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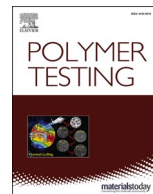
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The thermo-mechanical recyclability potential of biodegradable biopolyesters: Perspectives and limits for food packaging application[☆]

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ABSTRACT

Up to now, recycling has been opposed to biodegradability, although these two end-of-life options are complementary. If combined in an integrated system, recycling creates an after-use economy, while biodegradability eradicates definitely the issues of environmental spreading of the persistent plastic wastes. This paper reviews the current state on recyclability of some promising biodegradable polyesters, polylactide acid (PLA), polyhydroxyalkanoates (PHAs), bio-polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT), with emphasis on mechanical recycling. The effect of the mechanical reprocessing (multiple extrusion or injection-molding) on the chemical structure and thermomechanical properties of the polymers is reported. In addition, the application of upgrading strategies such as blends and/or composites to improve polyesters recyclability are considered. A further decontamination step is studied in order to achieve food contact aptitude in mechanical recycling for food packaging application. Finally, the challenges that should be faced in the future, to promote the recyclability of biodegradable polyesters are addressed.

1. Introduction

Since the early 1900's, the discovery of fossil-based polymers, especially thermoplastics has been the main driver behind the development of plastic industry. Strong, inexpensive, lightweight and versatile, plastics are used in thousands of products that add comfort, convenience and safety to our everyday lives. The current world production of plastic is about 370 million tons [1,2], with an annual growth in consumption of about 5% [3]. European plastics production accounts for 16% of the global market, with approximately 57.9 million tons in 2019 [1,2]. Packaging is the largest end-use market segment, accounting for just over 40% of total plastic usage. Polyolefins such as low and high density polyethylene (LDPE and HDPE) and polypropylene (PP), along with polyesters like polyethylene terephthalate (PET) are the most used thermoplastics in packaging sector [4,5]. These fossil-based materials are in ever-increasing demand because of their desirable thermal stability, mechanical properties and their good barrier properties to carbon

dioxide and oxygen.

However, rapidly increasing production of single-use plastic products overwhelms the world's ability to deal with them, with the emergence of severe environmental consequences. In 2019, 17.8 MT of food and drink packaging were collected in Europe, with 18,5% landfilled, 39,5% incinerated and 42% down-cycled, while the non-collected waste is still accumulated in the environment [1]. Plastic incineration generates toxic emissions, carbon dioxide and methane, which contribute to worldwide climate change [6] and air pollution. But the crucial consequence of linear plastic waste management is the persistent and invasive particles pollution interfering with our ecosystem and entering in food-feed chains. Plastics that are not incinerated are doomed to persist for centuries, slowly fragmenting into micro and nano-particles. These particles are able to absorb and transport ubiquitous organic pollutants and to diffuse in all environmental compartments including air, water, and living being's organs (by translocation) [7,8]. Numerous multi-lateral public and private initiatives are implemented such as the

[☆] We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

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European plastic strategy to develop a plastic circular economy by banning single-use plastic, increasing plastic recycling rate and curbing unrecyclable multi-layered materials.

The European directive 2008/98 set up the waste hierarchy from the most to the least favorable management scenario and ranks the recycling as the first action to be prioritized after re-use and prevention. In this way, the new Directive (UE) 2018/852 on packaging and packaging waste of the European commission targets 55% of plastic packaging to be recycled by 2030.

Nevertheless, it should be noted that the term “recycling” is most often improperly used for plastic as large-scale recycling such as mechanical recycling, is not applicable an unlimited number of time. The quality of the recycled plastic decreases after the first treatment cycle and the best recyclable plastic such as PET is doomed to end quickly as a persistent waste [9,10]. Processes called “recycling” are most often “down-cycling” or “re-using loops” since the process is not part of a closed loop of upgrading. The development of biodegradable plastics to substitute persistent conventional petrochemical plastics gives hope that such environmental and health problems might be solved or at least reduced. Biodegradation ensures that the waste is fully converted in a reasonable time into harmless molecules such as carbon dioxide and water, being able to reintegrate the carbon cycle via the photosynthesis [11]. Biodegradation means that no persistent particles of plastic waste will jeopardize our eco-systems and health in the future in many possible ways including their uptake, accumulation in organs or pollutant transport. However, up to now, biodegradable plastics are contrasted with recycled plastic. Recycling and biodegradation are considered as two separate and not compatible end of life options, which is not clearly supported by any scientific data. It is time to move beyond these bias and to consider that the recycling of biodegradable polymers could advantageously upgrade their biodegradation in a complementary way. On this basis, the waste hierarchy applied to the specific case of biodegradable packaging materials can be considered according to the

prioritization model presented in Fig. 1. Beyond the question of carbon savings, each pathway is associated with a time scale for which thermo-mechanical recycling technologies appears most valuable because of their convenience compared to the more expensive and time-consuming chemical recycling technologies [12].

In order to clarify the recycling ability of existing biodegradable plastic, the current review was undertaken. Our long-term vision is to contribute to resources saving while avoiding the production of persistent plastic waste, by promoting re-using loops of biodegradable plastic before biodegradation.

Biodegradable and compostable polymers were classified into four categories [13] (I) naturally occurring polymers such as starch, cellulose, proteins ...; (II) biopolymers produced directly by natural or genetically modified organisms, such as microbial polyesters; (III) polymers obtained from the conventional/chemical transformation of bio-based monomers, such as PLA; (IV) polymers chemically synthesized from fossil-based monomers (Fig. 2). A large number of biodegradable and compostable polymers have been produced recently and many of them are promising candidates to replace fossil-fuel-derived plastics in different applications. Among them, polyesters such as polylactide acid (PLA), polyhydroxyalkanoates (PHAs), bio-polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT) are undergoing a dynamic development [14,15] (Fig. 2).

According to European Plastics, the global capacity of bioplastic production was 2.11 million tons in 2019 (accounting for about 1% of plastics produced) and is forecasted to reach 2.44 million tons in 2024 [2]. The global PLA market was estimated to 300 Kt in 2019, and is expected to reach 330 Kt by 2024 [16]. Current global production of PHAs is about 25,320 tons which account for 1.2% total bioplastics compared to 13.4% for PBAT and 4.3% for PBS. However, due to its significant growth, it is expected to reach 6.6% of total bioplastic production in 2024 [17,18]. Thanks to technological advances in the productivity and functionality of PLA, several large companies such as

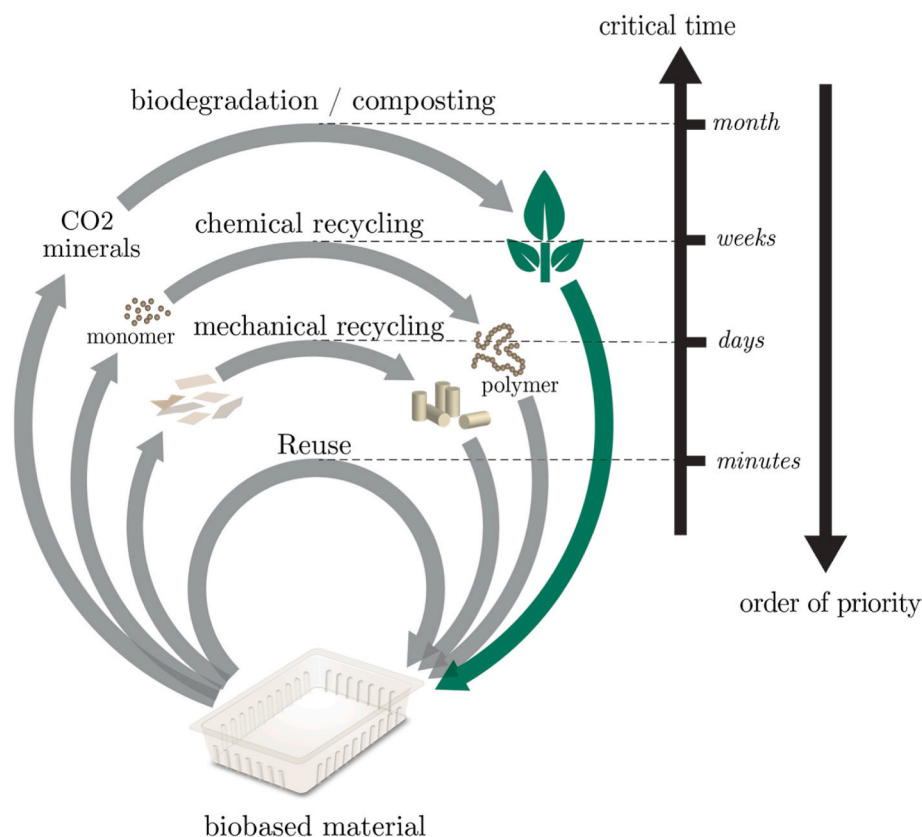


Fig. 1. Waste hierarchy approach applied to biodegradable packaging materials.

