Recycling of bioplastic waste: A review

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ABSTRACT

Replacing conventional plastics with bioplastics, i.e., plastics that are bioderived and/or biodegradable, does not necessarily solve the issues of resource depletion and plastic waste accumulation. To come to a truly sustainable plastics economy, the growing bioplastics production must be paralleled with effective end-of-life strategies for bioplastic waste, which is essential for all bioplastics, regardless of their biodegradability. While there is no doubt on the importance to recycle biobased non-biodegradable bioplastics such as bio-polyethylene terephthalate (bioPET), bio-polyethylene (bioPE), and bio-polypropylene (bioPP), the scenario is not as clear for biodegradable bioplastics, for which biodegradation is often seen as the only acceptable end-of-life option. However, biodegradation is normally not aimed at recovering plastic materials or monomers to be reintroduced in the life cycle of plastic products, while this is specifically the aim of other types of recycling options, such as mechanical and chemical recycling, which address both waste management and primary resource preservation. Hence, since bioplastics production is growing and such materials will coexist with conventional plastics for decades to come, it is vital to find the best end-of-life pathways for each of the most common bioplastics.
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1. Introduction

Plastic materials pervade our life. Even though the industrial-scale production of plastics started only in the 1950s, they have rapidly become essential for everyday life and high-end applications thanks to their low bulk density, high durability, good processability, excellent mechanical and barrier properties, and low cost [1]. Their versatility has triggered the rapid increase in the volume of plastic produced annually over the last few decades and this quantity continues to grow. Approx. 311 million tonnes (MT) of plastic were produced globally in 2014, the synthesis of which consumed 6% of the worldwide oil production [2]. The world plastics production was 350 MT in 2017 [3] and 368 MT in 2019 [4]. Of the overall plastics production in Europe in 2019, 39.6% by weight was devoted to packaging and 20.4% to construction, which by far represent the largest end-use markets [4], while the main polymers produced were polyolefins such as polyethylene (29.8%) and polypropylene (19.4%).

However, the same properties that render plastics so useful also make the increasing amount of plastic waste, if improperly managed, a substantial environmental threat [5]. In Europe, the amount of plastic waste sent to recycling has doubled in the period from 2006 to 2018, but 25 wt% of plastic post-consumer waste (i.e., 7.2 MT) in 2018 was still sent to landfill [4]. Current projections indicate that 12 billion tonnes of plastic waste will end up in landfills or the natural environment by 2050, compared to the 4.9 billion tonnes found in 2015 [6]. Moreover, it has been estimated that, from 2010 to 2025, 100 MT of plastic waste will have entered the marine environment, where it will slowly degrade and fragment to form microplastics [6,7]. Therefore, the issue of plastic waste collection and treatment, together with the non-renewable origin of most commercial plastics, has lately focused significant academic and industrial efforts towards more sustainable yet equally performing options [8].

A promising alternative is represented by bioplastics, defined as plastics that are biodegradable and/or derived from renewable resources [8–11]. Biodegradable bioplastics have alternative routes for waste disposal, thus limiting the amount of plastic waste ending up in our environment, while bioderived bioplastics allow a substantial reduction in the carbon footprint in the stage of resource extraction [12].

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List of acronyms

Acronym/symbol	Description
bioPAs	bio-polyamides
bioPC	bio-polycarbonate
bioPE	bio-polyethylene
bioPET	bio-poly(ethylene terephthalate)
bioPMMA	bio-poly(methyl methacrylate)
bioPP	bio-polypropylene
bioPTT	bio-poly(trimethylene terephthalate)
bioPVC	bio-poly(vinyl chloride)
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
DS	degree of substitution
FDCA	furandicarboxylic acid
HDPE	high-density polyethylene
HFM	5-hydroxymethylfurfural
kT	thousand tonnes
LCA	life cycle assessment
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MT	million tonnes
NIR	near-infrared
P(LLA-CL)	poly(L-lactic acid-co-ε-caprolactone)
P(LLA-TMC)	poly(L-lactic acid-co-trimethylene carbonate)
PA	polyamide
PAF	poly(2,5-alkylene furanoate)
PAT	poly(alkylene terephthalate)
PBA	poly(butylene adipate)
PBAT	poly(butylene adipate terephthalate)
PBS	poly(butylene succinate)
PBSA	poly(butylene succinate-co-adipate)
PBSL	poly(butylene succinate-co-lactate)
PCL	polycaprolactone
PDLA	poly(D-lactic acid)
PDLLA	poly (L, D-lactic acid)
PDO	1,3-propanediol
PE	polyethylene
PEF	poly(ethylene furanoate)
PES	poly(ethylene succinate)
PET	poly(ethylene terephthalate)
PGA	polyglycolic acid
PHAs	polyhydroxyalkanoates
PHB	poly(3-hydroxybutyrate)
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	poly(lactic acid)
PLLA	poly(L-lactic acid)
PP	polypropylene
PS	polystyrene
PTT	poly-trimethylene terephthalate
PVA	polyvinyl alcohol
RIC	resin identification code
SEI	socio-economic indicator
TA	terephthalic acid
T_g	glass transition temperature
T_m	melting temperature
TPS	thermoplastic starch
VFA	volatile fatty acid

The intense investigation of the last few decades resulted in the commercialization of several bioplastics of industrial interest, such as poly(lactic acid) (PLA) [9], polyhydroxyalkanoates (PHAs) [13,14], poly(butylene succinate) (PBS) [15], and thermoplastic starch (TPS) [16,17], but also bio-poly(ethylene terephthalate) (bioPET) and bio-polyethylene (bioPE), which are similar to their non-renewable counterparts [18,19]. However, although bioplastics have been studied for nearly a century, their extensive industrialization is still embryonic. According to the report of the European Bioplastics Association, global bioplastic production in 2019 was 2.11 MT, i.e. only 0.6% of the total plastics production [20], and it is predicted to reach 2.89 MT by 2025 [11,21] (Fig. 1). The main reasons for the limited application of bioplastics stem from the more expensive production and generally inferior mechanical properties compared to petrochemical plastics [22]. Nevertheless, as the world urgently needs an efficient alternative to petroleum-based plastics, the growth of the bioplastics market over that of petrochemical plastics is expected to be considerable in the next years.

However, replacing petroleum-based plastics with bioplastics does not necessarily solve the plastic waste issue. To increase the sustainability of bioplastics overall their whole life cycle, the increasing bioplastics production must be coupled with the implementation of effective strategies to manage bioplastic products at their end of life. Among these strategies, recycling, and mechanical recycling in particular, must play a prominent role, as it allows reducing emissions, the carbon footprint as well as the consumption of raw materials, as pointed out by many life cycle assessment (LCA) studies [23,24]. This is fundamental for all plastic products, included those made of bioderived and biodegradable plastics.

This review is focused on the most industrially interesting bioplastics and describes their disposal options, with particular attention on mechanical recycling. After a paragraph stressing the importance of bioplastics recycling (Section 1.1), this review describes the most promising bioplastics in terms of properties, applications, and market share (Section 2), and then discusses their main recycling and disposal options (Section 3), also presenting some case studies referred to PLA and PHAs recycling (Section 4). The most important outcomes of this analysis, together with the future perspectives, are presented in the concluding remarks (Section 5).

