

Review

Enzymes in Poly(Butylene-Succinate) Industry: An Overview on Synthesis Routes and Post-Processing Strategies

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2023, volume 3, issue 4
doi:10.21926/cr.2304026**Received:** June 16, 2023
Accepted: October 29, 2023
Published: November 08, 2023

Abstract

This paper will present some sectors in which enzymes can replace traditional catalysts in poly(butylene-succinate) industry, emphasizing the green chemistry aspects associated with these newer strategies.

Keywords

Bio-based polymers; biodegradable polyesters; poly(butylene-succinate); enzymatic polymerization; enzymatic degradation

1. Introduction

Sustainability is an everyday topic in the production fields, and it's reflected in the shared ambition of a future where chemical feedstock will switch from crude oil to other carbon sources [1]. Considering that the available resources on our planet are limited, improvements and changes in large-scale industrial processes are necessary. Carbon has been extracted from plants for decades,



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and compounds such as glucose from starch hydrolysates or soybean glycerol are still used as C sources in active commercial fermentations. When starch is diverted to bioethanol fuel's production line, its demand and price increase unequivocally.

This phenomenon is reflected in the higher food prices, and in a world where the population increases annually, the need for an alternative and more abundant carbon source appears obvious [2]. The development of technologies for non-food biomass hydrolysis started with this idea, and now we can witness the growth of research in plants that use diverse agricultural waste streams. Among the many possible sources of vegetable origin, lignocellulosic fibers constitute the most exciting biomass from an economic and availability point of view as they can be extracted from grains, seed hairs, stems, and leaves of various plants abundant in nature [3]. The case of lignocellulose production could be taken as a striking example: just 4.6 out of the total 181.5 billion tons per year of lignocellulose are produced as a waste of the agricultural industry. Comparing these volumes with the number of organic chemicals engendered per year, set at 400 million, it is clear that the available starting material is enormous [4].

This biomass can be converted through multiple technologies (e.g., biocatalysis) into valuable building blocks [5-7]. Enzymes can catalyze a wide range of biotransformations since they are an environmentally friendly alternative to traditional chemo-catalysis. Industrial applications of biocatalysts have been mainly studied for the synthesis of high-value - low-volume products, such as fine chemicals. As the enzyme application field develops, more commodities are also being produced through this method [8].

Polymers such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and its derived polyesters establish the 80% of the European plastic commodities market [9]. Petroleum-derived plastics have a daily and massive consumption per person, but they constitute a class of materials that tend to resist microbial degradation, which can be accumulated in the world environment. Moreover, the increasing price of refinery crude oil has increased interest in biodegradable polymers and bio-polymers [10].

Polymers can be classified according to their origin as synthetic or natural polymers: natural polymers can be found in living organisms with a defined chemical structure with a few exceptions, such as lignocellulose; synthetic polymers come from a chemocatalytic polymerization of chemicals. There is often confusion between biopolymers and biodegradable polymers.

The first category comprehends polymers synthesized from bio-based monomers (namely, renewable sources and not from petroleum fractions). In contrast, biodegradable polymers constitute a material that undergoes deterioration when exposed to microorganisms in a specific period. Not all bio-based polymers can be considered biodegradable materials [11].

In Germany's NOVA®-Institute full report, every bio-based polymer's market and relative productions can be found [12]. Figure 1 shows the worldwide production capacities of some bio-based polymers surveyed during the last decade. These data don't include bio-based polyurethanes, epoxy resins, cellulose acetate polyesters, and polyethylene terephthalate. Some of these polymers are brand new, so their markets cover smaller portions. Therefore, this will be where bio-based polymer production development should be carried out [13]. The look towards traditional catalysis in polymer science has shifted to the possibility of using heterogeneous catalysis conditions, often performed by enzymatic systems. The recent wave in the development of sustainable industrial

catalysts allowed many scientists to bind their efforts to replace traditional metallic-based methods with innovative and greener strategies under mild reaction conditions [14].

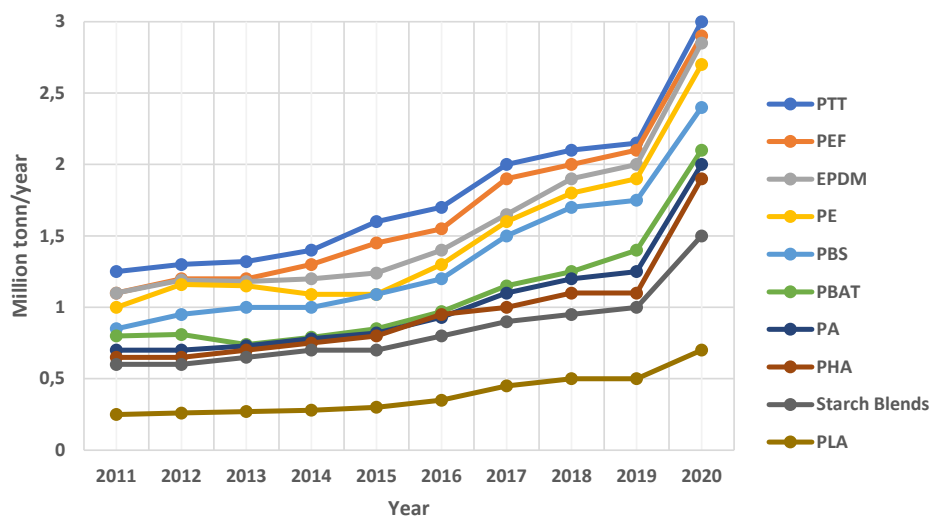


Figure 1 Worldwide production capacities of selected bio-based polymers from 2011 to 2020 [12].