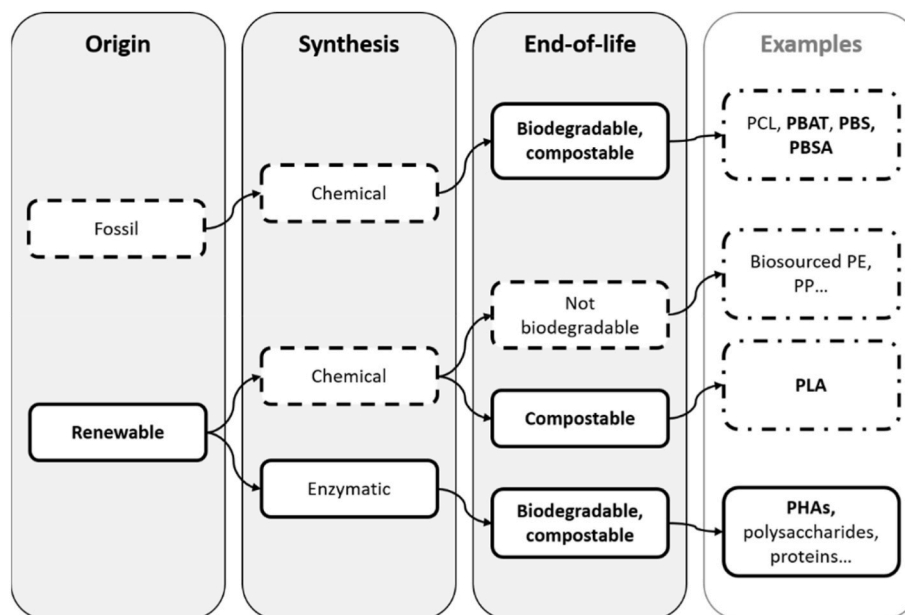


Fig. 2. Main groups of bioplastics according to Berthet [15].

McDonald's®, Bayer, DuPont, Nike, Danone ... Have already started to integrate its containers and packaging into their products [19,20]. For instance, Danone® is changing their yogurt cup from conventional PP to PLA, improving their packaging carbon footprint by 25% and DuPont® PLA materials are used in the production of cups, trays and films. This, together with the growing consumer demand for biodegradable plastics [21] is causing the production of these polymers to take off and probably exceed estimates.

As a consequence, biodegradable/compostable polymers will be increasingly used for common application like bottles, trays, packaging, etc. Hence, they would likely end up in waste streams and composting facilities which could not assimilate increasing flows of these polymers. Furthermore, Gioia et al. reported that biodegradation and composting of biodegradable plastics should be restricted to specific applications [22]. For example, biodegradation of agricultural mulch film where material fragmentation leads to soil contamination, or composting of food waste collection bags where separation between organic matters and plastics is not possible. For all these reasons, it would be advisable to promote solutions offering the possibility to extend the service lives of these materials, or to obtain added value before finally discarded them into biodegradable products facilities.

Previous reviews have focused on mechanical and chemical recycling of PLA and PLA derivatives [23–26]. This review covers the studies dealing with the mechanical recyclability of the main promising biodegradable polyesters PLA, PHAs, PBAT and PBS within the last ten years. A deep focus is given to relationship between chemical structure and polymer macroscopic properties during reprocessing steps. With a view to the potential use of these biodegradable polyesters as food packaging, their decontamination ability will be discussed.

The limitations likely to be encountered by the bioplastics recycling sector, and some challenges to be faced in the future are presented at the end of the review.

2. Recycling processes and life cycle assessment (LCA)

Different end of life (EOL) channels for plastic waste are now in place. (I) Landfilling is one of the oldest waste treatments based on the burial of post-used plastic [27]. (II) Incineration. The aim of this technology is to produce energy from plastic waste, since the calorific value of plastics such as polyolefins or polyvinyl is similar to that of fuel or oil used for its production [28,29]. (III) Mechanical recycling includes

waste sorting, size reduction, cleaning (or decontamination) and polymer remodeling [30]. This process is called primary recycling or closed-loop recycling and implies that performances and functionality of recycled materials are equivalent to the original virgin plastic (With a regular supply, only the recycling of PET and HDPE bottles is economically viable today [31]). The technology that currently prevails is secondary recycling (down cycling) which leads to a product with lesser value than to original plastic [32]. (IV) Chemical recycling, or tertiary recycling, involves the degradation of the polymer chain into monomer units (depolymerization) or randomly ruptured fragments (oligomers). The chain rupture is carried out either by solvolysis or thermodegradation (pyrolysis) [33,34].

Several studies have examined the environmental burden of the existing waste management options for both biodegradable and non-biodegradable plastics, based on the assessment of carbon footprint and the use of nonrenewable energy. For all plastics, mechanical recycling seems to be the favorable option, especially when it produces virgin-quality recyclates [35–40].

K. Changwichan et al. [41] have implemented eco-efficiency (E/E) indicator to compare landfilling, composting, mechanical recycling and incineration of takeaway food boxes made from PLA, PHA or PBS. E/E indicator is recognized as a single indicator which includes both economic and environmental aspects, with a view to increasing economic benefit while reducing environmental impact. Out of the four end-of life (EOL) options, 100% mechanical recycling showed the highest E/E values for all the bioplastic boxes. This high E/E value is mainly due to the avoidance of bioplastic production step which is responsible for negative environmental impacts (eutrophication, acidification, land use ...) and high costs. For the three polyesters tested, recycled PLA showed the highest E/E followed by PBS and PHA. In other words, the mechanical recycling of these polyesters and particularly PLA has shown a lower environmental impact and a higher economic benefit compared to the other EOL scenarios.

LCA analyses also support this outcome particularly because of the carbon savings that such a process can provide. Rossi et al. [42] concluded that landfill and industrial composting of PLA result in the worst environmental impact compared to mechanical recycling. This can be explained by the fact that recycling technology allows the polymer to be regenerated and reused, while composting leads to its replacement which is associated to the impact of the whole production process again (Fig. 3) [35]. Even within recycling processes, chemical

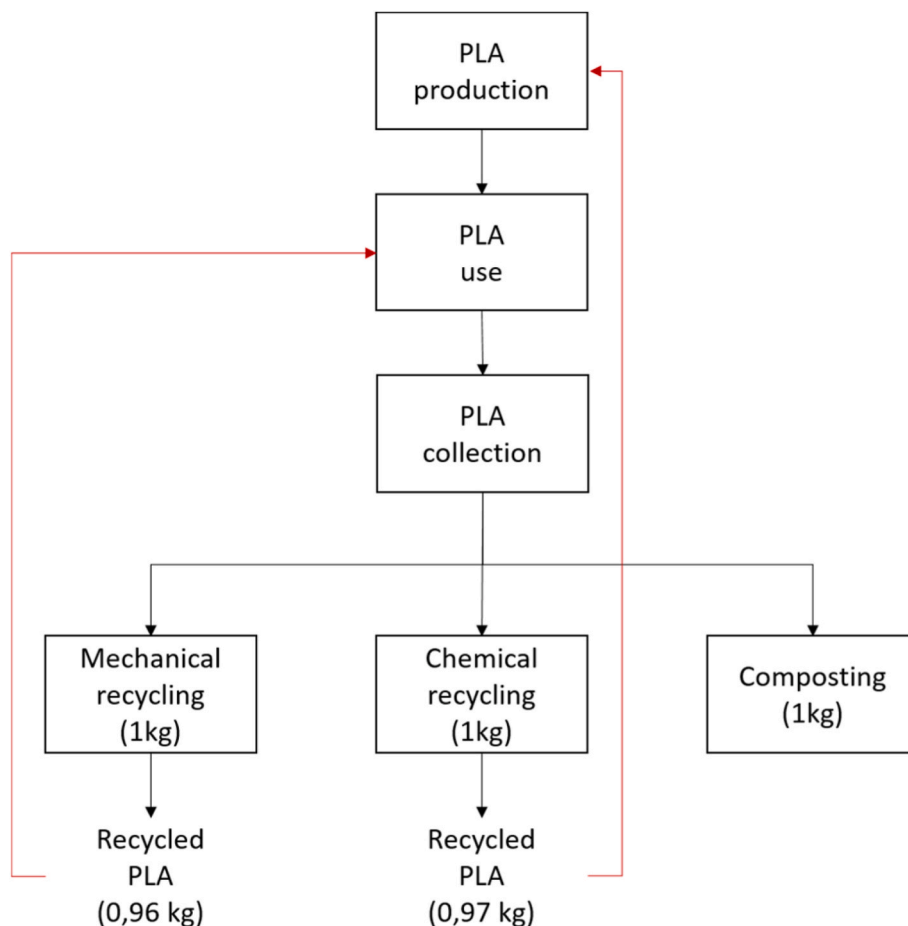


Fig. 3. PLA conversion yield through different end-of-life options according to Hottle et al. [35].

