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Understanding bioplastic materials - current state and trends

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Abstract: Plastic pollution is now considered one of the largest environmental threats facing humans and animals globally. Development of bioplastic materials may offer part of the solution as bioplastics include both nondegradable and biodegradable materials with both being important for sustainability. Bioplastic materials are currently being designed to encompass minimal carbon footprint, high recycling value and complete biodegradability. This review examines recent developments and trends in the field of bioplastic materials. A range of the most utilized bioplastic materials is presented (polylactic acid (PLA), polyhydroxyalkanoate (PHA), starch, cellulose, bio-based poly(butylene succinate) (bio-PBS) and bio-polyethylene (bio-PE)) including their production, application and degradation options.

Keywords: bioplastics; biopolymers; biodegradation; polylactic acid; sustainability polyhydroxyalkanoates

CONTENTS

INTRODUCTION

Bioplastics – definitions

Historic perspective of bioplastics

DESCRIPTION OF IMPORTANT BIOPLASTICS

Polylactic acid (PLA)

Polyhydroxyalkanoates (PHA)

Starch and Cellulose

Poly(butylene succinate) (PBS)

BioPE

(BIO)DEGRADATION AND RECYCLING OF BIOPLASTICS

CONCLUSIONS

INTRODUCTION

“Plastics” as synthetic polymers were introduced about 100 years ago and today they are one of the most produced, used, and most versatile materials.¹ Nevertheless, their biggest advantage, namely durability, turned out to be their

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biggest problem, as their degradation rate does not match their intended service life so the build-up in the environment is inevitable. Environmental pollution from plastic is a vast issue, given that in 2018 alone the worldwide production of plastics from fossil resources almost reached 360 million tons, while in Europe it reached 62 million tones.² This translates that each person consumes 50 kg of plastic per year in the European Union and 68 kg per year in the United States.³ Approximately half of the synthetic polymers end in single-use or short-lived products, which mostly end up on landfills and in oceans, where they get fragmented over time into ‘microplastics’ that harm and kill various organisms, finally ending up on our plates.⁴ In January 2018, the EU released its vision for a more sustainable plastics industry to be achieved by 2030. The new plastics strategy states that 100 % of plastics should either be reusable or recyclable by 2030.²

Environmental concerns over plastic pollution coupled with a growing debate over crude oil dependence and depletion have sparked and fueled interest in bioplastics. Bioplastics include both nondegradable and biodegradable plastics (Fig. 1) and both are important for sustainable solutions. The production and use of bioplastics are generally regarded as a more sustainable activity when compared with plastic production from petroleum (petrochemical plastics; petroplastics) because it relies less on fossil fuels as carbon source and also introduces fewer, net-new greenhouse emissions if it biodegrades.⁵ Bioplastics also significantly reduce hazardous waste caused by oil-derived plastics. However, the manufacturing of bioplastic materials is still often reliant upon petroleum as an energy and materials source.^{6,7}

Bioplastics – definitions

The term ‘bioplastic’ is often used by the public and in the scientific literature. However, the term ‘bioplastic’ refers to either the bio-based origin of plastic or the biodegradable character of plastic. These two aspects of plastic are not synonymous, and therefore the term ‘bioplastic’ is confusing. In this review, a clear distinction is made between bio-based and biodegradable plastics (Fig. 1). According to International Union of Pure and Applied Chemistry (IUPAC), a bioplastic is derived from “biomass or monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow”.⁸

It is also important to make the distinction between degradable, biodegradable and compostable. These terms are often incorrectly used interchangeably. Degradable plastic is plastic that will undergo some significant structural change in some definite environment. The ‘environment’ may as well be an industrial process instead of some naturally occurring microbial one. According to the IUPAC, biodegradable polymers are defined as “polymers, susceptible to degradation by biological activity, with the degradation accompanied by a lowering of its mass”.⁹ Some other definitions require a biodegradable material to

be mineralized into carbon dioxide, water, and biomass during biodegradation (standard CEN/TR 15351:2006).¹⁰

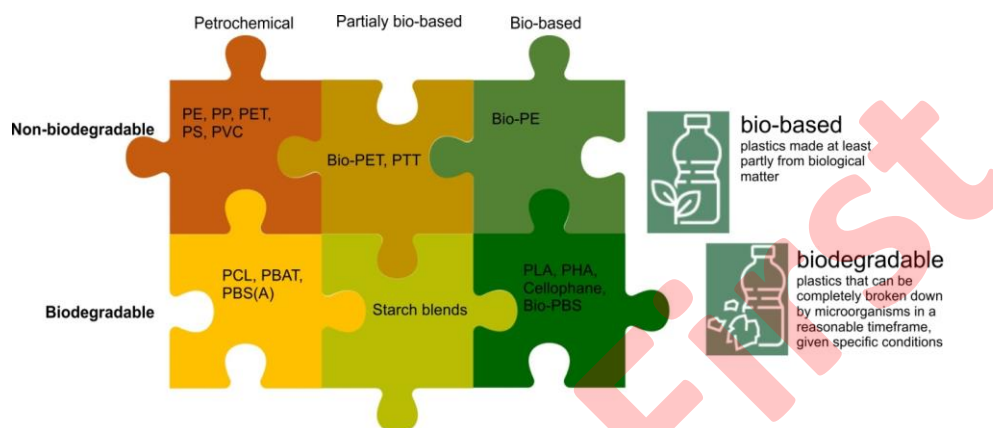


Fig. 1. Not all bio-based plastics are biodegradable, and not all biodegradable plastics are bio-based. PE=polyethylene; PP=polypolypropylene; PET=poly(ethylene terephthalate); PS=polystyrene; PVC=poly(vinyl chloride); PTT=poly(1,3-propylene terephthalate); PCL=poly(caprolactone); PBAT= poly(butylene adipate terephthalate); PBS(A)=poly(butylene succinate(adipate)); PLA=poly(lactide); PHA=polyhydroxyalkanoate.

Compostable plastic is a plastic “capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass, at a rate consistent with known compostable materials (e.g. cellulose) and leaves no toxic residue...” defined by the American Society for Testing and Materials.¹¹ Unfortunately, the term “biodegradable plastic” has also been used by producers of specially modified petrochemical-based plastics which appear to biodegrade. This is the case with the plastics to which a degradation initiator has been added to achieve a controlled UV/oxidation disintegration process. This type of plastic may be referred to as degradable plastic or oxy-degradable plastic or photodegradable plastic as the process is not initiated by microbial action. However, plastic bag manufacturers often misrepresent their product's degradability by misleading use of the terms biodegradable or compostable. It has been shown that even biodegradable plastics might not biodegrade in every environment.¹²

Historic perspective of bioplastics

Natural plastic materials (plant gum, shellac, starch) have been used for thousands of years.¹ The first plastics in the modern sense were celluloid and cellophane and they were bio-based. Cellophane, commercialized in 1912, is still in use today.¹³ In the early 1950s, Amylomaize (>50 % amylose content corn) was successfully bred and commercial bioplastics applications started to be

explored. Modern bioplastics started emerging in the 1980s when the environmental effects of plastic waste became obvious. The first bioplastics were blends of starch with conventional polymers so that certain biodegradability and the use of natural feedstock were partly achieved.

In 1982, Biopol (poly(hydroxybutyrate), PHB) was introduced as the first fully biodegradable plastic, but costing nearly 20 times its non-biodegradable competitors. In 2004, NEC developed a flame-retardant plastic, polylactic acid (PLA), without the employment of halogens and phosphorus compounds. In 2005, Fujitsu became one of the first technology companies to make personal computer cases from bioplastics, which were featured in their FMV-BIBLO NB80K line. In 2007, Braskem of Brazil announced it had developed a route to manufacture high-density polyethylene (HDPE) using ethylene derived from sugar cane.^{1,14}

There are three ways to produce bioplastics that include (i) using natural bio-based polymers such as starch with partial modifications to meet the requirements; (ii) producing monomers by fermentation followed by polymerization (PLA, poly(butylene succinate) (PBS), bio-based polyethylene, bio-PE) and (iii) producing them by bacteria directly (polyhydroxyalkanoates, PHAs).¹⁵ The first generation technologies focused on feedstock such as corn, starch, or rice to produce bioplastics which were deemed unacceptable in food vs. fuel debate, so the focus shifted towards various waste streams from wood and paper as well as food industries or to third generations from micro-algae, marine bacteria, sewage sludge).¹⁵⁻¹⁷

In the last decade, the production of bioplastics has been accelerated and reached substitution alternatives for major petrochemical plastics (Table I).

