



Innovative solutions and challenges to increase the use of Poly (3-hydroxybutyrate) in food packaging and disposables

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ABSTRACT

Poly(3-hydroxybutyrate) (PHB) has gain in recent years a huge interest in the food packaging field due to its renewable origin from waste as well as non-food crops, high mechanical strength, medium-to-high barrier performance, and inherent biodegradability in natural environments. Despite these advantages, PHB also shows a narrow processing window and high brittleness since this homopolyester shows low thermal stability and high crystallinity, limiting its industrial application. The present review provides an updated state of the art of the most relevant aspects in terms of processing and properties of PHB materials with a particular emphasis for their use in sustainable food packaging. It also describes the most potential strategies that can be applied to improve both the processability and mechanical properties of PHB, including the melt blending with green plasticizers and flexible biodegradable polymers as well as the development of more ductile co-polyesters. Finally, the waste management of the newly developed PHB-based articles is discussed, from their potential compostability to develop more biopolymers to more economically favored alternatives such as mechanical and chemical recycling technologies.

1. Introduction

Plastics show a good balance between different properties, including lightness, low production cost, durability, ease of processing, ability to be moulded into a multitude of shapes, and high thermal and mechanical properties. As a result, plastics are present in a wide range of industrial sectors, from agriculture to the automotive industry, building and construction, and electronics. However, the packaging sector is the one that concentrates the highest consumption of plastics, which is currently over 40% [1]. Among packaging applications, those related to food conservation represent around 90% of them that, in turn, result in one-single uses with an average shelf life of approximately 2 weeks [2].

Petroleum-derived plastics are one the most widely used materials in food packaging. During the last decades, there has been an increase in the production of petrochemical polymers. In 2019, the global production of synthetic plastics was estimated at 368 million tonnes, increasing

by 9 million tonnes compared to global production in 2018 [3]. However, the massive consumption of plastics is associated with a series of negative consequences for the environment. On the one hand, limited fossil resources are needed to produce these materials, whereas the current increasing production could accelerate their depletion. Although it is important to highlight that around 4 to 6% of all the oil and gas used in Europe is employed in the production of plastic materials, in the long term, plastics production should decouple from fossil-based feedstocks. In fact, it is expected that, in the future, the vast majority of plastics production move to alternative feedstocks including biomass, recycled oils or secondary plastics [3]. In addition, it should be taken into account that the production of petroleum-derived plastics generates other environmental problems, including the emission of large quantities of environmentally harmful gases such as carbon dioxide (CO₂) into the atmosphere. Furthermore, the main problem occurs after the product's end-of-life cycle since a large amount of synthetic plastics are still

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disposed of in controlled landfills after a short single use or, more importantly, leak out of the collecting systems, being accumulated in the environment [4]. In particular, in 2015, approximately 79% of the plastic waste generated globally ended up in landfills or as waste in the environment [5]. In this scenario, it has been projected that, by 2050, around 12 billion metric tonnes of plastic waste will be in landfills, while a high amount of them will reach the oceans producing high levels of microplastics [6].

The above-described environmental issues caused by the extensive use in food packaging applications of fossil derived plastics that are non-biodegradable have led to an increase in the research, development, and also production of more sustainable polymer materials. Although, recyclability of plastics has increased during the last years, in the case of food packaging their recyclability is very complex mainly because the use of multilayer packaging systems in the food packaging field [7–9]. In this regard, biopolymers are the most promising polymers that can offer a whole sustainable solution within the plastic packaging field. Biopolymers include “bio-based” polymers, polymers that are “biodegradable”, or polymers that exhibit both characteristics [10]. Multilayer structures based on biodegradable polymers, although are difficult of recycling, can be disintegrated under composting conditions as sustainable end-life option [7,11,12]. Polyhydroxyalkanoates (PHAs) belong to the most sustainable group since they are both, biobased and biodegradable.

PHAs are linear isotactic biodegradable polyesters that can be obtained from natural resources. In particular, PHAs are produced and accumulated intracellularly by a wide range of microorganisms under conditions of nutrient deficiency and in the existence of excess carbon source and which act as a carbon and energy storage body [13–15]. These biopolyesters are biodegradable in industrial composting conditions and, in some cases, also in natural environments. Therefore, PHAs can be integrated inside the so-called Circular Bioeconomy strategies that aim, mediated by microorganisms, to bring the carbon back to the soil [16]. In particular, this type of biopolyesters has gained a high interest in the food packaging sector due to its physical properties are similar to some petrochemical polymers used in packaging applications [17–22]. In particular, certain PHAs share some similarities in terms of mechanical performance and thermal and water resistances than polyolefins, for example polypropylene (PP) [23]. Fig. 1 summarizes the lifecycle of a PHA packaging, which is based on a sustainable closed cycle system. In this process, the PHA material is obtained from natural and renewable resources, even food and industrial waste, then it is used to produce the packaging article, which can be reused or mechanically recycled, similar to other polymers, and finally it can be composted at the end of its lifespan. If the resultant compost is used as a carbon source

to produce a new PHA, this process close the loop and it is sometimes so-called organic recycling [24].

There are a wide variety of different PHAs, whose monomer composition and physicochemical properties vary according to the bacterial strain, carbon source, and culture conditions used. Currently, >150 different monomers of PHAs are known to exist, being 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) the two most common and widely studied [25]. Poly(3-hydroxybutyrate) (PHB) is the best characterized PHA, consisting of only 3HB as the monomer unit, and also the most applied PHA for short-term applications [26,27]. It belongs to the group of short-chain length PHAs (*scl*-PHAs). Due to its high stereo-regularity, PHB easily crystallizes from the melt at a relative high temperature, with a crystallization temperature (T_c) of approximately 110 °C, and develops a high crystallinity degree (X_c over 80%) [28,29]. As a result of this, PHB shows higher oxygen and water vapour barrier properties than other biopolyesters as well as improved resistance to ultraviolet (UV) light, which make it a potential candidate for use in sustainable food packaging applications [23,30]. Thus, PHB and its copolyesters have been recently introduced to the plastic packaging market, with production in 2020 of around 35,870 tonnes and an estimated 10-fold increase in production over the next five years [31].

However, PHB also has a number of drawbacks that make difficult to introduce it on an industrial scale. One of the main problems of PHB is its high brittleness and low ductility due to its high crystallinity as well as the physical ageing process that the material undergoes during secondary crystallization, which results in the formation of irregular pores on the surface and limits the flexibility of the amorphous chains [32,33]. Indeed, whereas high crystallinity of PHB renders some of the above-described advantages that are fundamental for materials intended for food packaging [1,17,30,34–39], it also provides PHB with a brittle and fragile performance. Moreover, PHB has a narrow processing window as its melting temperature (T_m) is close to its degradation onset temperature (T_{onset}) [40]. These technical disadvantages, together with its current high cost, due to its synthesis is based on a biotechnological routes, means that its use in food packaging is still limited. Therefore, the market penetration of PHB into the packaging sector is still far away the high expectations of the scientific community since it is not yet competitive with petrochemical derived plastics [41].

Numerous research works are being currently underway to improve the processability and ductility of PHB to extend its industrial applications for food packaging and disposable articles. Some examples of these include co-polymerization of 3HB with high contents of 3HV and other monomers [42–45], the use of plasticizers and impact modifiers, and physical blending with more ductile biopolymers [18,46–49]. Among them, melt-mixing strategies have many advantages over other methodologies because they offer the chance to improve the physical performance of the final material through a relatively simple method that is cost-effective and makes use of a readily available processing technology at the industrial level [34]. In this context, plasticizing by means of additives is one of the cheapest, simplest, and most effective methods to improve the ductile mechanical properties, such as impact strength or elongation at break [37,50]. Natural and/or biodegradable additives, for instance, polyethylene glycol (PEG) [51–54], glycerol [51,55], chemically modified vegetable oils [32,56,57], citrates esters such as acetyl tributyl citrate (ATBC) and triethyl citrate (TEC) [50,58–60], among others, have been successfully used as plasticizers for PHB. Moreover, the flexibility of PHAs can be improved by melt blending with more flexible biodegradable polymers, for example thermoplastic starch (TPS), poly(butylene adipate-co-terephthalate) (PBAT) or poly(butylene succinate-co-butylene adipate) (PBSA) [61–63], and poly(lactic acid) (PLA) [37–39,64] and its oligomers (oligomeric lactic acid, OLA) [38,39,64,65].

This review aims to summarize the main applications of PHB for food packaging and food related disposable articles. With this propose, the synthesis and chemical aspects as well as the most emerging techniques for PHB recovery and/or end-life options are firstly described. Then, the

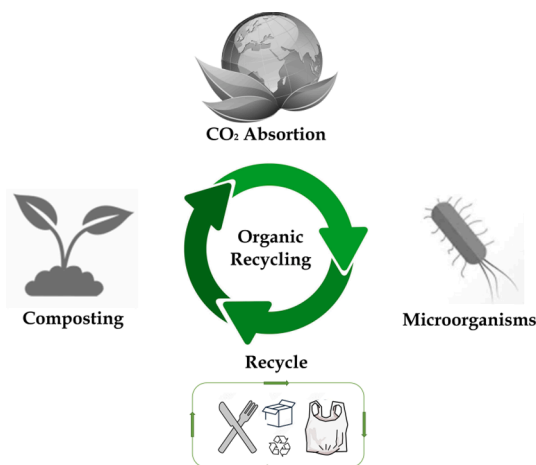


Fig. 1. Life cycle of polyhydroxyalkanoates (PHAs) for food packaging and disposable applications.

most typical processing aspects of PHB at the industrial level are described, being particularly focused on the ageing phenomenon of PHB and its narrow processing window. Finally, some cutting-edge research works focused on enhancing the PHB stretchability by means of melt blending are described, considering both plasticizers and more flexible biodegradable polymers. Therefore, it gathers the most relevant information regarding the possibility to extend the industrial applications of PHB in the food packaging field.

2. Bacterial production of PHB

PHAs are a group of microbial biopolyesters biologically synthesized as intracellular products of the secondary metabolism of several bacteria, archaea, and a limited number of yeasts, under controlled fermentation conditions. PHAs are biosynthesized through an aerobic process and further accumulated inside the microbial cell as storage materials in response to nutrient limitations, that is, nitrogen, phosphorus, oxygen, and/or trace elements [41,66]. Therefore, the yield of substrate-to-product conversion is limited by the carbon source [41]. Under abundant carbonaceous sources, such as glucose or sucrose, and/or lipids, for instance, vegetable oils or glycerin [66], microorganisms can accumulate up to 60–80% of dry cell weight in PHA as a source of energy to prevent starvation if an essential element becomes unavailable [67–69]. Thus, in the current scenario, PHAs can intrinsically not become competitive with traditional petrochemical derived plastics produce in chemical reactors. Indeed, the carbon substrate solely account for 20–45% of the total PHAs production costs [70]. Nevertheless, during the last years considerable research efforts has been focused on reducing the costs of biomass growth and subsequent PHA accumulation in the microbial cells by replacing costly organic carbon sources by agricultural and food industry wastes such as molasses, cheese whey, wheat, and rice bran, fruit pulps, glycerol, vegetable oils and vegetable oil residues, starch, oil mill, etc. [41,71–73], or even, more recently, wastewater or municipal biowaste [74]. Table 1 gathers some of the main waste materials that have been used as carbon feedstock for microbial PHA production [75–77].

The mechanism of synthesis of PHB at the industrial level can be summarized in three fundamental stages: (i) fermentation, (ii) extraction, and (iii) purification, which are schematically represented in Fig. 2. In this regard, *Alcaligenes eutrophus* glucose is widely used as carbon source for the production of PHB. Thus, it is frequently used as the main microorganism for the production of PHB mainly because it is easy to grow in a simple medium, offering the additional advantage that it can accumulate up to 80% of dry cell weight in PHA [23]. The cultivation of living microbial cells takes place in bioreactors and the biotechnological PHA production process is typically finished by stop of aeration and pasteurization. Then, a downstream process to separate PHA-rich biomass from the spent fermentation broths is required, which is usually conducted by sedimentation, flocculation, centrifugation, or filtration techniques. This separation step, which involves the recovery of intracellular PHAs from the surrounding non-PHA cells mass, highly

Table 1
Wastes materials used in the production of polyhydroxyalkanoates (PHAs).

Waste Materials for PHA production
Milk industry waste
Starch
Plant oils waste
Vegetable oils waste
Spent coffee grounds
Lignocellulosic waste
Sugar industry waste
Legume waste
Animal fats waste
Biodiesel industry waste
Lignin and lignin derivatives
Wastewater

impacts on the PHA production costs. For instance, various researchers have evaluated that approximately 50% of the PHAs production cost is associated with the extraction and purification steps [78–80]. Finally, the PHA drying yield from microbial biomass by thermal or lyophilization processes should also be carefully considered since the biopolymer must be recovered without negatively affecting its properties, such as the molecular weight (M_w) [41].