recycling has shown higher impacts due to the environmental burden associated with the re-polymerization step [43]. As an example, mechanical recycling spends 1.60 MJ of fossil energy to produce 0.96 Kg of PLA, which is 4 times lower than energy used for recycling the same amount of PLA through chemical process [35].

It is important to note that none of LCA studies has considered the deterioration of material properties within the mechanical processing and no standard test methods for the evaluation of the quality of the resulting recyclates have been developed. Thus, LCA identifies mechanical recycling as the preferred option in the short term over other waste management techniques, but the possibility of recycling the polymer by chemical or organic processes (AD, composting) could be useful in the long term (after several cycles of mechanical treatment). Today, LCA analyses do not provide a clear answer as to the combination of different end-of-life scenarios to reduce the environmental impact of biodegradable materials [44].

The study of degradation mechanisms during mechanical reprocessing and potential unlocking of these issues are the topic of the next part.

3. Mechanical recycling: reprocessing ability of biodegradable polymers

From a technical point of view, mechanical recycling which requires low investment, is an eco-friendly technology and is relatively simple to set up and applied. However, it often results in products whose properties are much poorer than those of the starting material. The degree of deterioration of the polymer properties as a function of the reprocessing cycles is an important techno-economic criterion which defines the recirculation potential of the material through mechanical recycling

[12]. This section will first shed light on the impact of mechanical recycling on the structure and properties of PLA, PHA, PBS and PBAT, with a focus on degradation mechanisms of these polyesters (Table 1) (Niaounakis et al. reported the patents related to the mechanical recycling of aliphatic polyesters, but these patents only focus of the mechanical recycling of PLA [45]). Then, the different methods that have been attempted to improve the properties of recyclates will be examined. It should be noted that no industrial recycling process has been implemented yet for this type of plastic. Hence, in all the studies presented herein, the term “recycling” refers to the material reprocessing, by means of extrusion or compounding, at lab scale.

3.1. Impact of the mechanical recycling on structure-properties of biodegradable polyesters

3.1.1. Mechanical recyclability and degradation mechanisms of PLA

PLA is a biopolymer obtained from the polycondensation of lactic acid or from the ring-opening polymerization of lactide (a cyclic dimer of lactic acid). PLA monomer derives from the fermentation of sugar feedstock, corn, etc, with a predominance of L-isomer in nature. Commercial PLA with high crystallinity is generally based on a 100% L-lactide isomers. The co-polymer with a few proportion of the D-lactide isomer is rather amorphous [5,46]. The two largest producers of PLA are NatureWorks and Mitsui Chemical, although some others companies produce smaller outputs. PLA presents optical and mechanical properties generally considered as similar to those of PS and PET and is approved by FDA for food-contact application [47]. PLA is widely described as a biodegradable plastic. However, this polymer is less susceptible to environmental degradation than other aliphatic polyesters. It was evidenced that its degradation is mainly due to abiotic

Table 1

Review of the impact of multiple reprocessing, on biodegradable biopolyesters and their blends.

	Polymer material	Reprocessing conditions	Thermomechanical properties	Ref
PLA	PLLA [Biomer]	Injection-molding at 175–195 °C	After 5 cycles, tensile strength from 64.1 to 58.7 MPa, Young's modulus stables at 2.6 GPA, elongation at break, from 3.4 to 3.0%. From the 6th cycle, sharp decrease in tensile strength and elongation at break.	[25]
	PLA (4.2% D-lactide content) [Natureworks]	Injection-molding at 160–190 °C	After 2 cycles, viscous molar mass is maintained, and it showed 50% decrease at the 5th cycle. After 5 cycles: decrease in the Young's modulus of 28%, overall increasing fashion of strain at break (10%), the impact resistance decreased by 10% after the first cycle, remaining unchanged after. Decrease of the cold crystallization temperature from the second cycle (drop of 6 °C). Loss of PLA performance after the second cycle.	[51]
	PLLA [Biomer]	Injection-molding at 175–190 °C	After 5 cycles, decrease of T _g from 66 to 56 °C, appearance of crystallization during cooling after 2 cycles, decrease of M _w by 50% after 3 cycles. Therefore, a rapid decrease of PLA performances was observed.	[52]
	PLA [Natureworks]	Extrusion (temperature not mentioned)	Mechanical properties decreased with extrusion numbers: after 10 cycles, impact strength decreased by 20%, and tensile test at break by 8%. MFR of the sample extruded 10 times was threefold higher than that of neat PLA. T _g was not affected. Cold crystallization temperature decreased from 125 to 115 °C. Tonset after one extrusion was 339 °C, and after 10 extrusions, it reached 332 °C. This recycled PLA is suitable to be used as additive to the neat PLA.	[55]
	PLA [Natureworks]	Extrusion (145–190 °C) + Injection (180–210 °C)	Extrusion + injection of neat PLA caused: increase in MFI from 7 to 10.7 g/10min, yellowish color, decrease in M _w from 212 to 162 KDa, degradation temperature was	[56]

Table 1 (continued)

	Polymer material	Reprocessing conditions	Thermomechanical properties	Ref
	PLA (4.2% D-lactide) [Natureworks]	Extrusion + compression molding at 180 °C	slightly lower for processed material 325 °C (compared to 331 °C for virgin PLA), significant increase in elongation at break (32–35%). After 5 cycles: decrease in M _w from 289 to 154 KDa, very slight increase in T _g , strong decrease in tensile modulus and ultimate stress at both 20 °C and 50 °C. No additional chemical functions (end groups) appearance.	[57]
	PHB [BIOCYCLE]	Extrusion + compression molding at 170 °C	After 3 cycles: decrease in tensile strength at break above 50%, increase in crystallinity after the first cycle (even more after the 2nd and 3rd cycles), T _{max} corresponding to degradation temperature was maintained at 297 °C, no modification in the chemical structure of the polymer.	[68]
PHA	PHBV (3% HV) [Tianan]	Extrusion (single screw) at 175–180 °C	After 3 cycles: decrease in M _n from 299 to 260 KDa, complex viscosity drastically reduced, slight decrease in tensile modulus from 4.3 to 3.8 GPa due to the enhancement in crystallinity, decrease in strain at break with more brittle material. Degradation from the 3rd cycle.	[76]
	PHBV (14% HV) [Zeneca Bioproducts]	Extrusion (twin screw) at 170 °C	Properties maintained up to the 4th cycle. After 4 cycles: decrease in M _w from 337 to 281 KDa, no modification in tensile strength, crystallinity rate was reduced from 54% to 42%, slight modification in Tonset.	[77]
PBS	PBS [Bionolle]	Extrusion (twin screw) at 160–210 °C	MFR reduplicate after 1 cycle. After 7 cycles, decrease in M _w from 156 to 119 KDa, T _g and melting temperatures not altered by reprocessing, modification in the shape of melting peak due to molecular degradation, at room temperature no significant change in storage modulus neither in Young's modulus, decrease in tensile strength and strain at break by 24 and 32% respectively. Loss of material properties throughout recycling.	[84]

[87]

(continued on next page)

Table 1 (continued)