TABLE I. Bioplastics alternatives for major petrochemical plastics

	LDPE ^a	HDPE	PP	PS	PVC	PET	PUR
PLA	+	++	++	++	-	++	-
PHA	++	+++	+++	++	+	++	++
Starch blends	++	++	++	+	-	++	-
Bio-PE	+++	+++	-	-	-	-	-

Source: Chemical Market Resources Inc. Substitution potential: +++- high; ++-medium; + low; - not foreseen. ^aLDPE = low density polyethylene; HDPE = high density polyethylene; PS = polystyrene; PP = polypropylene; PVC = poly(vinyl chloride); PET = poly(ethylene terephthalate); PUR = polyurethane; PLA = polylactide; PHA = polyhydroxyalkanoate.

In most cases they exhibit similar properties and can even exceed the performances of conventional plastics: *e.g.* PLA can replace fossil-based polystyrene (PS) and can be modified to replace conventional PE or polypropylene (PP); PHA can gradually substitute PP and low-density polyethylene (LDPE) with similar physicochemical, thermal, and mechanical properties; poly(hy-

droxybutyrate) (PHB) possesses better physical properties than PP for food packaging applications and is completely nontoxic. In addition, bio-based polyesters have the potential to prevent from releasing micro-plastics if they are formulated to be biodegradable or compostable. On the other side, the cost of bioplastics is currently still not competitive with that of petroplastics. Bioplastics do not yet reach the fossil fuel parity on fossil fuel-derived energy for their manufacturing, reducing the cost advantage over petroleum-based plastic.⁵

DESCRIPTION OF IMPORTANT BIOPLASTICS

Bioplastics contribute less than one percent to overall plastics production, but the market is growing. About half (44.5 % in 2019) of all bioplastics on the market are bio-based and not biodegradable (Fig. 2). Bio- PE, bio-based PET (bio-PET) and bio-based PTT (bio-PTT) account for the majority of these so-called drop-in materials. They are more or less equivalent to their fossil-based counterparts, so they are really convenient for the industry. Producers and recyclers can drop them into their existing infrastructure, however, they cause the same kind of pollution as petrochemical plastics. Besides PLA, which accounts for 14 % of the global production capacity for bioplastics (biodegradable and non-biodegradable), mainly starch blends (21 %), other biodegradable polyesters including PBS (4 %) and PHAs (1 %) are produced an industrial scale (Fig. 2).

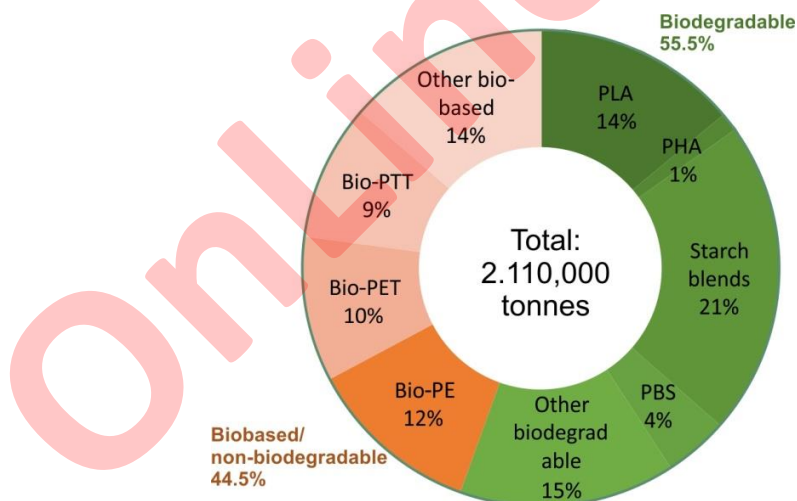
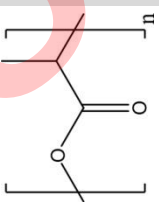
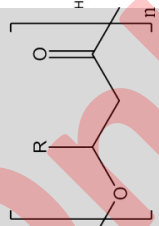
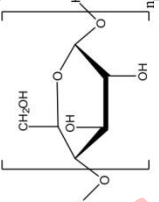
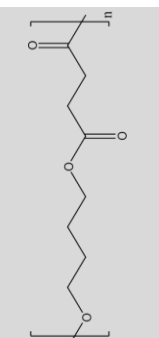
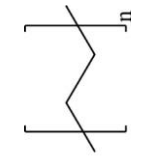


Fig. 2. Global production capacities of bioplastics in 2019 (data adapted from European Bioplastics¹⁸)

Five commercial bioplastics have been chosen for this review based on the volume of their production and the wide range of applications that they cover (Table II).

TABLE II. Biobased polymers described in this study (adapted from Hatti-Kaul and coworkers¹⁹)

Polymer	PLA	PHA	Starch	Bio-PBS	Bio-PE
Structure					
Biobased content, % ^a	100	100	100	Up to 100	100
Annual production, tons ^b	217 000	30 000	384 000	97 000	200 000
Trademarks/ Company	Ingeo/ NatureWorks, Lumony/ TotalCorbion, Lacty/Shimadzy, Vylomecol/Toyobo	Minerv-PHA/ Bio-On, PHBH/Kaneka, Nodax/Danimer Sci.	MaterBi/ Novamont	Bionolle 1000/Showa Denko, BioPBS/PTT MCC Biochem	I' m green/ Braskem
Application	Packaging, medical implants, 3D printing polymers, electronics, textiles	Packaging, compost bags, tissue engineering	Food packaging, compostable films and bags, disposable utensils	Films and sheets for food packaging, fishing nets, the automotive industry	Packaging films and bags

^aThe biobased content of the polymers is based on current information about commercially available products.^bThe annual production volume of the polymers was obtained from www.european-bioplastics.org/market/

Poly(lactic acid) (PLA)

PLA is a biobased and biodegradable aliphatic polyester that represents 13.9 % of global bioplastic production capacities in 2019 (Fig. 2²⁰). Lactic acid (2-hydroxy propionic acid) is the basic monomer of PLA produced either by bacterial fermentation of basic carbohydrates or by chemical synthesis. Industrial lactic acid producers, such as NatureWorks and Total Corbion, utilize the lactic fermentation process rather than synthesis.²¹ The use of corn starch, cassava roots, sugar cane, or potato as the carbohydrate source makes the industrial process of lactic acid production sustainable and renewable.²² PLA is one of the most efficient biopolymers, yielding 1 kg of polymer from 1.6 kg of the fermented amount of carbohydrate feedstock, while other biopolymers require 2-3 times more feedstock for production. PLA and PLA-blends generally come in the form of granulates with various properties and are used in plastics processing industry for the production of foil, moulds, cups, bottles and mulch films used in agricultural fields. On the other side, due to PLA's relatively low glass transition temperature, PLA cups cannot hold hot liquids, so much research is devoted to developing a heat resistant PLA. Additional research is also ongoing to come up with even more eco-friendly and economical methods of producing lactic acid by using crop residues such as stems, straw, husks, and leaves as carbohydrate sources.²³ Lactic acid can be used to produce the PLA of variable molecular weights, however, usually, only the high Mw PLA has major commercial value in various industries.

There are three routes for PLA production:

- 1) direct condensation polymerization: esterification of lactic acid monomers and free water removal using progressive vacuum and high temperatures, resulting in the less-desired low Mw PLA;
- 2) direct polycondensation in an azeotropic solution: PLA production by a direct condensation and continuously removing of condensation water by the azeotropic distillation;
- 3) polymerization through lactide formation (ring-opening method): industrially accomplished for high Mw PLA production using lactide as an intermediate state. This process results in a metal catalyst combining with a lactide to form larger PLA molecules.