In a context to reduce costs and promote the successful market penetration and commercialization of PHAs, the use of mixed microbial cultures (MMCs) represents an affordable approach due to sterile conditions and specific feedstock are not necessary [82]. MMC fundamentals are based on the fact that, in the presence of an external substrate, microorganisms have the option to use it either for growth or for accumulation of intracellular reserves. Conceptual models on PHA synthesis have previously assumed that accumulation occurs when growth is limited by internal factors, for instance an insufficient amount of ribonucleic acid (RNA) or enzymes required for growth, and/or external factors, such as a lack of nutrients [83]. However, some studies have demonstrated that storage of PHA by mixed cultures can also occur without any external or internal growth limitation in conditions of excess nutrients and sufficient experiment time for physiological cell adaptation [84]. Indeed, once the most optimal bacteria for PHA accumulation have been selected, they can simultaneously grow and store PHA. Thereafter, it is considered that the metabolic pathways for carbon consumption and PHA storage are the same as for pure cultures [85]. Therefore, the key to the effectiveness of MMC for PHA production processes in terms of both storage capacity and productivity mainly relies on culture selection, that is, enrichment in PHA-accumulating organisms, rather than the conditions imposed to the bioreactor [86]. These MMC processes are based on three-stage process, which have been summarized in Fig. 3. In stage 1 or first step, in the so-called anaerobic membrane bioreactor (AnMBR), the feedstock acidogenic fermentation takes place. Then during stage 2, the permeated fermented feedstock obtained, which is rich in organic acids, is subsequently used as influent for the aerobic enrichment of the PHA-producing culture. This second step is carried out in a sequencing batch reactor (SBR) that is subjected to feast and famine (FF) conditions. Finally, PHA accumulation occurs during stage 3, the so-called production stage, in a batch reactor inoculated with sludge from the culture enrichment of SBR and pulse-fed with the clarified fermented feedstock produced in first step. The PHA composition depends on the percentage of each volatile fatty acid (VFA) in the fermented feedstock produced in the acidogenic fermentation and supplied to the MMC. In this regard, it has been demonstrated that PHA production by MMC can be manipulated to produce copolymers with different monomer unit composition by controlling the operational conditions of the acidogenic reactor [87–89]. In any case, MMC processes for PHA production are fully compatible with the use of agro-industrial surplus and waste as feedstock [82].

Furthermore, transgenic plants induced with the PHA genes and synthesizing enzymes seems to be the most viable strategy for the agro-manufacturing of PHA (at least on laboratory scale) and at promising affordable cost for the plastic processing industry [6]. It seems that transgenic plants will allow the production of PHAs at high scale level and, thus, will allow their production at lower cost.

3. Processing aspects of PHB-Based formulations

Even though the properties of PHB are very promising, it still shows some disadvantages that are responsible for its low competitiveness with respect to commodity plastics and, thus, restrict its industrial applications as novel food packaging material. These drawbacks include not only the above-mentioned high cost to produce PHB (compared with conventional polyolefins) but also its extremely narrow processing window and high crystallinity, which makes it a highly brittle material with the consequent poor processability and low stretchability [91]. Furthermore, PHB shows a T_m in the 170–180 °C range, with a mean

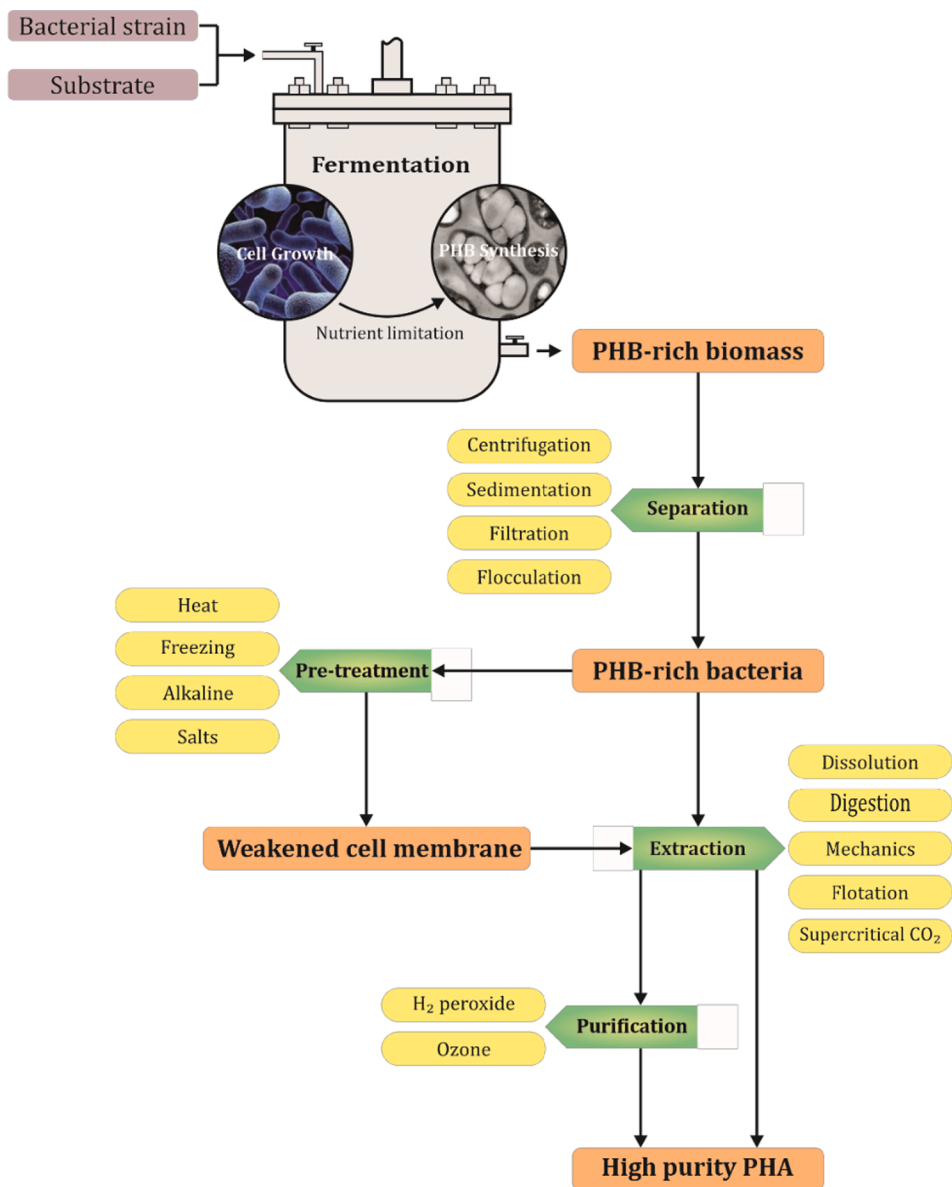


Fig. 2. Schematic representation of the synthesis of poly(3-hydroxybutyrate) (PHB) summarized in three fundamental stages: (i) fermentation, (ii) extraction, and (iii) purification. Adapted from Garcia-Garcia (2019) [81] under Creative Commons CC BY license.

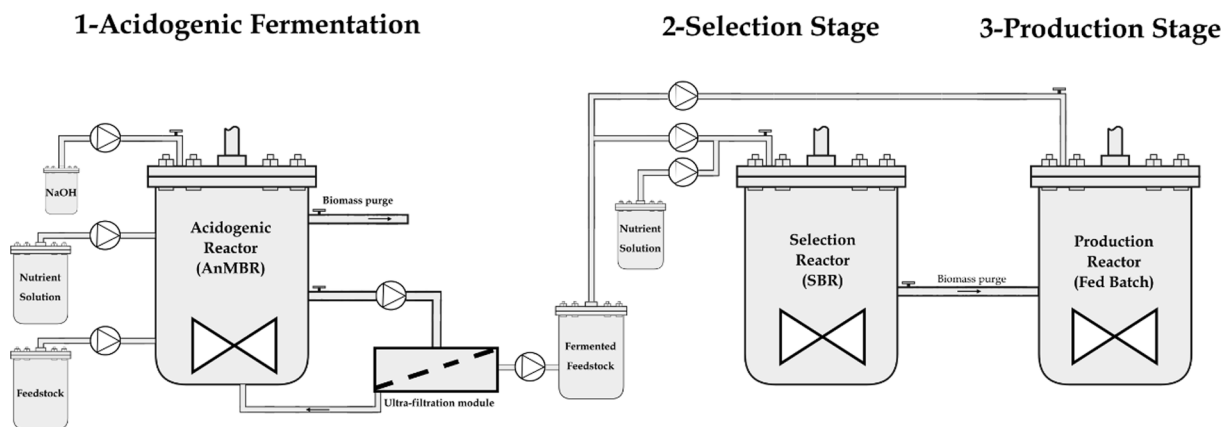


Fig. 3. Setup of the 3-stage polyhydroxyalkanoate (PHA) production process by mixed microbial cultures (MMCs). Reprinted from Duque et al. [90] with permission from Elsevier.

value at approximately 173 °C, which is close to its T_{deg} (at nearly 270 °C) [30,92]. In fact, PHB thermal degradation starts at a temperature near the processing temperature conditions, showing the T_{onset} values between 245 and 260 °C [37,56,57]. As a result, this very narrow processing window, provided by the high crystallinity and inherent PHB low resistance to thermal degradation, certainly limits the processing of PHB in the plastic industry [23,92–94]. To reduce PHB high crystallinity and facilitate its processability, several strategies have been addressed, including blending and co-polymerization. Blending strategies are considered simple, scalable, and cost-effective methods for the plastic processing industry since the processing technology needed are already available at most current plastic processing industries. In this sense, PHB has been widely blended with other biodegradable polymer matrices, for example PLA [17,26,36–38,92,93,95], but for film production other biopolyesters with higher flexibility are required. Among them, poly(ϵ -caprolactone) (PCL) has demonstrated to be one of the most interesting polymers for increasing the PHB stretchability [18,96–98].

The leading conversion methods for PHB-based blend formulations at the industrial level are those related to melt-processing techniques (e. g., extrusion, injection molding, thermoforming, film forming, etc.) [18,34,99], while more recently the electrohydrodynamic processing (EHDP), namely electrospinning and electrospraying, has also gained considerable interest [100,101]. Prior to melt processing, PHB should be dried to prevent water/humidity presence that can lead to a significant M_w drop due to the fact that ester groups are highly susceptible of hydrolysis. In fact, linear isotactic PHB can be obtained either as oligomer (OHB) or as a polymer and is characterized for having a M_w in the range of 1,000–3,000,000 $g\ mol^{-1}$ (with polydispersity of around two) [102] which is one of the main parameter characterizing the physical as well as the mechanical performance of the final product, contributing to high modulus and high strength [103]. Being OHB when M_w in the range of 1,000–10,000 $g\ mol^{-1}$, low molecular weight PHB when the M_w in the range of 10,000–20,000 $g\ mol^{-1}$ and PHB polymer when the molecular weight is higher than 20,000 $g\ mol^{-1}$. Thus, the reduction on the M_w will, thereafter, compromise the overall properties of the final PHB-based materials during their service. The viscosity of PHB decreases after melt processing with a consequent reduction of its M_w due to the thermal degradation by random scission of polymer chains. It was found that in extruded PHB products, the M_w value is proportional to the residence time, while it also decreases with increasing of processing temperature and screw speed, along with a significant reduction on the tensile strength and elongation at break without significant changes on the elastic modulus [104]. Additionally, additives as well as their amount should also be carefully selected since they can affect the kinetic of thermal degradation (i.e.: glycerol) [55].

Due to its low thermal stability, PHB processing temperature is habitually carried out at the lowest temperature possible, typically in the range of 160–200 °C for a few minutes. In this context, Janigová *et al.* studied the thermal degradation of PHB as a function of the annealing time and temperature, and they concluded that the degradation of PHB is minimal under 170 °C even in a presence of a rather effective pro-

degradant additive such as the case of glycerol [55]. Once PHB is melt-processed, then the biopolymer is modeled into the desired packaging products and, finally, cooled down to attain its desired dimensions. In this context, thermoforming and injection molding are some of the most popular production techniques used at the industrial level in the packaging sector. For instance, compression molding of PHB has been successfully performed with a pretreatment at 160 °C for 2 min, followed by the application of 4 tons for another 5 min at 160 °C, and cooled down to 60 °C [105]. Sanchez-Safont *et al.* [106] studied the thermoforming ability of PHB and were able to optimize the process to obtain thermoformed trays with good mold reproducibility. This process was carried out by a vacuum-assisted thermoforming technique at the pilot scale level, varying the heating (ranging between 20 and 45 s) and vacuum times (ranging between 3 and 20 s, respectively) (see Fig. 4).

