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SURVEY

**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 (poly(lactic 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; poly(lactic acid); sustainability polyhydroxyalkanoates.

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## 1. INTRODUCTION

“Plastics” as synthetic polymers were introduced about 100 years ago and today they are one of the most produced, used, and versatile materials.<sup>1</sup> Nevertheless, their biggest advantage, namely durability, turned out to be their biggest problem, as their degradation rate does not match their intended service life and so their 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 reached almost 360 million tons, while in Europe it reached 62 million tones.<sup>2</sup> 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.<sup>3</sup> Approximately half of the synthetic polymers are used in single-use or short-lived products, which mostly end up on landfills and in oceans, where they become fragmented over time into ‘microplastics’ that harm and kill various organisms, finally ending up on our plates.<sup>4</sup> 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.<sup>2</sup>

Environmental concerns over plastic pollution coupled with a growing debate over crude oil dependence and depletion have sparked and fuelled 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 more sustainable activities when compared with plastic production from petroleum (petrochemical plastics; petroplastics) because they rely less on fossil fuels as the carbon source. They also introduce fewer, net-new greenhouse emissions if they biodegrade.<sup>5</sup> Bioplastics also significantly reduce hazardous waste caused by oil-derived plastics. However, the manufacture of bioplastic materials is still often reliant on petroleum as a source of energy and materials.<sup>6,7</sup>

### *1.1. Bioplastics – definitions*

The term “bioplastic” is often used by the public and in scientific literature. However, the term “bioplastic” refers to either to the bio-based origin of the plastic or the biodegradable character of the 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 the International Union of Pure and Applied Chemistry (IUPAC), a bioplastic is derived from “biomass or monomers derived from biomass and which, at some stage in its processing into finished products, can be shaped by flow”.<sup>8</sup>

It is also important to make the distinction between degradable, biodegradable and compostable. These terms are often incorrectly used interchangeably. Degradable plastic is a 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”.<sup>9</sup> Some other definitions require a biodegradable material to be mineralized into carbon dioxide, water, and biomass during biodegradation (standard CEN/TR 15351:2006).<sup>10</sup>

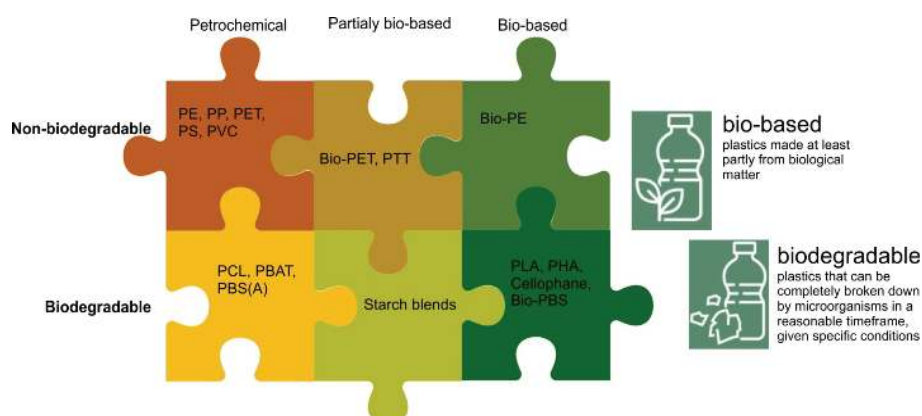


Fig. 1. Not all bio-based plastics are biodegradable, and not all biodegradable plastics are bio-based. PE=polyethylene; PP=polypropylene; PET=poly(ethylene terephthalate); PS=polystyrene; PVC=poly(vinyl chloride); PTT=poly(1,3-propylene terephthalate); PCL=poly(caprolactone); PBAT= poly(butylene adipate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

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.<sup>11</sup> Unfortunately, the term “biodegradable plastic” has also been used by producers of specially modified petrochemical-based plastics that 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 the degradability of their products by misleading the use of the terms biodegradable or compostable. It has been shown that even biodegradable plastics might not biodegrade in every environment.<sup>12</sup>