	Polymer material	Reprocessing conditions	Thermomechanical properties	Ref
	PBS [Natureplast]	Extrusion at 190–210 °C	After the 3rd cycle: viscosity increased by up to 31% indicating the occurrence of branching/recombination without crosslinking, decrease in M_w by about 20%, significant increase in the crystallization temperature up to 16 °C.	
Blend	PLA/PBS (50:50 wt%)	injection molding at 190 °C	After 7 cycles: a drop in the viscosity by –65%, decrease in PLA M_w , PBS accelerate the cold crystallization of PLA from cycle 4, stability of mechanical properties especially for stiffness and tensile strength. PBS is less degraded than PLA.	[107]
	PLA/PHBV (50:50 wt%)	Extrusion at 175–180 °C	After 6 cycles: M_n is reduced by 4.8% due to stabilization effect of PLA, increase in crystallization enthalpy from 33 to 46 J g ^{–1} due to the crystallization of PHBV, decrease in storage modulus by 9%, biphasic morphology of the blend, which does not affect its mechanical properties. Incorporation of PLA improved PHBV properties.	[76]
	PHBV/PBAT (35:65 wt%)	Extrusion at 140 °C	After only 3 cycles: MFR increased by 328%, shift of melting value to higher temperatures, increase in crystals size. Degradation mainly occurred in PBAT, with a phase separation in the blend.	[84]

hydrolysis rather than to microbial attack [48]. For this reason, PLA can only degrade under industrial composting conditions, including anaerobic conditions and elevated temperatures [49,50].

The mechanical recycling of PLA has been investigated at lab-scale by means of injection [25,51,52] and extrusion [53–55], during one [56], three [54], five [57], and ten [55] processing cycles. All studies showed a gradual decrease in M_w , which enhanced the mobility of the polymer chains and increased crystallization during cooling [57]. The cold-crystallization (T_{cc}) can be decreased down to 10 °C from the initial values, due to the liability of recyclates to nucleate crystalline domains, at lower temperatures, as a consequence of the presence of shorter chains generated by the degradation [23]. However, the influence of successive reprocessing cycles on glass transition temperature (T_g) and melting point (T_m) of PLA remained very limited.

With regard to changes in mechanical properties during reprocessing, various results have been reported. After seven injection cycles, Pillin et al. [52] observed that neither material strength in elastic domain, nor tensile modulus were affected by the thermomechanical treatment. Tensile modulus value remained constant as the potential decrease in M_w was probably balanced by the increase in crystallinity. However, stress and strain at break decreased from 66 MPa to 25 MPa, and from 6% to 0.8%, respectively. In contrast, Zenkiewicz et al. [55]

showed a slight decrease of 8.3% for stress at break and an unchanged strain at break after ten extrusion cycles. This was confirmed by Badia et al. [51]. and Lopez et al. [25] studies which reported that no significant modifications occurred in stress-strain at break of PLA over five reprocessing cycles. These variations between studies could be attributed to the variation in the ratio of D/L lactide isomers in PLA. In general, PLA reprocessing affected the macroscopic mechanical properties, resulting on materials with increased brittleness and stiffness [51,52,55].

By investigating water vapor and oxygen transmission rates versus extrusion number, it has been observed that permeability through PLA films significantly rise with the extrusion number. After ten extrusion cycles, the relative increase of transmission rates of water vapor and oxygen were 39% and 18%, respectively [55].

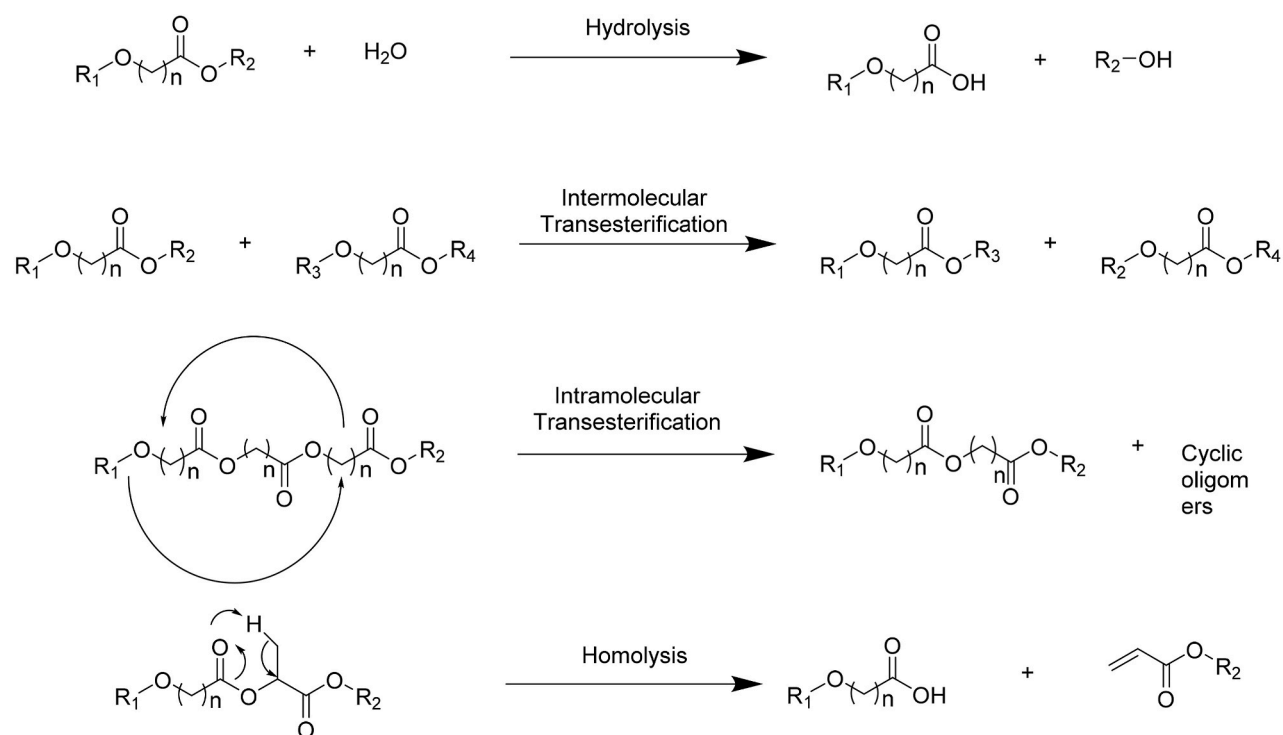
The influence of the washing step on properties of PLA recyclates was pointed out by Beltrán and coworkers [58]. In order to approach the real conditions of mechanical recycling, virgin PLA samples were first subjected to an accelerated aging process including photochemical and thermal degradations. Then, a portion of these samples was washed with a sodium hydroxide aqueous solution. Finally, all the samples were reprocessed by extrusion and compression molding. After one cycle, the recycled PLA, without washing step presented a small decrease in the intrinsic viscosity in comparison with the virgin polymer (around 5%). However, the intrinsic viscosity of the washed PLA was 20% lower than that of virgin PLA and 16% lower than that of recycled PLA without washing. This suggests that different factors contribute to the structural degradation of recyclates, including ageing, chemical washing and thermomechanical treatment.

Other studies questioned the influence of thermomechanical multi-processing on microbial degradation of PLA and it was found out that PLA recyclates are still industrially compostable after several cycles [54].

During thermal processing, PLA polymer is mainly subjected to chain scission reactions leading to a decrease in molecular weight and an increase in cold crystallization. Generally, the thermal degradation of PLA follows the postulated mechanistic routes of polyesters which are: (I) hydrolysis; in the presence of water; the cleavage of the ester linkages giving rise to carboxylic acid and hydroxyl linear oligomers. (II) intramolecular transesterification leading to the formation of cyclic or linear oligomers. (III) intermolecular transesterification which interchange ester units between different chains causing a variation in M_w distribution. (IV) homolytic chain scission at temperatures above melting [59]. The analysis of PLA recyclates by MALDI-TOF-MS revealed that the repeated thermomechanical treatments resulted on hydrolytic and homolytic chain rupture along with intermolecular transesterification mechanisms [59]. Mechanical forces taking place during the reprocessing (e.g. shear and elongation deformation during extrusion cycles) are converted in additional heat input, enhancing thermal degradation [59,60] (Fig. 4). In the presence of oxygen, the thermo-oxidative degradation is governed by intramolecular transesterification in first stage and radical degradation in the second stage initiated by the lowest dissociation energy of tertiary CH bond [61].

