-6.6 [122]	Polyethylene	1.1-1.5 [123]
PHA	4.4-6.1 [122]	PET	1.6-1.8 [124]
PLA	1.9-6.6 [122]	Polypropylene	1.3-1.8 [125]
Polyethylene	1.8-2.2 [122]	Polyvinyl chloride	1-1.8 [126]

Public perception has been another challenge faced by bioplastics researchers and developers. While the great benefits of bio-based polymers are generally acknowledged, they have sometimes been subject to criticism, and even ridicule, on the basis that they will not solve the world's plastics waste problem; that their productions use farmland and compete for food sources; that they produce methane greenhouse gas while biodegrading; that they have very limited applications and would not replace the majority of conventional plastics; and so on.[127-130] Whereas some of these concerns are warranted and may have arisen from misconceptions or confusions, the origins of unfounded criticisms and accusations are more elusive. However, it is certain that oil companies, already facing challenges posed by the rapid development of electric vehicles, would suffer further losses in their profit share in the event of major advancements in bioplastics market. With the belief that the benefits of bio-based polymers far outweigh their disadvantages, we hereby share our opinions on some of the most frequently raised concerns in the following myth/fact discussions.

Myth: Bio-based polymers = biodegradable polymers.
Fact: Not necessarily. Whether a polymer is biodegradable depends ultimately on its structure, rather than how it is produced. While most Class A and Class B bio-based polymers happen to be biodegradable, only a few Class C polymers (e.g. PBS and PBAT) are. In other words, PLA, even if chemically synthesized, would still be biodegradable; conversely, polyethylene, bio-based or oil-based, is always nonbiodegradable.

Myth: Bio-based polymers are actually not biodegradable, as they are claimed to be, and thus will not solve the plastics crisis.
Fact: Bio-based polymers and bioplastics do not directly address the accumulation of plastics waste; biodegradable plastics and plastics recycling are the primary means to address waste. The primary advantage of bioplastics is the use of renewable biomass as raw material instead of nonrenewable oil and gas. Nevertheless, since 58.1% of bioplastics produced in 2020 are biodegradable,[11] increased use of bioplastics would likely also reduce plastics waste.

Myth: Bioplastics, even if biodegradable, do not degrade fast enough under normal conditions, and composting facilities must be used.
Fact: Again, biodegradability is only a side benefit of some bioplastics. Slow degradation is common to all biodegradable plastics, not just those that are bio-derived; blaming the latter for the problem would be analogous to criticizing electric cars for not being able to travel twice as fast as cars that use internal combustion engines. Furthermore, too fast degradation would undermine a plastic product's usefulness.

Biodegradable mechanisms are complicated, and some pathways are more environmentally friendly than others.

Myth: Bioplastics are only good for packaging applications and would not replace all conventional plastics.

Fact: Applications for bioplastics have diversified significantly, especially with developments of Class C bio-based polymers. The proportion of bioplastics produced for packaging in 2020 was 47%,[11] only slightly higher than 40% for conventional plastics.[131]

Myth: The production of bio-based polymers takes up much agricultural land and impacts human and animal food production.

Fact: In 2019, 0.016% of the world's total agricultural land was used to produce feedstocks for bio-based polymers.[132] It means that, even if all plastics produced today were bio-based, and even assuming the land area used increases proportionally with production volume, the proportion of farmland used would not exceed 2%.

We hope the above discussions will help raise public awareness of the value of bio-based polymers. At this stage, subsidies and regulations in favor of bioplastics are likely critical to their market expansion. These will be more likely to happen if bioplastics' benefits and challenges are unambiguously communicated to governments and the public.

5. Conclusion

We have discussed in this review the development status of bio-based polymers, with a focus on publication trends in the journal and patent literature, and attempted to provide clarifications on some common confusions and misconceptions. Bio-based polymers can be produced from biomass feedstocks via a variety of routes, and the past two decades have seen strong overall growth of research and development activities. Frequent and wide adoption of bioplastics, made from bio-based polymers, will reduce our dependency on fossil fuels, with the added benefits of lower carbon footprint and biodegradability. However, in the absence of key technical breakthroughs and government support, bioplastics' relatively high production costs have limited their ability to gain more market share from conventional plastics. Decreases in oil prices (and thus in the costs of oil-based polymers) after 2013 has likely had a negative impact on research around the development of bio-based polymers as viable alternatives. As there seems to be plenty of inaccurate perceptions and confusions about bioplastics among the general public, we encourage scientists and entrepreneurs to actively engage in knowledge

sharing and public education, which would be vital to bioplastics gaining favorable public attention as well as government policies.

Acknowledgements

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