A fundamental aspect of biocatalysts can be identified in their optimal performance in different reactive environments, so using these alternative catalysts appears to be one of the most suitable and versatile choices from the point of view of green chemistry principles [15, 16].

Enzymatic polymerization is the *in vitro* polymerization of artificial substrate monomers catalyzed by an isolated enzyme via non-biosynthetic pathways. Some of the first examples of *in vitro* enzymatic polymerization are constituted by (i) the synthesis of polysaccharides from alpha-D-glucose-1-phosphate (G1P) by a phosphorylase enzyme isolated from muscle extract and (ii) the reversible synthesis of starch from G1P through the application of an enzyme isolated from pea seeds. These are two of the most relevant examples of the first employment of biocatalysis for the production of medium-high molecular weight compounds. Still, there are other synthesis paths where enzymes are commonly employed, such as the production of cellulose and natural rubber [17].

Among the great variety of available biocatalysts and related specific enzymes to be employed according to the desired pathway, it is necessary to mention the poly-(hydroxy-alkanoates) (PHAs). They constitute the perfect example of how humans can exploit microorganisms for the production of commodities since they have been taken into consideration also for the production of biodegradable polyesters starting from fossil-based monomers [14].

According to the 'transition-state analog substrate' (TSAS) principle, the structure of monomers has to be as similar as possible to the transition-state conformation of the *in vivo* enzyme that carries out the reaction [18]. This can be translated into the need to choose the correct enzyme for the response taken into account, and, therefore, also the reaction conditions that we are interested in optimizing.

In the following paragraph, an in-depth discussion will be shown regarding the different synthetic strategies involving the use of enzymes, which can be undertaken as renewable alternatives to the traditional metal-catalyzed pathways.

2. Synthesis

With this Section, an overview was carried out on the possible fields of application of various biocatalysts to obtain both monomers as bio-based compounds and to carry out the polymerization of poly(butylene-succinate) (PBS).

2.1 Polyester Enzymatic Polymerization

There are three main routes for the synthesis of aliphatic polyesters: (i) a polycondensation of a hydroxy acid or of a diol and a diacid which has the drawback of a low degree of polymerization leading to low molecular weight polymers and makes their use problematic for the production of block copolymers; (ii) a ring-opening polymerization (ROP) of lactones and other cyclic diesters such as lactide and glycolide which under appropriate conditions can lead to high molecular weight polyesters with limited secondary reactions; (iii) an enzymatic polymerization that can be carried out under mild reaction conditions without the need to use toxic reagents and with the possibility of recycling the catalyst. This latter synthetic strategy has been the most explored in this paper thanks to its technological innovation and the characteristics of regio and stereoselectivity that enzymes can play. Therefore, the direct synthesis of functional polyesters can be carried out without using protected monomers, and enzymatic polymerization block copolymers can be obtained. However, this strategy is hampered by the relatively low molecular weight of the polymer materials obtained [19].

The innovation of the proposed synthetic methods will be highlighted, citing a few peculiar characteristics of the biocatalytic alternatives for synthesizing polyesters. The first proposed example is the study published by Tsujimoto *et al.* [20] in which CALB in free form was used to polymerize divinyl sebacate and glycerol. In this work, the polycondensation carried out with a commercial biocatalyst in the presence of unsaturated higher fatty acids allowed to obtain polyesters with unsaturation in the side chain. In the early 2000s, this group reported maximum yields of 77% of non-soluble material in 24 hours at 60°C in 95:5 MeOH:H₂O: the obtained polymers showed different molecular weights but a narrow dispersity index of Mw/Mn 3.3 [20].

Marcilla *et al.* [21] used Novozym 435, a commercial immobilized CALB lipase sample, to produce aliphatic polyesters in innovative solvents. Indeed, the group achieved an ROP of ϵ -caprolactone and the polycondensation of aliphatic diesters and 1,4-butanediol in a broad spectrum of ionic liquids employed as polymerization solvents. For example, they were able to obtain 44% yield in polycaprolactone (PCL) through an enzymatic ROP performed at 60°C when [bmim][Tf₂N] was employed as a solvent to be compared to 55% of yield when traditional toluene was used as reaction solvent. Similar results were obtained in the polycondensation reaction, reaching 56% of work within the first 24 hours at 70°C in [bmim][PF₆] or [bmim][BF₄] [21].

Novozym 435 was also employed by Kadokawa *et al.* [22] in three primary reactions: (i) enzymatic Ring Opening Polymerization (eROP) of *D,D*-lactide, (ii) chemoenzymatic synthesis of pentablock copolymers of polystyrene (PS), polycaprolactone (PCL) and polyethylene oxide (PEO) and (iii) polycondensation of methyl ricinoleate in the presence of molecular sieves. In all cases, the authors obtained the desired materials under mild reaction conditions and temperatures of 50-70°C [22].