PLA has versatile applications in the food-packing industry, medical and cosmetics industry, textile industry, structural applications and 3D printing (Table II). The global PLA market was valued at USD 673.88 million in 2018 and is estimated to generate net revenue of approximately USD 2277.57 million by 2027. PLA market is dominated by 1–5 major players such as NatureWorks, Total Corbion, Synbra Technology BV, Futerro and Sulzer Ltd, with NatureWorks and Total Corbion being the major producers, with a capacity of 1.5×10^5 and 0.75×10^5 metric tons per year, respectively (Table SI).²⁴

In the past 10 years, the vast majority of patents regarding PLA production is related to methods of processing PLA into materials for particular applications such as 3D printing wires, fibers, sheets, etc., or to modification of available PLA in order to improve their properties (CN108705753A, CN106738783A, CN104138310A, US2015337097A1, CN104356365A). When it comes to patents concerning the production of raw material, they are mainly focused on methods of obtaining high molecular weight PLA (US9023953B2, US9062006B2, CN106750199A). Additionally, two patents should be pointed out since they are dealing with the production of lactic acid using agricultural feedstock and sideline products, thus making PLA production process ecologically and environmentally even more viable (US7507561B2, CN104592500A).

As mentioned, PLA has some significant shortcomings such as low melt strength, poor processability, high brittleness, low toughness, and slow biodegradation rate, which hamper specific PLA applications.²⁵ Therefore, PLA is often blended/combined with a range of different polymers, additives, and fillers in order to improve material properties, reduce costs and open up new opportunities for PLA application.²⁶ Some of the most studied PLA blends with other polymers are listed below:

- The development of PLA blends with biobased and biodegradable thermoplastic starch (TPS) is of great interest for food packaging applications and could also be considered in biomedical applications, due to achieved improvements in toughness²⁷;
- Addition of biobased and biodegradable PHB to PLA enhances its crystallinity, which is important for food packaging applications in order to increase the barrier performance of PLA based materials²⁸;
- PLA blends with biodegradable PCL have improved ductility and toughness compared to neat PLA, and increased tensile strength compared to neat PCL, and as such, they are utilized in tissue engineering and grafts, as well as in packaging applications with easy-open peelable feature²⁹;
- PLA and biodegradable PBS blends exhibit a ductile behavior with gradual losses of strength and modulus during biodegradation, so they have potential in food packaging applications. In addition, PBS/PLA blends have excellent mechanical properties and suitability as materials for 3D printing^{30,31};
- PLA and synthetic, non-degradable PEG blends have decreased viscoelasticity, and increased hydrophilicity and degradation rate, and often are used for drug delivery and scaffolds. 3D-printed scaffolds were also recently produced using PLA/PEG blends.³²

Recycling, as one of the possible plastic disposal routes, has been extensively studied on PLA. Currently, only 10 % of PLA waste is returned to the PLA production process.³³ PLA can undergo mechanical or chemical recycling. An easy and the cost-effective way to recycle post-consumer PLA is

mechanical recycling that involves recovering, sorting, regrounding, and reprocessing the waste plastic and that became common practice in the industry.³⁴ However, this method has limitations affecting PLA quality, thus limiting the range of products in which it can be used and reducing the economic viability.³⁵ An alternative is chemical recycling, during which PLA is hydrolyzed at a high temperature to yield lactic acid, which can be readily polymerized to high Mw PLA. NatureWorks is an example of successful offgrade Ingeo™ recycling using a chemical method, while Galactic started the pilot unit to produce recycled PLA using a chemical recycling process (Loopla). However, chemical recycling is still a complex and expensive process. Although PLA is potentially recyclable, no separate recycling stream for PLA yet exists.³⁶ Presence of PLA in the current plastic recycling infrastructure, even at low concentration, causes contamination of the recycling stream and production of inferior recycled material. Thus, it is crucial to sort out PLA from other plastics and also to establish single streams of materials like PLA in order to recycle them. In addition, PLA is assigned the Resin Identification Code (RIC) number “7-OTHER” (ASTM D7611), with several other, rather new, polymers, and that is not considered accurate for the identification and (pre)sorting of PLA from a waste mixture.³⁵

Another end-life scenario for PLA and the natural way of recycling is biodegradation. Numerous literature data are dealing with PLA degradability in soil and compost. Majority of these studies used industrially produced PLA for testing, and polymer weight loss or molecular weight loss as methods to assess degradability. PLA degradation upon disposal in the environment is very challenging due to PLA resilience to microorganisms' actions in soil or sewage under ambient conditions.²¹ No significant PLA degradation was observed when the polymer was buried in the real soil environment, or in soil under controlled temperatures of 25 °C and 37 °C, even after 24 months of exposure.³⁷⁻⁴⁰ However, PLA - including commercially available PLA bottles and PLA deli containers, could be degraded in the compost after only 45–60 days, but high temperatures of 50–60 °C are required to hydrolyze the polymer into smaller molecules, which are then degraded by microorganisms to CO₂ and H₂O.^{41,42} A search of patents from the previous decade revealed a large number of patented microorganisms and corresponding enzymes with PLA degrading activity (Table III).

Since PLA must first be hydrolyzed at elevated temperatures to reduce the molecular weight before biodegradation can commence³⁸, it is more accurate to say that PLA is compostable, but due to a specific temperature and moisture conditions necessary for proper PLA composting, the path to zero waste is complicated and unattainable at this moment. In contrast to soil and compost, only a few studies deal with PLA biodegradation in aquatic environments. Since

after 10 weeks no evidence of microbial degradation was found, authors suggested that marine microbes have a limited ability to degrade PLA.^{43,44}

TABLE III. Examples of patented microorganisms for PLA degradation

Patent number	Year	PLA-degrading microorganism (enzymes)
CN110317762A	2019	<i>Pseudomonas</i> sp. LXM88/protease
WO2017198786A1	2017	
CA2937569A1	2017	<i>Alcanivorax borkumensis</i> , <i>Rhodopseudomonas palustris</i> /hydrolase
WO2016146540 A1	2016	<i>Micromonospora</i> sp./hydrolase
WO2016062695A1	2016	<i>Actinomadura keratinilytica</i> T16-1/hydrolase
AU2014325231A1	2016	protease
EP2483429A1	2012	<i>Ochrobactrum</i> sp.
CN102380180A	2012	<i>Lentzea waywayandensis</i> , <i>Tritirachium album</i> , <i>Amycolatopsis orientalis</i>
CN102181378 (A)	2011	<i>Pseudomonas</i> sp. DS1001
JP4273504B2	2009	<i>Aspergillus oryzae</i> , <i>Aspergillus soya</i> /serine hydase

Polyhydroxyalkanoates (PHA)

PHAs are a family of natural biodegradable polyesters, usually produced by prokaryotes as cytoplasmatic water-insoluble storage compounds of carbon and energy.⁴⁵

Since the discovery of the simple PHB homopolymer by Lemoigne in the 1920s, a family of over 150 different aliphatic polyesters of the same general structure was revealed. As a result, the polymer properties demonstrated by this family are very broad.⁴⁶ Although their shape, size, structure, and physical properties depend on the producer organism and cultivation conditions, all polyesters are thermoplastic, water-insoluble, non-toxic, relatively resistant to hydrolytic degradation, biocompatible and biodegradable.⁴⁷ PHAs are classified into two major subdivisions by the carbon chain length of their monomeric units: short-chain-length-3-hydroxyalkanoates (scl-3HA) have 3–5 carbon atoms and medium-chain - length - 3 - hydroxyalkanoates (mcl-3HA) with 6–16 carbon atoms.⁴⁵

PHB was the first bacterial PHA identified. The unique properties of PHA are recognized as better oxygen barrier than PP and PET, better water vapor barrier (than PP), and the fat/odor barrier. Such superior physicochemical properties of PHA (*e.g.* in reference to PP) have promoted its usage in various fields including food packaging.⁴⁸ However, the poor mechanical performance and melt processing behavior of PHB, *i.e.* high brittleness, low thermal stability and difficult processing, along with insufficient barrier properties, limit its widespread use.⁴⁹