PHB has also been processed by injection molding with a maximum temperature of 160–180 °C [23,32]. In this context, Bucci *et al.* [23] processed PHB-based food packaging materials into jars and caps with the same injection molding equipment used for PP at the industrial level. It was then demonstrated that PHB can be processed with the injection molding processing technology already available in the industrial facilities. However, PHB showed very different physical and mechanical properties to those of PP, such as higher density and higher fluidity level, and thus it was needed to refrigerate the molds with water at around 20 °C, leading to a longer injection cycles than PP. Nevertheless, it was concluded that the production cycle times of PHB can be reduced by using specific designed molds for PHB and the application of heat with temperatures at around 60 °C in order to give higher crystallization rate for the PHB material.

EHDP is another processing technology that has gained considerable interest during the last years, both in the form of electrospraying and electrospinning [107]. For instance, the use of electrospun PHB fibers in tissue engineering is very promising to replace damaged or poorly grown nerves and tissue regeneration [108]. Moreover, during the last years, the production of electrospun materials has been gradually transferred from the laboratory to industrial level [64,100,109]. Truthfully, the production of ultrafine electrospun PHB-based fibers in the form of nonwoven mats by means of electrospinning has shown a great potential in several industrial applications, including the food packaging sector [100,109]. In fact, electrospinning is one of the latest technologies to process PHAs in the form of monolayer and multilayer films by the application of high electric voltages and annealing treatments [110]. The latter process, therefore, opens up the incorporation thermolabile substances into electrospun biopolymer films, including natural extracts, for the development of active packaging systems [7,72,110]. In this new trend, PHB has begun to have a greater impact, both individually and with polymer mixtures such as PLA, polyanilines, or lignins [64,101,108,111–113]. In particular, the combination of PLA and PHB biopolyesters, since both are bio-based thermoplastic polyesters, results very promising for packaging and other short-term applications [64,101]. Then, the electrospinning process offer several advantages for PHB mats manufacturing due to the fact that it is



Fig. 4. Thermoformed tray based on poly(3-hydroxybutyrate) (PHB) reinforced with cellulosic rice husk fibers and compatibilized with hexamethylene diisocyanate (HMDDI): (a) bottom-side view, (b) top-side view and (c) bottom view. Reprinted from Sánchez-Safont *et al.* [106] under Creative Commons CC BY license.

relatively simple and versatile [101]. The foremost advantage of electrospinning technique is that it allows the production of PHB-based mats operating at room temperature and thus avoids thermal degradation during processing [64,101,110]. In this context, Arrieta *et al.* [101] developed neat PHB mats by electrospinning and obtained uniform, straight, and bead-free electrospun fibers (Fig. 5). Authors ascribed the good processing conditions of PHB in comparison with other biopolyesters, such as PLA [101] or PCL [114], to the highly ordered stereochemical structure of PHB that leads to a highly crystalline polymer [64,101].

Similarly, solvent-casted coatings based on PHB allowed to obtain the advantages of PHB material avoiding thermal processing. Thus, during the last years, PHB has gain interest as paper coating systems [40,115]. For instance, Seoane *et al.* [40] in order to protect paper from moisture developed paper-based renewable packaging material by using PHB as coating. Authors prepared the PHB single layer coating by firstly dissolving PHB in N,N-dimethylformamide (DMF), further pouring the PHB solution onto cellulose paperboard, and finally evaporating the solvent at 80 °C for 12 h to eliminate the solvent [116]. This study successfully reported bilayer systems based on cellulose paperboard with PHB (in 15 wt% related to the paperboard weight). Similarly, Salgado *et al.* [115] developed bilayer systems based on soy protein isolate (SPI) and PHB with the aim of reducing the water vapor permeability of SPI films to improve their functionality as food packaging materials. PHB was dissolved in chloroform (CHCl₃) and then the PHB solution was poured onto already prepared SPI films in aqueous medium. Then, CHCl₃ was slowly evaporated at 15 °C and the PHB was allowed to crystallize, first at room temperature during 15 days and the for 2 additional days at 20 °C and 58% relative humidity (RH). The resultant film was finally peeled from the casting surface.

4. Embrittlement of PHB-based materials

The aging of semicrystalline polymers is a physical phenomenon involving molecular-level relaxation that is manifested in thermodynamic and macroscopic physical properties, such as enthalpy and volume, due to the non-equilibrium character of the glassy state [117]. The phenomenon was firstly deeply studied by Struik [118,119], while it was subsequently investigated for PHB by Scandola *et al.* [120]. The theory attributes embrittlement to a decrease in free volume by the so-called “amorphous phase densification”, due to the reorganization of polymer chains when the material is stored at temperatures close to but lower than its glass transition (T_g). Aging principles rely on the coexistence of two amorphous phase types, that is, an undisturbed phase that is far from crystalline lamellae and a disturbed one. The latter is close to crystalline lamellae and shows a restrict mobility due to interaction with the crystals. Several authors consider that physical aging of the PHB

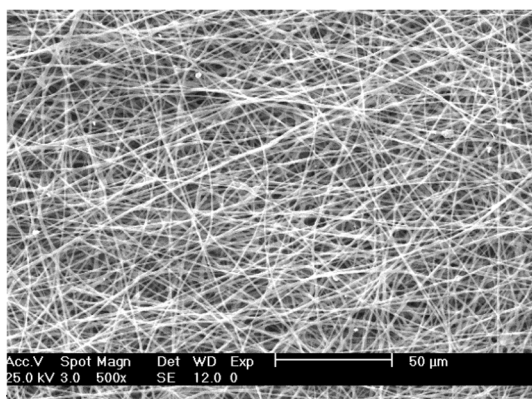


Fig. 5. An electrospun mat of poly(3-hydroxybutyrate) (PHB) fibers (500 × magnifications). Reprinted from Arrieta *et al.* [114] under Creative Commons CC BY license.

amorphous phase is responsible to cause the progressive brittleness of the material that is observed during both its storage at room temperature as well as during the PHB-based products service life [121]. In particular, this hypothesis is based on the fact that the physical ageing hinders the mobility of the amorphous phase adjacent to the crystalline layer, leading to the progressive PHB embrittlement with time [122–124]. However, this phenomenon has not been fully elucidated and there is no consensus on the explanation of the physical origin of the PHB embrittlement. Indeed, some authors such as Biddlestone *et al.* [125] or De Koning *et al.* [123,126] argued that PHB’s T_g is below room temperature (around 0 °C), which can be too low to enable the development of physical aging. Nevertheless, the presence of crystals in semicrystalline PHB can restrict the movement of the amorphous part, increasing the T_g with respect to that of the completely amorphous material, so that the temperature at which physical aging can occur is slightly higher [127]. Thus, other studies have revealed that a PHB morphology with three phases, namely, a crystalline phase, a mobile amorphous phase, and a third rigid amorphous phase whose mobility is much lower and, therefore, its T_g is higher, can allow the process of physical aging [128]. In addition to the classical physical aging of the amorphous phase, other assumptions consider that, after the primary crystallization that occurs during cooling, a secondary crystallization slowly takes place in PHB during the storage at room temperature [123,125]. De Koning *et al.* [123,129] reported that physical aging hardly contributes to the brittleness of PHB, and attributed it to a progressive crystallization during storage at room temperature (secondary crystallization), which resulted in the appearance of small crystallites that bridge the crystalline lamellae and strongly constrict the remaining amorphous PHB chains between the crystals, thus embrittling the material. Furthermore, some authors consider that embrittlement is caused by the overall crystal perfection over time, which restricts the mobility of the amorphous fraction of PHB [122,130,131]. Therefore, it is currently accepted that the PHB embrittlement process could be due to the two above-described phenomena occurring simultaneously, the physical aging as well as a secondary crystallization [121,132].

In any case, it is assumed that the interlamellar amorphous chains are progressively “frozen”, yielding an increase of the amorphous rigid fraction. Therefore, whereas freshly processed PHB exhibits ductile behavior, when the article is molded and stored at room temperature (“aged” PHB) it undergoes a progressive physical aging process that leads to its embrittlement and further causes a drastic decrease in elongation at break [133]. The effect of physical ageing and/or secondary crystallization can be easily determined by mechanical and dynamic mechanical thermal analysis (DMTA). In order to verify this, Crétois *et al.* [121] firstly heated and kept a PHB sample to 195 °C for 2 min to remove its thermal history and then, to avoid crystallization, the sample was quenched in liquid nitrogen. The resultant sample was studied by DMTA analysis in a refrigerated room (~-5 °C) to avoid crystallization before the starting of the experiment, and results are shown in Fig. 6.

The negative impact of secondary crystallization can be minimized by an annealing process at high temperatures, by which it is possible to alleviate the restrictions imposed by the crystals on the amorphous chains and in turns improves the toughness and ductility of the final material. Furthermore, subsequent secondary crystallization can be largely avoided, thus maintaining the toughness and ductility achieved after annealing [123,134]. Although annealing can offer a toughness improvement by “rejuvenating” PHB, this effect seems to be temporary. For instance, De Koning *et al.* [123] measured the mechanical properties of an annealed PHB at 110 °C for 10 h after 150 days of storage (“re-aged” PHB). Authors observed an increase of storage modulus from 0.92 to 0.94 GPa with a significant decrease of the elongation at break from 43% to 30% and the loss tangent from 0.10 to 0.065. Therefore, several authors have proposed alternative strategies to reduce PHB brittleness by plasticizing [60,131], blending with rubbers and elastomers [124,135], or co-polymerization of 3HB with 3HV or 3-

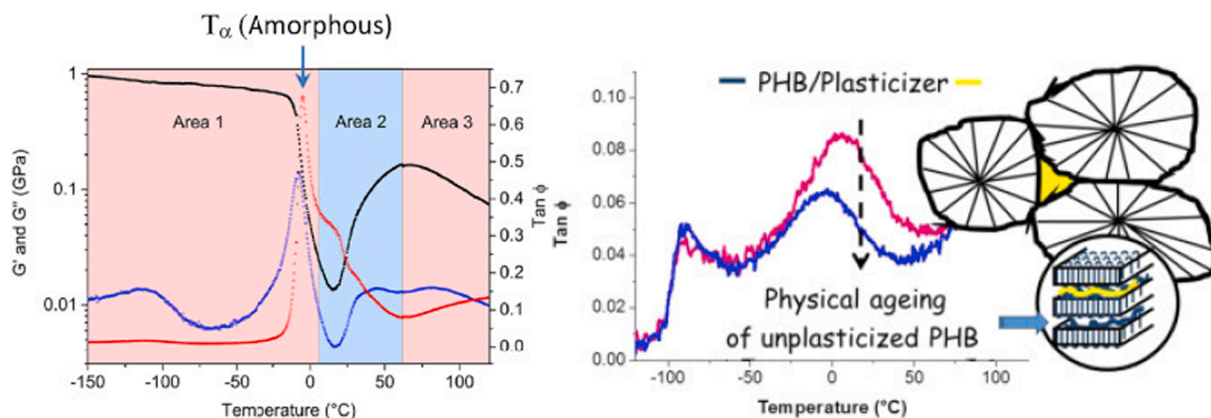


Fig. 6. Changes in the thermomechanical properties from amorphous to crystallized poly(3-hydroxybutyrate) (PHB): Storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \phi$). To make it easier to understand, the figure is divided into three clearly differentiated areas. From -150 to 5 °C (area 1), PHB is amorphous and the changes of G' , G'' , and $\tan \phi$ correspond respectively to β (~ -110 °C) and α (-3 °C) relaxations. From 5 to 60 °C (area 2), crystallization takes place and it is characterized by an increase of G' , which explains the enlargement of $\tan \phi$ peak originated by the mobility restriction of the remaining amorphous phase due to the constraint induced by the appearance and growth of the crystalline phase. From 60 to 110 °C (area 3), the shape of G' and G'' curves are typical of a semicrystalline polymer. Reprinted from Crétois *et al.* [121] with permission from Elsevier.

hydroxyhexanoate (3HH), which induces a reject of the co-monomer into the amorphous phases that could reduce the extent of secondary crystallization [136,137].

5. Processability and ductility enhancement of PHB

As mentioned above, PHB has a series of technical limitations, such as its high fragility and low thermal stability, that together with its high cost, impairs its use in packaging at the industrial level. Therefore, several research efforts have been focused on increasing PHB ductility mainly including plasticization [32], blending with more flexible biopolymers [1,34], or co-polymerization [138]. Similarly, cold-calendering has been also proposed to produce flexible films based on biopolyesters and could be interesting for the production of flexible films based on PHAs [139]. Among them, the most scalable methodologies to improve PHB processing and ductility are plasticization and physical blending due to the current industrial equipment can be employed. Meanwhile, although its scale up is less straightforward, co-polymerization with other hydroxy acids offers the advantages over the other strategies of avoiding potential plasticizer migration and/or phase separation [140]. In particular, the use of co-polymers of PHA favors the development of less crystalline materials than PHB, which offers several advantages such as higher flexibility [141,142].