### 1.2. Historic perspective of bioplastics

Natural plastic materials (plant gum, shellac, starch) have been used for thousands of years.<sup>1</sup> 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.<sup>13</sup> In the early 1950s, amylo maize (>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, poly(lactic 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.<sup>1,14</sup>

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); *iii*) producing them by bacteria directly (polyhydroxyalkanoates, PHAs).<sup>15</sup> The first generation technologies focused on feedstock such as corn, starch, or rice to produce bioplastics, which were deemed unacceptable in the 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).<sup>15–17</sup>

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; source: Chemical Market Resources Inc.; substitution potential: +++ - high; ++ - medium; + - low; - - not foreseen

| Bioplastic       | LDPE <sup>a</sup> | HDPE <sup>a</sup> | PP <sup>a</sup> | PS <sup>a</sup> | PVC <sup>a</sup> | PET <sup>a</sup> | PUR <sup>a</sup> |
|------------------|-------------------|-------------------|-----------------|-----------------|------------------|------------------|------------------|
| PLA <sup>a</sup> | +                 | ++                | ++              | ++              | -                | ++               | -                |
| PHA <sup>a</sup> | ++                | +++               | +++             | ++              | +                | ++               | ++               |
| Starch blends    | ++                | ++                | ++              | +               | -                | ++               | -                |
| Bio-PE           | +++               | +++               | -               | -               | -                | -                | -                |

<sup>a</sup>LDPE = 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(hydroxybutyrate) (PHB) possesses better physical properties than PP for food packaging applications and is completely nontoxic. In addition, bio-based polyesters have the potential to avoid the release of micro-plastics if they are formulated to be biodegradable or compostable. On the other hand, the cost of bioplastics is currently still not competitive with that of petroplastics. Bioplastics do not yet reach fossil fuel parity of fossil fuel-derived energy for their manufacture, reducing the cost advantage over petroleum-based plastics.<sup>5</sup>

2. DESCRIPTION OF IMPORTANT BIOPLASTICS

Bioplastics contribute less than one percent to the 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 very 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 on the industrial scale (Fig. 2).

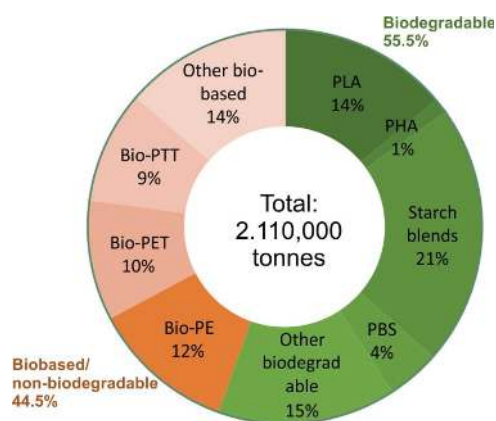

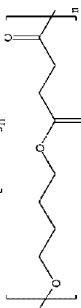
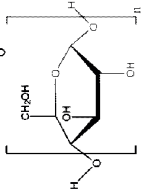
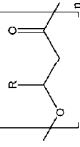
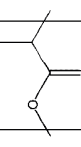


Fig. 2. Global production capacities of bioplastics in 2019 (data adapted from European Bioplastics<sup>18</sup>).

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 co-workers<sup>19</sup>)

| Polymer | Structure  | Biobased content, % <sup>a</sup> | Annual production, t <sup>b</sup> | Trademarks/Company   | Application  |
|---------|--|----------------------------------|-----------------------------------|--|--|
| Bio-PE  |   | 100                              | 200 000                           | I'm green/Braskem  | Packaging films and bags   |
| Bio-PBS |   | Up to 100                        | 97 000                            | Bionolle 1000/Showa Denko, BioPBS/PTT MCC Biochem                        | Films and sheets for food packaging, fishing nets, the automotive industry |
| Starch  |   | 100                              | 384 000                           | MaterBi/Novamont   | Food packaging, compostable films and bags, disposable utensils            |
| PHA     |   | 100                              | 30 000                            | Minerv-PHA/Bio-On, PHBH/Kaneka, Nodax/Danimer Sci.                       | Packaging, compost bags, tissue engineering                                |
| PLA     |  | 100                              | 217 000                           | Ingeo/ NatureWorks, Lumony/ TotalCorbion, Lacty/Shimadzu, Vytocel/Toyobo | Packaging, medical implants, 3D printing polymers, electronics, textiles   |