1.1. Benefits and challenges of bioplastics recycling

The life cycle of plastics, regardless of their origin and biodegradability, is truly sustainable only if the disposal options include recycling. Although everyone agrees on the convenience of recycling non-biodegradable plastics, regardless of their origin, the same is not true for biodegradable plastics, for which biodegradation is often seen as the only appropriate disposal option. However, most commercial biodegradable bioplastics (e.g., PLA and PHAs) degrade slowly under ambient conditions, even in presence of microorganisms, which may strongly limit the theoretical advantages of using bioplastics to avoid environmental pollution [20]. Moreover, the biodegradation of plastics in the environment or landfills can lead to uncontrolled methane emissions, with a negative environmental impact [20]. Biodegradation of commercial bioplastics must be performed in specific composting plants, but this should be seen as the very last life cycle step, after many steps of reuse and recycling. In fact, bioplastics disposal results in discarding valuable bioderived molecules and raw materials (e.g., lactic acid for PLA). In this optics, chemical recycling can transform waste bioplastics into alternative feedstocks for monomers and
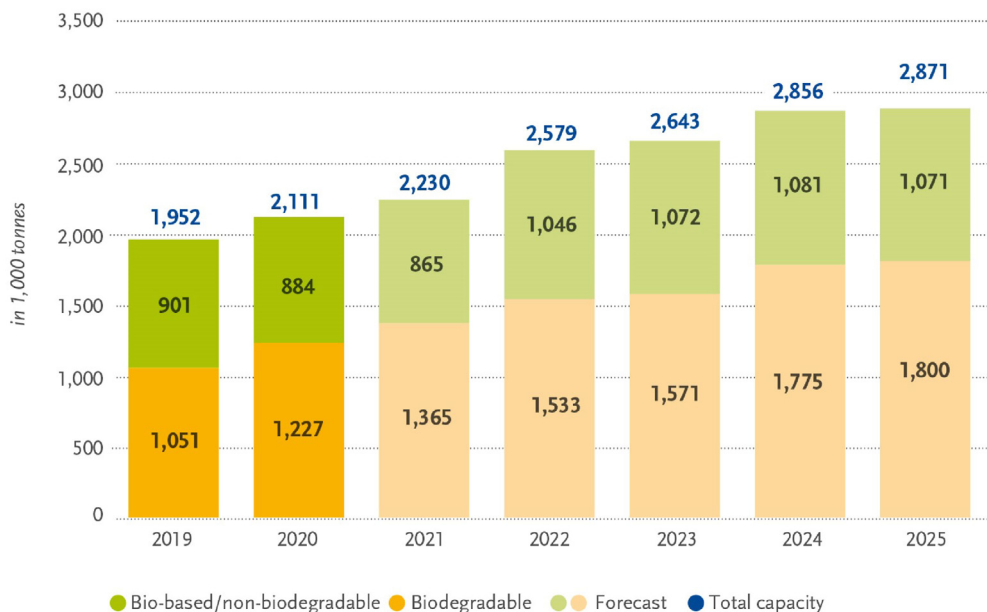
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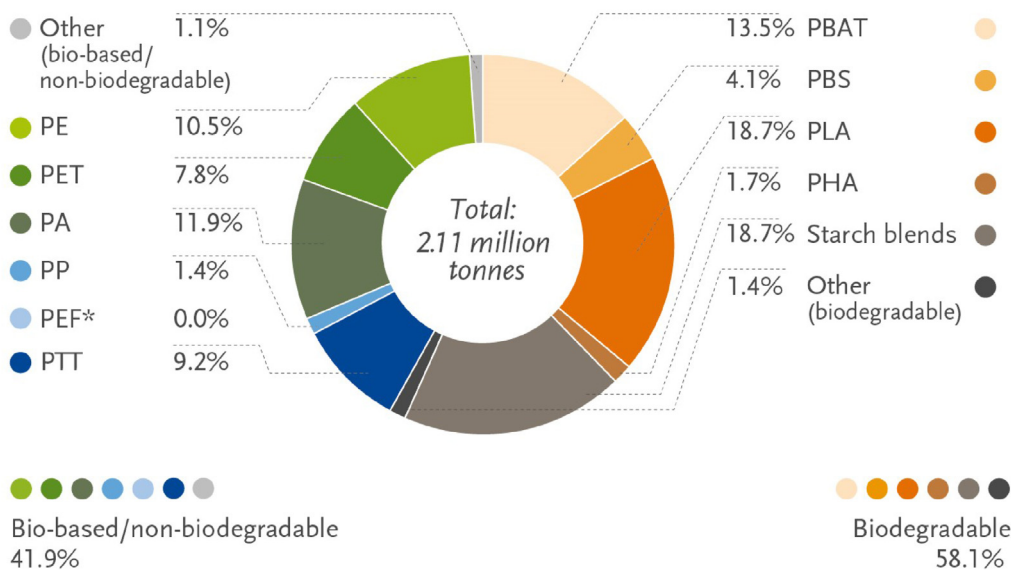
(b)

Fig. 1. Global production capacity of bioplastics in 2020. (a) Total production of biodegradable and non-biodegradable plastics and forecasts; (b) production capacities by material type (reprinted with permission from Ref. [25]).

intermediate products, thereby preserving primary renewable re-sources and further decreasing the bioplastics' environmental impact [20].

Furthermore, whilst bio-based non-biodegradable polymers such as bioPET or bioPE can be mixed with their petrochemical-derived counterparts and recycled in the same recycling facilities, this does not always apply for biodegradable bioplastics [26]. For example, the current plastic bottle reclaiming industry, which

mainly processes PET and high-density polyethylene (HDPE), has well-established working technologies, satisfied customers, raw materials, and investors. If the current materials mix is expanded with new materials, this will require satisfying all these re-quirements also for those materials [27]. Biodegradable bioplastics, especially those used for packaging, are entering both the streams of plastics recycling and green-waste composting, and this could result in increased sorting cost, yield loss, and decreased processability

and quality of the recycled or composted output [26]. On the other hand, implementing independent recycling streams would be subordinated to reaching a critical mass of collected bioplastic waste and to developing technologically viable, effective, efficient, and economical recovery systems and end markets for post-consumer bio-based materials [27].

In conclusion, since the bioplastics market is predicted to grow in the next years, bioplastics and conventional plastics are expected to coexist for many years to come, and it is thus essential to address the issue of recycling both biodegradable and non-biodegradable bioplastics and to study their most effective recycling pathways.

2. Classification of main commercial bioplastics: properties and applications

According to European Bioplastics Association, "bioplastics are either bio-based, biodegradable or feature both properties" [21]. The practical meaning of these two words, "bio-based" and "biodegradable", is defined by international standards [3]. Biodegradable plastics are certified according to several standards defining precise conditions for composting, such as ISO 17088:2012, ISO 14855-2:2018, EN 13432:2000, EN 14995:2006, ASTM D6400-19, ASTM D5338-15, and AS 4736. For example, ASTM D6400-19 states that three main requirements must be satisfied to identify a product as compostable in municipal or industrial aerobic facilities, i.e., (i) the product should disintegrate during composting in 84 days so that a maximum of 10% of its original weight remains after sieving on a 2-mm sieve, (ii) 90% of the organic carbon should be converted to CO_2 within 180 days, and (iii) the product should not negatively influence the ability of composts to support plant growth when compared to biowaste-derived composts not containing that product.

On the other hand, bio-based polymers, regardless of their biodegradability, are mainly certified according to EN 16640:2015, EN 16785-1:2015, ISO 16620 4:2016, and ASTM 6866-18, which measure the renewable, "young" carbon fraction through ^{14}C measurements or radiocarbon and elemental analysis [20], although there are notable exceptions to this classification, as discussed in Section 2.1.1.2. Therefore, bioplastics can be divided into three groups (Fig. 2):

- Biodegradable plastics produced from biobased resources, such as PLA, PHAs, TPS, and PBS;
- Biodegradable plastics produced from petrochemical resources, such as poly(butylene adipate terephthalate) (PBAT) and poly-caprolactone (PCL);
- Non-biodegradable or partially biodegradable plastics from biobased monomers, such as bioPE, bioPET, bioPP, but also bio-derived technical polymers, such as poly-trimethylene terephthalate (bioPTT) or some polyamides (bioPAs).

Among biodegradable plastics, PLA and starch blends account for the largest market share (18.7% each) (Fig. 1), while PBAT follows with a share of 13.5%. Among non-biodegradable bioplastics, the four major players are bioPE (10.5%), bioPET (7.8%), bioPAs (11.9%) and bioPTT (9.2%) [3], while other interesting biobased non-biodegradable bioplastics are bioderived polycarbonate (bioPC), poly(methyl methacrylate) (bioPMMA) and poly(vinyl chloride) (bioPVC) [29]. Among the applications of bioplastics (Fig. 3), packaging is the largest market, accounting for more than 53% of the total weight share (1.14 MT in 2019) [20,21]. However, bioplastics are being employed in an increasing number of markets, such as the agriculture, textiles, and automotive sectors.

The following paragraphs cover the main commercial bioplastics classified into one of the three categories identified in Fig. 2, i.e., biobased biodegradable, petrochemical-based biodegradable, and biobased non-biodegradable bioplastics.

2.1. Biodegradable plastics

Although biodegradable plastics have attracted considerable academic and industrial attention only over the last three decades, these materials have a history of more than 100 years. Scientists have tried to synthesize biodegradable and biobased plastics since the late 1800s, when a biodegradable plastic called Galalith™ was synthesized starting from the milk protein casein, while in 1925 polyhydroxybutyrate (PHB) was synthesized as the first bioplastic made from bacteria [3]. However, in the early 1900s, as petroleum became the primary source of fuel and chemicals, these biobased and biodegradable bioplastics have been replaced by inexpensive, durable, and versatile petrochemical plastics. In the early 2000s, the environmental pollution resulting from the wrong use and disposal of such plastics have focused again the public attention on biodegradable plastics, due to their alternative disposal pathways and the related environmental benefits [3]. Plastics biodegradability depends on material chemistry, product morphology, and environmental conditions such as temperature, pressure, oxygen concentration, and bacterial population. It should be stressed that biodegradable plastics are mainly designed to degrade under specific conditions, most commonly in industrial composting plants in a controlled environment. Unless they are designed to biodegrade in a specific environment, e.g., soil or marine water, they will not degrade in these environments, or their degradation will be very slow [3].

The synthesis of biodegradable polymers can per performed via [3]:

- mechanochemical modification of a natural polymer, such as cellulose or starch;
- chemical synthesis from a monomer produced by biotechnological conversion of a renewable resource (e.g., PLA from lactic acid produced via sugar fermentation) or by chemical processing of non-renewable resources (e.g., polyvinyl alcohol (PVA));
- bacterial synthesis of polymers from microorganisms (e.g., PHB).

Processing biodegradable plastics is similar to that of conventional plastics and can be performed using the same equipment, but some important aspects must be considered, linked especially to moisture absorption and thermal degradation. Generally speaking, many biodegradable plastics tend to be considerably hygroscopic, and moisture can cause an uncontrolled reduction in viscosity, undesired foaming, and acceleration of hydrolysis. Hence, moisture must be carefully eliminated from the material before and during processing. Moreover, biodegradable plastics are susceptible to thermal degradation, so they must be processed with the mildest possible temperature and residence time, to avoid chain scission and depolymerization [3].

Biodegradable plastics have found use in many single-use applications where biodegradability can be exploited as a fundamental beneficial feature, such as in packaging, food services, and agriculture. Biodegradable plastics are used to produce compostable waste bags, mulch films, catering or food service products, and packaging for fresh and perishable food. A special category of biodegradable plastics is that of biomedical bioresorbable polymers, whose capability of biodegrading in living organisms makes them suitable to produce resorbable sutures, staples, wound dressing products, screws, plates, and drug release agents [3].