3.1.2. Mechanical recyclability and degradation mechanisms of PHAs

PHAs are a family of biopolyesters, produced by bacterial fermentation of sugars and lipids. This class of polymer includes a variety of molecular structure depending on the type of bacteria, the monomer used as substrate and the process parameters. The most widespread PHAs are the homopolymer polyhydroxybutyrate (PHB) and the copolyester polyhydroxybutyrate-co-hydroxyvalerate (PHBV) [62]. Some companies such as Tianan (China), Kaneka (Japan), Telles (USA) and Cheil Jidang (South Korea) produce PHAs at industrial scale, from 2000 to 50,000 tons/year [63]. For the time being, PHAs represent a low volume of the biopolymer market but they are attracting commercial interest [64], as they exhibit thermomechanical properties close to those of polypropylene. PHAs present good barrier properties, compliance



The most reported degradation products for PLA, PHA, PBS and PBAT

Mechanism Polymer	Hydrolysis	Intermolecular transesterification	Intramolecular transesterification	Homolysis	Reference
PLA	$R_1-O-CH(CH_3)-COOH + R_2-OH$	$R_1-O-CH(CH_3)-CO-O-R_3 + R_2-O-CH(CH_3)-CO-O-R_4$	$R_1-O-CH(CH_3)-CO-O-CH(CH_3)-CO-O-R_2$ + 	$R_1-O-CH(CH_3)-COOH + CH_2=CH-C(=O)-O-R_2$	46, 47
PHA PHB: $R_3 = CH_3$ PHBV: $R_3 = CH_2-CH_3$	—	—	—	$R_1-O-CH(R_3)-COOH + CH_2=CH-C(=O)-O-R_2$	58, 60, 65
PBS	—	—	—	$HO-CH_2-CH_2-C(=O)-R_1 + CH_2=CH-CH_2-CH_2-O-R_2$	77
PBAT	$HO-CH_2-CH_2-CH_2-CH_2-C(=O)-R_2 + HO-C_6H_4-C(=O)-O-R_1$	—	—	$CH_2=CH-CH_2-CH_2-C(=O)-R_2 + HO-C_6H_4-C(=O)-O-R_1$	81

Fig. 4. Thermal degradation mechanisms of aliphatic polyesters.

with food contact material regulations and biocompatibility, making them suitable for food packaging applications [5,63]. In natural environment such as soil, lake water and marine water, PHAs degrade in 5–6 weeks into water, carbon dioxide and biomass [3,65]. However, global use and industrialization of PHAs are still limited due to the high production costs, inducing high price.

Unlike PLA, only few studies have been carried out on the mechanical recyclability of PHAs probably due to their good biodegradability and their still limited market share.

PHAs are known to be very sensitive to thermal degradation during melt processing due to the narrow temperature window between melting and degradation temperatures.

PHB decomposes easily near its melting point [66]. After several grinding or extrusion cycles, there is a rapid decrease in molecular weight associated with a dramatic drop in viscosity at temperatures just above its melting point [67–69]. As consequence, significant change in mechanical properties was observed. After the third cycle, tensile strength decreased above 50% and elongation at break has declined so much that it impeded further extrusion [68,70]. However, neither Young's modulus, nor melting and glass transition temperatures were affected by heat treatments.

The random β -elimination scission has been widely regarded as the main degradation mechanism of PHB, based on a typical structures of degradation products, namely crotonic acid and oligomers with crotonate end-groups (Fig. 4) [71]. Later on, an E1cB (Elimination Unimolecular conjugate Base) elimination mechanism proceeding via α -deprotonation by a carboxylate anion to produce the same products was proposed [72]. β -elimination scission and/or E1cB elimination produce a large number of carboxylic compounds which would auto-catalyze the random degradation. These carboxylic compounds randomly attack ester groups on polymer chains to induce transesterification reactions, resulting on the reproduction of carboxyl groups associated with a remarkable decrease in molecular weight [73].

The auto-acceleration of the random degradation is dependent on carboxylic groups self-proliferation in bulk. The unzipping reaction occurring at the end of molecules is a 0th-order reaction, just kinetically favored scission of polymer chains that repeatedly generate a large number of crotonic acids. This is an ideal self-proliferation reaction of carboxyl compounds and is the key factor in the auto-accelerated random degradation [74,75].

The mechanical recyclability of PHBV with different % valerate was tested at laboratory scale in two studies. Zembouai et al. [76] monitored the behavior of PHBV with 3% HV content, during 6 extrusion cycles at 180 °C. Zaverl and coworkers [77] investigated the effect of 5 extrusion cycles, at 170 °C, on properties of PHBV with 14% HV content. They both reported a decrease in M_w (22,9% for PHBV-3%, after 6 cycles and 16,6% for PHBV-14%, after 5 cycles). It was observed that the mechanical properties (tensile strength, elongation at break and toughness) slightly decreased in the case of PHBV-3%, making it a little more brittle after multiple processing cycles, while PHBV-14% maintained its mechanical properties up to the fourth cycle. Thermal properties did not change during reprocessing, except for melting enthalpy of PHBV-3%, which increased by 9%. This is due to the decrease in M_w which enhances the polymer chains mobility and induces higher crystallization. The increase of the amount of valerate (up to about 10%) leads to a decrease of copolymer melting point (172 °C for PHBV-3% against 156 °C for PHBV-14%), which results in improvement in ductibility and flexibility and enhancement of its workability and thermal stability.

As for PHB, the degradation mechanism of PHBV is dominated by a random β -elimination reaction involving a six-membered ring transition state [73,78]. For both PHB and PHBV, the presence of oxygen did not induce or accelerate the degradation reactions at melting temperature [79].

3.1.3. Mechanical recyclability and degradation mechanisms of PBS

PBS is a biopolymer produced from the condensation of succinic acid

and 1,4-butanediol. In the past, PBS was exclusively obtained from fossil raw materials, but can be now entirely biobased thanks to the production of its monomers by bacterial fermentation, succinic acid and 1,4-butanediol resulting respectively from the fermentation of sugars like glucose and dextrose [80,81]. Companies producing PBS in commercial scale of 20,000 tons/year are Mitsubishi Chemicals, Hexing Chemical and Xinfu Pharmaceutical [66]. PBS mechanical properties present similarities with those of PP and PE, with a melting point exceeding 100 °C which proved to be suitable for applications requiring high temperatures. Its copolymers PBSA and PBST show higher flexibility, making them potential candidates for a wide panel of food packaging applications [66]. According to the European standard DIN EN 13432, PBS is biodegradable and compostable [82,83].

The mechanical recycling of polybutylene succinate (PBS) was simulated by repeated polymer extrusion for up to seven times, followed by granulation [84]. In such conditions, the Melt Flow Rate (MFR) of PBS doubled already after one reprocessing cycle. This correlated with GPC analysis results, which showed a significant decrease in M_n (virgin 78832, after 7 cycles 57866) and M_w (virgin 156157, after 7 cycles 119796). PBS structural degradation resulted on decrease in tensile strength and strain at break by up to 24% and 32% respectively. At ambient temperature, Young's modulus showed a marginal increase with the increasing number of reprocessing cycles (increase by maximally 7% of the initial value) and no impact was observed on storage modulus. These results may be related to general soft and flexible material features in this temperature range. Thermal parameters such as glass transition and melting temperatures were not altered by repeated treatments. However, a change in the shape of the melting peak has been noticed. A distinct double peak was observable for virgin PBS, which is most probably caused by polymorphism and may also involve a melt-crystallization. In comparison, the reprocessing yielded a single melting peak with a preceding exothermal effect. Others studies report the same changes of melting peak with decreasing of PBS molecular weight [85].

In other studies dealing with PBS reprocessing by means of 3 cycles of compression [86] and 5 cycles of extrusion [87], viscosity and M_w of polymer were found to decrease after the first extrusion run. However, they strongly increased thereafter [86]. Also, a decrease in crystallinity was observed [87]. This was attributed to the occurrence of branching/recombining reactions that increased the viscosity and disrupted the regularity of the polymer chains.