Several companies have developed PHA copolymers in order to improve the properties of PHAs. The incorporation of secondary different hydroxy acid (HA) monomers other than PHB such as 3-hydroxyvalerate (3HV), 3-hydroxyhexa-

noate (3HH), 3-hydroxypropionate (3HP) and 4-hydroxybutyrate (4HB) into the polymer chain to form copolymers is a common strategy.⁴⁷

One of the first copolymers that were manufactured in the industry was Biopol®, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). This copolymer is a thermoplastic and has a melting temperature in the range of 140–180 °C. It has a range of uses such as packaging, shampoo bottles, disposable razors, disposable cups, surgical stitches, surgical pins, disposable knives and forks, woven medical patches and nappy linin.⁴⁷ The mole percentage of 3HV is important in determining the properties of the copolymer since the composition of P(3HB-co-3HV) can range from 0 to 30 mol % 3HV. Li *et al.* found better tensile strength and Young's modulus of P(3HB-co-3HV-co-3HHp) in comparison to P(3HB).⁵⁰ The P(3HB-co-4HB) copolymer exhibits a broad array of morphologies such as high crystalline to elastomeric based on the concentration of 4HB.⁵¹

PHB has a comparable melting temperature with PLA, and thus allows for the blending of both polymers in their melted state.⁵² Blends of PHAs with natural raw materials from sustainable resources are well discussed.⁵³ The most common are PHA blends with starch, lignin and cellulose derivatives.^{54,55}

Many years of research efforts have led to the large-scale production of PHA and its copolymers. Procter and Gamble have developed Nodax® (Table II), PHA polymer consisting of PHB and a comparatively small quantity of medium chain length (mcl) monomers. The mcl units used include 3HH, 3-hydroxyoctanoate (3HO) and 3-hydroxydecanoate (3HD). Tianan's biopolymer Enmat® is PHBV copolymer contains about 5 % 3HV which improves the flexibility of the polymer. The USA based company Newlight Technologies chose methane as the carbon source for fermentation with a planned capacity of 43,000 tones per year within the next 20 years. Other commercial PHAs are produced by Bio-on (MINERV®), Metabolix (Mvera®, Mirel®), PHB Industrial (BIOCYCLE®) among other manufacturers (Table SII). Worldwide, more than 20 companies are known to be engaged in PHA production and applications. China, Italy, the USA and Brazil represent the main producers of PHAs using corn, cassava, sugar beet juice and sugarcane.⁵⁶

PHA has been produced with limited success in the market mostly due to the high production cost and instability on thermo-mechanical properties resulted from changing molecular weights and structures, that are related to varying PHA synthase activity.⁵⁷ The mechanical properties and biocompatibility of PHA can also be changed by blending, modifying the surface or combining PHA with other polymers, enzymes and inorganic materials, allowing a wider range of applications.

Although 300 types of natural PHA producers have been identified, only a few bacteria have been adopted for commercial production of PHA. Such

bacteria, including *Alcaligenes latus*, *Bacillus megaterium*, *Cupriavidus necator*, and *Pseudomonas oleovorans*, are found to convert different kinds of carbon sources into PHA.⁴⁸ The main carbon sources are glucose, fructose and fatty acids such as lauric acid. In particular, the feedstock cost for PHA production represents half of the overall production cost.⁵⁸ The enormous studies have been conducted to find low-cost feedstocks for the PHA production at industrial scale. Although food waste is a good initial feedstock for the production of bioplastics, it must be pretreated to improve or modify the physicochemical and biological properties.⁵⁹

Gerngross and coworkers reported for the first time the *in vitro* production of PHB.⁶⁰ This finding brought a new perspective and insight to economical processes for the synthesis of PHAs, using enzymes as a catalyst will offer a possibility of carrying out reactions in aqueous solution, which is a cheaper and more environmentally benign medium. Unusual PHAs can be synthesized from a wide range of substrates mediated by commercially available enzymes such as lipases and cutinases. Major disadvantages of this approach include high consumption of organic solvents, a progressive increase of medium viscosity over time and relatively low Mw of polymers obtained.⁶¹ To commercialize the enzymatic process, the production and purification costs of the enzyme need to be reduced.⁶² Today industries are still using the more robust and conventional way to synthesize PHAs, which is microbial fermentation.

Three techniques have been investigated, including mechanical, chemical and biological recycling.⁶³ PHAs can be mechanically recycled with some loss of molecular weight and mechanical properties.⁶⁴ Recently, PHBV has been mechanically recycled by Zaverl *et al.*⁶⁵, showing that PHBV is recyclable for up to five cycles because the reprocessing cycles did not significantly affect the mechanical properties (tensile and flexural testing, and impact toughness). The main disadvantage of mechanical recycling is that it is not applicable for the collected bioplastics from the waste which is expected to be heterogeneous. Chemical recycling of PHAs by thermal degradation has resulted in a transformation of PHAs into vinyl monomers.⁶⁶ Ariffin and coworkers used alkali earth compound catalysts (CaO and Mg(OH)₂) to enforce smooth and selective degradation of the polymer at a lower temperature. The obtained monomers, crotonic acid and 2-pentenoic acid, were then used as feedstock for the production of poly (crotonic acid-co-acrylic acid) through copolymerization.

PHAs are an appropriate candidate for biological recycling as its biodegradation can occur under both aerobic and anaerobic conditions.^{67,68} Numerous bacteria, streptomycetes, and fungi isolated from the different terrestrial and aquatic environments produce extracellular PHA depolymerases in order to hydrolyze solid PHA into water-soluble monomers or oligomers to be used as nutrients.⁶⁹ In this sense, many scl-PHA depolymerases have been

purified and characterized in contrast to a limited number of mcl-PHA depolymerases. It is very difficult to compare the activities of PHB depolymerases because of the various set of conditions used in tests. Martinez-Tobon and coworkers compared the activity of strains with proven and predicted PhaZ activity for PHB film degradation, which helped to identify strains displaying high degradation activity. Strains *Crupriavidus* sp. and *Comamonas testosteroni* 31A showed the highest percentage of weight loss after 7 days, 90 % and 53 %, respectively.⁷⁰ There are some examples of highly tolerant enzymes in harsh conditions such as PhaZs depolymerases from *Comamonas testosteroni* YM1004, *Schlegelella* sp. KB1a, *Schlegelella thermodepolymerans*, *Streptomyces* sp. IN1 and *Thermus thermophilus* HB8. These biocatalysts could be employed in the degradation of polymers from industrial wastes that may require high pH and/or temperatures since polymer solubility is increased and microbial contamination is reduced.⁷¹

Several factors can influence the time needed for total biodegradation, including polymer characteristics, surrounding conditions, and the type of degrading organisms. The "real-life tests" separate composting, soil burial and field testing.⁶⁸ In a study by Hablot *et al.*, the degradation of PLA/PHA nonwoven mulches was performed using simulated weathering. At 63 °C, the repetition of UV irradiation and the water spray system promoted the degradation of the PLA/PHA blend and molecular weight loss of 90 % was achieved after 180 days.⁷² When the PHB films were immersed in the sea at a depth of 1.5m, their weight loss after 4 weeks was about 90 %. On the contrary, the biodegradation in seawater by lab test method for 4 weeks was around 50 %.⁷³ Biodegradation tests carried out in artificial environments lack transferability to real conditions and, therefore, there is the necessity of environmentally authentic and relevant field-testing conditions.

In the patent base for the last 10 years, the great number of innovations related to the advancement of the PHA production process has been described (Table SIII). Many inventions are focused on downstream feedstock costs (WO2014032633A1, US20190360008A1). The microbial production of PHA copolymers from two raw materials (sugar cane and sugar beet) containing sucrose is disclosed (EP2780461A1). Isolation of new PHA-producing microorganisms and genetic modification of existing ones is also the purpose of many inventions. In WO2012149162, the organisms are engineered to efficiently utilize ethanol (or in some cases xylose) as the carbon source to produce a range of PHA copolymers with a cost-effective yield.