5.1. Plasticization of PHB

Plasticization produces an increase of the polymer chains mobility causing a decrease in the viscosity of the material and an increase in the melt index, which as a result facilitates processability. In this regard, the preparation of a preformed masterbatch is an extensively used strategy at the industrial level that leads to more homogeneous blend formulations and enhances the overall performance of the final polymer materials during service [36,92,143]. In plasticized PHB-based systems, the masterbatch approach helps to obtain a homogeneous distribution of plasticizer within the biopolyester chains [35]. The preparation of this type of masterbatch involves the pre-mixture of neat PHB with the plasticizer and its further processing into the final plasticized PHB-based products (for instance, films or parts). Furthermore, during the preparation of the masterbatch, other additives such as antioxidants or nucleating agents can be added. In this context, to guarantee the PHB-based packaging material's green nature, natural antioxidants are gaining interest in the food packaging industry [144,145].

In general terms, a high affinity between all the components of the

polymer blends is required to obtain effective blend-based formulations of PHB. This affinity can be theoretically predicted through the solubility parameters (δ) of each component of the blend formulation. Therefore, two substances with similar δ should be miscible. In particular, the solubility parameter value of PHB is within the range of 18.5 – 20.1 $\text{MPa}^{1/2}$ [37,135]. Another important parameter is T_g since when two polymers are miscible no phase separation of the amorphous phase is expected and, consequently, only one T_g value is observed. Although it is possible to process two polymers into blends for a wide range of compositions to obtain a homogeneous material from a macroscopic point of view with no discontinuities on blend morphology, the presence of two different T_g suggests the formation of an immiscible or partially miscible polymer system [146]. In the case of PHB, its T_g ranges between 1 and 5 °C (Table 2) [46]. In this context, PHB has been plasticized with citrate esters, such as ATBC, which possess very close solubility parameter ($\delta = 20.2$ $\text{MPa}^{1/2}$ [37]). Glycerol ($\delta = 16.5$ $\text{MPa}^{1/2}$) can also be used for PHB formulations since it is a natural plasticizer widely used for bioplastic plasticization [51,147,148]. Glycerol is a by-product of biodiesel production and, thus, it can be recovered as low-grade by-product and further used as biopolymers plasticizer [148–150]. While the addition of 5 wt% of glycerol did not affect the PHB's T_g value, the incorporation of 20 wt% slightly reduced it [51]. However, it also led to an immiscible formulation since a clear exudation appeared approximately one week after its preparation [51]. Moreover, glycerol has been suggested as a pro-degradant for PHB [55,151], particularly when it is used in content only up to 10 wt% [55]. This behavior has been ascribed to the alcoholysis reaction produced by the alcohol moiety is attached to the end of the shorter polymeric chains produced after scission of the PHB main chain. In fact, it has been observed that degradant effect of alcoholysis is even higher than hydrolysis by moisture. In this context, Janigová *et al.* ascribed such behavior to a better interaction between the polymer and alcohol, which is less polar than water [55]. At higher glycerol content it seems that certain level of recombination of the PHB fragments with the glycerol moieties through condensation reactions take place due to the plasticization produce lower viscosity at higher plasticizer content [55].

PHB has been also plasticized by 200 $\text{g}\cdot\text{mol}^{-1}$ poly(ethylene glycol) (PEG-200) (PEG $\delta = 16.7$ $\text{MPa}^{1/2}$ [37], T_g at -82.4 °C [51]). PEG-200 effectively reduced the T_g of PHB from 1 to -8 °C and -23 °C, after the addition of 5 and 20 wt%, respectively [51]. However, the plasticized PHB samples still resulted too brittle and unfeasible for tensile testing measurements [51]. Low concentrations (5 and 7 wt%) of Lapol plasticizer (Lapol 108, $M_w = 80,000$ $\text{g}\cdot\text{mol}^{-1}$, a polyester plasticizer

Table 2Glass transition temperature (T_g) of poly(3-hydroxybutyrate) (PHB)-based formulations.

Formulation	T_g (°C)	Processing method	References
Neat PHB	1–5	Melt blending	[46]
PHB	–2	Solvent casting	[40]
PHB + 5 wt% Gly	1	Melt blending	[51]
PHB + 20 wt% Gly	–1		
PHB + 5 wt% PEG	–8		
PHB + 20 wt% PEG	–23		
PHB + 5 wt% TEGB	–7		
PHB + 20 wt% TEGB	–23		
PHB + 5 wt% Penta	–17/–2		
PHB + 20 wt% Penta	–10		
PHB + 5 wt% Lapol	5.8	Melt extrusion	[46]
PHB + 7 wt% Lapol	4.6		
PHB + 10 wt% TB	–6.5	Solvent casting	[152]
PHB + 20 wt% TB	–7.0		
PHB + 30 wt% TB	–11.5		
PHB + 10 wt% PDEGA	–12.2		
PHB + 20 wt% PDEGA	–15.0		
PHB + 30 wt% PDEGA	–18.8		
PHB + 10 phr ELO	–7.0	Melt extrusion	[57]
PHB + 5 phr MLO	–3.9	Melt extrusion	[32]
PHB + 10 phr MLO	–3.6		
PHB + 15 phr MLO	–3.5		
PHB + 20 phr MLO	–3.4		
PHB + 5 phr EFAE	–3.3		
PHB + 10 phr EFAE	–1.7		
PHB + 15 phr EFAE	–1.6		
PHB + 20 phr EFAE	–1.7		
PHB + 5 wt% DOA	–5.8	Melt extrusion	[156]
PHB + 10 wt% DOA	–7.0		
PHB + 20 wt% DOA	–6.9		
PHB + 30 wt% DOA	–6.8		
PHB + 5 wt% DOP	–4.8		
PHB + 10 wt% DOP	–8.8		
PHB + 20 wt% DOP	–9.4		
PHB + 30 wt% DOP	–10.8		
PHB + 5 wt% TAG	0.5		
PHB + 10 wt% TAG	–9.7		
PHB + 20 wt% TAG	–16.7		
PHB + 30 wt% TAG	Not detectable		
PHB + 5 wt% PA	–4.1		
PHB + 10 wt% PA	–8.3		
PHB + 20 wt% PA	–16.0		
PHB + 30 wt% PA	–21.8		

Gly = glycerol; PEG = poly(ethylene glycol) ($M_w = 200$); TEGB = tri(ethylene glycol) bis(2-ethylhexanoate); Penta = pentaerythritol; Lapol = Lapol 108 Bioplasticizer; TB = tributyrin; PDEGA = poly[di(ethyleneglycol) adipate]; ELO = Epoxidized linseed oil; MLO = maleinized linseed oil; EFAE = epoxidized fatty acid ester; DOA = Dioctyl adipate; DOP = Dioctyl phthalate; TAG = triacetyl glycerol; PA = Polyadipate.

derived from >50% renewable resources with the T_g value at around -0.7 °C yielded to PHB films showing a single T_g (see Table 2), suggesting the formation of a fully miscible system [46].

Furthermore, to obtain PHB-coated films with adequate deformability, the use of plasticizers are also necessary [40]. In this sense, Seoane et al. [152] studied the plasticization of PHB ($M_w = 600,000$ g mol $^{-1}$, Biocycle) for coating applications by solvent casting technique with increasing amounts (10, 20, and 30 wt%) of tributyrin (TB) and poly[di(ethyleneglycol) adipate] (PDEGA). Only one T_g with a significant shift to lower values was observed for all the PHB-based coating films, showing good miscibility between PHB and both plasticizers (TB and PDEGA) in the amorphous region.

In recent years, there has been increasing interest in the study and use of plasticizers obtained from natural resources, which are characterized by low toxicity, low migration, and are more environmentally friendly than petrochemical plasticizers. Among these, vegetable oils are of particular interest due to their many advantages such as they are abundant around the world, cost effective, biodegradable, non-toxic, and show lower migration than other plasticizers [153]. In particular,

vegetable oils present two chemical characteristics that make them good plasticizers for PHAs [154]. On the one hand, their fatty acid chains can better mix and intercalate between polymer chains, increasing intermolecular space and facilitating mobility. On the other hand, the ester groups can chemically interact with the polymer chains to improve compatibility [154]. The chemical structure of vegetable oils in which the terminal $-OH$ groups of glycerol are not present, since they have been esterified, avoid the already mentioned alcoholysis reaction. In addition, some of the triglyceride structures of vegetable oils show insaturations that allow chemical modifications to prepare multiple reactive groups that can increase compatibility during extrusion at high temperatures [155]. This chemical functionalization includes, for instance, maleinization, epoxidation, acetylation, transesterification, etc. The effect of unmodified and chemically modified vegetable oils on the PHB properties has been scarcely studied, though some studies have demonstrated its effectiveness through an increase in the ductile mechanical properties as well as a reduction in T_g when compared with unplasticized PHB [32,57]. However, the overall amount of plasticizers should be restricted to low quantities for food applications to avoid exceeding their migration limit and imposing safety issues, particularly in the case of epoxidized vegetable oils.

The deterioration of PHB properties with time, which is drastic for neat biopolymer compositions, seems to be less intense when using plasticizers since plasticized formulations are less affected by aging [131]. But it should be highlighted that when it comes to work with plasticized PHB formulations, the selection of the suitable plasticizer as well as its appropriate amount are of outmost importance to optimize the processing conditions. Plasticizers allow minimizing the effects of PHB ageing, thus they allow avoiding the need for a post-processing thermal treatment, which moreover could trigger the migration of plasticizer and consequently will deteriorate the mechanical performance of the plasticized materials [131]. The formation of short oligomers of 3-hydroxybutyrate (OHB) as a consequence of thermal processing at high temperatures should be avoided by controlling the processing conditions, since OHB can act as plasticizers but also can migrate from the plastic material to the food stuff. While OLA has been widely used to plasticize biopolyesters [7,39], OHB has been less explored as plasticizer. In fact, although the thermal degradation of PHB has been suggested as a useful way to obtain vinyl oligomers that can be used as component for synthesis of block copolymers, while it can be also used as OHB plasticizer for biopolyesters such as PLA [157].

5.2. Blending of PHB with flexible biopolymers

PHB has been blended with flexible biodegradable polymers, such as PCL, poly(butylene succinate) (PBS) and PBSA, TPS, PBAT, among others, with the aim of obtaining final products with a more ductile performance [1,18,47,49]. This strategy has been carried out not only for improving the performance of PHB in packaging applications but also, in some cases, for cost reduction. In particular, several studies have reported the development of PHB/PLA blends based mainly on a cost reduction strategy [158] since the improvement in the ductile performance is minimal [61]. However, it has been observed that to increase the flexibility of PLA-PHB blends plasticizers are required not only to increase the elongation at break but also to increase the compatibility between both polymeric matrices [17,37,38,46]. Physical blending approaches provide several advantages to develop new materials with the desired properties by simple mixing two or more dissimilar polymers without the need of chemical agents [31,159]. Moreover, blending can be carried out either in the melt state (for instance, extrusion, injection molding, film-forming, etc.) or in an appropriate solvent (for example, electrospinning, casting, coating, etc.) and using currently available plastic processing machinery [159]. Table 3 gathers the most relevant binary and ternary blends of PHB with the preparation methodologies carried out to prepare them.

PCL is a soft semicrystalline biodegradable thermoplastic polymer

Table 3

Binary blends of poly(3-hydroxybutyrate) (PHB) with biodegradable polymers and preparation methodologies.

Formulation	Processing method	References
PHB/PLA	Melt-blended solvent casting	[26,158,160,161] [162]
PHB/PCL	Melt-blended solvent casting	[1,18,163,164] [57,165]
PHB/PBS	Melt-blended solvent casting	[47,166,167] [168,169]
PHB/PBSA	Melt-blended	[166]
PHB/PBAT	Melt-blended solvent casting	[170] [171]
PHB/TPS	Melt-blended solvent casting	[49] [172]

PLA = Polylactide; PCL = poly(ϵ -caprolactone); PBS = poly(butylene succinate); PBSA = poly(butylene succinate-co-butylene adipate); PBAT = poly(butylene adipate-co-terephthalate); TPS = thermoplastic starch.

that derives from the petrochemical caprolactone monomer. PCL is a great candidate to improve the ductility of PHB-based materials since, at room temperature, it behaves as a flexible plastic due to the fact that it possesses the glass transition region well below the room temperature (T_g around -60 °C) and T_m is around 60 °C [18,173]. PHB has been blended with PCL in 75:25 (wt/wt) proportion resulting in promising biodegradable formulations that offer higher thermal and impact resistance and improved flexibility than neat PHB [96]. Similarly, binary PHB/PCL blends containing 25–75 wt% PCL yielded elongation-at-break changes from 11.2 % up to values over 1000 %, even though these were immiscible [18]. However, it should be also taken into account that thermal stability of the resultant PCL-containing blends will be more limited due to the low melting point of PCL and most applications would be restricted to applications at room temperature.