<sup>a</sup>The biobased content of the polymers is based on current information about commercially available products; <sup>b</sup>the annual production volume of the polymers was obtained from [www.european-bioplastics.org/market/](http://www.european-bioplastics.org/market/)

### 2.1. Poly(lactic acid) (PLA)

PLA is a biobased and biodegradable aliphatic polyester that represented 13.9 % of global bioplastic production capacities in 2019 (Fig. 2<sup>20</sup>). 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.<sup>21</sup> 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.<sup>22</sup> 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 the plastics processing industry for the production of foil, moulds, cups, bottles and mulch films used in agricultural fields. On the other hand, due to the relatively low glass transition temperature of PLA, PLA cups cannot hold hot liquids, so much research is devoted to the development of a heat resistant PLA. Additional research is also ongoing to find even more eco-friendly and economical methods for producing lactic acid by using crop residues, such as stems, straw, husks, and leaves as carbohydrate sources.<sup>23</sup> Lactic acid can be used to produce PLA of variable molecular weights, however, usually, only high *M<sub>w</sub>* 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 a less-desired low *M<sub>w</sub>* PLA;
- 2) direct polycondensation in an azeotropic solution: PLA production by direct condensation and continuous removal of condensation water by azeotropic distillation;
- 3) polymerization through lactide formation (ring-opening method): industrially accomplished for high *M<sub>w</sub>* 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 it is estimated that it will generate a net revenue of approximately USD 2277.57 million by 2027. The PLA market is dominated by 1–5 major players, *i.e.*, NatureWorks, Total Corbion, Synbra Technology BV, Futerro and Sulzer Ltd., with NatureWorks and Total Corbion being the major producers, with a

capacity of  $1.5 \times 10^5$  and  $0.75 \times 10^5$  metric t per year, respectively (Table S-I of the Supplementary material paper to this paper).<sup>24</sup>

In the past 10 years, the vast majority of patents regarding PLA production are related to methods of processing PLA into materials for specific applications, such as 3D printing wires, fibbers, sheets, *etc.*, or the modification of available PLA in order to improve the properties (CN108705753A, CN106738783A, CN104138310A, US2015337097A1 and 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 and CN106750199A). Additionally, two patents should be emphasized since they deal 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.<sup>25</sup> 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.<sup>26</sup> 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 toughness;<sup>27</sup>
- 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 materials;<sup>28</sup>
- 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 feature;<sup>29</sup>
- PLA and biodegradable PBS blends exhibit ductile behaviour 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;<sup>30,31</sup>
- 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. Recently, 3D-printed scaffolds have also been produced using PLA/PEG blends.<sup>32</sup>

Recycling, as one of the possible disposal routes for plastic, has been extensively studied on PLA. Currently, only 10 % of PLA waste is returned to the



PLA production process.<sup>33</sup> PLA can undergo mechanical or chemical recycling. An easy and the cost-effective way to recycle post-consumer PLA is mechanical recycling, which involves recovering, sorting, regrinding, and reprocessing the waste plastic, has become common practice in the industry.<sup>34</sup> However, this method has limitations affecting the PLA quality, thus limiting the range of products in which it could be used, and reducing the economic viability.<sup>35</sup> An alternative is chemical recycling, during which PLA is hydrolyzed at a high temperature to yield lactic acid, which could be readily polymerized to high Mw PLA. NatureWorks is an example of successful off-grade Ingeo™ recycling using a chemical method, while Galactic started a 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.<sup>36</sup> The presence of PLA in the current plastic recycling infrastructure, even at low concentrations, causes contamination of the recycling stream and production of inferior recycled material. Thus, it is crucial to remove PLA from other plastics and to establish single streams for materials such as 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.<sup>35</sup>