Biodegradable plastics can be divided into two groups, regarding whether they are synthesized from renewable or non-renewable resources. The following two sub-paragraphs present the most industrially interesting biodegradable polymers classified according to their origin.
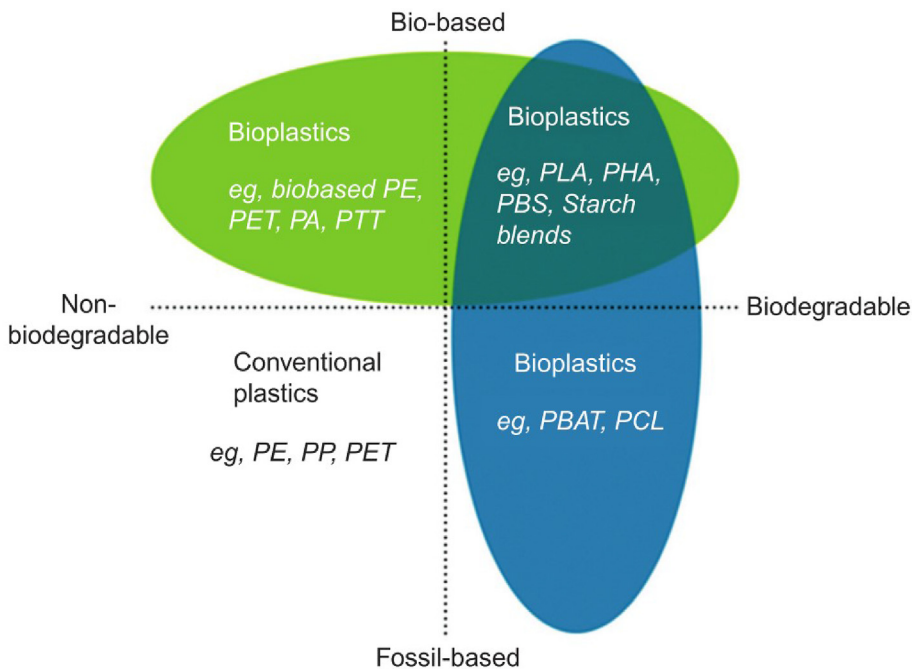
Fig. 2. Classification of plastic materials based on their origin and biodegradability (reprinted with permission from Ref. [28]).
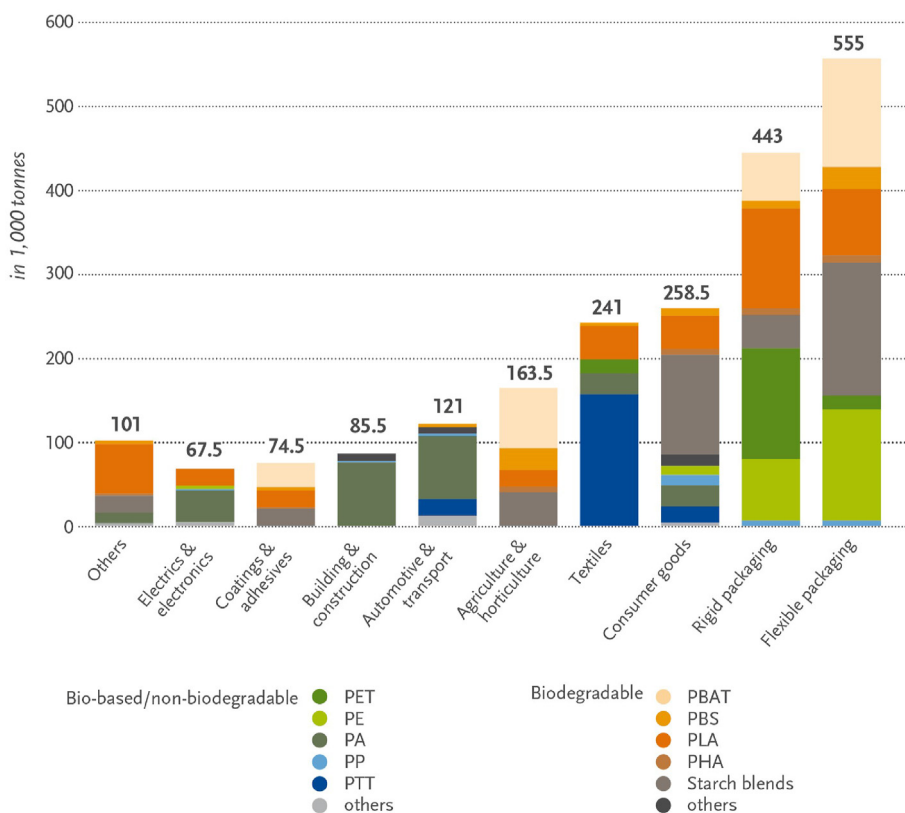

Fig. 3. Bioplastics application by market segment (reprinted with permission from Ref. [25]).

2.1.1. Biodegradable plastics from biobased resources

2.1.1.1. Polylactic acid (PLA). Polylactic acid or polylactide (PLA), one of the most interesting and widely used biodegradable bioplastics, was first synthesized by the DuPont scientist Carothers in 1932 and became the first bioderived and biodegradable polymer produced at an industrial scale in the late 1990s [3]. PLA is a linear aliphatic polyester synthesized by the ionic polymerization of lactide, which is produced by the dehydration-condensation of two lactic acid molecules. Lactic acid is obtained via the fermentation of glucose, which can be derived from various biosources such as sugar cane,

corn, potatoes, and tapioca [30,31]. Since lactic acid exists in two optical forms, i.e., L-lactic acid and D-lactic acid, there are three lactide isomers, namely L-lactide, D-lactide, and D-L-lactide (or meso lactide) [32,33]. The polymerization of L-lactide and D-lactide results in poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), respectively, semicrystalline polymers with very similar properties [34,35]. Commercial PLA is generally PLLA with a small content (2−4%) of D-lactide [36]. On the other hand, the polymerization of meso lactide yields the amorphous poly (L, D-lactic acid) (PDLLA) [37,38].

PLA degrades in the environment in 6−24 months, depending on the size and shape of the product, its isomer ratio, and temperature. PLA is water-insoluble but unstable if exposed to halogenated hydrocarbons, and shows good thermomechanical properties, similar to PET and PP, although it has some inherent shortcomings, such as brittleness and elevated moisture uptake [3,9]. The mechanical properties of PLA also depend on the annealing/orientation treatments as well as the degree of crystallinity. PLLA generally shows high tensile modulus (approx. 3 GPa), good mechanical strength (approx. 60 MPa), high workability, and transparency [9]. For all these reasons it has been intensively applied especially in packaging applications, to produce disposable cups, bowls, films, bottles, and jars. PLA is also applied to produce clothes and furniture textiles, hygiene products, disposable cutlery, and mulch films for agriculture. Foamed PLA is used as an insulator and represents an alternative to polystyrene (PS) foam [39−41].

2.1.1.2. Polyhydroxyalkanoates (PHAs). Polyhydroxyalkanoates (PHAs) are bioderived and biodegradable aliphatic polyesters synthesized via the polymerization of β-, γ-, and δ-hydroxyalkanoic acids, which are obtained mainly through the fermentation of sugar and lipids (i.e., glucose, sucrose, vegetable oils) coming from a wide variety of feedstocks [42,43]. However, other sustainable carbon sources have been considered, such as wood chips, cardboard cutouts, and waste plastic bottles and bags [44,45]. In this very last case, if the plastic waste is of petrochemical source, the resulting PHAs will not contain a significant fraction of "young" carbon (please refer to Section 2), but they can still be classified as bioderived polymers.

Hydroxyalkanoic acids can be polymerized by a wide variety of bacteria, which synthesize PHAs as a carbon and energy reserve when subjected to stressful conditions [46]. These bacteria can combine more than 150 monomers, thereby obtaining different homopolymers and copolymers according to the type of bacteria and the culture conditions [47−49]. PHA synthesis is encouraged in conditions of shortage of phosphorus, nitrogen, and oxygen and excess of carbon, and the quantity of PHA may represent up to 80% of the cell dry weight. Large-scale PHA production involves expensive fermentation, isolation, and purification processes, and therefore a real market breakthrough for PHAs will be achieved only after a considerable increase in the process yields [50−52]. In any case, PHAs are driving the growth of the biodegradable bioplastics market and, in the next five years, the production capacity of PHAs is expected to triple [21].

The general chemical formula of PHAs is reported in Fig. 4. The most diffused PHAs are poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). PHB has a high elastic modulus and is a better barrier than PLA for water vapor and UV−visible light, but it shows a high brittleness and low thermal stability in the molten state, which narrows the temperature processing window and poses considerable processing challenges. These two shortcomings are partially solved in the PHBV copolymer, which has achieved certain economic importance because of its PP-like properties. PHBV, commercially available with a hydroxyvalerate (HV) content of up to 15%, shows enhanced flexibility and
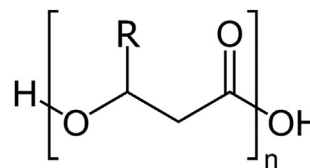
Fig. 4. General formula of polyhydroxyalkanoates (PHAs). $R = CH_3$ for poly(3-hydroxybutyrate) (PHB), while $R = C_2H_5$ for poly(3-hydroxyvalerate).

a lower processing temperature than PHB. A further toughness increase would be achieved by increasing the HV content, but this is currently not commercially viable due to the excessive production cost [3].

Similar to PLA, PHAs have various applications as single-use items in the packaging and biomedical fields. For example, thanks to their high biocompatibility, PHB and PHBV are under investigation to produce bioresorbable surgical sutures, wound dressings, tissue scaffolds, bone fracture fixation plates, and porous sheets for stimulation of tissue regeneration in injured soft tissues [22,43]. The biodegradability of PHAs mainly depends on chain configuration, crystallinity, and processing conditions. For example, copolymers have a higher degradation rate than homopolymers. Among the advantages of PHAs is also the relatively high degradation rate in marine environments. After one year in a marine environment at 30 °C, PLA only biodegrades by approx. 8%, while PHBV by approx. 80% [11].