The process of producing monomers from PHA by depolymerization is in the focus of many inventions (CN104328062A, WO2016085396A1). A method for efficiently decomposing PHA and converting it to biogas containing methane as a main component, particularly under anaerobic conditions has been disclosed

by Kaneka (WO2015122190A1). Additionally, major PHA producers disclosed several patents related to the improvement of the production process, processing, and functional modification of PHAs (US2017369908A1, WO2018021046A1, US2020109423A1).

Starch and Cellulose

The interest toward polysaccharides as biomaterials is increasing continuously during the past decade owing to their applications in pharmaceuticals, biomedical use, food supplements, and cosmetics. The fact that these polymers, such as cellulose and starch are extracted from natural resources has led to the impression of good biocompatibility and biodegradability.⁷⁴

Starch is a well-known, versatile, inexpensive, and primary energy reserve polysaccharide in plants. Generally, the native starch isolated from different plants tends to have limited shear resistance, thermal resistance, thermal decomposition, and a high tendency toward retrogradation. Additionally, starch dissolves in the aqueous media, and it shows low mechanical and shapes stabilities in liquids. To overcome these limitations, starch can be combined with stable, synthetic, thermoplastic polymers.⁷⁵ For example, pairing starch with PCL resulted in improved processability of starch, reduced high stiffness, and overcome high moisture sensitivity of starch, which is one of the greatest weaknesses of starch as a biomaterial. On the other hand, starch improves the biodegradability of PCL and, as the cheapest biomaterial on the planet, starch can substantially lower the high cost of the final product.^{76,77} Development of starch blending techniques tends to be more interesting while potential applications are extensive and they can be able to substitute an older material that exhibits the same properties. Among its tissue-engineering applications, starch is most famous for its use in generating scaffolds for bone regeneration due to its bone-bonding behaviour when reinforced with hydroxyapatite, good mechanical properties, non-cytotoxic and biocompatible nature, excellent support for cell adhesion, and thermoplastic behaviour when combined with thermoplastic polymers.^{78,79}

The plant material is grounded in water, the debris is filtered from the slurry, and starch granules are obtained after centrifugation from the suspension.⁸⁰ The content of amylose and amylopectin in starch varies and largely depends on the starch source. Typically, the amylose content is between 18-28 %. The ratio of amylose and amylopectin in the starch may affect starch behaviour during processing and the properties of the end product. As the amylose content increases, the crystallinity of starch-based products is increasing as well resulting in texture firming.⁸¹ Several techniques may be applied to develop starch-based biomaterials with improved properties: thermoplasticization, cross-linking, esterification, and blending with different polymers.

Most of the starch produced worldwide is derived from corn, but other types such as cassava, sweet potato, potato, and wheat starch are also produced in large amounts.⁸² Italy-based Novamont is a manufacturer of starch-based plastic called Mater-Bi used to make BioBag branded certified compostable bags (Table II). BioBag® is the world's largest brand of certified compostable bags and films made from Mater-Bi. SpudWare® was one of the first bioplastic starch-based cutleries brought to the market. It stood out for its ability to withstand high heat. BioMass Packaging® uses TSP to manufacture water-soluble packing (<http://www.biomasspackaging.com/education/bioplastics/>). Some fishing hooks are also made from starch-based polymers. Since corn starch can absorb 1000 times its weight in moisture, it is used in disposable diapers (Tethis™), fuel filters to remove water (Super Absorbent Co.), and as a treatment for burns (Sonett).⁸³

Cellulose is the most abundant renewable resource on the planet and the major structural component in plant cell walls. Besides plants, some species of bacteria and algae produce cellulose. In general, cellulose, regardless of the source, is a highly crystalline and high molecular weight biopolymer and is, usually, a fibrous, tough and hydrophilic but insoluble in water and other common solvents. The chemical structure of cellulose makes it suitable to form hydrogels which are used in tissue engineering, cartilage modelling, bone implantation, cell culture scaffolds, enhanced drug delivery, heavy metal absorbance, and in retaining soil water and efficient fertilizer release for agricultural efficiency. Because of its abundance, cellulose can serve as a virtually inexhaustible source of raw material in the production of sustainable bioproducts.^{84,85} The nanocomposites of cellulose have revolutionized the medical field and are being used in tissue engineering, ligament engineering and wound healing. In addition, cellulose-based ethanol production help to reduce the pressure on conventional energy sources.^{86, 87} As its anhydroglucopyranose unit contains reactive hydroxyl groups, cellulose has potential use in designing advanced polymeric materials. So far, most of the industrial modifications of cellulose to improve its properties have been cellulose esters, ethers and graft copolymers, obtained by changing the hydroxyl groups of the cellulose molecules.⁸⁸

Cellulose can be produced by two means: natural synthesis procedures including plant photosynthesis and microbial synthesis.⁸⁹ Cellulose is present in small quantities in all brown algae, most of the red and golden algae. The most effective producers of bacterial cellulose (BC) are *A. xylinum*, *A. hansenii* and *A. pasteurianus*.⁹⁰⁻⁹² BC is chemically pure, free of lignin, hemicellulose, and pectin. Current methods of BC production include static culture, submerged fermentation through aerated or agitated cultivation and airlift bioreactors.⁹³ In static cultures, BC is formed at the liquid-air interface as hydrogel-like membranes, with thickness from millimeters to centimeters. Microfibrillar structure of BC is responsible for most of its properties such as high tensile

strength, high crystallinity index and a higher degree of polymerization.^{94,95} The modification of BC can be performed during its biogenesis by the introduction of different substances into the BC-producing growth medium or by modification of bacterial cells. The other approaches for modification of cellulose (plant or bacterial) include the use of physical factors, such as ultrasound irradiation (or sonication), static magnetic field (SMF), or rotating magnetic field (RMF) exposure. BC can be modified by cultivation with an AgNO₃ solution which results with the BC membrane containing silver nano-particles. The new properties of BC can also be achieved by incorporating reinforcing particles into the membrane structure.^{96,97}

It is challenging to estimate the time that cellulosic material will be available to microbial degradation because of the limited number of microbial organisms able to degrade solid cellulose and due to different crystalline forms of cellulose. As a result, microbial degradation of solid cellulose can often be the rate limiting step. The deconstruction of cellulose contained in the plant cell wall requires the action of specific enzymes able to release degradation products from this substrate.⁹⁸ Enzymatic degradation of cellulose is generally carried out by hydrolases. Biodegradation of cellulose wastes by fungal or bacterial enzymatic activities represents a large area of research experiments concerning the influence of different physical and biochemical factors.⁹⁹

NatureFlex™ by Futamura (Japan) is a major source of renewable cellophane film (natural biopolymer made of cellulose from plants). Nature Flex bags generally degrade in several weeks in a home compost pile or a commercial compost facility. BioMass Packaging carries cellophane products made with Nature Works LLC, a 100 % cellulose biopolymer with excellent oxygen, grease, oil and moisture barrier characteristics. They are used as a packaging film for bakery product wraps, other food wraps, and food-grade transparent bags. Bio-process®, XCell®, and Biofill® are bacterial cellulose-based products already available commercially for topical application in wound healing,¹⁰⁰ <http://www.biomasspackaging.com/education/bioplastics/>). BC is extensively used in the food industry, packaging and acoustic diaphragms for audio speakers and headphones. Large surface area and great absorbance properties enable the use of very low BC concentration/amount to form an excellent binding, thickening and coating agents. Papers that are coated with BC are extremely strong and smooth as the coating protects the underlying fibres from moisture.¹⁰¹

The biodegradation of starch-based materials depends on the starch processing method used as well as on the biodegradability of other components. The main elements in biodegradability testing are the incubation of the sample under conditions conducive to microbial attack and/or their enzymes, and evaluation of the degree of degradation. Polyvinyl alcohol (PVA) and starch are biodegradable in some microbial environments: they are compatible and their

blends present good film properties. Several wheat starch/PVA/glycerol blends prepared using a solution casting technique under ISO 14855 were examined by composting for 45 days. Starch and glycerol were absolutely degraded while PVA appeared practically intact.¹⁰² The biodegradation of co-extruded starch/PLA films was studied in liquid, inert solid, and composting media using experimental ISO methods. The percentage of mineralization in the compounds was higher than the minimum required 60 % that allows a compound to be classified as biodegradable. Researchers found that the addition of starch enhanced biodegradation of the PLA component, especially in liquid media.¹⁰³ Studies also showed that ternary blends composed of PLA, PCL, and starch buried in soil, degraded rapidly in the first 8 weeks.¹⁰⁴