PBS, and its copolymer PBSA, are ductile types of biodegradable condensation polyesters of succinic acid and 1,4-butanediol. In most cases, these monomers are obtained from petroleum, but they can also be derived from renewable resources via fermentation [174,175]. Although these biopolyester are not miscible with PHB, Qiu *et al.* [169,176] reported some limited miscibility at low contents in solution systems. To increase compatibility between the two biopolyesters, dicumyl peroxide (DCP) was added at 0.5 wt% as a free-radical grafting initiator to induce a radical reaction between PHB and PBS, forming PHB-g-PBS copolymer at the phase interface, which subsequently acted as compatibilizer and partially cross-linked networks in the blends [47]. This process of reactive compatibilization resulted in improvements in the elongations at break from < 10 to 400% for the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/PBS (80:20 wt/wt) blend, with a 12.7% HV molar content in the copolymer, whereas the unnotched Izod impact toughness was improved from values of 10 to 50 $\text{kJ}\cdot\text{m}^{-2}$ for the PHB/PBS (70:30 wt/wt) blend. In another study, ternary blends of PHB with PLA and PBS or PBSA were developed by reactive extrusion in a co-rotating extruder using epoxidized vegetable oils as compatibilizers in order to obtain biodegradable materials with high toughness [177]. Authors reported that contents of 30 wt% of the two succinic acid derived biopolyesters, that is PBS and PBSA, positively contributed to increasing the ductile properties of PHB-based materials with a subsequent improvement on impact toughness. PHB/PBSA blends with increased flexibility blends have been recently developed by Righetti *et al.* [166] by adding different contents of PBSA, ranging from 15 wt% to 85%, that is, PHB/PBSA blends of 85/15, 70/30, 50/50, 30/70 and 15/85 wt/wt.

Starch is considered as an attractive biopolymer due to it is highly abundant, it shows low cost and low density, its biodegradable nature, while it presents a nonabrasive nature. Plasticization by incorporating suitable amounts of water and/or glycerol results in the “gelatinization” process of the starch granules and the development of flexible TPS that can be melt-processed and shaped into different articles [178]. In terms

of blends, Garrido-Miranda *et al.* [179] developed PHB/TPS (65:35 wt/wt) and observed that TPS was able to reduce the melting temperature of PHB (around 6 °C). Blends of TPS and PHB were also developed by Lai *et al.* [62] by adding PHB in different proportions (i.e.: 1, 3, 5, and 7 wt%), showing that the mechanical properties in terms of tear strength were improved due to the addition of PHB.

Finally, the PBAT co-polyesters, derived from the polycondensation reaction of 1,4-butanediol, adipic acid, and terephthalic acid, are polymers with tunable balance in terms of physical performance and biodegradation with a high potential for biopolymer blending applications [180]. In comparison to other biodegradable polymers, PBAT is very flexible (elongation at break as high as 700%) and it is mainly used to produce flexible films in the packaging and agricultural industries [181]. As a result, PBAT has been widely explored to develop binary and ternary blends with PHB and other PHAs. For instance, Beber *et al.* [182] prepared melt-extruded blends of PHB with PBAT contents ranging from 25 to 75 wt%, analyzing the mechanical properties at both room temperature and -40 °C. When compared with the samples tested at room temperature, the Young's Modulus and tensile strength values were remarkably higher and elongation at break lower at -40 °C. However, the maximum deformation at break nearly remained unchanged at lower temperatures. These results indicate that the PHB/PBAT blends are great candidates for food containers, among other applications, that are able to support relatively high stresses and keep adequate elongations for refrigerator and freezer storage.

6. Properties of PHB articles

PHB-based materials have properties that are similar to other synthetic thermoplastic polymers that are currently widely used in the food packaging sector, such as polypropylene (PP) and low-density polyethylene (LDPE). These properties, combined with the fact that feedstocks for PHB production include renewable and sustainable sources, such as food waste, and its inherent biodegradation nature when exposed to active biological environments, make PHB a leading candidate for sustainable packaging applications [183].

6.1. Thermal stability

As shown above, one of the foremost drawback of PHB-based formulations for melt-processing conversion methods is the low thermal stability of this biopolyester. Since PHB thermal degradation can start right after melting, this results in a very limited processing window. In particular, formulations of PHB and PHBV co-polymers with low 3HB contents are typically melt-processed with a melt temperature in the 170 – 190 °C range [185], whereas these PHAs are unstable from approximately 165 °C [186]. This degradation is stereoselective with an activation energy of 235 kJ [187]. Thermal degradation of PHB mostly includes *cis*-elimination reaction (non-radical random chain scission on the ester bond), which facilitates the formation of oligomers, crotonic acid (CA) as well as dimeric, trimeric, and tetrameric volatiles (Fig. 7-a) [125,188–190]. It consequently leads to a M_w reduction, significantly affecting its mechanical properties and its molten state viscosity [58,104,191]. Furthermore, at moderate temperatures, above 120 °C, the PHB terminal groups can degrade. In fact, when PHB possesses the terminal groups in the form of carboxylate ions, instead of carboxylic acid, and the carboxylate end groups of PHB can induce thermal degradation of PHB and the decomposition pathway of those terminal groups is via intermolecular α -deprotonation by carboxylate groups [192]. According to Kawalec *et al.* PHB follows the mechanism of the degradation reaction showed in Fig. 7-b, the carboxylate end group of PHB (see 1 in Fig. 7-b) abstracts the acidic proton at C2 of PHB with the formation of carbanion (see 2 in Fig. 7-b). The carbanion can tautomerise to an enolate form (see 3 in Fig. 7-b). The carbanion then undergoes the elimination reaction, leading to chain scission with the generation of two polymer chain fragments: the *trans*-crotonate terminal

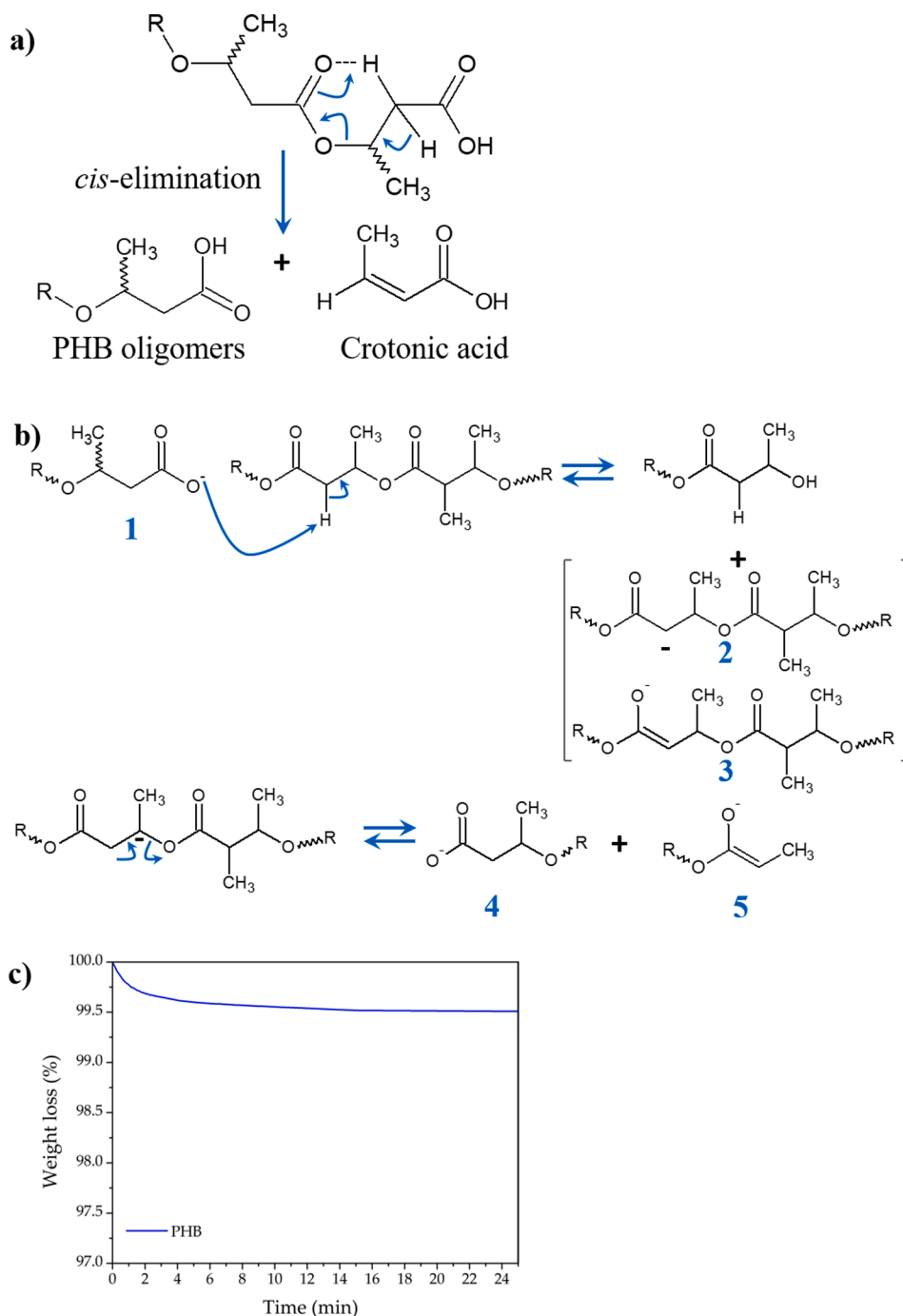


Fig. 7. (a) Non-radical thermal degradation of poly(3-hydroxybutyrate) (PHB) by *cis*-elimination. Adapted from Arrieta (2014) [195] under Creative Commons CC BY license; (b) Degradation mechanisms of PHB induced by carboxylate ions. Adapted with permission from Kawalec *et al.* (2007) [192] Copyright 2007 American Chemical Society. (c) Thermogravimetric analysis (TGA) isothermal curves of PHB pellets (P226 Biomer®) at 180 °C. Reprinted from Arrieta *et al.* [37] with permission from Springer Nature.

group (see 4 in Fig. 7-b) and a carboxylate end group (see group 5 in Fig. 7-b).

Thus, to ascertain the thermal stability of PHB at the required processing conditions, the thermal degradation of neat PHB has been assayed by means of isothermal thermogravimetric analysis (TGA). In this regard, Arrieta *et al.* [37] analyzed the thermal stability of as-received commercial PHA pellets by means of studying isotherms at 180 °C in air atmosphere (Fig. 7-b). It was observed that neat PHB presented a mass loss of <0.5% in 25 min, which was considerably higher than the one attained during by melt-blending and film-forming processes (approximately 6 min). However, it should also consider that PHB is very sensitive to the rotational rate and shear forces during extrusion and melt mixing. It is therefore very important to carefully set the processing parameters since a high rate reduces the processing time,

but a too high rate will lead to increased decomposition of PHAs [193]. Previous studies in this sense have reported that PHB's M_w decreased not only with increasing processing temperature, but also residence time, where the shear forces can significantly contribute to this reduction [194].