A review worth mentioning for the quality of the study is undoubtedly the recent work by Hevilla *et al.* [23], in which the authors thoroughly explore a broad spectrum of applications of commercial enzymes (especially immobilized *Candida antarctica* Lipase B). To name a few, they presented the

production of complex polymers such as polybutadiene block copolymers with 1,5-cyclooctadiene from an ester precursor called ROMP and the subsequent enzymatic ROP of ω -pentadecalactone (PDL). The synthesis of amphiphilic polymers by copolymerization of 10,11-dihydroxy undecanoic acid (DHU) in the presence of methoxy-PEG with different lengths was also reported [23].

Aspergillus niger, *Bacillus subtilis*, *Candida antarctica* or *rugosa*, *Pseudomonas cepacia*, and *Thermomyces lanuginosus* are the most common microorganism exploited for lipase production. CALB is one of the most popular lipases thanks to its unique advantages of broad substrate scope, high catalytic activity in polymerization reactions, and high thermal stability, up to 100°C in its immobilized form, such as Novozym 435 [24].

An eROP of lactones with different numbers of carbon atoms performed by Wang *et al.* [25] led to polyesters with straight or branched chains with excellent results when Novozym 435 was employed as a biocatalyst. In the same study, polycondensation of different hydroxyacids, diols, diacids, or diols and diacid derivatives was also evaluated, including the possibility of synthesizing PBS catalyzed by Novozym 435 [25].

The following section will report a study on the new frontiers of enzymatic polyester synthesis.

2.2 PBS Synthesis

PBS is a polyester with a repeating unit structure, as shown in Figure 2. This biodegradable polymer is primarily used as a commodity material, and it is currently produced by fossil-based routes in most of the process productions on an industrial scale [26].

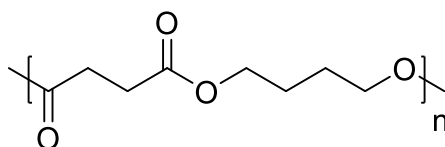


Figure 2 PBS repeating structural unit.

Like other polyesters such as PET, there are two known routes to synthesize PBS: (i) via esterification of succinic acid (SA) with 1,4-butanediol (BDO) or (ii) transesterification of diethylsuccinate (DES) or dimethyl succinate (DMS) with BDO [27]. The chemical structures of the above-mentioned monomers are shown in Figure 3.

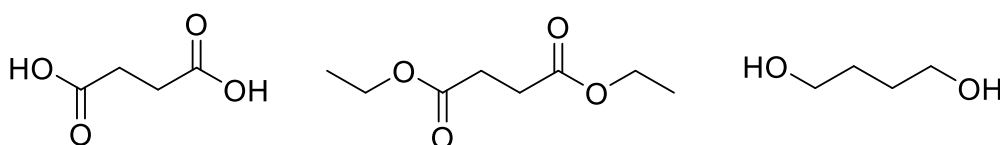


Figure 3 Monomers structures from the left: succinic acid (SA), diethyl succinate (DES), and 1,4-butanediol (BDO).

PBS is considered one of the best candidates among the biodegradable aliphatic polyesters to be 100% bio-based, produced from monomers derived from renewable sources. The reality is that only one of the two monomers needed for the polymerization is currently available as a bio-based building block, which is bio-based succinic acid [28]. On the other hand, biobased BDO is not yet economically viable compared to its counterpart from the refinery chain.

This aspect will be considered in Section 2.3., while in this section, the limitations of traditional synthetic strategies and possible solutions involving the use of enzymes will be discussed.

The most common formation of this material can be experienced from a wide range of publications regarding the PBS synthesis. Most of these pathways involve harsh reaction conditions and the use of catalysts of metal-based core, commonly Mn, Zn, Ti, Ca, Co, MgAc₂, Sb₂O_x, Fe_xO_y, etc. [26-29]. High temperatures and vacuum conditions are often used to remove the reaction's by-products and obtain polymeric products with higher molecular weights.

Traditional catalysts employed in the PBS production process are usually characterized by three main problems: (i) low selectivity leading to the formation of undesired products, (ii) high price compared to their turnover number, and (iii) proven toxicity. The latter aspect must be considered, especially when the polymeric product is designed for food packaging applications or for controlled biomedical drug delivery systems. What has been described above has led to the search for new catalysts for the production process of PBS and other commodity plastics. In particular, this work will focus the reader's attention on using biotechnological catalysts as a greener alternative [18].

Usually, the conventional PBS synthesis exploits the esterification equilibrium, while the alternative enzymatic polymerization pathways use a transesterification reaction process [30]. This choice can be attributed to the higher specificity of the employed enzyme (commonly a lipase enzyme) towards esters and alcohols rather than towards acid substrates employed in the esterification. All equilibrium polycondensation reactions need an efficient removal system of the by-product [31]. Using diesters such as DES or DMS instead of dicarboxylic acids can shift the equilibrium towards the polymerization product because more volatile results (alcohols) are obtained concerning water.