Biodegradability of cellulose is dependent on cellulose's degree of crystallinity, structure, functional groups, cross-linking and molecular weight.¹⁰⁵ Two general types of substrates were used to measure cellulose biodegradation: relatively unaltered natural substrates (pure crystalline cellulose or biomass), and modified cellulosic substrates (substituted or dyed celluloses). Studies showed that PHB/BC composite biodegraded at a greater rate and extent than that of PHB alone, reaching 80 % degradation after 30 days, whereas PHB did not reach this level of degradation until close to 50 days of composting.^{106,107} Even though biodegradation of some cellulose samples has been studied, there is still a lack of a comprehensive study on biodegradability of a variety of cellulose-based packaging materials that can potentially replace synthetic packaging films.¹⁰⁸

A list of patents related to starch and cellulose is presented in Table SIV. The process described in WO2017130106A1 relates to the production of starch from microalgae which is more efficient in comparison with conventional production. Method of producing a starch-based biodegradable polymer, using processed cannabis waste as a carbon source is described in WO2020037394A1, while the process for producing biodegradable plastic from agricultural by-products renewable resource-based is covered in WO2019155398A1. Patent WO2018125897A1 is related to the production of material formed from one or more starches, a plasticizer and water, resulting in improved sustainability, biodegradability and increased strength. CN102585485B relates to the preparation of composite material (starch combined with thermoplastic polyurethane). This material has the advantages of high mechanical property, low cost, biodegradability, and the process of preparation is simple. WO2016138593A1 also covers the potential of starch to combine with one or more biodegradable polymers (PCL, PBS, PLA, PHA) in order to get biocomposites with tailored properties. WO2018041779A1 and WO2020034958A1 are describing the application of starch and its modifications in food packaging with low tensile strength products, while WO2017091463A1 provides methods of making coated particles using different kinds of starch. Patent WO2019209834A1 relates to new additive materials that

are physically blended with polymeric materials, such as starch, to impart biodegradability to polymers that are not otherwise biodegradable. Patent WO2020014762A1 relates to the production of nanocellulosic material based on fractioning a cellulosic pulp stream originating from pre-treatment or mechanical defibrillation. WO2019221535A1 presents a method for manufacturing crystal nanocellulose and WO2020015884A1 describes a device and a method for producing nanocellulose from natural raw materials. WO2017160218A1 also relates to a method of manufacturing a cellulose product from cellulose fibers. On the other hand, bacterial cellulose production on cassava bagasse as suitable feedstock and its processing is covered in WO2016029432A1. Methods for production and processing of multi-phase biomaterials based on bacterially synthesized nanocellulose are presented in WO2016113400A1. WO2017192476A1 presents an invention which provides a pulp product with nanocellulose as a tool for improving the strength properties. Cellulose derivative with excellent thermo-plasticity, waterproofness, elastic modulus and impact strength and its producing method are presented in WO2017061190A1. Patent WO2018187782A1 provides a method for modification of the surface of polymer-based materials (bacterial nanocellulose, nanocellulose, and a cellulose derivative) and compositions generated thereby. WO2016174104A1 relates to the use of the bacterial nanocellulose composite in chip technology and material engineering, and furthermore, for medical purposes (skin, tissue, or neuro transplant). WO2020035734A1 is also connected with medical usage of cellulose nanofibrils describing a method of producing three-dimensional autologous fat graft.

Poly(butylene succinate) (PBS)

PBS is an aliphatic biodegradable polyester produced by polycondensation from 2 raw materials: succinic acid (SA) and 1,4-butanediol (BDO). The mechanical properties of PBS are similar to low-density polyethylene (LDPE) or polypropylene (PP)^{109, 110} but it can be biodegraded in contrast to LDPE and PP.¹¹¹ Beside the production of PBS by polycondensation, recently a lipase-catalysed synthesis of PBS was developed.¹¹² PBS synthesized by lipase has a narrower polydispersity index than that synthesized by the polycondensation, but the remaining lipase may cause a problem in the following thermal processing.¹¹²

In the beginning, PBS was biodegradable but petro-based polyester and currently, large plants for producing renewably sourced SA were developed and Mitsubishi commercializes bio-based PBS (bio-PBS) that is obtained by using bio-based SA (bio-SA). Furthermore, bio-based BDO (bio-BDO) can be produced at an industrial scale, as well. Nowadays, products of 100 % bio- PBS can be found in the markets. Bio-PBS is produced in various demo and pilot plants, mainly from sugarcane and cassava monomers.¹¹³ The production of bio-PBS includes the productions of BDO and SA, and the production of BDO includes the production of bio-ethanol and SA (Argonne National Laboratory,

2014).¹¹³ The production of bio-ethanol using sugarcane is separated into three major stages: the sugarcane plantation, the conversion of sugarcane into molasses by sugar milling and refining, and the processing of molasses into bio-ethanol by fermentation.¹¹³ In a more recent study, a novel, nonphosphorylative pathway was used to convert biomass sugars to BDO with a 100 % theoretical maximum molar yield.¹¹⁴ In that pathway assimilation of sugars into the TCA cycle is allowed and afterward built of artificial biosynthetic pathways to BDO using 2-ketoacid decarboxylases and alcohol dehydrogenases enzymes.¹¹⁴ Bio-SA is mainly produced by several microorganisms as a fermentation product. Bioamber built the first plant in 2008 that uses *Escherichia coli* as a host microorganism and wheat-derived glucose as a substrate for SA production. Four years later, Reverdia, a joint venture between DSM and Roquette, started production of bio-SA from starch using low-pH yeast technology, and Myriant technologies set up a SA plant with the production capacity of 30 million pounds from unrefined sugars as feedstock using *E. coli* as a host organism.¹¹⁵ Derived from natural resources, such as sugarcane, cassava and corn, bio-PBS is compostable into biomass, carbon dioxide and water. There are already several producers with existing commercial capacities for the production of bio-PBS and additional dedicated and non-dedicated capacities are expected to start up in the coming years (Table SV). Bio-PBS is currently being employed in a wide range of industries such as packaging, agriculture, pharmaceutical, consumer goods, electronics and electricals, textile, automotive and interiors.¹¹⁶ It is also utilized to produce bowls, plates, plastic utensils, and diapers.¹¹⁶ Amongst others biopolymers, bio-PBS has strengths in flexibility, natural fiber compatibility, heat resistance and biodegradability under specific conditions (according to DIN EN 13432). It was found that the PBS polymer was more ductile if some adipic acid/lactic acid or some other monomer was added during the standard polymerization of SA and BDO.¹¹⁷ These results indicate that copolymerization of PBS is essential for improving its characteristics. Depending on the monomer and the stereochemical nature of the monomer, different PBS (bio-PBS) copolymers have been registered, such as: PBSA (poly(butylene succinate-co-adipate)), PBST (poly(butylene succinate-co-terephthalate)), PBSF (poly(butylene succinate-co-fumarate)), PBS-DLS (poly(butylene-succinate-dilinoleic succinate)), P(BS-BMS) poly(butylene succinate-co-butylene 2-methylsuccinate), PBS-PLA blends, etc. Amongst the different possibilities for PBS copolymers, PBSA, PBST and PBS-PLA blends are the most commonly mentioned in literature. PBSA copolymer is better degraded than PBS due to its lower crystallinity and glass transition temperature¹¹⁸, and together with PBS it was manufactured under the trademark Bionolle® (series 1000 and 3000, respectively) by Showa Highpolymer Co., Ltd for application as trash bags, plant pots, filaments, bottles, gloves, containers, laminated paper, trays, etc.⁷¹ PBST

copolymer has a lower crystallinity than PBS, but in contrast to PBSA biodegrades more slowly.¹¹¹ PBST like other aliphatic-aromatic copolymers may be used as a film or coating in disposable food packaging. PBS-PLA blends with low toxicity have potential in food packaging, biomedicine, and agricultural markets.¹¹⁹ Commercial PBS-PLA blends have been utilized for food service ware production by NatureWorks LLC.⁶⁴ Based on extensive research, PBS-PLA blends have been successfully modified and processed into fibers, blown films, flat films, and sheets.²⁵ PBS and its copolymers are biodegradable in lipase solution, soil burial, water, activated sludge and compost.¹²⁰⁻¹²²