According to the stability issues faced by PHB during its melt processing, several strategies have been explored to increase thermal stability by means of plasticizers. For instance, Grillo Fernandes *et al.* [51] developed PHB formulations using several polyols as plasticizers, which contain different types and amounts of hydroxyl groups. However, authors observed that both glycerol and PEG-200 decreased the thermal stability of PHB, 289 to 280 °C with 20% PEG-200 (slope = 2%/K). This thermal stability impairment was ascribed to a synergistic effect produced by the moisture and the polyol presence. Meanwhile, tri(ethylene

glycol) bis(2-ethylhexanoate) (TEGB) and pentaerythritol (Penta) did not significantly affect the thermal stability of PHB. Similarly, Abdelwahab *et al.* [46] studied PHB plasticized with 5 and 7 wt% of Lapol 108 Bioplasticizer (Lapol® LLC, Santa Barbara, California, USA), a mixture based on OLA with glycerin, diethylene glycol (DEG), and maleic anhydride (MAH), observing that thermal stability remained neatly unchanged (calculated at 5 wt% mass loss). More effective results have been observed by the use of vegetable oils. For instance, Panaitescu *et al.* [56] studied the effect of epoxidized soybean oil (ESO) on the thermal properties of PHB. It was observed that the incorporation of 5 wt% ESO slightly increased T_{onset} of PHB by about 3 °C (calculated at 10 wt% mass loss), without affecting its T_m value, thus maintaining its thermal stability. In another study, Garcia-Garcia *et al.* [32,57] studied the effect of different commercial chemically modified vegetable oils, namely epoxidized linseed oil (ELO), epoxidized soybean oil (ESBO), maleinized linseed oil (MLO), and an epoxidized fatty acid ester (EFAE). Additions from 5 to 20 parts per hundred resin (phr) were tested and it was observed that all these novel vegetable oils yielded an increase in the T_{onset} value (onset degradation temperature was taken as the temperature for a mass loss of 5%), accompanied with a decrease in T_m of PHB, due to they provided a lubricating effect that increased chain mobility. Therefore, vegetable oils resulted in an increase of the processing window of PHB by both delaying thermal degradation and favouring processing at lower temperatures. Similarly, Melo-Giaquinto *et al.* [196] developed a formulation of PHB plasticized with canola oil (CO). Authors reported that, as the CO content in the PHB matrix increased, the value of T_m decreased, successfully achieving a reduction by about 8 °C for a plasticizer content of 10 wt%. In addition, because CO is a natural biocide, the resultant materials also showed high potential for antimicrobial packaging.

6.2. Crystallization behavior

As above discussed, PHB is a highly semicrystalline biopolyester with T_g and T_m values of approximately 1–5 °C and 180 °C, respectively [46]. PHB materials studied by X-ray diffraction analysis (XRD) show reflection peaks at 13.5° and 16.8°, corresponding to the (020) and (110) planes, and three weak peaks at 19.1°, 22.2°, and 25.5°, crystallizing in the form of a orthorhombic structure [46]. In this regard, the use of additives, such as plasticizers, and biopolymer blends can also affect its crystallinity and, thus, the performance of the resultant PHB-based materials. In most cases, the incorporation of plasticizers has further increased the crystallinity of PHB. For instance, Abdelwahab *et al.* [46] studied melt-processed neat PHB and PHB plasticized with Lapol 108 Bioplasticizer by XRD, observing that the typical diffraction peaks of PHB at $2\theta = 13.5^\circ$ and 16.9° increased in intensity in the plasticized PHB formulation with 7 wt%. Similarly, Seoane *et al.* [40] studied the isothermal crystallization of PHB ($M_w = 600,000 \text{ g mol}^{-1}$, BIOCYCLE® 1000, PHB Industrial Brasil S.A, São Paulo, Brazil) plasticized TB and PDEGA, at contents of 20 and 10 wt% of each plasticizer, by means of cross-polarized optical microscopy (POM). The PHB plasticized films were obtained by solvent casting using DMF and these were crystallized after melting (at 196 °C), further quickly cooled until 70 °C, and maintained at 70 °C. On the one hand, the characteristics concentric rings of PHB with the typical Maltese cross [51] were clearly observed in neat PHB (Fig. 8-a). On the other, regarding plasticized PHB formulations, no macroscopic phase separation was observed and the spherulitic morphology showed that PHB was able to crystallize in the presence of each plasticizer (Fig. 8-b and Fig. 8-c) as well as when both plasticizers were combined (Fig. 8-d). Moreover, in the PDEGA-containing PHB samples, a different band spacing of the spherulites structure was observed (Fig. 8-c and Fig. 8-d). Conversely, Grillo Fernandes *et al.* [51] plasticized PHB with glycerol at 5 wt% and the characteristics concentric rings of PHB were lower than in neat PHB, while the typical Maltese

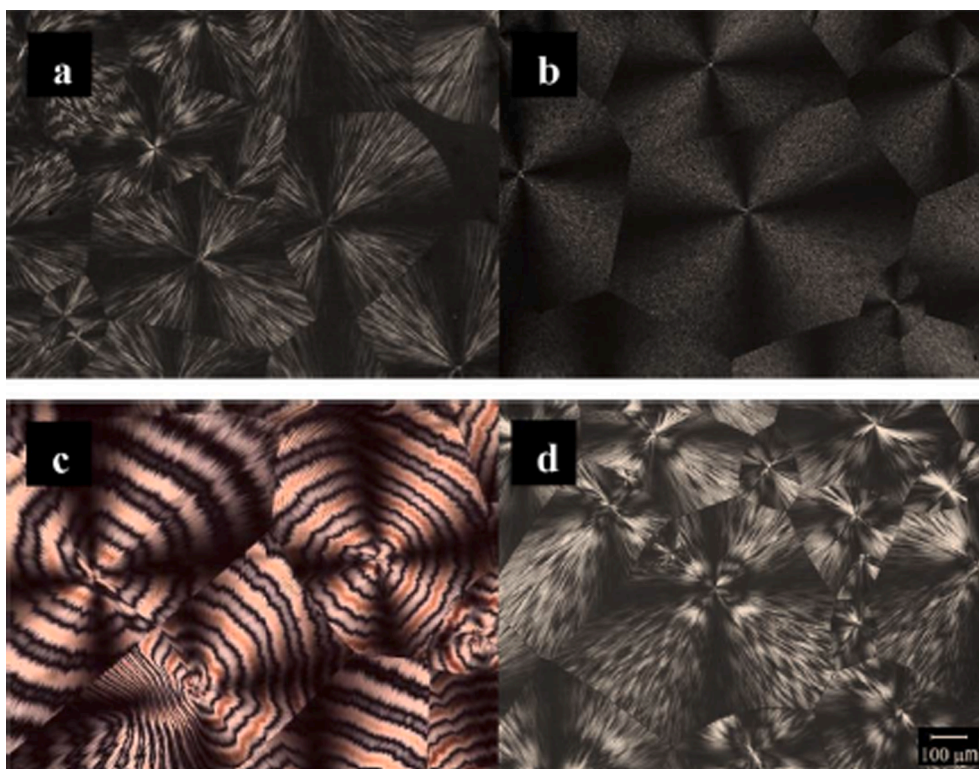


Fig. 8. Spherulitic morphology of different poly(3-hydroxybutyrate) (PHB) samples crystallized at 70 °C: (a) PHB; (b) PHB with 20 wt% tributyrin (TB); (c) PHB with 20 wt% poly[di(ethylene glycol) adipate] (PDEGA); (d) PHB with 10 wt% TB and 10 wt% PDEGA. Reprinted from Seoane *et al.* [152] under Creative Commons CC BY license.

cross were not clearly seen in the plasticized PHB sample. In fact, PHB required at least 20 wt% of glycerol to increase the degree of crystallinity, from 56% in neat PHB, to 62% in plasticized PHB [51].

In terms of biopolymer blends, Qui *et al.* [169] studied the crystallinity of PHB blended with PBS by non-isothermal crystallization by differential scanning calorimetry (DSC) and observed that the blend samples in 40:60 and 60:40 wt/wt proportions showed two crystallization peak temperatures, corresponding to the T_c values of PHB and PBS, respectively, centered at approximately 70 and 85 °C. Meanwhile, for PHB/PBS blends in 80:20 and 20:80 wt/wt proportions, it was observed only one crystallization peak temperature. However, the crystals of both biopolymers actually co-existed since two melting endotherms were clearly observed, corresponding to the respective melting of PHB and PBS crystals. Furthermore, Lovera *et al.* [165] studied PHB blended with PCL and observed that the incorporation of PCL was able to decrease the crystallization capacity of PHB. In fact, the PHB crystallization becomes more difficult and a decrease in PHB nucleation density was clearly detected. Indeed, if the PHB content in PCL/PHB blends was lower than 50 wt%, it was no longer possible to distinguish a crystallization exotherm for PHB in DSC analysis. The authors ascribed this behavior to a reduction in overall crystallization rate brought about by the transfer of heterogeneities from PHB to PCL that, in turn, delays its primary nucleation in such a way that PHB crystallization was only conceivable upon subsequent heating. Furthermore, it is also worthy to note that in the case of PHB blends with other PHA, including PHBV copolymers, crystallization of PHB can be affected by incomplete melting of the biopolymer crystals attained upon exposure at high temperatures due to a self-nucleation phenomenon [197].

6.3. Mechanical properties

PHB is characterized by a tensile strength and an elastic modulus similar to, or even higher, than other synthetic thermoplastic polymers widely used in the packaging field such as PP and LDPE. However, PHB shows higher rigidity and, more importantly, significantly higher brittleness with an elongation-at-break value of around 5% and very low toughness or impact strength [46]. Some authors have reported tensile strength values of standard PHB articles ranging from 28 MPa to 40 MPa and Young's modulus of 1.2 ± 0.8 GPa, while values of elongation at break was in 2–8% range [184,198]. Table 4 shows the most relevant mechanical properties of PHB and their comparison with those of the petrochemical and non-biodegradable PP and LDPE polyolefins.

In this regard, crystallinity plays a major role in the high brittleness of PHB, contributing by means of different factors. Firstly, the low nucleation density together with the high degree of crystallinity and the low crystallization rate, cause PHB to slowly crystallize from the melt. As a result, PHB forms large spherulites, which may present internal cracks, both circumferential and radial, due to the thermal stresses produced during cooling from the high crystallization temperatures to room temperature. These cracks can act as stress concentration points, embrittling the material [199–201]. Secondly, as indicated above, changes in the mechanical properties of PHB are observed with aging

Table 4

Physical properties of injected-molded pieces of poly(3-hydroxybutyrate) (PHB) and the commonly used synthetic polymers polypropylene (PP) and low-density polyethylene (LDPE) [184].

Properties	Polymer		
	PHB	PP	LDPE
Tensile strength (MPa)	40	38	10
Elastic modulus (GPa)	3.5	1.5	0.2
Elongation at break (%)	5	400	620
Melting temperature (°C)	175	176	110
Glass transition temperature (°C)	4	−10	−30
Density (g cm ^{−3})	1.26	0.91	0.92

due to a progressive embrittlement of the biopolymer microstructure with time, caused by crystal perfection over time, that restricts the mobility of the amorphous fraction [122,130,131]. Then, both the process of secondary crystallization of the amorphous phase during storage at ambient temperature as well as the physical ageing phenomenon due to the proximity of PHB's T_g to the ambient temperature [124] further contribute to its low toughness. As a result, the high fragility of PHB, derived from its high crystallinity, is one of the main drawbacks that limits its industrial applicability.

Plasticizers have been used to both improve PHB melt processing, by reducing melt temperature, and flexibility, which is of particular interest for film intended applications in food packaging. Table 5 summarizes some of the main plasticizers that have been explored to improve the mechanical performance of PHB, including the values reported. For example, Grillo Fernandes *et al.* [51] plasticized PHB with several polyols, reporting that PEG-200 and, particularly, glycerol significantly decreased the Young modulus. Moreover, authors demonstrated that TEGB shows a slight effect on the Young modulus, whereas pentaerythritol can provide a filler effect since it was able to increase the rigidity of PHB. All these previously reported plasticizers did not produce highly flexible PHB materials since elongation at break was, in all cases, lower than 20%. In addition, PHB plasticized with 5 wt% Lapol 108 Bioplasticizer produced a decrease of the PHB's Young modulus, without significant affecting the elongation at break.

Similar to the improvements showed in thermal properties, vegetable oils seem to be more effective in increasing the mechanical flexibility of PHB, achieving higher elongation-at-break values. For example, Panaitescu *et al.* [56] also studied the effect of ESO on the mechanical PHB properties. The results showed that the addition of 5 wt% of oil increased the elongation at break of PHB by 45% and slightly reduced its tensile strength and elastic modulus. In this work, authors additionally studied the effect of other plasticizers, such as ATBC and two medium- M_w PEGs, that is, of 4000 g/mol (PEG-4000) and 6000 g/mol (PEG-6000). However, higher ductile improvements were attained by ESO, though it is also worth to note that, among the all the plasticizers studied, ATBC induced the most notable plasticizing effect in terms of T_m , viscosity, and crystallinity reduction, showing an increase in ductility similar to that achieved by ESO. In any case, ATBC also produced a greater decrease in tensile strength and elastic modulus of PHB. The study of Garcia-Garcia *et al.* [32,57], who reported the effect of ELO, ESBO, MLO, and EFAE on the mechanical properties of PHB, demonstrated that the addition of low contents of all these chemically modified vegetable oils resulted in an increase in the elongation at break and impact-energy absorption, except for ESBO. In particular, the best ductile properties of PHB were obtained after the incorporation of 5 phr of EFAE, increasing the elongation at break of PHB by 40% and impact strength by 109%, from 9.7% and 2.1 kJ m^{−2} of PHB to 13.6% and 4.4 kJ m^{−2} for the sample plasticized with 5 phr of EFAE, respectively. Nevertheless, the use of large quantities, that is, 15 and 20 phr, resulted in a decrease of the ductile mechanical properties due to a phenomenon of phase separation caused by oil saturation in the biopolyester matrix. Similarly, Melo-Giaquinto *et al.* [196] studied the effect of incorporating different CO content into PHB, observing that 10 wt% resulted in a decrease in the tensile strength and elastic modulus of about 50% and 57%, respectively, resulting in a more flexible material.