In most bio-synthetic routes, a two-stage polymerization with increasing vacuum and temperature is applied to achieve materials with higher molecular weights. Figure 4 shows an example of the polymerization reaction through transesterification catalyzed by N435, a commercially available enzyme produced by Novozymes® A/S [32]. This demonstrates how an enzymatic transesterification can be conducted to exploit the enzymatic catalyst's capabilities.

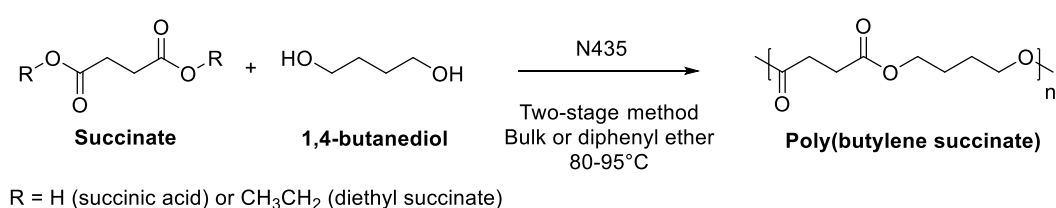


Figure 4 Enzymatic polycondensation of succinate with BDO using a two-stage method [33].

The company patents the exact catalyst formulation, but its composition is known as a lipase immobilized on a poly(methyl-methacrylate) resin support cross-linked with divinyl-benzene. Immobilization consists of a synthetic strategy to obtain heterogeneous catalysts, which involves using a carrier (organic, inorganic, or blend) to bind chemo or biocatalyst [34].

As for the type of catalysts related to this work, immobilization is a commonly used tool to improve the properties of enzymes, such as stability and reusability. Using this technique, the costs associated with the catalyst synthesis and formulation may be fully compensated by the quality of the obtained product and the enzyme turnover number or frequency [32].

Despite the advantages of the above-mentioned enzymatic methods, polycondensation of monomers by metal catalysis is still the industry's preferred way of PBS synthesis today. Table 1 shows only a few examples of the catalysts commonly employed in the reaction of interest.

Table 1 Some types of catalysts commonly employed in the chemocatalytic synthesis of PBS [35].

Catalysts	References	Hazard identification [(EC) No 1272/2008] [36]
Zr(OBu) ₄	[26]	H226, H314, H318, H336, H335
Hf(OBu) ₄	[26]	H226, H318, H317
Sb ₂ O ₃	[29]	H315
Sn(Oct) ₂	[29]	H318, H317, H361, H412
Ti(OBu) ₄	[29]	H226, H315, H318, H336, H335
SnCl ₂	[37]	H290, H302, H332, H314, H318, H317, H335

Polymeric products obtained by the two-stage method catalyzed by the compounds shown in the table usually do not reach the purity grades and molecular weights required by the manufacturing market. The second parameter is the most problematic because if the molecular weight is not equal to the desired one, it can affect the mechanical and rheological properties of the obtained material [38].

Two main strategies can be undertaken to achieve higher molecular weights: (i) synthesize a cyclic monomer and then proceed with a ring-opening polymerization (ROP) or (ii) proceed with a co-polymerization of succinic acid and BDO with succinic anhydride [39].

The first strategy, presented in Figure 5, is an example of ROP performed on cyclic monomers resulting from the transesterification between DMS and BDO.

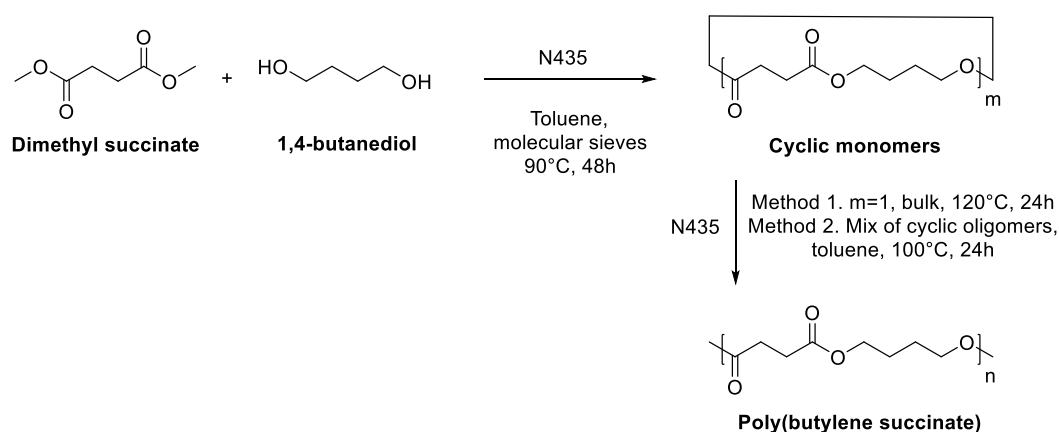


Figure 5 Ring Opening Polymerization (ROP) strategy [40].