Another end-life scenario for PLA and the natural way of recycling is biodegradation. Numerous literature data deal with PLA degradability in soil and compost. The 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 the resilience of PLA to the actions of microorganisms in soil or sewage under ambient conditions.<sup>21</sup> No significant PLA degradation was observed when the polymer was buried in a real soil environment, or in soil under controlled temperatures of 25 and 37 °C, even after 24 months of exposure.<sup>37–40</sup> 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 CO<sub>2</sub> and H<sub>2</sub>O.<sup>41,42</sup> 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 commence,<sup>38</sup> 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, the authors suggested that marine microbes have a limited ability to degrade PLA.<sup>43,44</sup>

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> ,<br><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> ,<br><i>Amycolatopsis orientalis</i> |
| CN102181378 (A) | 2011 | <i>Pseudomonas</i> sp. DS1001  |
| JP4273504B2     | 2009 | <i>Aspergillus oryzae</i> , <i>Aspergillus soya</i> /serine hydrolase                          |

## 2.2. Polyhydroxyalkanoates (PHA)

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

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.<sup>46</sup> Although their shape, size, structure, and physical properties depend on the producing organism and cultivation conditions, all polyesters are thermoplastic, water-insoluble, non-toxic, relatively resistant to hydrolytic degradation, biocompatible and biodegradable.<sup>47</sup> 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.<sup>45</sup>

PHB was the first bacterial PHA identified. The unique properties of PHAs are recognized as better oxygen barrier than PP and PET, better water vapour barrier (than PP), and fat/odour barrier. Such superior physicochemical properties of PHA (*e.g.*, in reference to PP) have promoted their usage in various fields, including food packaging.<sup>48</sup> However, the poor mechanical performance and melt processing behaviour of PHB, *i.e.*, high brittleness, low thermal stability and difficult processing, along with insufficient barrier properties, limits its wide-spread use.<sup>49</sup>

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.<sup>47</sup>

One of the first copolymers to be manufactured in the industry was Biopol<sup>®</sup>, 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 linen.<sup>47</sup> 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).<sup>50</sup> The P(3HB-co-4HB) copolymer exhibits a broad array of morphologies, such as highly crystalline to elastomeric based on the concentration of 4HB.<sup>51</sup>

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

Many years of research efforts have led to the large-scale production of PHA and its copolymers. Procter and Gamble have developed Nodax<sup>®</sup> (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<sup>®</sup> is a PHBV copolymer containing 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 t per year within the next 20 years. Other commercial PHAs are produced by Bio-on (MINERV<sup>®</sup>), Metabolix (Mvera<sup>®</sup>, Mirel<sup>®</sup>) and PHB Industrial (BIOCYCLE<sup>®</sup>) among other manufacturers (Table S-II). 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.<sup>56</sup>

PHA has been produced with limited success on the market mostly due to the high production costs and instability of thermo-mechanical properties resulting from changing molecular weights and structures, which are related to varying the PHA synthase activity.<sup>57</sup> 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.<sup>48</sup> 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.<sup>58</sup> An enormous number of studies have been conducted to find low-cost feedstock for PHA production on the industrial scale. Although food waste is a good initial feedstock for the production of bioplastics, it must be pre-treated to improve or modify the physicochemical and biological properties.<sup>59</sup>