2.1.1.3. Starch-based plastics. Starch is the second most abundant organic compound on earth after cellulose. It belongs to the family of carbohydrates and is produced by plants as a food reserve. Starch consists of two major polysaccharides, i.e., the linear amylose (10−30%) and the highly branched amylopectin (70−90%). Commercially available starch is mainly derived from plants such as wheat, rice, corn, potato, and barley, for which starch composes 60−90% of the dry weight [53]. Starch-based materials are attracting increasing interest as they biodegrade completely and relatively quickly and are largely available from renewable sources at low cost [17,54,55].

To produce starch-based plastics, native starch must first be destructurized to make it thermoplastic and melt-processable. This is achieved by using plasticizers such as water, glycerin, or other polyols, and/or by thermomechanical processes. This results in obtaining thermoplastic starch (TPS), which can be processed with standard equipment used for synthetic plastics and can be blended and additivated to adjust its physical−mechanical properties, such as stiffness, strength, and water solubility [56−59]. Quickly biodegradable starch-based plastics are used to produce packaging products such as bags for biowaste disposal and thermoformed trays, agricultural items such as mulching films and plant pots, and hygiene and cosmetic products [55,60].

2.1.1.4. Cellulose-based plastics. Cellulose is the most abundant polymer on Earth and is produced by plants as a structural polymer, but it can be also synthesized by acetic acid bacteria. Plant cellulose is generally mixed with other polymers such as lignin, hemicelluloses, and pectin, whereas bacterial cellulose has a very high purity [3].

Similarly to starch, cellulose is a complex polysaccharide, and it is a linear homopolymer composed of monomeric glucose units interconnected with β-1,4 linkages. Cellulose is more resistant to hydrolysis than starch due to the stronger hydrogen bonds. Like starch, native cellulose is not a thermoplastic polymer as it degrades before melting, and therefore it must be modified to obtain a

thermoplastic material. Among the most diffused cellulose derivatives are cellulose esters and ethers such as cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB), which generally are very stiff but also brittle and very hygroscopic [61,62]. The biodegradability of cellulose derivatives depends on the degree of substitution (DS), i.e., the number of substituents per anhydroglucose unit, ranging from 0 to 3. For example, cellulose acetates with a DS of 1.5 degrade relatively rapidly, while those with a DS of 2.5 can still be biodegraded, but only by certain microorganisms and at a very slow rate [62—64].

2.1.2. Biodegradable plastics from petrochemical resources

Synthetic polymers are generally obtained from crude oil, but also from natural gas and coal. Since these polymers do not occur in nature, most of them are not biodegradable or compostable. However, degradability can be achieved by integrating unstable (amide, ether, or ester) bonds that can undergo hydrolysis under certain conditions [3]. The result is represented by a small group of biodegradable fossil-based plastics, used mainly in blend with biobased biodegradable polymers to enhance their thermo-mechanical properties, but showing some niche applications also as homopolymers. The most prominent polymers of this group are PBS, PCL, PVA, and PBAT, whose chemical formula is shown in Fig. 5.

2.1.2.1. Poly(butylene succinate) (PBS).
PBS is a biodegradable aliphatic thermoplastic polyester synthesized from 1,4-butanediol and succinic acid by condensation polymerization [65,66]. PBS belongs to the family of poly(alkylene alkanoate)s similarly to the less common poly(ethylene succinate) (PES), poly(butylene adipate) (PBA), and poly(butylene succinate-co-adipate) (PBSA). PBS can be produced from renewable or non-renewable monomers, but the vast majority of commercially available PBS is produced from fossil-based resources.

PBS is a semicrystalline thermoplastic polymer with a glass transition temperature (T_g) of $-45/-10$ °C, a melting point (T_m) of 90/120 °C, and a high strain at break (up to 330%), comparable with that of PE and PP [66]. On the other hand, the high crystallinity degree determines a relatively slow biodegradation rate. PBS is used for many applications such as food packaging films, shopping bags, agriculture mulch film, plant pots, hygiene products, while it is not largely employed in the biomedical field due to the scarce biocompatibility and bioactivity. PBS is also used in blends and composites, where fillers are added to improve thermal

conductivity, mechanical performance, gas-barrier properties, or flame resistance [67—69].

2.1.2.2. Polycaprolactone (PCL).
PCL is a linear aliphatic biodegradable polyester belonging to the family of poly(ω-hydroxyalkanoate)s and produced through the ring-opening polymerization of caprolactone. PCL is a semicrystalline polymer with high toughness and flexibility, showing a glass transition temperature of -60 °C and a melting point of approx. 60 °C [70]. Its biocompatibility and slow degradation in *in vivo* conditions (1—2 years) also enable its use for medical applications that require slow bioresorbability, such as some sutures, drug delivery systems, and tissue engineering scaffolds [71—73]. Similarly to other biodegradable plastics of petrochemical origin, PCL is also used in blends with biobased biodegradable plastics, as starch-based polymers, PLA, PHAs, and PBS [74].

2.1.2.3. Polyvinyl alcohol (PVA).
Polyvinyl alcohol (PVA) is a thermoplastic, biodegradable, and biocompatible polymer obtained through the hydrolysis of poly(vinyl acetate). PVA is water-soluble but resistant to most organic solvents. Its properties depend on the degree of hydrolysis, which can be full or partial and typically varies between 80% to more than 99% [75]. The higher the degree of hydrolysis, the higher the crystallinity and water solubility [76].

It is commonly used in multilayer assembly for food packaging applications due to its excellent film-forming capability and oxygen-barrier properties. Applications also include chemicals for water treatment, dyes, detergents, disinfectants, and agricultural products [76—78]. It is also largely employed to produce fibers through various spinning techniques including electrospinning. PVA fibers are used especially in the biomedical field and to increase the mechanical properties of cementitious materials [77,79,80].

2.1.2.4. Poly(butylene adipate terephthalate) (PBAT).
Poly(butylene adipate terephthalate) (PBAT) is a biodegradable aliphatic-aromatic random copolyester, derived from a poly-condensation reaction of adipic acid, terephthalic acid, and 1,4-butanediol. PBAT possesses excellent toughness, improved wear and fracture resistance, good chemical resistance to water and oils, high strain at break (700%), but low tensile strength (approx. 30 MPa). It is widely used for compostable organic waste bags, agricultural mulch films, as well as for packaging (wrapping) films, and disposable tableware [81,82]. Similarly to PCL, it is also widely
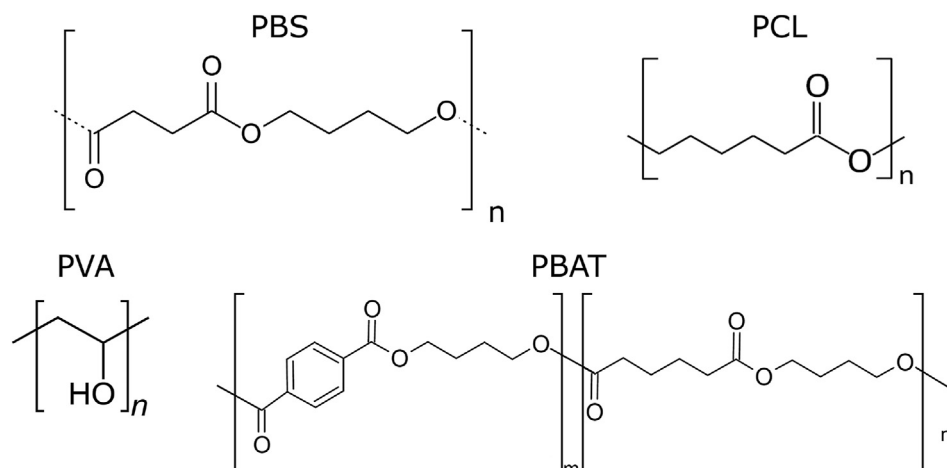

Fig. 5. Chemical formula of poly(butylene succinate) (PBS), polycaprolactone (PCL), polyvinyl alcohol (PVA), and poly(butylene adipate terephthalate) (PBAT).

used in blends with starch-based plastics, PLA, and PHAs, but also with engineering polymers like polycarbonate [69,83].

2.2. Non-biodegradable or partially biodegradable plastics from biobased monomers

The last group of bioplastic materials is that of biobased non-biodegradable plastics. Biobased plastics refer to all plastics obtainable from fermentation and dehydration of biomass, which comprises all non-fossilized and biodegradable organic material from plants, animals, and microorganisms, as reported in the standard UNI EN 17228:2019 [3]. Although biomass is biodegradable, this does not apply to all intermediates and polymers produced from it.

Bioderived non-biodegradable bioplastics do not feature the interesting alternative disposal option of biodegradation and present the same problems of waste accumulation as traditional petrochemical plastics. Nonetheless, they can increase the sustainability of plastics products especially in the first stages of the life cycle, concerning raw materials extraction, which explains the ever-growing interest in this plastics class.

The most commercially attractive non-biodegradable plastics fully or partially derived from renewable resources are the bio-counterparts of the most widely used petrochemical plastics, such as PE, PP, and PET. However, other bioderived polymers are approaching the market, such as polyethylene furanoate (PEF) and other polyesters derived from 2,5-furandicarboxylate [18].