A heterogeneous catalyst can be employed, thus exploiting all the advantages of this sustainable approach listed above. Sugihara *et al.* performed the two-step synthesis of PBS using N435 as a catalyst: the cyclic monomer production was carried out at 90°C for 48 hours, and the actual polymerization step at 100 or 120°C for 24 hours [40].

Given the reaction temperatures required for the polymerization process, it is evident that using a heat-resistant catalyst is mandatory. In this case, the enzyme immobilization strategy also comes

into play the enzyme immobilization strategy, which prevents the natural degradation of non-extremophile proteins at the examined temperatures.

The polymerization process can also be performed in bulk conditions, producing a product of high optical transparency and allowing the formulation of materials suitable for large casting [41]. The process shown in Figure 6 falls into the category of two-stage polymerization between SA, BDO, and succinic anhydride. This process ensures that average molecular weight values are achieved in 4 hours when the second step is performed at 85°C.

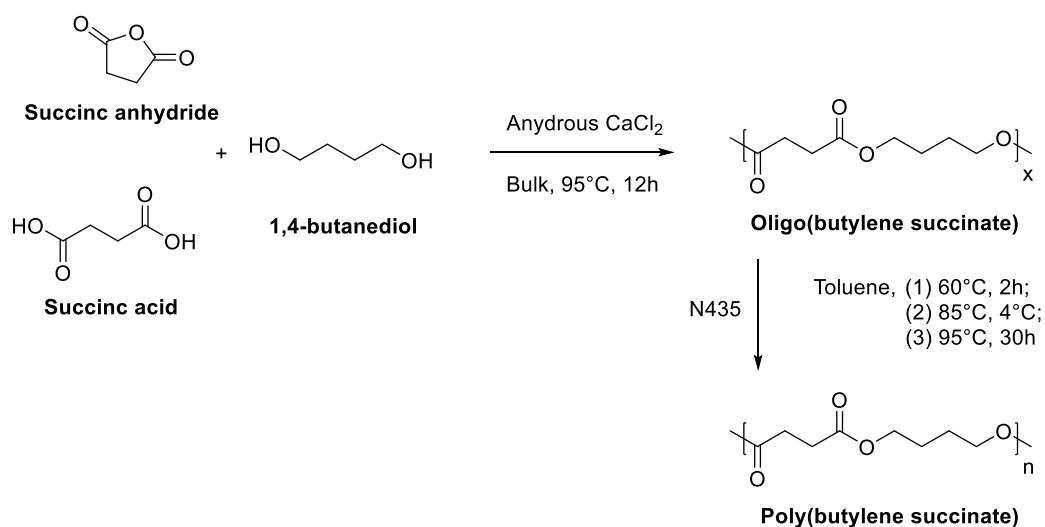


Figure 6 Co-polymerization strategy [42].

Azim *et al.* reported the advantage of employing *Candida Antarctica* Lipase B (CALB) in PBS synthesis [43], assessing that the easy recovery of the catalyst before a new reaction cycle and the total sustainability of the biocatalytic process allow overcoming the obstacles encountered using the traditional synthetic route.

To give context to the reader, succinic anhydride is a commodity mainly used in polymer science to synthesize alkyd resins, polyesters synthesized by the reaction between dicarboxylic acids and polyfunctional alcohols that are modified with fatty acids. These types of wax are commonly employed in the paint industry; thanks to their chemical structure, alkyd resins are used to create thin protective films with fast-drying properties at low cost.

Succinic acid SA can also be used as a diol in synthesizing these materials, which can be performed with specially engineered enzymes [21]. For further examples of the fields of application of biocatalysis in the synthesis of polymeric products, such as polyesters, some valuable references are cited [33, 41-48].

CALB has also been successfully employed in the production of biobased aliphatic unsaturated polyesters starting from DES, BDO, and various itaconates [49] and co-polyesters of PBS with poly((R)-3-hydroxybutyrate) [50].

Thus, it is also possible to obtain different polymeric materials based on the PBS structure through two-stage co-polymerizations which exploit the action of biocatalysts, whether homogeneous or heterogeneous.

The results of the three polymerization strategies shown above can be summarized by reporting the average molecular weights (Table 2).

Table 2 PBS molecular weights can be obtained through the synthetic strategies discussed in Section 2.1.

Strategy	Theoretical Mw [g/mol]	Dispersivity
Standard enzymatic two-stage polycondensation	45000	3.7
Ring Opening Polymerization	130000	1.6
Co-polymerization	73000	1.7

Therefore, to obtain the polymeric product with the required molecular weight according to the material intended use, the most suitable synthetic method has to be chosen wisely [51, 52].

2.3 Monomer Synthesis

Thanks to this research, it will be possible to make improvements aimed at synthesizing the PBS synthesis route starting from 100% bio-based monomers with polymerization catalyzed by sustainable biocatalysts.

Succinic acid is a chemical compound used directly in large-scale food, automotive, or pharmaceutical applications or as an intermediate to produce different resins and polymeric materials. The C₄ dicarboxylic acid is considered one of the most promising building blocks that can be created via fermentation from renewable sources.