Gerngross and co-workers reported for the first time the *in vitro* production of PHB.<sup>60</sup> This finding brought a new perspective and insight into economical processes for the synthesis of PHAs using enzymes as a catalyst and will offer the 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 the obtained polymers.<sup>61</sup> To commercialize the enzymatic process, the production and purification costs of the enzyme need to be reduced.<sup>62</sup> 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.<sup>63</sup> PHAs can be mechanically recycled with some loss of molecular weight and mechanical properties.<sup>64</sup> Recently, PHBV was mechanically recycled by Zaverl *et al.*,<sup>65</sup> 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 waste, which is expected to be heterogeneous. Chemical recycling of PHAs by thermal degradation has resulted in a transformation of PHAs into vinyl monomers.<sup>66</sup> Ariffin and co-workers used alkali earth compound catalysts (CaO and Mg(OH)<sub>2</sub>) 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 their biodegradation can occur under both aerobic and anaerobic conditions.<sup>67,68</sup> Numerous bacteria, streptomycetes, and fungi isolated from 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.<sup>69</sup> 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 the tests. Martinez-Tobon and co-workers compared the activity of strains with proven and predicted PhaZ activity for PHB film degradation, which helped to identify strains displaying high degradation activity. The strains *Crupriavidus* sp. and *Comamonas testosteroni* 31A showed the highest percentage weight loss after 7 days, 90 and 53 %, respectively.<sup>70</sup> There are some examples of highly tolerant enzymes in harsh conditions such as PhaZs depolymerases from *C. 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.<sup>71</sup>

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.<sup>68</sup> In a study by Hablot *et al.*, the degradation of PLA/PHA non-woven 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.<sup>72</sup> When the PHB films were immersed in the sea at a depth of 1.5 m, their weight loss after 4 weeks was about 90 %. On the contrary, the biodegradation in seawater by the laboratory test method for 4 weeks was around 50 %.<sup>73</sup> Biodegradation tests performed 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, a great number of innovations related to the advancement of the PHA production process have been described (Table S-III). 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 in a cost-effective yield.

The process of producing monomers from PHA by depolymerisation is the focus of many inventions (CN104328062A, WO2016085396A1). A method for efficiently decomposing PHA and converting it to biogas containing methane as the main component, particularly under anaerobic conditions, was 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, and US2020109423A1).

### 2.3. Starch and cellulose

The interest in polysaccharides as biomaterials has been 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.<sup>74</sup>

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.<sup>75</sup> 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.<sup>76,77</sup> 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.<sup>78,79</sup>

The plant material is grounded in water, the debris is filtered from the slurry, and starch granules are obtained after centrifugation from the suspension.<sup>80</sup> 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 increases as well, resulting in texture firming.<sup>81</sup> 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.<sup>82</sup> Italy-based Novamont is a manufacturer of starch-based plastic called Mater-Bi used to make BioBag branded certified compostable bags (Table II).

BioBag<sup>®</sup> is the world's largest brand of certified compostable bags and films made from Mater-Bi. SpudWare<sup>®</sup> 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<sup>®</sup> 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 for disposable diapers (Tethis<sup>TM</sup>), fuel filters to remove water (Super Absorbent Co.), and as a treatment for burns (Sonett).<sup>83</sup>

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, 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 for retaining soil water and efficient fertilizer release for agricultural efficiency. Due to its abundance, cellulose can serve as a virtually inexhaustible source of raw material in the production of sustainable bioproducts.<sup>84,85</sup> 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 helps to reduce the pressure on conventional energy sources.<sup>86,87</sup> As its anhydroglucopyranose unit contains reactive hydroxyl groups, cellulose has potential use in the design of 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 exchange of the hydroxyl groups of the cellulose molecules.<sup>88</sup>

Cellulose can be produced by two means: natural synthesis procedures including plant photosynthesis and microbial synthesis.<sup>89</sup> Cellulose is present in small quantities in all brown algae, and most of red and golden algae. The most effective producers of bacterial cellulose (BC) are *A. xylinum*, *A. hansenii* and *A. pasteurianus*.<sup>90-92</sup> 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.<sup>93</sup> In static cultures, BC is formed at the liquid-air interface as hydrogel-like membranes, with thickness from millimetres to centimetres. The microfibrillar structure of BC is responsible for most of its properties, such as high tensile strength, high crystallinity index and higher degree of polymerization.<sup>94,95</sup> 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) inc-

lude 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 AgNO<sub>3</sub> solution, which results with the BC membrane containing silver nanoparticles. The new properties of BC can also be achieved by incorporating reinforcing particles into the membrane structure.<sup>96,97</sup>

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.<sup>98</sup> Enzymatic degradation of cellulose is generally performed 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.<sup>99</sup>