2.2.1. Bio-polyethylene (bioPE)

Polyethylene (PE) represents approx. 30% of total plastics production [4]. It is synthesized through the polymerization of ethylene via different conditions of temperature and pressure and in presence of various catalysts, which results in different PE types (e.g., HDPE, low-density PE (LDPE), linear low-density PE (LLDPE)). The versatility of PE can be further expanded by copolymerization, for example by using other alkenes as comonomers, such as 1-propene, 1-butene, 1-pentene, 1-hexene, 4-methyl-pentene-1, 1-heptene, and 1-octene. Ethylene was mainly produced from ethanol until the early 1900s and then from the steam cracking of hydrocarbons at 750—950 °C, due to the inexpensiveness of crude oil, but it can also be produced from fully renewable resources [11]. BioPE is obtained from the polymerization of bioethylene, in turn obtained from the dehydration of bioethanol using solid acid catalysts such as alumina or silica-alumina at approx. 400 °C [18,19,22].

At the beginning, the production of bioethylene was not considered to be cost-competitive compared to fossil-based ethylene, but since 2008 the price of a barrel of ethanol from sugar cane (approx. $115 US) has become competitive with the price of a barrel of crude oil (approx. $80 US). Nowadays, 1 kg of bioPE is approx. 30% more expensive than petrochemical PE [3,18,28]. The industrial production of bioPE started in 2010, when the Brazilian company Braskem started producing 200,000 tonnes of bioPE yearly, with the support of a well-developed sugar cane industry and ethanol fuel economy. BioPE is chemically identical to its non-renewable counterpart and can be used in the same applications, but its environmental footprint is considerably lower [3,19,84].

2.2.2. Biopolypropylene (BioPP)

Propylene is the second most important organic building block for polyolefin production after ethylene, and PP is the second most important polymer after PE, with a market share of 20% in 2019 [4,18]. PP can be obtained from biological resources by fermentation of glucose to obtain isobutanol, which is subsequently dehydrated to obtain biobutylene and then bio-polypropylene, from which bioPP is obtained via polymerization [18].

As for bioPE, the Brazilian company Braskem was the first to produce bioPP on a pilot-plant scale, but their process route is still confidential. BioPP production has been less explored than that of bioPE, which explains the exiguous market share of bioPP [18]. However, according to Bioplastics Europe, the production capacities of PP are expected to almost sextuple by 2024 [21].

2.2.3. Bio-poly(ethylene terephthalate) and bio-poly(trimethylene terephthalate) (BioPET and BioPTT)

Poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT) are examples for partly biobased polyesters, synthesized from fossil-based terephthalic acid (TA) and biobased 1,3-propanediol (PDO) or ethylene glycol. Their biobased carbon content is approx. 20% for bioPET and 27% for bioPTT [19,22].

Biobased ethylene glycol production starts from the dehydration of bioethanol to obtain ethylene, followed by oxidation to ethylene oxide, and finally hydration to ethylene glycol. The Coca-Cola Company applied this process to produce bottles made of partly biobased PET (PlantBottle™), and since its introduction to the market, more than 35 billion bottles were distributed in the period 2009—2018. Biobased PDO is produced via microbial fermentation of glucose, via a process developed by DuPont and Genencor in 2003 [85]. This biotechnological route yielded highly pure and economically competitive PDO, which resulted in more applications of this building block in biopolymers and other chemical products [86].

Although the commercially available bioPET and bioPTT are only partially bioderived because they are made of petrochemical-derived TA, it is currently possible to produce bioderived TA starting from several biobased intermediates, such as isobutanol, limonene, muconic acid, or furan derivate molecules such as hydroxymethylfurfural [18].

A comment should also be made about PET biodegradation. PET, generally considered non-biodegradable or non-compostable, is reported to be naturally degraded by several enzymes, but the degradation rate is generally very slow. Recently, a novel bacterium has been identified able to use low-crystallinity PET as a carbon source thanks to PET-hydrolyzing enzymes such as PETase, and this can open new opportunities for bio-recycling of PET [87].

2.2.4. Biobased polyamides (BioPAs)

Polyamides (PAs) are condensation polymers with repeating amide links in their molecular chain, which contribute to the formation of inter-chain hydrogen bonds and therefore to an ordered microstructure and a high crystallinity degree. This is at the basis of their high mechanical properties, such as good impact strength, high hardness, and good abrasion resistance. PAs can either be synthesized from the condensation reaction of a diacid and a diamine, or they are based upon a single repeating unit comprising both the carboxylic and amine reactivities.

Biobased polyamides held approx. 12% of the global bioplastic market in 2019 [21]. BioPAs that are commercially available are either based on sebacic acid or undecanoic acid, both of which can be derived from castor oil. The more common and commercially available PA derived from this biomolecule is polyamide 11 (PA11), but it is possible to produce fully or partially bioderived versions also of other polyamides, such as PA610, PA1010, PA510, PA6, PA66, and PA12 [19,88].

2.2.5. Polyesters based on 2,5-furandicarboxylate

Unlike the bioderived non-biodegradable plastics reported so far, aliphatic polyesters based on 2,5-furandicarboxylate do not have a commercially available petrochemical counterpart. Yet, this

class of polymers is approaching the market as the "sleeping giant" of the world of bioplastics.

Aliphatic polyesters based on 2,5-furandicarboxylate, or poly(2,5-alkylene furanoate)s (PAFs) (Fig. 6) are synthesized from the polycondensation between an alkylene glycol and 2,5-furandicarboxylic acid (FDCA). FDCA is produced by the oxidative conversion of 5-hydroxymethylfurfural (HFM), in turn obtained by dehydrating simple sugar molecules such as glucose and fructose [89]. FDCA is widely recognized as a major bioderived building block, and in fact it was listed among the top 12 highly valuable chemicals from biorefinery of carbohydrates by the United States Department of Energy in 2004 [90] and 2010 [91].

PAFs represent a promising bioderived alternative to fossil-based poly(alkylene terephthalate)s (PATs), which are nowadays only partially renewable. PAFs feature thermal, mechanical, and gas barrier performance in some cases superior to those of the corresponding PATs, which makes them suitable for packaging and textile products, as well as for more technical and high-added-value applications [92—96].

The most prominent member of the PAF family is poly(ethylene furanoate) (PEF), studied as the fully bioderived alternative to PET [97,98], but PAFs have also been produced with longer-chain diols, containing up to 12 carbon atoms [95]. A longer alkyl chain increases molecular mobility, thereby enhancing the crystallization kinetics and ductility and decreasing the transition and melting temperatures [95,99—101].

3. End-of-life options for bioplastic waste

The best end-of-life option for any waste product depends on the material, its volume on the market, and available collection and processing infrastructure. According to the European Directive on waste management [102], waste should be managed according to a precise hierarchy indicating a priority order in the legislation and policy for waste prevention and management: (i) prevention; (ii) preparing for re-use; (iii) recycling; (iv) other recovery, e.g. energy recovery; and (v) disposal (Fig. 7).

Since recycling is the second-best option for waste management after preparing for reuse, the life cycle of every plastic material is really sustainable only if its disposal options include recycling. Although everyone agrees on the convenience of recycling non-biodegradable plastics, be they bioderived or not, for biodegradable plastics biodegradation is often seen as the only appropriate end-of-life option. However, most commercial biodegradable bioplastics degrade slowly under ambient conditions, even in presence of microorganisms, as they have been engineered to degrade in specific conditions, for example in composting plants [20]. Although biodegradation can be regarded as a recycling option, and it is sometimes called "organic recycling" [88], it is normally not aimed at recovering plastic materials or monomers to be reintroduced in the life cycle of plastic products. Conversely, this is specifically the aim of other types of recycling options, such as mechanical (primary or secondary) and chemical (tertiary) recycling. For example, as long as the material quality is high, biodegradable plastics could be
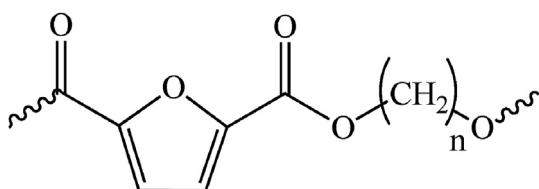
Fig. 7. Waste hierarchy of the European Directive on waste management (reprinted from Ref. [103]).

mechanically recycled by primary recycling, in which the recycled plastic has the same purpose as the virgin plastic, and/or by secondary recycling, in which the recycled plastic is used for less demanding applications [104]. When the material quality decreases under a certain threshold, bioplastics could be chemically recycled to recover valuable monomers that could be used as building blocks for new polymers or valuable chemicals Finally, with very low material quality, bioplastic waste could be biodegraded, when possible, and/or quaternary recycled via incineration (Fig. 8).

Therefore, it should not be *a priori* assumed that biodegradation is always the best end-of-life option for biodegradable plastic waste, but all available recycling strategies should be explored, in order to maximize the environmental benefits of these materials.

The rest of this Section discusses the end-of-life options for bioplastic waste, summarized in Fig. 9. The discussion will focus especially on biodegradable polymers, as non-biodegradable polymers such as bioPET, bioPE, and bioPP are indistinguishable from their petrochemical counterparts and can be recycled in the traditional plastic waste stream.

3.1. Identification and sorting

Identifying and sorting the different plastic materials composing the post-consumer waste is of fundamental importance for the subsequent recycling steps. The use of powerful and cost-effective technologies to separate plastic waste, able to guarantee high quality and purity, is necessary to produce market-competitive secondary materials [105,106]. However, the sorting step can be challenging not only because of the many types of different polymers present in the waste collection stream, but also due to the presence of compound- or layered items, constituted by different materials that can hardly be separated.