BASF, Corbion's Succinity, and Myriant's biotechnology did not seem to invest in the transition to bio-SA production until the development of Reverdia Technology of commercial scale Biosuccinium™ in 2013. SA was produced exclusively from crude oil and natural gas. LCY Biosciences actively offers the license of its bio-succinic acid production technology (previously developed by BioAmber) to the best buyer. TechnipFMC plc already has licensed technology for polymerizing PBS by using Biosuccinium™ as a monomer, so acquiring Biosuccinium technology will allow the company to leverage the entire PBS value chain. Therefore, it is clear that this topic is very much discussed among the prominent manufacturers of chemical products.

Table 3 and Table 4 show the data on SA production using the traditional and recently developed biocatalytic processes, thus allowing an immediate comparison between the quantities involved.

Hydrogenation of liquid maleic anhydride catalyzed by Pd or Ni at 120-180°C followed by a hydration step with hot water characterizes the SA petrochemical synthesis. The product can then be recovered by crystallization, filtration, and an additional drying step.

Table 3 Quantity of raw materials necessary for producing one ton of SA from maleic anhydride and related output amounts [53].

Input		Output	
Maleic anhydride	890.08 kg	Succinic acid	1000.00 kg
Hydrogen	254.31 kg	Waste (generic)	319.00 kg
Water	304.62 kg		
Nitrogen	72.88 kg		
Palladium catalyst	0.01 kg		
Natural gas	101.72 kg		

Electricity	356.03 kW h		
Total	1319.00 kg	Total	1319.00 kg
	356.03 kW h		

Table 4 Quantity of raw materials necessary for the production of one ton of SA from grain sorghum Reverdia and related output amounts [53].

Input		Output	
Grain sorghum grits	5339.20 kg	Succinic acid	1000.00 kg
Potable water	1578.99 kg	Ethanol	1250.00 kg
Underground water	53685.61 kg	Wastewater	12631.91 kg
Natural gas	0.0023 kg	Sanitary sewer	378.96 kg
Diesel	0.89 kg	Waste (generic)	45343.82 kg
Electricity	2204.62 kg		
Total	60604.68 kg	Total	60604.68 kg
	2204.62 kW h		

Biorefineries employ saccharifiable starting material, such as grain sorghum grits, to undergo microbial fermentation and obtain glucose. Reverdia elevated the SA production process by getting ethanol as a co-product.

The fermentation process of this alcohol by using genetically modified bacteria generates a sufficient energy stock to support bio-SA production. A distillation step is required to recover ethanol and concentrate the SA solution, followed by filtration and aging of the product crystals. Therefore, one of the monomers for synthesizing PBS can be produced environmentally and economically sustainably using already established biotechnological methods.

1,4-butanediol (BDO) is a highly reduced C₄ compound containing two hydroxyl groups that is mainly used as a building in polymer synthesis. Its global market was above 2.5 tons per year in 2016 and has grown exponentially. Traditionally, the production of BDO involves transforming petrol-based chemicals such as acetylene, butane, maleic anhydride, and butadiene.

One of the first attempts to produce BDO from renewable sources was carried out by Yim *et al.* 2011 by a thorough study in which an engineered *E. coli* strain allowed the production of bio-BDO starting from a mixture of hydrolyzed C₅ and C₆ sugars in a fed-batch fermentation reactor [54].

Liu *et al.* have optimized the previously reported production through a *de novo* pathway using an enzymatic reactor starting from D-xylose, leading exclusively to the production of bio-BDO [55].

In the meantime, the potential environmental benefit of using bio-BDO instead of fossil-based BDO has been assessed. Still, at the same time, the problems related to this type of biotransformation have been highlighted, as well as the type of feedstock production and the total energy demand of the process [56].

Thanks to the USA Genomatica's process developments, biobased BDO was produced from renewable sources through a technology that exploits the mechanism of action of a modified *E. coli* strain to obtain BDO directly from reducing a sugar-derived Biosuccinium™ [26].

A commercially relevant target of 2 g/L per hour of bio-BDO was successfully obtained from sucrose, dextrose, and cellulosic biomass (C₅ + C₆) with an engineered *E. coli* strain.

A detailed Life Cycle Assessment (LCA) was performed on the production mentioned above, highlighting how by producing bio-BDO with this strategy instead of the traditional petrochemical methods, the quantities of CO₂ emitted and required fossil energy are reduced by 83% and 64%, respectively [57].

In 2017, an engineered *Klebsiella oxytoca* diol dehydratase was employed to produce bio-BDO. Unfortunately, this study had only 209 mg/mL of product. Still, it is one of the first examples of the possibility of expanding the catalytic activity of diol hydratases toward non-native C₄ [58]. In fact, since the year following this study, an increase in publications on bio-BDO production has been observed, and an evaluation of bio-BDO as a profitable alternative to oil-derived BDO has been assessed [59]. Therefore, the problematic aspects of the biotechnological process, such as the process temperature or the pH conditions, have been studied in more depth [60] and overcome with new and innovative technological strategies [61].

The Cheng *et al.* study is the first example of bio-BDO synthesis on an industrial scale, reaching a production of 140 g/L with an engineered CoA-dependent *E. coli* able to transform renewable carbohydrate feedstock in the product of interest [62].