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 packaging films for bakery product wraps, other food wraps, and food-grade transparent bags. Bioprocess®, XCell® and Biofill® are bacterial cellulose-based products already available commercially for topical application in wound healing,<sup>100</sup> <http://www.biomass-packaging.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 concentrations/amounts to form 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.<sup>101</sup>

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 the solution casting technique under ISO 14855 were examined by composting for 45 days. Starch and glycerol were absolutely degraded while PVA appeared practically intact.<sup>102</sup> 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 the biodegradation of the PLA component, especially in liquid media.<sup>103</sup> Studies also showed that ternary blends composed of PLA, PCL, and starch buried in soil degraded rapidly in the first 8 weeks.<sup>104</sup>

Biodegradability of cellulose is dependent on the degree of crystallinity, structure, functional groups, cross-linking and molecular weight of the cellulose.<sup>105</sup> Two general types of substrates were used to measure the biodegradation of cellulose: 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 those 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.<sup>106,107</sup> Even though the biodegradation of some cellulose samples have been studied, there is still a lack of a comprehensive study on the biodegradability of a variety of cellulose-based packaging materials that could potentially replace synthetic packaging films.<sup>108</sup>

A list of patents related to starch and cellulose is presented in Table S-IV of the Supplementary material. The process described in WO2017130106A1 relates to the production of starch from microalgae, which is more efficient in comparison to the conventional production. Method of producing a starch-based biodegradable polymer, using processed cannabis waste as the carbon source, is described in WO2020037394A1, while the process for producing biodegradable plastic from renewable resource-based agricultural by-products 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 a composite material (starch combined with thermoplastic polyurethane). This material has the advantages of high mechanical property, low cost, biodegradability and the preparation process is simple. WO2016138593A1 also covers the potential of starch to combine with one or more biodegradable polymers (PCL, PBS, PLA, and PHA) in order to obtain biocomposites with tailored properties. WO2018041779A1 and WO2020034958A1 describes the application of starch and its modifications in food packaging using low tensile strength products, while WO2017091463A1 provides methods for 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 a nanocellulosic material based on fractioning a cellulosic pulp stream originating

from pre-treatment or mechanical defibrillation. WO2019221535A1 presents a method for the manufacture of 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 fibres. On the other hand, bacterial cellulose production on cassava bagasse as a suitable feedstock and its processing is covered in WO2016029432A1. Methods for the production and processing of multi-phase biomaterials based on bacterially synthesized nanocellulose are presented in WO2016113400A1. WO2017192476A1 presents an invention that provides a pulp product with nanocellulose as a tool for improving the strength properties. Cellulose derivative with excellent thermoplasticity, waterproofness, elastic modulus and impact strength and its production method are presented in WO2017061190A1. Patent WO2018187782A1 provides a method for the 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 a 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 a three-dimensional autologous fat graft.

#### 2.4. *Poly(butylene succinate) (PBS)*

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

In the beginning, PBS was a biodegradable but petro-based polyester, while currently, large plants for producing renewably sourced SA have been developed and Mitsubishi commercializes bio-based PBS (bio-PBS) that is obtained using bio-based SA (bio-SA). Furthermore, bio-based BDO (bio-BDO) can also be produced on an industrial scale. Nowadays, products of 100 % bio- PBS can be found on the markets. Bio-PBS is produced in various demo and pilot plants, mainly from sugarcane and cassava monomers.<sup>113</sup> 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).<sup>113</sup> 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.<sup>113</sup> In a more recent study, a novel, nonphosphorylative pathway was used to convert biomass sugars to BDO with a 100 % theoretical maximum molar yield.<sup>114</sup> In this pathway, assimilation of sugars into the TCA cycle is allowed and afterward built of artificial biosynthetic pathways to BDO using the enzymes 2-ketoacid decarboxylases and alcohol dehydrogenases.<sup>114</sup> Bio-SA is mainly produced by several microorganisms as a fermentation product. In 2008, Bioamber built the first plant that uses *Escherichia coli* as the host microorganism and wheat-derived glucose as the 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 a production capacity of 30 million pounds from unrefined sugars as feedstock using *E. coli* as the host organism.<sup>115</sup> 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 S-V). Bio-PBS is currently being employed in a wide range of industries, such as packaging, agriculture, pharmaceutical, consumer goods, electronics and electrical, textile, automotive and interiors.<sup>116</sup> It is also utilized to produce bowls, plates, plastic utensils, and diapers.<sup>116</sup> Amongst others biopolymers, bio-PBS has strengths in flexibility, natural fibre compatibility, heat resistance and biodegradability under specific conditions (according to DIN EN 13432). It was found that 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.<sup>117</sup> 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 the literature. PBSA copolymer is better degraded than PBS due to its lower crystallinity and glass transition temperature,<sup>118</sup> 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.*<sup>71</sup> PBST copolymer has a lower crystallinity than PBS, but biodegrades more slowly in contrast to PBSA.<sup>111</sup> 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.<sup>119</sup> Commercial PBS-PLA blends have been utilized for production of food service ware by NatureWorks LLC.<sup>64</sup> Based on extensive research, PBS-PLA blends have been successfully modified and processed into fibres, blown films, flat films, and sheets.<sup>25</sup> PBS and its copolymers are biodegradable in lipase solution, soil burial, water, activated sludge and compost.<sup>120–122</sup>