Currently, about 75 % of the plastic waste is disposed in sanitary landfills and about 25 % is recycled.¹²³ In general, bioplastics can degrade under anaerobic conditions in landfills releasing methane, but with a proper composting facility, bioplastics can be converted to compost and recycled.¹²⁴ Recycling of plastic waste and bio-based waste, like bio-PBS, may be done through several processes: mechanical, chemical and organic processes. Chemical recycling of bio-based PBS and its copolymers is environmentally harmful, thus the use of polyester-degrading enzymes is an eco-friendly alternative. Many hydrolases from several fungi and bacteria have been discovered and successfully evaluated for their activity against different aliphatic and aromatic PBS polymers and copolymers.^{71,125} Bio-PBS produced by PTT MCC Biochem has industrially compostable and home compostable grades, but the current grade used for paper coating is only industrially compostable.¹²⁶ Bio-PBS can be easily separated from the paper when soaking under water without damaging paper pulp and paper pulp can be recycled to produce paper again, or like backyard compost, or in the case of a leak to the environment, it will degrade eventually in limited time.¹²⁶ Testing the degradation phenomena of bio-PBS plastics in the environment can be classified into three categories: field tests, simulation tests, and laboratory tests.¹²⁷ The performed degradation studies of a commercially available PBS and PBSA copolymer in various environments have shown that the most favorable degradation environment was compost, which contains microorganisms and natural enzymes that support degradation.¹²⁸ In those studies, degradation after four to six weeks was observed, followed by a strong mass loss in compost, due to interaction with enzymes. In addition, the strength of polymers was significantly reduced. Biodegradation test in the soil gave the same results like biodegradation in compost, but the changes in the molecular parameters were less intense because of lower concentration of microorganisms, enzymes and lower temperature of the process.¹²⁸

According to the patents base, in the last 10 years, most patents are based on bio-PBS biodegradability. Mostly, patents deal with the promotion of methods for preparing new bio-PBS materials which have improved mechanical properties, compatibility, controlling of degradation speed, and with whom the cost of bio-

PBS production is effectively reduced (CN109608835A, CN103709688A, CN110240788A, CN109867921A, CN106589854B, CN105670248A). Bio-PBS materials with improved properties have been used through patents in the last 10 years mainly in the form of coated paper, synthetic fiber, trash bag, coffee capsule cutlery, *etc.* (US20180058010A1, US20140021574A1, WO2010151798A2, WO2016105217A1).

Bio-polyethylene (BioPE)

PE consists of long chain polymers of ethylene and it is produced as either HDPE or LDPE, or linear low density polyethylene (LLDPE).¹²⁹ PE is chemically synthesized by polymerization of ethane.¹²⁹ Bio-based PE (bio-PE) is chemically identical to fossil-based PE, it has the same technical properties and it is not biodegradable.¹³⁰ Bio-PE is used to produce high value products using low pollution processes and contributing to the global environmental balance. The process involves: pretreatment, enzymatic scarification, fermentation, dehydration, and polymerization.¹³¹ Ethanol produced by fermentation from renewable resources can be used as a raw material for polyethylene production. Production of bio-PE from renewable resources consists of three steps¹³⁰:

- 1) synthesis of ethanol by a fermentation process from sugars, extracted from natural materials *e.g.* sugarcane;
- 2) chemical dehydration reaction transforming of ethanol into ethylene;
- 3) “classical” reaction of polymerization of ethylene into polyethylene to make the various grades of PE (HDPE, LDPE, LLDPE).

Bio-based PE produced this way is used in packaging applications like carrying bags, plastic films and bottles, automotive fuel tanks, injection molded parts, tubes.¹³² The most used PE copolymer is HDPE. HDPE is a rigid polymer with polymer chains packed closer one to other resulting in greater intermolecular forces. The presence of a strong intermolecular forces results in a dense, highly crystalline material form. It is a relatively tough and resistant polymer that can withstand high temperatures, up to 120 °C, without any effect on material properties. Furthermore, HDPE is an extremely resistant material to many chemicals, hence its widespread use in healthcare and laboratory environments. It is resistant to many acids, alcohols, aldehydes, esters, bases and oils. Braskem company is the world-leading supplier of bio-PE (HDPE, LDPE, LLDPE) and the current Braskem bio-PE grades are mainly targeted towards food packaging, cosmetics, personal care, automotive parts and toys, but there are many other companies in the world producing bio-PE (Table SVI.). Bio-PE is a bio-based polymer but it's not biodegradable. It is well known that polyethylene is resistant to degradation due to chemical and biological inertness, which is a result of its high molecular weight, three-dimensional structure and hydrophobic nature, all of which interfere with polyethylene availability for the action of microorganisms, light, water, *etc.* According to some research^{133,134}, the

addition of antioxidants and stabilizers protects polyethylene against oxidation at the production stage, which further increases its resistance to degradation.

The degradation of a commercial environmentally degradable PE was investigated in two stages: firstly, by abiotic oxidation in an air oven to simulate the effect of the compost environment and secondly, in the presence of selected microorganisms.^{135,136} It was observed that microbial growth occurred in the presence of PE samples that had been compression molded to thick sections but had not been deliberately pre-oxidized. Changes of molecular weight distribution occurred after preheating in the air at 60 °C and not at ambient temperatures, but colonization of microorganisms occurred on all samples.¹³⁵ Also, erosion of the film surface was observed in the vicinity of the microorganisms and the decay of oxidation products in the surface of the polymer film was found to be associated with the formation of protein and polysaccharides, due to the growth of microorganisms (*Rhodococcus rhodochrous* ATCC 29672, *Cladosporium cladosporioides* ATCC 20251, *Nocardia asteroides* GK 911).^{135,136} Nowadays, bio-PE is accepted for recycling in many recycling centres, especially HDPE. The recycling process consists of collecting and separating the plastic, using sink-float separation or Near-Infrared Radiation (NIR) techniques, then homogenizing and melting the plastic, and finally cooling the plastic into pellets that can be reused for the production of, for example, toys, rope, piping etc.¹³⁷ Recycling HDPE has many benefits such as cost-efficiency of manufacturing a product from recycled HDPE instead of producing 'virgin' plastic.

According to the base of patents in the last 10 years, most patents are based on PE biodegradability and recycling. Patents are focused on improving PE materials (HDPE, LDPE) in terms of advancing their mechanical properties and production of materials with a simple structure that is easy to recycle. Many patents have marketed products such as blow molding, injection molding and foam products and showed that from recycled PE materials new materials of excellent quality and biodegradability can be produced (CN207467268U, US9593177, US9637626B2, US2016/0108217A1). Analyzing the commercial application of patents over the last decade, it has been shown that bio-PE has found its application in bags, boxes, bottles, toys, pipes, *etc.* (Table SVI).

(BIO)DEGRADATION AND RECYCLING OF BIOPLASTICS

In January 2018, the EU released its vision for a more sustainable plastics industry to be achieved by 2030. The new plastics strategy states that 100 % of plastics should either be reusable or recyclable by 2030. Prevention, re-use, collection and recycling should always be the first choice in efforts to achieve some of these goals. As mentioned, to overcome both oil dependence, price fluctuations and enhance resource efficiency, bioplastic materials constitute an applicable route that has to be explored as a part of the solution. Plastics that are

currently marketed as “biodegradable” will themselves contribute to plastic pollution if they are lost or littered. They do not break down as quickly and completely in the environment and can thus harm wildlife and ecosystems. To reinforce the positive impact of bioplastics, successful recycling strategies also need to be clearly proposed and applied. In general terms, the purpose of recycling is to convert the production of postconsumer waste into building blocks for the production of new polymers.