Guo *et al.* identify the bottleneck of bio-BDO production with engineered *E. coli* in the last step, namely reducing 4-hydroxy butanaldehyde with aldehyde dehydrogenase/alcohol dehydrogenase [63].

Therefore, in recent years, the research has specialized in optimizing the process steps by improving the catalytic properties of enzymes thanks to protein engineering [64]. At the same time, milder production conditions for bio-BDO have been sought, defined as greener and safer [65]. Over the course of this year, it has been demonstrated that biological engineering is suitable for the sustainable synthesis of building blocks, constituting the future of sustainable chemistry in the area under consideration. However, the economic aspect of investing necessary capital and resources includes the ambit in which future optimizations will indeed be required [66].

In this paragraph, the scientific path regarding the possibility of producing the monomers necessary for synthesizing PBS with innovative methodologies that involve the use of enzymes, both in their native form or subjected to protein engineering processes, has been illustrated. As mentioned above, further research must be carried out to allow bio-BDO to be economically advantageous compared to bio-SA.

3. Post-processing

3.1 Biodegradation

Given that 60% of total plastic waste in Europe is made up of disposable packaging materials, it is clear why this field is one of the starting points for the evolution towards a sustainable global market. Aliphatic polyesters are usually easily susceptible to biological attacks; therefore, the possibility of using them in various fields has attracted attention.

Nowadays, poly(lactic acid) PLA holds the record as a biodegradable polymer that can also be used in direct contact with food, but its cost is a non-negligible disadvantage [67].

PBS and poly(butylene-succinate-co-adipate) (PBSA) are two of the primary candidates as aliphatic biodegradable polyesters intended for the food packaging field [68]. Indeed, chemical structure, composition, sequence distribution, and crystallinity of PBSA copolymers play a

fundamental role in post-use degradation chances associated with this class of polymeric materials [69].

To facilitate the understanding of the biodegradation phenomenon of a polymeric material, a study performed with a specific type of lipase under standard reaction conditions [70] will be presented below.

For example, PBS and PBA homo-polymers are not suitable for enzymatic degradation by hydrolysis over 90 hours. The biodegradability of the samples was assessed through a simple percentage of the weight loss compared to the starting material. This observed phenomenon of lower mass loss characteristic of PBS-rich copolymer could be attributed to the higher degree of crystallinity [71].

When hydrolysis is performed in a buffer solution with *Candida cylindracea* lipase at 30°C, the highest enzymatic degradation rate is observed for PBAS-50 (co-polyester containing 50 mol.% of butylene succinate units), as shown in Figure 7 and confirmed by the correlation between composition and physical-chemical properties available in the literature [70].

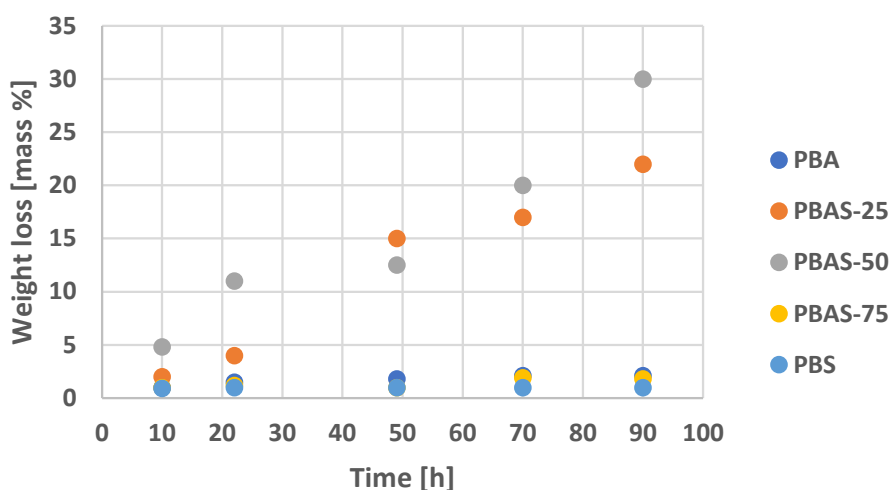


Figure 7 Co-polyesters biodegradation performed by *Candida cylindracea* lipase [70].

Since the 1990s, microbial degradation of polymeric materials has attracted worldwide attention [72] thanks to the ability of microorganisms to be used as the “cleanup of man-made pollutants” released into the environment.

Over the past thirty years, a wide variety of hydrolysis reactions have been successfully used for the enzymatic treatment of PET. Recent studies have reported some interesting results regarding the classes of microorganisms employed in the biodegradation of PET.

For example, Kawai *et al.*[73] have determined the five main aspects that affect the biodegradability of PET-based polymeric materials: (i) the hydrolysis reaction temperature that should be above the temperature of glass transition T_g (70-80°C for PET), (ii) the percentage by weight of water that can be absorbed by the polymer that is directly related to its surface topology, (iii) the percentage of crystalline and amorphous phases in the material, (iv) the spatial orientation of the polymeric chains and (v) the melting temperature characteristics of polyesters. More generally, it is known that when the reaction is carried out at higher temperatures, an acceleration of the degradation process is usually observed.