Degradation mechanism of PBS within multiple processing cycles was not investigated. Only few studies have examined the mechanism of PBS thermal degradation in absence and presence of oxygen [88,89]. Without oxygen influence, The thermal degradation of PBS is mainly governed by β -elimination mechanism [90]. Rizzareli and co-workers [89] investigated the thermo-oxidative degradation of PBS under atmospheric air at 170 °C for up to 6 h. The structure modification and oligomer end-groups produced during polymer degradation were identified using MALDI-TOF-MS analysis. It contributed to establish the global degradation mechanism, described in Fig. 5. The initial step consists of a hydrogen abstraction from the methylene group adjacent to the ester linkage, leading to the formation of an hydroperoxide intermediate. Unstable hydroperoxide derivative undergo elimination of hydroxyl radical to produce oxy radical which can decompose into oligomers with different end-groups through different routes. A comparison with PBS behavior under nitrogen confirmed that oxygen is a key parameter in the degradation process.

3.1.4. Mechanical recyclability and degradation mechanisms of PBAT

PBAT (poly(butylene-adipate-co-terephthalate)) is an aliphatic-aromatic co-polyester, synthesized by polycondensation of 1,4-butanediol (BDO) with both adipic and terephthalic acids (AA and PTA). It is mainly produced by BASF (Germany), KINGFA (China) and Novamont (Italy) at a rate of less than 60,000 tons/year [91]. Although PBAT is synthesized from fossil-based derivatives, it can cover a wide range of

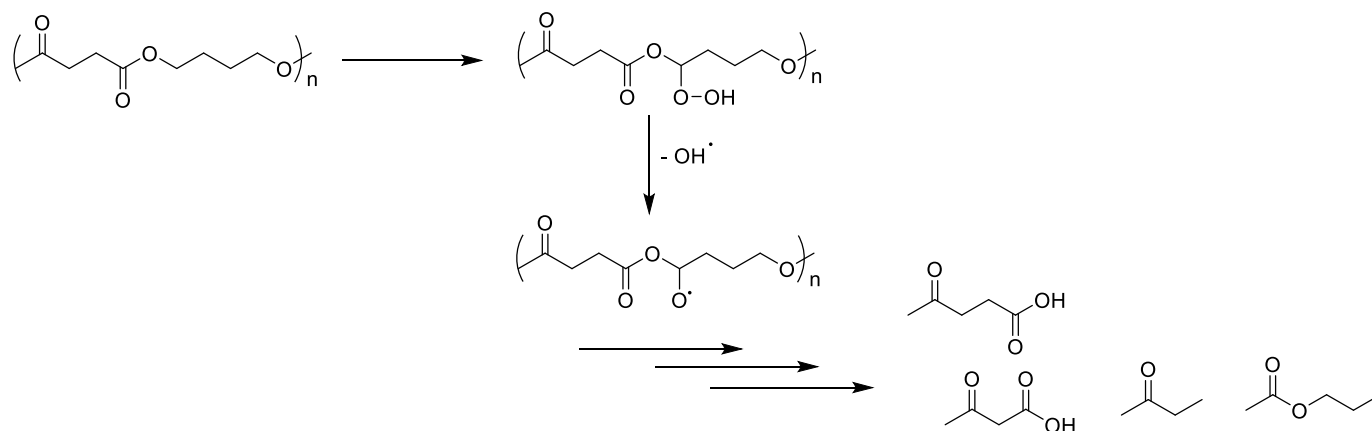


Fig. 5. Overall thermal-oxidation processes in PBS according to Rizzarelli et al. [89].

packaging applications as it exhibits properties similar to those of low density polyethylene thanks to the aromatic unit in the molecule chain [92], and it completely biodegrades in soil [93]. Despite this, expending PBAT producing is still hampered by its high production cost (between PLA and PHAs) and low thermomechanical resistance. One of the strategies to improve the mechanical properties of PBAT is the increasing of the terephthalate content. However, a specific ratio between terephthalate and aliphatic components (30–50 mol% of terephthalate units) should be respected in order to maintain the biodegradability of the polymer [22,92]. Because of its relatively poor performance, very few studies have been conducted on the PBAT recycling. Scaffaro et al. found that the addition of organoclays to PBAT polymer under UV irradiations enhances the polymer crosslinking, leading to the formation of porous structure, which can be further used for the production of high-value Materials. In this case, also, the biodegradability of the material is affected [94]. The thermal degradation of PBAT is mainly governed by an oxidative chain scission as discussed in several studies. Thus, after extrusion at 180, 190 and 200 °C [95] or after processing on a torque rheometer at 180 °C and 200 °C for 10 min [96], a decrease in molecular weight and viscosity was observed, indicating the thermo-degradation of PBAT governed by scission chain reactions probably competed with cross-linking reactions (Fig. 4). Chaves and Fechine [96] reported an increase of absorbance at 400 nm of PBAT solution after processing at 180 or 200 °C, which may be due to an increase of chromophore groups or cross-linking in polymer. The same processing under nitrogen flow [95,97] and/or with the use of antioxidants additives [96] showed a lower reduction in molecular weight and viscosity, which confirms the influence of oxygen in the degradation process. Chain scission mechanisms of PBAT were proposed by Al-Itry and coworkers [95] as depicted in Fig. 4.

On the other hand, a study reported by Signori and Bronco [97] revealed that processing PBAT in a mixer at temperature range of 150 °C–200 °C during 10 min did not affect the molecular weight and thermal properties of the polymer. This may be attributed to the relatively mild processing conditions compared to the other studies.

3.2. Tentative to upgrade polyesters properties during mechanical recycling

Although the treatments described above do not simulate realistic conditions of the mechanical recycling process, the various studies highlighted the structural degradation of PLA, PHA, PBS and PBAT under the influence of thermal, thermomechanical and thermo-oxidative treatments.

In order to prevent or minimize degradation during these “recycling” processes, different strategies have been considered including thermal and chemical treatments, or the production of blends, bio-composites or

nanocomposites based on bio-polyesters.

3.2.1. Thermal and chemical treatments

Several studies have examined the potential effect of some thermal and chemical treatments on the improvement of PLA properties during/after reprocessing. By choosing appropriate temperatures between 75 °C and 135 °C range, it is possible to modify the amorphous-to-crystalline ratio of PLA during processing. Thus, Carrasco et al. [56] and Nascimento et al. [98] subjected PLA samples, previously extruded and injected during one cycle, to thermal annealing at 120 °C during 6 h. The resulting increase of crystallinity induced an increase of Young's modulus and yielded strength, while a decrease of elongation at break was observed. The use of additives is a common strategy to improve the material processability. Since the thermal degradation mechanisms of biopolyesters are often enhanced by the presence of oxygen, many studies investigated the addition of antioxidants to stabilize them during recycling. These antioxidants may have the capacity to trap free radicals, limiting oxidative phenomenon and maintaining thereby polymer chain length. For instance, the addition of quinones or tropolone to PLA at 200 °C, under air, led to the effective stabilization of thermal and mechanical properties [52,99]. Typical antioxidant stabilizers (Irganox® and Irgafos®) were also added to PBS [87] and PBAT [96]. The thermo-mechanical degradation was suppressed for PBS and strongly reduced for PBAT. Properties of recycled PLA was significantly improved by the use of phosphites [100,101]. The use of chain extenders and branching agents by reactive extrusion has also proven its efficiency. The addition of multifunctional epoxides to PLA [95,102,103] or PBAT [95] contributed to the stabilization of molecular weight of these polyesters, improving thereby their mechanical, thermal and rheological properties.

3.2.2. Polymer blends

Since this review is specifically dedicated to biodegradable polyesters, blends made by adding non-biodegradable polymers are not discussed here and the focus is on blends combining virgin and recycled polymers.

The properties of blends made up of cleaned post-consumer PLLA bottle flakes and virgin PLLA resin were assessed [104]. After cleaning, blends were extruded and thermoformed into trays, to be then characterized. Up to 40% PLLA recycled content, no significant difference was observed in M_w , thermal and mechanical properties of blends with just slight difference in sheets color.

La Mantia et al. [105] investigated the effect of five extrusion cycles on the thermal, rheological and mechanical properties of PLA/PBAT blend (45:55 wt%). Throughout the processing cycles, an increase in the viscosity was observed and correlated with the presence of branched macromolecules in PBAT. Regarding the mechanical properties, the

elastic modulus increased while the elongation at break decreased with the number of extrusions, due to the decrease in molecular weight and the increase in crystallinity mainly in the PBAT phase. However, the five extrusion cycles did not significantly affect the thermomechanical properties of the blend, indicating that it can withstand more reprocessing cycles. The addition of PBS to PLA to improve its toughness and crystallization has been widely studied. These blends offer specific material properties. However, their favored biphasic composition, mainly leads to a restriction of their applications [106]. Thus, in PLLA/PBS blend (50:50 wt%), PBS nodules were included in PLLA matrix, acting as crystallization nuclei agents. After seven injection cycles of the blend, an increase of the crystallinity and a drop of the elongation at break were observed, and correlated with PLLA degradation. On the other hand, Young's modulus and the tensile strength remained relatively stable [107].