The identification and sorting steps can be performed (i) manually, on the basis of markers and labels, and/or (ii) automatically, though techniques based on differences in density, optical systems (e.g., near-infrared (NIR) techniques), fluorescent and coloring dyes, or solvents [20,107]. Manual sorting consists in the identification of different plastics by the operator on the basis of shape, color, appearance, or trademark. This technique is useful when plastic components are large enough to justify the time and effort involved, since it is very labor-intensive and measures must be taken to avoid an unhealthy working environment for the operators [20,106]. To facilitate manual sorting, various markers and labels could be used to identify biopolymers in the plastic waste stream. However, for instance, PLA is identified with the Resin Identification Code (RIC) "7-OTHER", which is not accurate for the identification of an increasing fraction of PLA in the plastic waste [20]. A more reliable way to identify and separate biodegradable
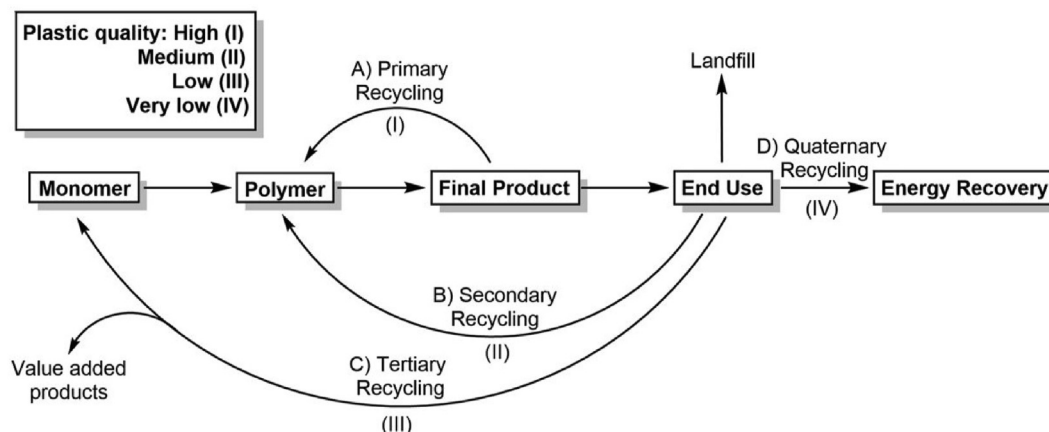
Fig. 6. General formula of poly(2,5-alkylene furanoate)s (PAFs).

Fig. 8. Quality of plastic material associated with the various end-of-life options for plastic waste (reprinted with permission from Ref. [11]).
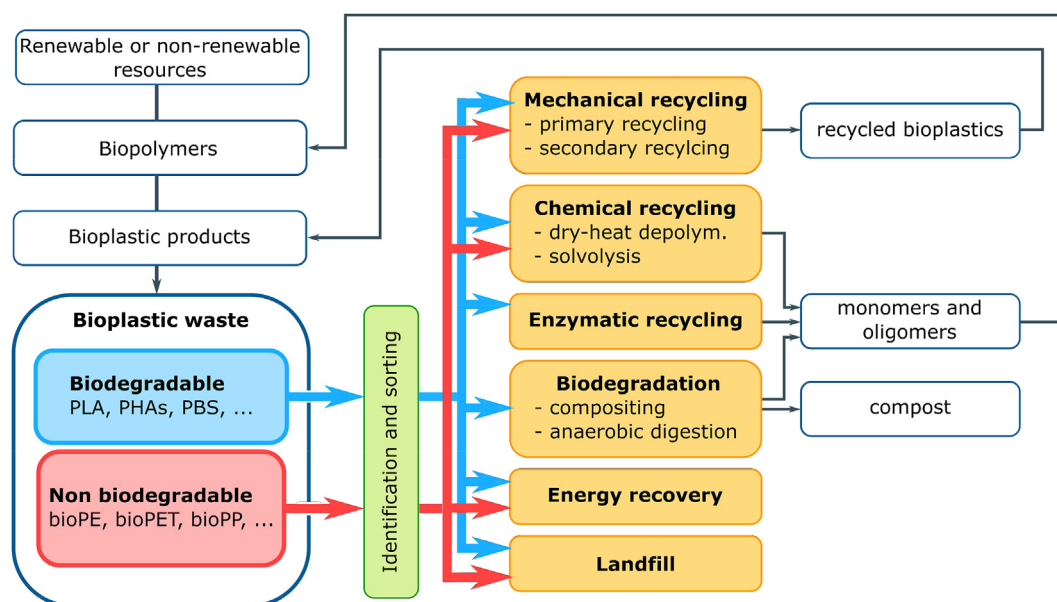

Fig. 9. End-of-life routes for biodegradable and non-biodegradable bioplastic waste.

and compostable polymers is based on international product labels, attributed by certification organizations (e.g., European Bioplastics, DIN CERTCO) to products that meet the criteria detailed in the standards. In general, manual sorting would be still necessary at the beginning of the recycling process to remove films, paper, cardboard, and bulky items [105].

Automatic sorting techniques could be also useful to identify and separate bioplastics. For example, the differences in density between PLA (1.25–1.49 g/cm^3), PHB (1.21–1.26 g/cm^3), and polyolefins (<1 g/cm^3) can be used to separate these materials through air classifiers or float-sink separation techniques with appropriate solvents. These density differences could also be accentuated by adding suitable additives during processing [20].

Another separation technique is near-infrared spectroscopy (NIR), which is likely the most diffused technology in plastic sorting and recycling. It is based on collecting reflected spectra of polymers in the wavelength range 700–1000 nm, and these spectra are different according to the specific polymer [105,108]. For bioplastics, NIR has been proven successful to separate PLA from PET waste. In fact, NatureWorks has collaborated with some NIR

equipment manufacturers and reached an efficiency of 97.5% in PLA removal from PET stream, thus identifying NIR as the most promising technique for automatically separating PLA from a PET waste stream. However, this was questioned by various recycling associations, such as the Association of Plastic Recyclers (APR), which expressed concerns that the output quality and yield are not high enough. Anyway, NIR systems could be too expensive as a sorting technique for biopolymers, given the current limited PLA fractions in the waste streams, and this may explain the lack of patents related to NIR sorting of bioplastics [20].

3.2. Recycling options

3.2.1. Mechanical recycling

Mechanical recycling can be defined as the processing of waste by physical means and is regarded as the main approach for plastic recovery, as it is generally less expensive, requires relatively simple technology, and has a lower environmental impact than chemical recycling [11,107]. Mechanical recycling starts with waste collection, screening, and manual and/or automatic sorting, and is

composed of several steps such as grinding, washing, drying, compounding/extrusion, and granulation. These steps may also occur in a different order and more than one at a time, according to the size, shape, and composition of the feed plastic waste [105].

Mechanical recycling comprises both primary and secondary recycling. Primary recycling is a closed-loop recycling technique that can only be performed on plastic waste of high quality and known history. Through primary recycling, the recycled material is used for applications with characteristics and performance equivalent to those of corresponding virgin plastics. It is generally not related to post-consumer plastics, but to the reconversion of uncontaminated plastic waste (e.g., production scraps) into its original pellet or resin form within the same production plant, and thus it does not require sorting and cleaning [108].

Secondary recycling is the mechanical reprocessing of waste, post-consumer plastics. At the end of secondary recycling, the recycled material generally shows poorer mechanical properties than the virgin product, due to a reduced material purity and degradation processes occurring during the product life. Therefore, recyclates are normally destined for the production of less demanding applications [11]. In any case, secondary recycling is only economically feasible when the waste is not constituted by too many materials and/or contaminated, which would otherwise require long and expensive separation and purification steps [109].

Although mechanical recycling is a well-established recycling route for traditional plastics, its application to bioplastics should be handled with care, especially in the case of biodegradable plastics. Most of the polymers of this class, including PLA, PHAs, and polyglycolic acid (PGA), are aliphatic polyesters, and thus quite thermosensitive [3]. For example, PLA and PGA are highly susceptible to thermal degradation, which causes coloration and leads to a decrease in mechanical properties. This problem is worsened by their high hygroscopicity, and the absorbed water favors hydrolytic breakdown of the molecular chains at high temperatures, thereby accelerating the thermal degradation. Therefore, while mechanically reprocessing these bioplastics, it is fundamental to accurately dry these materials before reprocessing. Furthermore, efficient drying can be complicated by paper impurities, which can also contain humidity [88]. For PLA, an additional issue is represented by the low T_g (55–60 °C), above which the material becomes sticky. This feature, combined with the low crystallization kinetics, makes it difficult to dry and/or crystallize amorphous waste plastic items, such as films. Analogously, thermoplastic starch is sensitive to hydrolysis during use and recycled material must be generally intended for downgraded applications. Moreover, it is immiscible with traditional packaging plastics and cannot be co-recycled into high-performance secondary products [11,20].

Conversely, non-biodegradable bioplastics as bioPET, bioPE, or PEF can be mechanically recycled together with their non-renewable counterparts. PEF, in particular, could be introduced in the current PET waste stream in low amounts (up to 2 wt%) without compromising the final quality of the recyclates [20].

3.2.2. Chemical recycling (tertiary recycling)

Chemical recycling, also called tertiary recycling, is a steadily growing recycling route related to the transformation of waste products into useful chemicals, such as monomers and/or oligomers re-introducible in the polymer value chain and re-used for polymerization [22]. For biopolymers, tertiary recycling is performed particularly on aliphatic polyesters, which are depolymerized in a controlled way with the main aim of saving primary resources, rather than reducing the amount of waste generated by slowly degrading biopolymers. Compared to mechanical recycling, some chemical recycling techniques (e.g., pyrolysis) can be performed also on low-quality, heterogeneous, degraded, or contaminated plastic waste and convert it into high-added-value chemicals, with the further advantage of enabling a truly circular economy of polymer products. On the other hand, it generally requires higher temperatures and is more energy-consuming. Chemical recycling can be performed through dry-heat depolymerization techniques (e.g., pyrolysis) or solvolysis methods (e.g., hydrolysis, alcoholysis) [23,110].