The degree of biodegradation varies with temperature, polymer stability, and available oxygen content. Consequently, most bioplastics will only degrade in the tightly controlled conditions of industrial composting units. Apart from starch-based bioplastics, in compost piles or simply in the soil/water, most bioplastics will not degrade.¹³⁸ Bioplastics are still plastics and being made from plants or having the potential to biodegrade under limited conditions does not make them “planet-safe.” At the moment, there is a need for more transparency about environmental claims of bioplastic products. A ban on labelling plastic products as “biodegradable” or as “compostable”, unless they meet strict standards, is urgently needed. There are currently few international organizations which have established standards and testing methods for compostability¹³⁹, namely:

- American Society for Testing and Materials - ASTM-6400-99
- European Standardization Committee (CEN) - EN13432
- International Standards Organization (ISO) - ISO14855 (only for biodegradation)
- German Institute for Standardization (DIN) - DIN V49000

The ASTM, CEN and DIN standards specify the criteria for biodegradation, disintegration and eco-toxicity for a plastic to be called compostable.

- Biodegradability is determined by measuring the amount of CO₂ produced over a certain time period by the biodegrading plastic. The standards require 60 % conversion of carbon into carbon dioxide within 180 days for resins made from single polymer and 90 % conversion of carbon into carbon dioxide for copolymers or polymer mixes.
- Disintegration is measured by sieving the material to determine the biodegraded size and less than 10 % should remain on a 2 mm screen within 120 days.
- Ecotoxicity is measured by having concentrations of heavy metals below the limits set by the standards and by testing plant growth by mixing the compost with soil in different concentrations and comparing it with controlled compost.

The EN 13432 industrial standard is arguably the most international in scope and compliance with this standard is required to claim that a product is compostable in the European marketplace. In summary, it requires biodegradation of 90 % of the materials in a laboratory within 180 days. The ASTM-6400

standard is the regulatory framework for the United States and sets a less stringent threshold of 60 % biodegradation within 180 days, again within commercial composting conditions.

The most accurate standard test method for anaerobic environments is the ASTM D5511 – 02 Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials under High-Solids Anaerobic-Digestion Conditions. Another standard test method for testing in anaerobic environments is the ASTM D5526 - 94(2002) Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions. However, this latter test has proven extremely difficult to perform. Both of these tests are used for the ISO DIS 15985 on determining anaerobic biodegradation of plastic materials.

One should bear in mind that none of the standards for plastics labelled as biodegradable or compostable today makes them suitable for disposal in the open environment. However, the most likely destination of many biodegradable products currently is the landfill as numerous composting facilities focus on food scraps and either won't accept biodegradable packaging or will still frequently screen it out along with other plastics for shipment to a landfill. The environmental consequences of landfilled biodegradable materials have led some researchers and advocates to push for more universal access to compost collection, as well as the development of altogether new materials.^{7,140}

As mentioned, for biodegradation, PLA needs industrial composting conditions, including temperatures above 58 °C. It needs to be properly managed and routed to specialized industrial composting or recycling facilities. Under the right circumstances, microorganisms can turn the material into carbon dioxide and water within a couple of weeks. However, if it becomes littered or dumped, PLA sticks around for much longer. When pure PLA ends up in seawater, it does not seem to biodegrade at all. Other kinds of bioplastics are known to better biodegrade in marine environments.¹⁴¹ However, whether that really happens in a specific case, and how long it will take, is highly unpredictable.

Improved recycling strategies have to be developed for bioplastics. In particular, bio-based polyesters (PLA, PHA/B and PBS) have demonstrated the potential for either mechanical or biochemical recycling.⁶³ Ongoing research includes bio-upcycling efforts¹⁴² as well as the improvement of chemical recycling processes.¹⁴³ On the other side, research is intensive on the side of the material design, where molecular triggers are explored.¹⁹

CONCLUSIONS

Bioplastics are a large family of materials with widely varying properties. As with conventional plastics, the end-of-life options depend entirely on the application, the way the product is disposed of by its user, and the available

infrastructure in the region where the product is being disposed of. Therefore, “biodegradable”, a magic word for environmentally-minded consumers, isn’t always a green magic bullet. Claims that bioplastics reduce environmental impact still lack sufficient evidence.¹⁴⁰ Whether bio-based plastics are more sustainable than fossil-based ones, and what contribution they could have as a building block for sustainable development of an innovative bioeconomy, still can not be answered conclusively due to insufficient data.¹⁴⁰ It is evident that there is a lot of branding around biodegradability and that a demand for biodegradables continues to climb - with packaging, take-out containers, even designer jeans and athletic shoes now carrying this designation. It is important that we, as consumers, do not allow biodegradable marketing tactics to influence our purchasing decisions and to trade one set of environmental problems for another. It is evident that bioplastics won’t solve the plastic waste crisis, so tackling consumption remains key.

ABBREVIATIONS

3HH	- 3-hydroxyhexanoate
3HD	- 3-hydroxydecanoate
3HO	- 3-hydroxyoctanoate
3HP3	- hydroxypropionate
3HV	- 3-hydroxyvalerate
4HB4	- hydroxybutyrate
BC	- bacterial cellulose
BDO	- 1,4-butanediol
bio-BDO	- bio-based 1,4-butanediol
bio-PBS	- bio-based poly(butylene succinate)
bio-PE	- bio-based polyethylene
bio-PET	- bio-based poly(ethylene terephthalate)
bio-PTT	- bio-based poly(1,3-propylene terephthalate)
bio-SA	- bio-based succinic acid
HDPE	- high-density polyethylene
IUPAC	- International Union of Pure and Applied Chemistry
LDPE	- low-density polyethylene
LLDPE	- linear low density polyethylene
mcl-3HA	- medium-chain - length - 3 - hydroxyalkanoates
NIR	- near-infrared radiation
PBAT	- poly(butylene adipate terephthalate)
PBA	- poly(butylene adipate)
PBS	- poly(butylene succinate)
PBSA	- poly(butylene succinate-co-adipate)
PBST	- poly(butylene succinate-co-terephthalate)

PBSF	- poly(butylene succinate-co-fumarate)
PBS-DLS	- poly(butylene-succinate-dilinoleic succinate)
P(BS-BMS)	- poly(butylene succinate-co-butylene 2-methylsuccinate)
PCL	- poly(caprolactone)
PE	- polyethylene
PET	- poly(ethylene terephthalate)
PHA	- poly(hydroxyalkanoate)
PHB	- poly(hydroxybutyrate)
PHBV	- poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	- polylactic acid
PP	- polypropylene
PS	- polystyrene
PTT	- poly(1,3-propylene terephthalate)
PUR	- polyurethane
PVA	- poly(vinyl alcohol)
PVC	- poly(vinyl chloride)
SA	- succinic acid
scl-3HA	- short-chain-length-3-hydroxyalkanoates
TPS	- thermoplastic starch

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ИЗВОД

РАЗУМЕВАЊЕ БИОПЛАСТИЧНИХ МАТЕРИЈАЛА: ТРЕНУТНО СТАЊЕ И ТРЕНДОВИ

САЊА ЈЕРЕМИЋ¹, ЈЕЛЕНА МИЛОВАНОВИЋ¹, МАРИЈА МОЈИЋЕВИЋ², САЊА ШКАРО БОГОЈЕВИЋ¹ и ЈАСМИНА НИКОДИНОВИЋ-РУНИЋ¹

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Зарађање пластиком сада се сматра једном од највећих претњи по животну средину по људе. Развој биополимерних материјала може бити део решења јер биопластика укључује и неразградиве и биоразградиве материјале, а обе су важне за одрживи развој. Биопластични материјали се у овом моменту дизајнирају тако да имају минималан угљенични отисак, високу могућност рециклирања и потпуну биоразградивост. Овај преглед приказује недавна дешавања и трендове у области биопластичних материјала. Представљен је низ биопластичних материјала који се најчешће користе: (поли-(млечна киселина) (PLA), поли(хидроксиалканоат) (PHA), скроб, целулоза, поли(бутилен-сукцинат) на бази обновљивих материјала (био- PBS) и полиетилен од обновљивих сировина (био-PE)), укључујући њихову производњу, могућности примене и деградацију

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