The observations mentioned above could be applied in research on biodegradation of PBS [74], considering that it is a white crystalline thermoplastic polymer with a melting temperature range of 90-120°C and T_g between -45 and -10°C [75]. Thanks to the same degree of characteristic temperatures, this can be translated into the similar mechanical properties of PBS and poly(olefins), such as poly(propylene) and low-density poly(ethylene) [76].

Recently, groups of scientists interested in this phenomenon have reported that *Amycolatopsis sp.* HT-6 and some *Penicillium sp.* strains can de-polymerize PBS, while other microorganisms have been found to consume 50% (w/v) of some emulsified PBS samples [77-85].

Pan *et al.* demonstrated the direct correlation between the different molecular weights of PBS films and the enzymatic degradation performed by an *Aspergillus fumigatus* cutinase [86].

From the data shown in Figure 8, it is clear that the different degrees of degradation estimated as weight loss are closely related to the other poly-dispersivity indices of the four samples. The same study also considers the influence of the various degrees of crystallinity of the starting material.

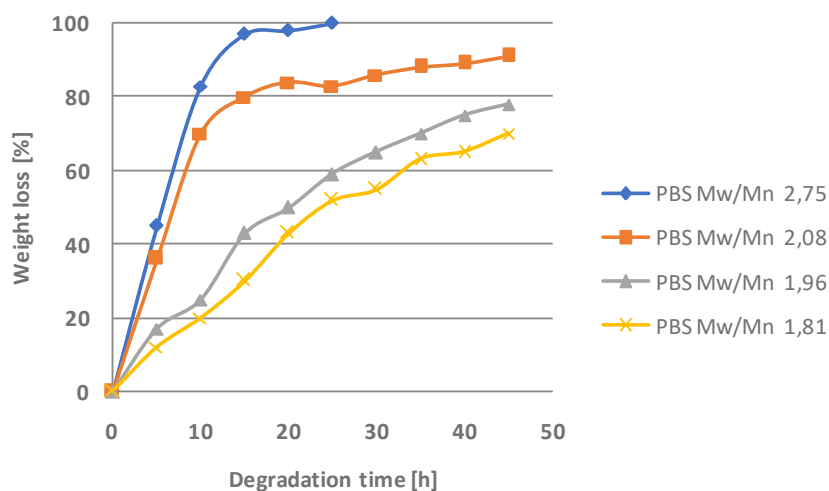


Figure 8 Effect of different average molecular weights on weight loss of PBS samples subjected to enzymatic degradation [86].

3.2 Further Applications

Enzymes are not considered solely for their ability to degrade polymeric materials. Still, they have also been evaluated as excellent candidates to improve their characteristics in terms of already-known properties and the introduction of new ones [4, 87-89].

One of the most commonly used strategies for formulating materials with modified specific properties is the copolymerization of the section whose performance has to be improved with an area allowing this task to be achieved.

In the literature, a wide variety of copolymers of succinic acid and other dicarboxylic acid copolymers have been successfully synthesized and studied as poly(butylene succinate-co-butylene terephthalic acid) P(BS-co-BTA) [69], poly(butylene succinate-co-butylene malate) P(BS-co-BM) [90] or poly(butylene succinate-co-2,5-tetrahydrofuran methanol) P(BS-co-TS) [91].

To synthesize materials intended for biomedical applications such as drug delivery, compatible implants, scaffolds for tissue engineering, or low molecular weight compound release systems,

aliphatic polyesters are excellent candidates as they resist human metabolism in proportion to their structural characteristics [92]. Consequently, the compatibility between the materials and the receiving organism should be evaluated by exploratory tests. Instead, for the use of these materials in the food packaging field, the passage of oxygen or moisture has to be controlled as they can cause degradation of the content of the packaging.

Namely, the gas barrier capabilities of the biopolymers produced are essential. They must be added to the need to formulate biodegradable polymeric materials per the principles of the circular and sustainable economy [93].

Therefore, enzymes can take on the role of process catalysts and be used in new areas as propriety implementers of new Special Adsorbent Polymers (SAP) for agricultural, food, or biomedical sectors and other purposes [94-98].

4. Conclusions

In this review, the spectrum of use of enzymes in the PBS industry was presented. Possible fields of use of some biocatalysts have been examined, starting from the synthesis of the monomers 1,4-butanediol (BDO) and succinic acid (SA), then considering different polymerization strategies to obtain high molecular weights poly(butylene-succinate) PBS. Finally, the focus was shifted to polymer post-synthesis treatments, such as enzymatic biodegradation and manufacturing industries where these sustainable materials can be used. In this investigation, the negative and positive aspects of a possible replacement of traditional catalysis with innovative enzymatic methods were highlighted, considering some of the principles of green chemistry. Future research will undoubtedly identify the potential of biocatalysts and demonstrate how they could be used on an industrial scale in the field of PBS production.

Author Contributions

Armani D. and Dr. Petri A. were involved in data collection. Armani D. planned and drafted the manuscript, was responsible for the bibliographic collection and designed the figures. Dr. Petri A. supervised the work, interpreted the results and worked on the manuscript. All authors discussed the results and commented on the manuscript.

Competing Interests

The authors have declared that no competing interests exist.

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