3.2.2.1. Pyrolysis.
Among chemical recycling routes, pyrolysis is one of the most promising methods for plastic waste that is difficult to be mechanically recycled or depolymerized. It can be performed at considerably lower temperatures than incineration and does not require as many pre-treatment steps as mechanical recycling [109].

Pyrolysis is the degradation by heating plastic waste in an oxygen-free atmosphere at moderate temperatures (300–700 °C). During pyrolysis, thermal degradation of polymer chains can be accomplished with or without a catalyst, and the process is called catalytic pyrolysis or thermal pyrolysis, respectively [109,111]. The degradation of polymer chains into smaller and less complex molecules results in solids (char), gases (non-condensable substances), and also liquids (condensable vapors or oils) that can be converted into high-added-value chemicals. The relative yields of these products are determined by the process conditions and feedstock composition, and the proximate analysis is a very useful tool to assess the feedstock composition in terms of volatiles, fixed carbon, and inorganic waste (ash). Since the volatile fraction of all synthetic plastics is very high (97–99%) and the ash content is low (1–3%) [109], plastics can yield a very high amount of oils (>90 wt %). On the other hand, the yield of this process can be decreased by additives such as fillers, flame retardants, plasticizers, and dyes, which increase the char fraction.

Pyrolysis is a well-established route for polyolefin waste, yielding small hydrocarbons, but also for polymers as polystyrene (PS), poly(methyl methacrylate) (PMMA), PET, and PA, yielding styrene, methyl methacrylate, terephthalic acid, and ε-caprolactam, respectively. Biodegradable aliphatic polyesters can also be suitably treated by pyrolysis. For example, pyrolysis of PLA results in its depolymerization and obtainment of lactide [20]. However, the reaction has a low monomer yield and is very slow, and thus it must be performed at high temperatures (300–600 °C) and in presence of a catalyst. The high temperature may promote undesired side reactions, such as lactide racemization, thereby hindering the attainment of high-quality products. Some solutions involving special catalysts that lower the reaction temperature, such as metal oxides and hydroxides like MgO, CaO, BaO, and Al(OH)$_3$ [109,112], have been recently proposed.

3.2.2.2. Solvolysis.
Solvolysis refers to all depolymerization and partial depolymerization techniques involving a solvent, sometimes coupled with heat. Common solvolysis techniques are hydrolysis, alcoholysis, glycolysis, methanolysis, acidolysis, aminolysis, and ammonolysis. The most suitable polymers are step-growth polymers such as polyesters, polyamides, and polyurethanes, for which solvolysis can be regarded as the reverse reaction to polycondensation.

Hydrolysis is composed of two steps, i.e., water diffusion into the bulk polymer and the hydrolysis reaction properly said. For low water diffusion rates, polymer degradation occurs first on the surface (heterogeneous erosion), whereas for high water diffusion rates, the polymer is subjected to homogeneous erosion. When the degradation rate in the solid state is slow, a possible solution is a

temperature increase. High-temperature hydrolysis is somewhere referred to as hydrothermal depolymerization, which may also involve high water pressure. The high temperature (above the polymer's melting point) and pressure accelerate the degradation reaction, which can take place in subcritical and supercritical conditions either with or without oxidizing agents [22].

Other important solvolysis techniques in the chemical recycling of polyesters are alcoholysis and glycolysis. In alcoholysis, the nucleophilic alcohol group cleaves ester bonds, thereby promoting a transesterification reaction, while glycolysis refers to the insertion into the polymer chains of a glycol, thus replacing ester bonds with hydroxyl groups. For example, some solvolysis reactions of PET with different solvents are reported in Fig. 10, with the corresponding output products.

For biodegradable plastics, chemical recycling, and solvolysis in particular, has not been a very important end-of-life option, but it is promising from an economic and ecological point of view. For example, for PLA, obtaining lactic acid from hydrolytic degradation of PLA waste can require less energy than producing it from biomass fermentation [3,110].

3.2.3. Enzymatic and microbial recycling

Enzymatic and microbial depolymerization are new promising techniques that harness the action of enzymes and microorganisms to degrade biodegradable bioplastics in a selective and controlled way, with the aim of recovering monomers and other valuable chemicals. This aim is what makes this technique a truly recycling method, thus distinguishing it from biodegradation and composting, which are instead disposal methods. Enzymatic and microbial recycling could be listed among the chemical recycling techniques, but since they are relatively new methods, they are discussed in a separate paragraph.

Several research works and patents (Table 1) have been published on the enzymatic depolymerization of biodegradable aliphatic polyesters such as PLA, PCL, PBS, PTT, poly(butylene adipate) (PBA), using especially lipase or Proteinase-K followed by the depolymerization of the obtained oligomers. However, the technology of enzymatic depolymerization is still at the early stages. This recycling method is quite slow, especially for highly crystalline polymers with high intermolecular forces, and the reaction kinetics

cannot be enhanced by increasing the temperature, not to degrade the enzymes [20].

3.3. Degradation and disposal options

Degradation and disposal options differentiate from the recycling options discussed in Section 3.2 because the main aim is to eliminate waste rather than to recover polymers or monomers to be reintroduced in the plastics value chain.

Besides the degradation and disposal options suitable for conventional plastics and non-biodegradable bioplastics, i.e., quaternary recycling with energy recovery and landfilling, biodegradable bioplastics have the additional option of biodegradation, sometimes called organic recovery or organic recycling. Biodegradation can be performed through industrial or home composting, anaerobic digestion, or biodegradation on agricultural land, among which industrial composting is the predominant option. The time to complete the biodegradation depends not only on the chemistry and microstructure of the specific bioplastic, but also on the chosen end-of-life route and the biotic and abiotic factors such as the temperature, oxygen, and moisture concentration, and population of microorganisms.

3.3.1. Biodegradation or organic recovery

Biological waste treatments are end-of-life options peculiar to biodegradable plastic, and they can be performed either aerobically (with oxygen, e.g., composting) or anaerobically (without oxygen, e.g., anaerobic digestion). Composting is performed by fungi, bacteria, and actinomycetes either at low temperature ($<35\ ^\circ$C for home composting) or at higher temperature ($50-60\ ^\circ$C for industrial composting). Similarly, anaerobic digestion is performed by bacteria — not fungi — either at low temperature ($<35\ ^\circ$C for mesophilic digestion) or at higher temperature ($50-60\ ^\circ$C for thermophilic digestion).

Biodegradation rate is very dependent on the degradation technique and environment, being faster in compost, followed by soil, fresh water, marine water, and finally landfill, since biodegradation is faster at higher temperatures and in the presence of fungi, which are active only in compost and soil environments. Moreover, not all biodegradable plastics degrade in all biological degradation environments, so the correct biodegradation route must be chosen for each type of biodegradable bioplastics [3].

3.3.1.1. Composting. Composting is the controlled biological aerobic conversion of organic waste into CO_2, H_2O, heat, and minerals, biomass, and humus useful for plant growth. This conversion is activated by microorganisms such as bacteria, yeasts, and fungi [42]. In the European Union, composting is encouraged primarily by the EU Council Directive on Landfill of Waste (1999/31/EC) [114], which urges member Countries to limit the quantity of biodegradable waste that ends up in landfills, and by the 2008/98/EC Directive on Waste [102], which encourages the separate collection and safe treatment of biodegradable waste.

It is important to note that compostable plastics are a subcategory of biodegradable plastics. Compostable plastics, such as PLA and TPS, decompose in a relatively short time under composting conditions, while for biodegradable plastics the biodegradation may be slower. Hence, all compostable plastics are biodegradable, while not all biodegradable plastics are compostable [3].

3.3.1.2. Anaerobic digestion. Anaerobic digestion converts organic matter into three main substances, i.e., biogas, rich in methane and used as a fuel, biosolids, i.e., microorganisms grown on the organic matter, and liquor, i.e., dissolved organic matter, both used as fertilizers.
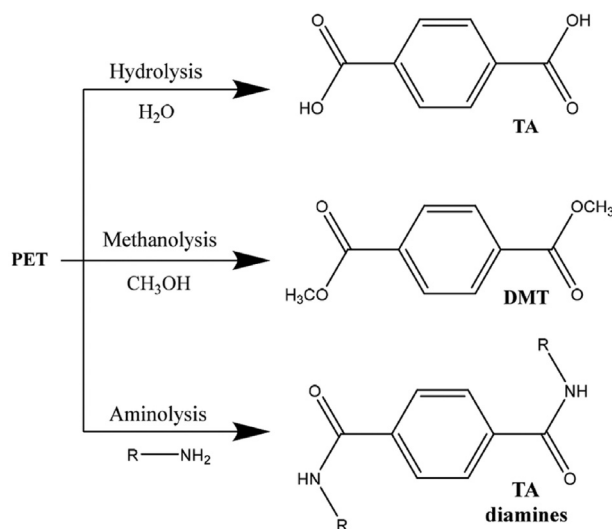

Fig. 10. Hydrolysis, methanolysis, and aminolysis reactions of PET that yield terephthalic acid (TA), dimethyl terephthalate (DMT), and TA diamines, respectively (reprinted with permission from Ref. [113]).

Table 1
Patents related to the enzymatic and microbial recycling of biodegradable polymers (adapted with permission from Ref. [20]).