Blends of PBS or PBSA with PHB can retain composting and the renewable characteristics of PHB whereas, at the same time, PBS and PBSA can increase its flexibility. In this regard, Righetti *et al.* [166] showed that the ductility of the PHB/PBS and PHB/PBSA blends increased with the PBS or PBSA content. For instance, PBSA increased the flexibility of PHB, with a consequent reduction of the elastic modulus, which was found properly described by the rule of mixtures in the whole composition range. Authors concluded that, in the case of PHB/PBS 50/50 and 30/70 wt/wt blends, the mechanical compatibility between both biopolymer matrices can be attributed to the co-continuous morphology in which the voids between the two separate

Table 5

Mechanical properties from tensile tests of melt-processed poly(3-hydroxybutyrate) (PHB) articles plasticized by different additives.

Formulation	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	References
PHB	1670–2600	30–50	2–7	[17,18,46]
PHB + 5 wt% Lapol	1750 ± 110	29 ± 2	7.2 ± 1.0	[46]
PHB + 7 wt% Lapol	1830 ± 140	26 ± 2	5.6 ± 1.0	
PHB + 5 phr ELO	1406 ± 79	21.6 ± 0.2	12.8 ± 0.2	[57]
PHB + 10 phr ELO	1347 ± 72	20.3 ± 0.2	13.6 ± 0.4	
PHB + 15 phr ELO	1323 ± 47	18.7 ± 0.4	12.0 ± 0.8	
PHB + 20 phr ELO	1326 ± 8	16.2 ± 0.7	8.2 ± 0.2	
PHB + 5 phr ESBO	1532 ± 90	19.2 ± 0.4	9.1 ± 0.5	[57]
PHB + 10 phr ESBO	1475 ± 49	18.8 ± 0.8	8.8 ± 0.6	
PHB + 15 phr ESBO	1393 ± 40	17.2 ± 0.7	8.4 ± 1.3	
PHB + 20 phr ESBO	1354 ± 38	15.4 ± 0.6	8.6 ± 0.5	
PHB + 5 phr MLO	1665 ± 49	18.7 ± 0.2	12.4 ± 1.0	[32]
PHB + 10 phr MLO	1596 ± 68	17.1 ± 0.6	10.4 ± 1.7	
PHB + 15 phr MLO	1623 ± 56	17.2 ± 0.5	10.2 ± 1.3	
PHB + 20 phr MLO	1548 ± 56	13.8 ± 0.4	8.3 ± 0.5	
PHB + 5 phr EFAE	1617 ± 67	19.0 ± 0.5	13.6 ± 1.1	[32]
PHB + 10 phr EFAE	1418 ± 71	17.9 ± 0.3	12.5 ± 0.7	
PHB + 15 phr EFAE	1475 ± 78	17.4 ± 0.3	12.0 ± 0.3	
PHB + 20 phr EFAE	1424 ± 75	17.7 ± 0.4	11.4 ± 1.3	
PHB + 2 wt% CO	592 ± 12	16.5 ± 1.6	4.1 ± 0.4	[196]
PHB + 6 wt% CO	375 ± 22	10.4 ± 0.1	4.0 ± 0.1	
PHB + 10 wt% CO	345 ± 24	10.4 ± 0.3	3.4 ± 0.1	
PHB + 5 wt% DOA	650 ± 60	21.4 ± 0.9	6.1 ± 0.6	[156]
PHB + 10 wt% DOA	745 ± 10	20.7 ± 0.4	5.7 ± 0.1	
PHB + 20 wt% DOA	576 ± 30	16.1 ± 0.3	6.2 ± 0.2	
PHB + 30 wt% DOA	557 ± 45	13.1 ± 0.7	4.3 ± 0.1	
PHB + 5 wt% DOP	680 ± 18	26.6 ± 0.6	8.8 ± 0.5	
PHB + 10 wt% DOP	554 ± 22	22.9 ± 0.2	10.5 ± 0.8	
PHB + 20 wt% DOP	448 ± 44	18.0 ± 2.3	10.1 ± 0.4	
PHB + 30 wt% DOP	340 ± 20	12.6 ± 0.4	8.6 ± 0.6	
PHB + 5 wt% TAG	683 ± 37	22.2 ± 0.4	5.7 ± 0.3	
PHB + 10 wt% TAG	520 ± 37	20.0 ± 0.4	7.4 ± 0.5	
PHB + 20 wt% TAG	238 ± 6	14.1 ± 0.3	10.3 ± 0.3	
PHB + 30 wt% TAG	186 ± 13	11.3 ± 0.7	15.5 ± 1.3	
PHB + 5 wt% PA	745 ± 20	27.6 ± 0.2	8.6 ± 0.3	
PHB + 10 wt% PA	683 ± 51	22.9 ± 1.2	6.8 ± 1.5	

Table 5 (continued)

Formulation	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	References
PHB + 20 wt% PA	523 ± 39	17.6 ± 0.5	8.8 ± 1.0	
PHB + 30 wt% PA	424 ± 23	14.4 ± 0.2	10.5 ± 0.5	

Lapol = Lapol 108 Bioplasticizer; ELO = Epoxidized linseed oil; ESBO = epoxidized soybean oil, MLO = maleinized linseed oil; EFAE = epoxidized fatty acid ester; CO = canola oil; DOA = Dioctyl adipate; DOP = Dioctyl phthalate; TAG = triacetyl glycerol; PA = Polyadipate.

phases were practically negligible (about 0.05 μm) and the phase size was about 0.5–1 μm . Meanwhile, this physical adhesion between matrix and dispersed phase was ascribed to the result of shrinkage that had taken place during sequential crystallization of the two biopolymer components. Authors established that PBSA provides higher flexibility to PHB and slightly reduces the stiffness in biopolymer blends. Similarly, Ma *et al.* [47] improved tensile strength and elongation at break of another PHA, that is, PHBV, by the incorporation of PBS. Whereas neat PHBV, with a 12.7% HV molar content, showed a low elongation at break of 4.5%, PBS was very ductile with an elongation at break of 260% and a strength at yield of 35 MPa. Contrarily TPS has had a major limitation due to its poor mechanical properties. However, TPS has been successfully blended with PHB to broaden its application in the packaging sector. In this regard, Lai *et al.* [62] blended TPS with different contents of PHB, not only observing an improvement in the flexibility of PHB, but PHB also provided an improvement in the tensile strength of TPS. Similarly, Garrido-Miranda *et al.* [179] developed PHB/TPS blend at a 65:35 wt/wt and observed that the elastic modulus decreased compared to that of the neat PHB (1560 MPa), reaching values of 1175 MPa, while the TPS elastic modulus was only 109 MPa. Since PCL is a ductile polymer with a high elongation at break, it has been widely used to increase the stretchability and reduce the fragility of PHB. In this regard, Garcia-Garcia *et al.* [18] studied PHB/PCL blends, covering the full composition range at 25 wt% additions. Authors were able to increase the flexibility of the material with the PCL content increase, with a consequent reduction of the elastic modulus and tensile strength. In fact, PHB/PCL blends with the highest PCL content (PHB: 25 wt% and PCL: 75 wt%) did not break during the tensile test assay and this formulation showed the maximum displacement of the tensile test machine, with elongation values of over 1000 % since PCL acted as the blend matrix. Although the strategy to blend PHB with PCL improved processability, the blends with PCL contents lower than 50 wt%, in which PHB acted as the matrix (PHB: 75 wt% and PCL: 25 wt%), led to materials with still low ductility (elongation at break of PHB75/PCL25: 11%), slightly higher than that of neat PHB (8%).

6.4. Optical properties

In the field of food packaging, the visual aspect of films is an important consumer requirement for materials to be used in this field [19,160,202,203]. In this sense, one of the most important aspects of packaging materials for consumer acceptance is transparency since consumers want to see the packed food [17,204]. Neat PHB films tend to show an amber hue and low transparency, or more correctly contact transparency, in the visible region of the spectrum (400–700 nm) [34]. The chromatic model $L^* a^* b^*$ or CIELab (spherical color space) is used to analyse this type of values. L^* stands for the luminance, where $L^* = 0$ represents dark and $L^* = 100$ indicates clarity or lightness. The a^*b^* pair represents the chromaticity coordinate, where $a^* > 0$ is red, $a^* < 0$ is green, $b^* > 0$ is yellow, and $b^* < 0$ is blue. In this sense, this tonality of PHB is characterized by a positive values for both a^* coordinate (green–red) and mainly for b^* coordinate (blue–yellow) in the CIELab space [36,37]. The a^* values, are in the range of 1.5 [17]. In terms of L^* ,

PHB is characterized by high lightness values of around 80 [205]. Furthermore, it has been reported that the transparency (T) and opacity (O) values of PHB/PHBV blends was 8.480 and 0.099, respectively, confirming that PHAs are slightly opaque [206]. Although, for certain applications, a low transparency may seem a disadvantage it can also be beneficial since it allows for improved stability and protection against some wavelengths [206,207].

Furthermore, plasticization can considerably reduce the amber tonality of PHB and lead to more transparent films, which can extend its applications in the food packaging field [17,35,37]. Some authors have also studied the color changes produced in PHB films during migration tests after exposition to food simulants [208]. It was observed that the color changes were almost comparable to that occurred in other polymers, such as the PLA biopolyester and the petrochemical high-density polyethylene (HDPE), confirming the suitability of PHB in the food packaging sector.

6.5. Barrier properties

Gas and vapor barrier, and particularly oxygen permeance, is one of the most important concerns for the food packaging industry since the presence of oxygen may lead to detrimental changes in foodstuff quality and reduce the food shelf life [37]. Among biopolyesters, the family of PHAs possesses high-barrier properties against oxygen. In fact, oxygen is a non-condensable small gas molecule and its permeability is mainly a diffusivity-driven property. As a result of this, the high crystallinity of PHB provides a high-oxygen-barrier performance since its crystals generate a more tortuous path for small molecules to pass through the amorphous matrix, restricting their mobility and reducing the small molecule access [160,209]. Several research studies have demonstrated the lower oxygen permeability of PHB compared to petrochemical polymers used in packaging such as polyolefins (e.g. PP, LDPE, and HDPE) [37] or even polyethylene terephthalate (PET) [208,210]. For instance, the oxygen permeability (OP) of PHB and PHBV were reported in the $1\text{--}10 \times 10^{-19} \text{ m}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ depending on the humidity conditions and the film-preparation methodology [72,210,211].

In terms of water permeability, PHAs are significantly more hydrophobic than other natural polymers, for example starch, cellulose, caseinates, etc. Indeed, water vapor is also mainly a diffusivity-driven property in PHAs due to their low water sorption nature. As a result, PHB shows water vapor permeability (WVP) of $5.2 \times 10^{-15} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ [211], which is in the range of medium-barrier thermoplastics widely used in the packaging field, such as PET ($2.3 \times 10^{-15} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$) [212]. Based on its low permeability to water vapor, PHB has been used as coating material to improve the barrier performance of paper and other biopolymers. For instance, Seoane *et al.* [40] successfully obtained bilayer systems based on cellulose paperboard with PHB (in 15 wt% related to the paperboard weight) in which PHB was able to protect paper against moisture, since the PHB-coated paperboard materials showed reduced water vapor permeability. Similarly, Salgado *et al.* [115] developed bilayer system based on soy protein isolate (SPI) coated with PHB. The resultant bilayer films showed improved water barrier properties, achieving a reduction of 70%. Furthermore, a high-aroma-barrier performance is very important for materials intended for food packaging applications since it will preserve the flavor of foodstuff [213]. In this regard, it has been also observed that PHB shows a β -limonene permeability (LP) of $3.2 \times 10^{-15} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ [211], which is a standard compound used to test the barrier performance for aromas, being more barrier than PET ($1.17 \times 10^{-13} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$) [210]. In any case, this value is relatively low since, as opposed to moisture, limonene is a strong plasticizing component for PHAs and, therefore, solubility plays a more important role than diffusion in permeability. In general terms, however, the incorporation of plasticizers tends to increase the polymer chain mobility reducing the gas barrier performance [214].