Currently, about 75 % of plastic waste is disposed in sanitary landfills and about 25 % is recycled.<sup>123</sup> 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.<sup>124</sup> Recycling of plastic waste and bio-based waste, such as bio-PBS, may be realised 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.<sup>71,125</sup> 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.<sup>126</sup> Bio-PBS can be easily separated from paper when soaking under water without damaging the paper pulp, which can be recycled to produce paper again, or as backyard compost, or in the case of a leak to the environment, it will degrade eventually in a limited time.<sup>126</sup> Testing the degradation phenomena of bio-PBS plastics in the environment can be classified into three categories: field tests, simulation tests, and laboratory tests.<sup>127</sup> The performed degradation studies of a commercially available PBS and PBSA copolymer in various environments have shown that the most favourable degradation environment was compost, which contains microorganisms and natural enzymes that support degradation.<sup>128</sup> In these studies, degradation after four to six weeks was observed, followed by a strong mass loss in the compost, due to interaction with enzymes. In addition, the strength of polymers was significantly reduced. Biodegradation test in soil gave the same results as biodegradation in compost, but the changes in the molecular parameters were less intense because of the lower concentration of microorganisms, enzymes and lower temperature of the process.<sup>128</sup>

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 having improved mechanical properties, compatibility, control of degradation rate, and effective reduction of the cost of bio-PBS production (CN109608835A, CN103709688A, CN110240788A, CN109867921A, CN106589854B and 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 fibre, trash bag, coffee capsule cutlery, *etc.* (US20180058010A1, US20140021574A1, WO2010151798A2 and WO2016105217A1).

### 2.5. Bio-polyethylene (Bio-PE)

PE consists of long chains of ethylene and it is produced as either HDPE or LDPE, or linear low density polyethylene (LLDPE).<sup>129</sup> PE is chemically synthesized by polymerization of ethane.<sup>129</sup> Bio-based PE (bio-PE) is chemically identical to fossil-based PE, it has the same technical properties and is not biodegradable.<sup>130</sup> Bio-PE is used to produce high value products using low pollution processes and contributing to the global environmental balance. The process involves: pre-treatment, enzymatic scarification, fermentation, dehydration and polymerization.<sup>131</sup> The 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 steps:<sup>130</sup>