The melt molding recycling of PLA/PHBV (50:50 wt%) blend was studied by Zembouai et al. [76] up to six repeated processing cycles. M_n value of the blend was only reduced by 4.8% after six reprocessing cycles and the stability was relatively improved compared to the neat PHBV. Mechanical properties were maintained after processing cycles as tensile modulus and strain at break did not significantly change. However, the crystallization enthalpy of the blend increased from 32.9 J g^{-1} in the first cycle to 46.5 J g^{-1} after the sixth one, revealing a decrease in the molecular weight of PHBV which enhanced the polymer chain mobility and the crystallization kinetic. The addition of PLA may be a promising route to the thermomechanical stabilization of PHBV. In the same vein of PHBV stabilization, a blend of PHBV/PBS (50:50 wt%) was produced and processed six times by extrusion [108]. Blend viscosity was higher than that of neat polymers and crystallinity and mechanical properties were kept constant during recycling. This may be ascribed to chemical interactions between PHBV and PBS chains which delayed the PHBV degradation. However, seven cycles extrusion of PHBV/PBAT blend (35:65 wt%) resulted in a considerable increase in MFR after only three processing cycles. This was associated to a growing band intensities in the wavenumber range between 3200 and 3600 cm^{-1} in FT-IR fingerprint, indicating the formation of carboxylic groups. This exceptional strong rise in flowability was not reflected in the results of GPC which revealed a rather moderate decrease in M_n and slight increase in M_w . Due to moderate processing temperatures (between 135°C and 150°C), degradation is not likely for PHBV but repeated processing provoked hydrolytic degradation of PBAT leading to a dramatically decrease in viscosity [84].

3.2.3. Biocomposites and nanocomposites

The use of fibers and particles to reinforce biodegradable polyesters is a common strategy to improve the performance, the water sensitivity and the sustainability of these polymers while reducing the often high production costs. The production of reinforced PLA has been widely reported, while the recyclability of such materials is still under investigation.

The mechanical recycling of PLA compounded with 30 wt% of wood fibers was simulated through repeated extrusion and injection molding [109]. Compared to neat PLA, the bio-composite was able to sustain five cycles of reprocessing without a significant drop in its mechanical properties, except for elongation at break. Its degradation occurred after the sixth or seventh cycle. However, the ageing of the bio-composite through immersion in water at 50°C , clearly affected the morphology of the bio-composite, accelerating its degradation under reprocessing conditions. The reinforcement effect of natural fibers was highlighted in other studies. Composites consisting of 30% PLA and 70% cellulose fibers (v/v) were prepared by compression molding and ground to be used as fillers for virgin PLA [110]. The reprocessing of these materials by repeated cycles of injection molding showed that the composite material with 20 wt% filler could be processed six times, with an acceptable reduction in mechanical properties while the composite with 50 wt% filler suffered a significant degradation already after one cycle of

injection molding. Bio-composites based on PLLA and flax fibers, with fiber content of 20 and 30 wt%, have shown mechanical properties close to those of glass fiber/PP composite and superior to hemp/PP and sisal/PP materials [111]. After several injection cycles of PLLA/flax fiber composites, the mechanical properties were conserved until the third injection, even if polymer M_w and fiber length were slightly reduced. Bourmaud et al. [107] studied the recycling ability of a 50:50 wt% blend of PLLA-PBS, containing 30 wt% of flax fiber, through seven successive injection cycles. As expected, the introduction of flax fibers induced a strong increase of composite viscosity due to the fiber-polymer and fiber-fiber interactions restricting chain mobility. The mechanical properties during the first three injection cycles were maintained enough to consider recycling as an end-of-life option for these composites. On the other hand, Lopez and co-workers [25] reported that PLLA reinforced with 30 wt% cellulosic fibers obtained from a softwood chemithermo-mechanical pulp (CTMP) is an un-recyclable material since the mechanical properties of the composite strongly decreased after just one processing cycle, made it too brittle to be reprocessed. The large water affinity of CTMP fibers might cause an increase in the water content and then a faster hydrolytic degradation of the matrices.

Concerning nanocomposites, some studies investigated the main effects of reprocessing PLA with nanoparticles such as cellulose nanocrystals (CNCs) [112] and nanofibers (CNF) [113], non-organic nanoparticles such as clay [114] or chalk [115], or carbon nanosources like Graphene nanoplatelets (GnP) [116].

Cellulose nanocrystals are widely used for the reinforcement of PLA matrix [112]. However due to their hydrophilic nature, they often agglomerate and initiate degradation of the PLA backbone. To improve the dispersion of the CNCs, Dhar and co-workers [112] employed radical initiator dicumyl peroxide (DCP) to covalently crosslink PLA and CNCs. The resulting nanocomposite was processed by extrusion three times. NMR and FTIR structural analysis revealed the formation of C-C covalent linkages between PLA and CNCs during reactive extrusion. This led to improved processability, and higher melt and thermal stabilities of PLA-CNC nanocomposites. The maximum degradation temperature increased by $\sim 7\text{--}12^\circ\text{C}$, and viscosity and storage modulus were improved by ~ 10 and ~ 50 times, respectively.

In the study conducted by Heidarian and co-workers, recycled PLA was reinforced by bagasse CNFs with a diameter of 35 nm [113]. Nanocomposites containing 1 and 3 wt% CNFs have shown a good dispersion of nanofibers in the matrix and a drastic improvement in recycled PLA mechanical properties, especially for Young's modulus and strength at break. Nevertheless, recycled PLA with 3 wt% CNFs showed a slower biodegradability, compared to the neat polymer. This was attributed to the more diffusion resistance ability of compounds due to the presence of nanocellulose in the polymer amorphous domain.

The influence of thermomechanical treatments on PLA/mineral nanocomposites was studied through repeated extrusion cycles. Composites of PLA with nanoclay were reported to have better thermal stability and improved barrier properties compared to neat PLA [114]. Nanocomposites based on PLA and chalk (CaCO_3) 30 wt% were found to be mechanically reprocessable up to six times without suffering significant change in mechanical and thermal properties [115]. PLA reinforced with graphene (GnP) was submitted to five extrusion cycles [116] and the presence of GnP reduced the degradation rate of nanocomposite throughout the recycling processes.

The presence of nanoparticles provides better PLA stability during thermomechanical treatments. However, the biodegradability of the resulting nanocomposites must be questioned in view of the possible impact of non-biodegradable nanomaterials on the action of the microorganisms involved.

3.3. Conclusions about mechanical "recycling" of biopolyesters

To date, all the studies on the mechanical recycling of biodegradable bioplastic are based on thermomechanical reprocessing, and are still

performed at laboratory scale, since no industrial facility is yet available. The post-consumer recycling of bioplastics materials may be implemented, as soon as the commercial volumes and sales increase sufficiently to cover the investments required to install separate recycling streams. However, their thermal and thermos-oxidative instability is an obstacle to their mechanical recycling, condemning them to be down-cycled (despite certain efforts to stabilize them). Key innovation is to design closed-loop recycling strategies able to preserve the quality of recyclates and to promote their utilization in food and beverage packaging sector.

Next section will discuss the challenge and limitations related to the closed-loop recycling of biodegradable polyesters in food packaging applications.

4. Application for food contact: Decontamination of recycled biodegradable polymers

Recycled plastic intended to food contact requires special attentions and is subject to specific regulation by the European Commission. The issue of consumer safety is at the heart of the regulatory framework which must ensure the harmlessness of recycled materials. Post-consumer plastic may contain undesirable contaminants due to previous packaging use and/or domestic misuse, to contaminations during waste disposal (cross-contaminations, presence of non-food grade polymers), and also to the presence of additives and polymer degradation products. The persistence of these contaminants in the recycled packaging may pose a risk to human health by migrating into food. Therefore, mechanical recycling processes for food contact applications are subject to regulations and must meet specific requirements to ensure the safety of recycled packaging.