7. Waste management of PHB articles

It is widely known that biopolyesters biodegrade at ambient conditions very slowly. In fact, they need specific conditions of humidity to hydrolyze the polymeric chains into shorter polymer chains and temperature (around 60 °C) to increase the activity of the microorganism and, thus, the degradation rate [215,216]. Industrial composting, also so-called organic recycling when the resultant compost is used to produce new biopolymers, is currently regarded as the most appropriate end-life option of PHB articles [24]. PHB is biodegradable in industrial compost facilities but also in natural environments at slower rate due to its ester bonds are accessible to be hydrolyzed by water and then can be biodegradable by a large variety of microorganisms, including bacteria, *Streptomyces*, and fungi [217]. These microbial strains can release enzymes, such as lipase, proteinase K, pronase, hydrogenase, etc., providing a catalytic activity during PHB biodegradability [218,219]. Briefly, disintegration is initiated by a hydrolysis process, followed by an aerobic fermentation mediated firstly by thermophilic bacteria during the first 90 days and, then, by mesophilic bacteria which prefer temperatures between 25 and 35 °C to growth. The composting process of biodegradable polymers under industrial conditions finally ends in humus-rich soil [34]. The disintegration process takes place initially in the amorphous phase of the polymer matrix at the same time as the polymers experiences a loss of transparency at the initial steps of composting (usually during the first day), which are ascribed to changes on the refraction index [17,35,220]. Additionally, the compostability of PHB depends on both the composting medium, humidity, and temperature. In fact, the degradation pathway of PHB is mostly followed by an enzymatic disintegration mediated by numerous enzymes that firstly erodes PHB surface [26]. Afterwards, when microorganisms remain in direct contact with PHB in the compost medium, they are able to secrete enzymes that possess the ability to break down the biopolymer chains into smaller ones, that is oligomers, decreasing the average M_w [23,34]. For instance, PHB can be enzymatically degraded either by the action of intracellular or extracellular depolymerases in the presence of both PHB-degrading bacteria and fungi [221].

The disintegration in compost at room temperature of PHB and other biodegradable polyesters, such as PLA, was studied by Zhang *et al.* [26]. Authors reported an increase in the sample weight at the beginning of the composting assays, which was ascribed to a swelling effect.

Water absorption was higher in the PHB samples compared with those of PLA. Indeed, it was observed that the mass loss value of PLA remained almost constant after the first three weeks, confirming that PLA is not compostable or, at least, degrades slowly at room temperature. In the case of PHB, an induction period of time of 56 days was required for biodegradation to start and, thereafter, a fast weight loss was observed for over a period of seventeen weeks.

Regarding the compostability of plasticized PHB articles, the presence of the plasticizer habitually speeds up the disintegration process under composting conditions due to the increased mobility of the biopolymer chains. This effect facilitates the initial hydrolysis process, which is further followed by the actions of enzymes from microorganisms in the composting medium [17,35,206,220]. In the case of PHB blends, the disintegration under composting conditions is highly dependent on the crystallinity of each biopolymer in the blend. For instance, in PHB/PLA blends, PHB delayed the disintegration rate of PLA since PHB is more crystalline than PLA [17]. In the case of PHB/PCL blends, PHB disintegrated faster than the blend samples due to the fact that PCL increased the crystallinity of the system (Fig. 9) [96]. In another study, Seoane *et al.* [40] developed paperboard coated with PHB and the resultant bilayers successfully disintegrated under composting conditions in around 50 days. Authors observed that the PHB presence did not significantly delay the disintegration time of paperboard, highlighting that PHB did not affect the biodegradable character of paper. In the case of PHB/TPS blends, it was observed that the weight loss of the blend samples tends to increase with increasing the TPS content, which

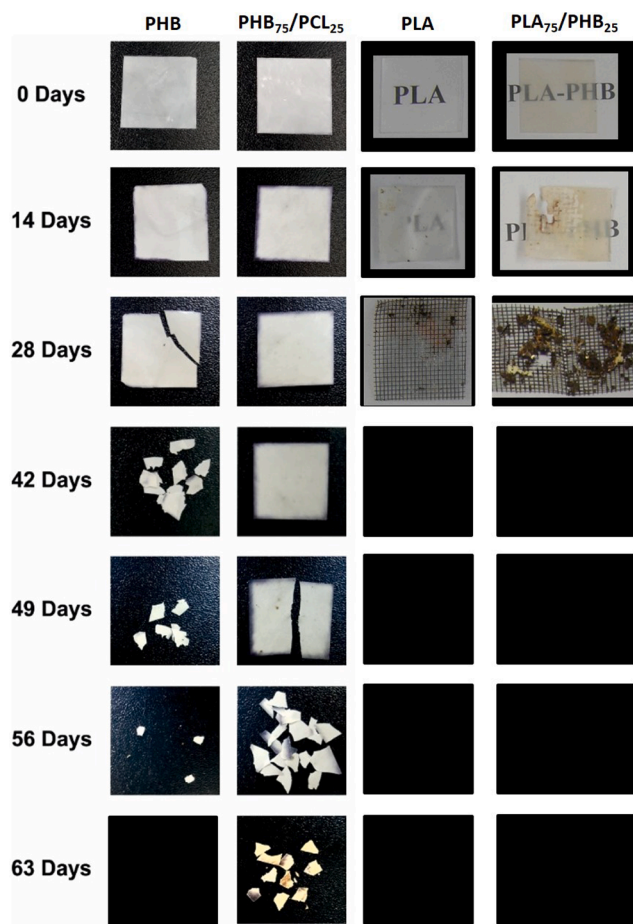


Fig. 9. Disintegration under composting conditions of poly(3-hydroxybutyrate) (PHB) and its blends with poly(ϵ -caprolactone) (PCL) and polylactide (PLA). Adapted from [96] and [17]. Reprinted from Garcia Garcia *et al.* [96] and Arrieta *et al.* [17] with permission from Elsevier.

was ascribed to the easier diffusion of water molecule. In fact, TPS is highly hydrophilic, and water absorption firstly increases due to the hydrogen bonding of $-OH$ groups of TPS and water. Thus, TPS is then more susceptible to hydrolytic attack, which is followed by enzymatic degradation. Furthermore, the presence of glycerol in the TPS matrix, which is in turn a carbon source for microorganisms, favors the disintegration process [62].

Other sustainable end-of-life pathways of PHB are technically feasible in addition to composting. Among them, the mechanical (secondary) and chemical (tertiary) recycling processes of post-consumer PHA waste are very promising in reducing the environmental impact of plastic packaging. Nowadays, some efforts have been made for mechanically recycling biopolyesters with promising results, particularly in the case of PLA [222–224]. However, there are very few studies dealing with the secondary recycling of PHB mainly due to its high brittleness and sensitiveness to thermal degradation during reprocessing. For instance, Plavec *et al.* [158] recently studied the mechanical recyclability of PHB when blended with PLA, concluding that PLA/PHB blends have better resistance against degradation at multiple thermomechanical process than unblended recycled PLA and PHB biopolymers. In fact, the solid state polymerization (SSP) has been proposed as a way to increase the molecular weight of biopolyesters to be further mechanically recycled [225], particularly when they come from well-known streams [224]. However, there are not studies on the solid state polymerization of neat PHB coming from industrial waste. Meanwhile, there are some studies reporting the increase of molecular weight of PHB through the polymerization of co-polymers of PLA and PHB by means of SSP and

using chain extenders (i.e.: pyromellitic dianhydride) [226]. Thus, due to its low thermal stability, it seems that the future of the mechanical recycling process of PHB is in combination with other biopolyesters such as PLA, either from blends or by producing new PLA-co-PHB copolymers. In any case, nowadays consumers still have restricted information about the correct disposal of compostable packaging, and they are under the risk to be mixed with petrochemical polymers waste. As a result, compostable plastics, including PHB, could negatively interfere with plastic mechanical recycling efforts since they could be rather acting as contaminants for traditional recycled plastics in industrial recycling lines [227,228].

While mechanical recycling of PHAs has shown poor viability due to the low thermal stability of PHAs, chemical recycling seems to be more promising. Thus, the chemical recycling of PHB articles can offer a novel solution to synthesize hydroxy acids, which are high-value monomers that could play a main role in the new so-called Circular Bioeconomy of biopolymers since the chemical recycling process allow to obtain the starting monomers closing the loop. Thus, starting from the polymerization of monomers, processing of the polymers in industrial products, disposal and followed by chemical recycling to obtain the monomers again PHB complies well the Circular Economy concept [140]. In this scenario, PHB has been successfully hydrolytically depolymerized by Tang and Chen [229], who obtained 3HB or its cyclic dimer (diolide, DL) and trimer (triolide, TBL) that, in all cases, could enable subsequent repolymerization to develop isotactic PHB according to the proposed a chemical recycling scheme shown in Fig. 10. Briefly, this is achieved by dimerization of the 3HB monomer to obtain racemic cyclic diolide (*rac*-DL), followed by isolation and isoselective ROP of *rac*-DL to isotactic PHB (isotacticity > 99%) by various classes of chiral or achiral catalysts and, finally, subsequent hydrolysis of PHB back to 3HB [229]. For abiotic hydrolysis of PHB, Yu *et al.* [230] recently studied the hydrolysis process of PHB films in acid and base media by monitoring the formation of 3HB and CA, the two monomeric hydrolytic products. The optimal conditions were found using concentrated acid solution. However, these conditions still yielded only 2% of 3HB and 90% of CA so that is was concluded that more selective hydrolysis of PHB to 3HB should be developed. In this regard, Li and Strathmann [231] performed PHB depolymerization in water media with temperatures slightly higher than 200 °C, improving the 3HB/CA ratio according the pH selected.

8. Conclusions

PHB has shown to be one of the most interesting biopolymers for food packaging applications since it comes from non-food grade natural resources and its articles can be fully compostable. In particular, this homopolyester can be melt-processed or dissolved in proper solvents to be processed by already existing processing technologies at industrial level, i.e.: extrusion, injection molding or electrodynamic technologies as well as used as coatings over paper or other biopolymers. However, both the low processing window and high brittleness of PHB materials are currently limiting its application in food packaging. This review has gathered the most promising strategies developed to solve these technical drawbacks and to contribute to extending the uses of this biodegradable homopolyester. Among them, the use of melt-blending processing technologies focusing on blending with plasticizers and/or more flexible biopolymer seems to offer the most sustainable and easily scalable solutions due to these formulations can be prepared in current processing industrial facilities. However, further studies will be needed in terms of optimizing the actual processing and performance of the resultant materials and also to find a more effective management of the future PHB-based packaging waste generated. In this regard, the compostability or, when possible, the mechanical and chemical recycling of PHB articles will open up new sustainable and more economically viable scenarios.

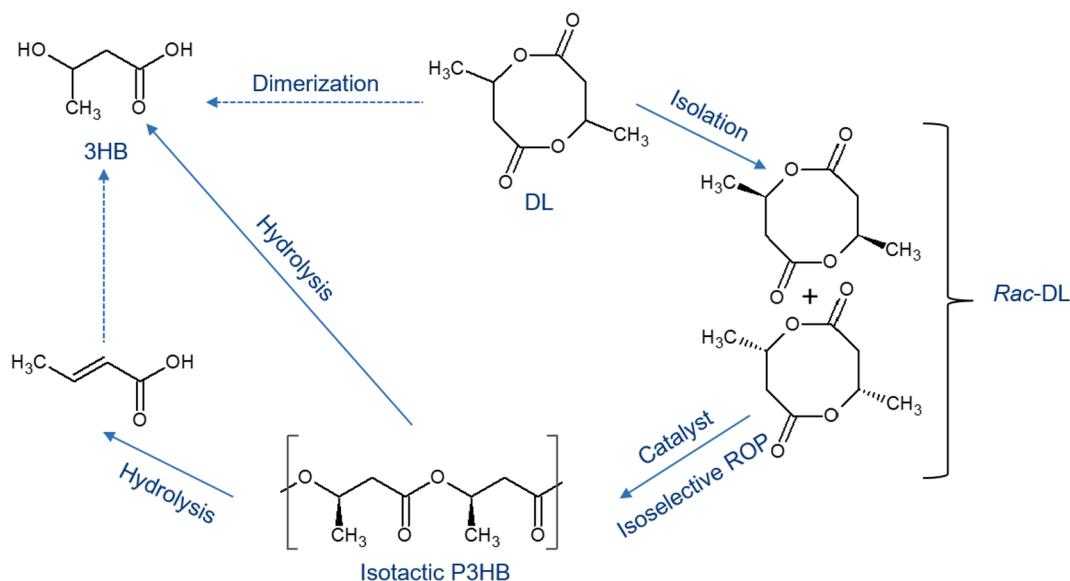


Fig. 10. Chemical recycling of poly(3-hydroxybutyrate) (PHB) via dimerization of 3-hydroxybutyrate (3HB) to cyclic dimer (DL), followed by isoselective ring-opening polymerization (ROP) of racemic cyclic diolide (*rac*-DL) to isotactic PHB, and hydrolysis of PHB back to 3HB. Adapted from Tang and Chen [229] with permission from Elsevier.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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