- 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, such as carrying bags, plastic films and bottles, automotive fuel tanks, injection melded parts, tubes.<sup>132</sup> 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 the properties of the material. 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. The Braskem Company is the world-leading supplier of bio-PE (HDPE, LDPE and 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 S-VI.). Bio-PE is a bio-based polymer but it is not biodegradable. It is well known that polyethylene is resistant to degradation due to its chemical and biological inertness, which is the 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,<sup>133,134</sup> 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.<sup>135,136</sup> It was observed that microbial growth occurred in the presence of PE samples that had been compression moulded to thick sections but had not been deliberately pre-oxidized. Changes in the molecular weight distribution occurred after preheating in air at 60 °C and not at ambient temperatures, but colonization of microorganisms occurred on all samples.<sup>135</sup> Also, erosion of the film surface was observed in the vicinity of the microorganisms and the decay of oxidation products on 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 cladosporoides* ATCC 20251, *Nocardia asteroides* GK 911).<sup>135,136</sup> Nowadays, bio-PE is accepted for recycling in many recycling centres, especially HDPE. The recycling process consists of the collection and separation of the plastic using sink–float separation or Near-Infrared Radiation (NIR) techniques, then homogenization and melting of the plastic, and finally cooling the plastic into pellets that can be reused for the production of, for example, toys, rope, piping *etc.*<sup>137</sup> Recycling HDPE has many benefits, such as cost-efficiency of the manufacture of 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 moulding, injection moulding and foam products, which showed that new materials of excellent quality and biodegradability can be produced from recycled PE materials (CN207467268U, US9593177, US9637626B2 and US2016/0108217A1). Analysing the commercial application of patents over the last decade, it has been shown that bio-PE has found application in bags, boxes, bottles, toys, pipes, *etc.* (Table S-VI).

### 3. (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 be either 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, 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.<sup>138</sup> Bioplastics are still plastics and being made from plants or having the potential to biodegrade under limited conditions does not make them “planet-safe”. Presently, 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 that have established standards and testing methods for compostability,<sup>139</sup> 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 in order for a plastic to be called compostable.

Biodegradability is determined by measuring the amount of CO<sub>2</sub> produced over a certain 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.

Eco-toxicity 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 a product be compostable in the European market. 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 Biodeg-

radation 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.

It should be born 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, currently, the most likely destination of many biodegradable products is the landfill as numerous composting facilities focus on food scraps and either will not accept biodegradable packaging or will still frequently screen it along with other plastics for shipment to a landfill. The environmental consequences of land filled biodegradable materials have led some researchers and advocates to push for more universal access to compost collection, as well as to the development of altogether new materials.<sup>7,140</sup>

As mentioned, PLA needs industrial composting conditions for biodegradation, 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 remains 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.<sup>141</sup> 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.<sup>63</sup> Ongoing research includes bio-upcycling efforts<sup>142</sup> as well as improvement of chemical recycling processes.<sup>143</sup> On the other hand, research is intensive on the side of material design, where molecular triggers are explored.<sup>19</sup>

#### 4. 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. Therefore, “biodegradable”, a magic word for environmentally minded consumers, is not always a green magic bullet. Claims that bioplastics reduce environmental impact still lack sufficient evidence.<sup>140</sup> 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 cannot be answered conclusively due to insufficient data.<sup>140</sup> 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 consumers do not allow biodegradable marketing tactics to influence their purchasing decisions and to trade one set of environmental problems with another. It is evident that bioplastics will not solve the plastic waste crisis, so tackling consumption remains the 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- <i>co</i> -adipate)                    |
| PBST      | poly(butylene succinate- <i>co</i> -terephthalate)              |
| PBSF      | poly(butylene succinate- <i>co</i> -fumarate)                   |
| PBS-DLS   | poly(butylene-succinate-dilinoleic succinate)                   |
| P(BS-BMS) | poly(butylene succinate- <i>co</i> -butylene 2-methylsuccinate) |
| PCL       | poly(caprolactone)  |
| PE        | polyethylene  |
| PET       | poly(ethylene terephthalate)                                    |
| PHA       | polyhydroxyalkanoate  |
| PHB       | poly(hydroxybutyrate)   |
| PHBV      | poly(3-hydroxybutyrate- <i>co</i> -3-hydroxyvalerate)           |
| PLA       | poly(lactic 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                   |

## SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/index>, or from the corresponding author on request.

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## ИЗВОД

## РАЗУМЕВАЊЕ БИОПЛАСТИЧНИХ МАТЕРИЈАЛА: ТРЕНУТНО СТАЊЕ И ТРЕНДОВИ

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Загађење 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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