4.1. Safety of recycling processes for food contact plastic packaging

According to article 3 of the framework regulation (EC) No 1935/2004, any food contact material should not transfer constituents to food in quantities which could endanger human health, change the composition of the food or deteriorate its organoleptic characteristics. In the absence of specific directives or regulations, the application of this inertia principle for biodegradable materials is covered by regulation (EC) N°10/2011 [117], which sets out the procedures for checking the compliance of plastic materials. For all materials produced from a recycling process, the main concern about their suitability for food contact is their possible post-usage contamination. Post-consumer plastic packaging may contain a range of substances that can accumulate throughout the packaging life, from production (additives), use/misuse, and recycling (degradation products) [118,119].

Considering that the contaminants are very diverse and that it is not possible to test every packaging, the safety of the final product is ensured by controlling the quality of the raw material and the efficiency of recycling process to remove contaminants [120]. Thus, in Europe, each recycling process must be evaluated by EFSA (European Food Safety Authority), in order to obtain an authorization for the production of food-contact recycled plastic by submitting a evaluation following specific guidelines [121].

The decontamination efficiency of the recycling process is evaluated by specific challenge tests. These tests are implemented according to a worst-case scenario simulating high levels of contamination in plastic waste [122]. Most technologies, designed for bottle-to-bottle recycling of PET, rely on cleaning steps to reduce contaminant levels mainly by a thermal treatment under vacuum or inert gas to promote contaminant desorption. This thermal treatment usually occurs in the solid state (flakes or pellets incubated in a reactor) and sometimes in the melt phase (in the extruder) [119]. Surface treatment with non-hazardous chemicals are also found in some recycling processes. At process output, concentrations of residual surrogates (C_{res}) are analyzed to assess the cleaning efficiency, and compared to a modelled surrogate

concentration (C_{mod}) which represent the maximum surrogate concentration in plastic that corresponds to an acceptable upper limit of dietary exposure whose threshold is set to avoid any toxicological effect. C_{mod} is calculated by generally recognized diffusion models overestimating the real migration of contaminant into food. To satisfy the evaluation criterion, the recycling process has to demonstrate its ability to decontaminate the contaminated plastic up to a residual concentration (C_{res}) not higher than the modelled concentration (C_{mod}) [123]. Surrogates are organic compounds (also known as “model contaminants”) with different molecular weights, volatilities and polarities, with a variety of functional groups, representative of possible chemical classes of contaminants concern. Several studies have been carried out to identify and quantify the potential contamination of collected plastics. PET is the most frequently studied material. In Europe, the EU project FAIR-CT98-4318, provided a set of PET surrogates such as Toluene, Chlorobenzene or Phenyl cyclohexane, as a result from extensive experimental and analytical experiments [124]. A review of the literature data can also be found in a report from Franz et al. [125].

From 2010 to 2018, EFSA evaluated more than 130 processes for food-contact recycled plastics. In most cases, the evaluated processes concern PET recycling, since it presents a relatively high inertness and resistance to higher temperature than other polymers, it does not need much additives like antioxidants and plasticizers, and all PET raw materials are food grade [126]. The other recycling processes mainly refer to polyolefins (PP and/or HDPE) which require further cleaning because of their higher permeability to contaminants, and a higher migration rate (into food) compared to PET. In addition, polyolefins are much less temperature resistant, making more challenging their effective decontamination. However, it is not relevant to use the same surrogate panel as PET for the polyolefins challenge tests, since the barrier properties are strongly different [118]. To date, EFSA has not received applications for any others types of plastic. From 1990 to 2018, the US FDA has given 206 favorable opinions with 153, 22, and 21 submissions referred to PET, PS, and polyolefins food contact recycling processes respectively.

4.2. Food safety of recycled biodegradable biopolymers

As the market of biodegradable biopolymers is still very emerging, their mechanical recycling has not been addressed yet, and even less for food applications. Indeed, mechanical recycling of biodegradable plastics is a controversial issue. The supporters of this type of recycling claim that commercial biodegradable biopolymers such as PLA degrade slowly under ordinary conditions, even in the presence of microorganisms, with the risk to contribute to plastic soup in the future. Biodegradable plastics disposed in landfills may lead to methane and CO₂ emissions, with a negative climate impact. Further, the recycling of biopolymers is crucial in reducing the consumption of renewable resources needed for the synthesis of the corresponding monomers. At the opposite, the mechanical recycling opponents point out two main limitations which might curb the implementation of such process. First, bioplastics represent today less than 1% of the total amount of plastics, and it is not realistic to develop separate recycling streams for them to date. So, when they end up in mixed fraction (with other plastics) or in residue during sorting, they are not currently isolated and are eventually incinerated [127]. Indeed, to preserve the quality of recycled PET, the PLA contamination should be maintained below 0.1% [128]. In the case of PP, the amount of PLA or PHB should not exceed 5% [129]. Moreover, they argue that the recyclates resulting from such materials show lower mechanical and thermal properties compared to original plastics and do not produce secondary material of high quality. The arguments of the detractors of the mechanical recycling of biodegradable plastics can be now considered as unfounded. The increase in PLA and PBS production will lead to the new separate recycling stream that should be implemented in the short to medium term (it is estimated that one type of bioplastic should reach 5–10% volume within plastic recycling system [130]). In addition, in the case of mixed plastic waste streams, biobased

and biodegradable polymers can be sorted out by employing NIR (Near Infra-Red) technology. For example, at a commercial scale, PLA has been sorted by means of NIR, with a minimum sorting efficiency of 97,5% [131]. On the other hand, the polymer degradation during the recycling process is not something peculiar to bioplastics. Even conventional plastics are prone to degrade under recycling conditions. If feeding with virgin plastic was the solution adopted to improve the quality of recycled oil-based plastics, it is imperative not to be restricted to this idea, and to exploit the wide field of opportunities that bioplastics recycling still offers. For instance, it would be interesting to strengthen studies in additives and stabilizers, especially natural molecules and macromolecules. These latter are not harmful for environment and human health and can play an important role in improving bioplastics for durable uses by providing cost reduction, reinforcement, increasing thermal resistance and crystallization rate, inhibiting oxidation ... Another option is to invest on the implementation of combined valorization techniques. For example, favoring chemical and biological recycling, after several cycles of mechanical recycling.

Even more, many challenges remain to achieve mechanical closed-loop recycling of biodegradable plastics. With regards to their particular transfer properties and their ability to absorb different substances, the well-known approaches used for PET seems not be adequate to ensure the safety of biodegradable biopolymers [119]. There is a need of further studies dealing with the possible contaminants specific to these polymers and to implement specific challenge tests with an adequate representative panel of surrogates with different polarities and molecular weight. The decontamination of higher molecular weight contaminant should be carefully assessed since the desorption efficiency decreases with an increasing in contaminants molecular weight.

5. Conclusion

Although gathered under a common generic denomination, bioplastics and biodegradable plastics integrate a great variety of polymers. Their different structures provide a reactivity and differentiated properties which defines the opportunities and options for their end-of-life treatments. This review covers the studies dealing with the mechanical recyclability of the main promising biodegradable biopolyesters, PLA, PHAs, PBAT and PBS within the last ten years. The study of degradation mechanisms during reprocessing steps highlighted the structural degradation of all studied polymers under the influence of thermal, thermomechanical and thermos-oxidative treatments. It is assumed that the quality grade of the output raw material from the recycling process determines its range of use for food and non-food applications. If different methods have been attempted to improve the properties of recycled polymers including thermal and chemical treatments, production of blends, bio-composites or nano-composites, all these strategies raise new concern about their impact on the recycling process and on the suitability for food contact of the packaging derived from the secondary material.

Despite the promising preliminary results on the mechanical reprocessing of biodegradable biopolymers, the closed-loop recycling for food applications is still not studied. It seems certain that the approach currently used for assessing the safety of PET recycling technologies cannot be extrapolated to the biopolyesters. In addition to the economic and logistical considerations specific to each territory, the emergence of a recycling system for biopolyester-based materials requires indispensable technological progress, such as (I) the improvement of the performance of the processes which should as far as possible avoid/limit the degradation of more sensitive bio-polyesters than PET and (II) the provision of guidelines describing how to evaluate these processes, particularly in terms of decontamination efficiency. In this way, the safety assessment of the mechanical recycling process should be deeper investigated, taking into account the polymer specificities (transport and barrier properties) in order to implement an adequate challenge test.

Author agreement statement

We the undersigned declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

We understand that the Corresponding Author is the sole contact for the Editorial process. He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

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