Biopolymers	Enzymes/micro-organisms	Depolymerization products	Patents
PLA (PLLA, PDLA), PBS	Polypeptide comprising amino acid sequence (SEQ ID No: 1; or SEQ ID No: 5); or micromonospora strain S0002	Lactic acid	WO2016146540 A1 (2016, CARBIOS; CENTRE NAT RECH SCIENT; UNIV POITIERS)
PLA (PLLA, PDLA)	Polypeptide comprising amino acid sequence (SEQ ID No: 1; or SEQ ID No: 5)	Lactic acid, dimers of lactic acid	WO2016062695 A1 (2016, CARBIOS; AGRONOMIQUE INST NAT RECH; INST NAT SCIENCES APPLIQ; CENTRE NAT RECH SCIENT)
PLLA, PTT	Proteinase-K; recombinant strain of *Lactococcus lactis* or *Escherichia coli* excreting depolymerase; cutinase	Lactic acid; terephthalic acid	WO2014079844 A1 (2014, CARBIOS)
PLLA, PDLLA, P(LLA-CL) P(LLA-TMC)	Hydrolase; preferably lipase (Novozyme® 435); in organic solvent (xylene, hexane/chloroform) or supercritical fluid (CO_2)	Cyclic ester oligomers	WO2004013217 A1 (2004, UNIV KEIO)
PHA (PHB, PHBV), PBS	Hydrolase; preferably lipase (Novozyme® 435); in dichloroethane or acetonitrile	Cyclic ester oligomers	JP2002320499 A (2002, UNIV KEIO)
PCL	Hydrolase; preferably lipase (Novozyme® 435); in toluene	Dicaprolactone	JP2002017385 A (2002, UNIV KEIO)
PCL, PBA, PBS	Hydrolase; preferably lipase; in supercritical fluid (CO_2)	Cyclic caprolactone oligomer, cyclic ester oligomers	JP2003079388 A (2003, UNIV KEIO)
PHB, PCL, PBA, PLA-CL, PTT	Hydrolase; preferably lipase (Novozyme® 435); in supercritical fluid (CO_2) and toluene	Cyclic caprolactone oligomer, cyclic ester oligomers	WO2005026245 A1 (2005, UNIV KEIO)
PBSL	Esterase; preferably cutinase or lipase	Succinic acid	JP2004290130 A (2004, MITSUBISHI CHEM CORP)
PLA, PBS	Proteinase-K (PEOx), lipase CS_2; in ethanol	Monomer and/or oligomer	WO2010050482 A1 (2010, TOYO SEIKAN KAISHA LTD)

Anaerobic digestion is composed of four main steps. The first is hydrolysis, performed by the extracellular enzymes of bacteria onto complex biological macromolecules such as carbohydrates, lipids, and proteins to produce simple sugars, fatty acids, and amino acids. The second step is acidogenesis, in which the products of hydrolysis are absorbed by acidogenic microorganisms, which produce intermediates such as volatile fatty acids (VFAs). These intermediates are converted into acetate, hydrogen, and CO_2 during the third stage, acetogenesis. Finally, during the fourth step, methanogenesis, methanogenic organisms consume intermediates and produce CH_4 [3].

3.3.2. Energy recovery (quaternary recycling)

Incineration of plastic and bioplastic waste with energy recovery, although lower in the hierarchy of waste management options than recycling, can be useful to dispose of all the non-recyclable and non-biodegradable plastic waste fraction and is surely preferable over landfilling. Plastics have a high calorific value and can be used in waste-to-energy plants to reduce fossil fuel consumption [108].

Although incineration is not the desired end-of-life option for bioplastics, and biodegradable plastics in particular, they generally are made only of C, O, and H, and therefore they could be accepted into these waste-to-energy plants, also because they can have similar calorific value as conventional plastics (Fig. 11). When bio-based plastics are incinerated, they are considered to produce renewable energy [3].

4. Ideal recycling pathways for some biodegradable bioplastics

4.1. Recycling of PLA

PLA is nowadays the most widely used biobased and biodegradable plastic. Its increasing use to replace conventional non-biodegradable plastics represents an undoubted step towards a sustainable use of plastic materials. Nevertheless, biodegradation of PLA in environmental conditions is very slow, which may result in considerable environmental pollution, thus causing the same waste management problems encountered for non-biodegradable
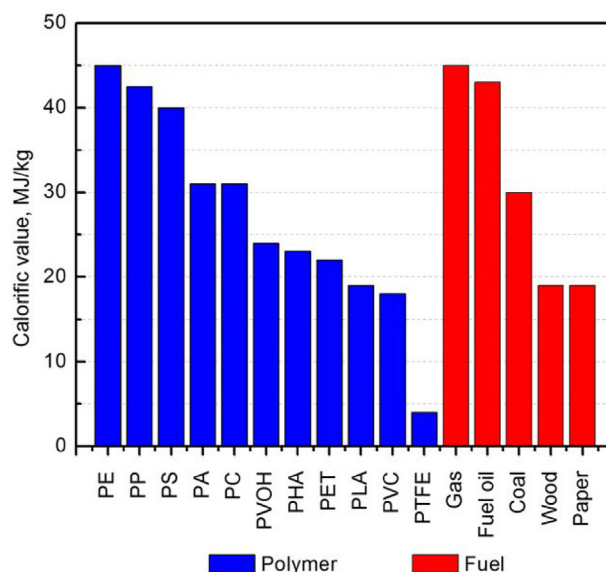

Fig. 11. Calorific value of some bio- and conventional plastics compared to those of some fuels (reprinted with permission from Ref. [115]).

plastics. Moreover, producing PLA precursors requires extensive amounts of croplands, which might result in issues related to food supply and overpricing, especially in poorer countries, and this contrasts with the objectives of a truly sustainable bioeconomy [24]. Hence, the growing diffusion of PLA must be coupled with a careful evaluation of its end-of-life options, to evaluate its recyclability via the available recycling routes, so to minimize its carbon footprint over the whole life cycle and save virgin PLA, which can be costly also from the environmental point of view.

The first challenge involves the evaluation of the best strategy for PLA waste collection and the opportunity to establish a recycling stream separated from that of the other plastic packaging materials. Attempts to recycle waste PLA bottles in the well-established PET recycling stream encountered considerable

resistance from PET recyclers, as PLA and PET bottles are very similar to each other and sorting can be challenging. A careful separation between PLA and PET is crucial because the presence of PLA, even in very low amounts (1 wt%), is detrimental for the final thermomechanical properties of PET recyclates, which must be then used for downgraded applications. The association of Plastics Recyclers Europe calls for the development of separate recycling streams for biodegradable plastics to improve waste management efficiency throughout Europe. It has been estimated that a recycling plant that processes a specific polymer is profitable only when the global production of that polymer reaches 200 thousand tonnes (kT) and the plant should be able to process 5–18 kT per year [11]. PLA production has grown steadily over the last years and approx. 200 kT have been produced globally in 2018 [24], which suggests that recycling streams and plants dedicated to PLA could soon be feasible.

4.1.1. Mechanical recycling of PLA

Mechanical recycling of PLA is the best option among the waste valorization methods for this polymer, as pointed out by several LCA studies [26]. However, several challenges must be faced to ensure its feasibility. Not only should reclaiming plants be adapted to introduce a separate stream for PLA, but it is also fundamental to tackle the degradation and decrease in mechanical properties that come along with mechanical recycling, which might negatively affect the marketability of recycled PLA. Thermomechanical degradation during mechanical reprocessing can be partially avoided by adding proper additives, such as functionalized clays, chain extenders, crosslinking agents, and even organic and bioderived fillers, which do not impair the final biodegradability of the material [24]. Among these organic fillers are silk fibroin nanoparticles and functionalized chitosan, which have a nucleating effect on PLA and help to mitigate the decrease in thermal stability, tensile strength, toughness, and gas barrier properties of the recyclate [24].

According to a recent study, mechanical recycling was proven the best option for PLA-based packaging also from a socio-economic point of view (Fig. 12) [116]. This study proposes a socio-economic indicator (SEI) that compares different end-of-life options according to their impact on several social actors, such as the workers, the consumers, the general society, the local community, and the value chain actors (i.e., plastic producers, distributors, waste management companies). The results indicate that value chain actors are the most influential stakeholder category in waste management and that key factors of this management are

the waste disposal cost, resource efficiency, and end-of-life responsibility [116].

4.1.2. Chemical recycling of PLA: hydrolysis and alcoholysis

The second-best option for PLA waste is chemical recycling, and in particular hydrolysis and alcoholysis are the best chemical recycling alternatives. In fact, PLA can be hydrolyzed to lactic acid with a 95% conversion within 2 h at 160−180 °C [110]. The hydrolysis rate depends on the concentration of polymer bonds, water, and acidic hydrolysis products [110]. Moreover, the hydrolysis of PLA is autocatalytic, as hydrolysis generates carboxyl groups which further catalyze the reaction. The hydrolysis rate depends on several factors such as polymer crystallinity, pH, temperature, but also the amount of absorbed water, the diffusion coefficient, and solubility of degradation products [117].

However, the lactic acid resulting from complete hydrolysis of PLA must be dehydrated, polycondensed to an oligomer, and depolymerized to obtain the lactide, which is the most common industrial starting point to PLA polymerization. Therefore, close-loop PLA production from complete hydrolysis of PLA waste is regarded as complicated and not very advantageous from an economical point of view. Moreover, dehydration and polycondensation increase the fraction of D-lactic acid over the L-fraction by partial racemization. A solution to this problem could be represented by the partial hydrolysis of PLA to oligomers and depolymerization of these oligomers to directly obtain lactide [20].

In general, chemical recycling allows obtaining lactic acid with much lower energy consumption than obtaining it from corn biomass fermentation. The amount of energy required to produce 1 kg of lactic acid from biomass is 55 MJ, while from PLA hydrolysis it is only 14 MJ [11].

PLA can be chemically recycled also via alcoholysis, in which several alcohols (e.g., methanol, ethanol, propanol) can cleave ester bonds via a transesterification reaction to produce lactate esters (e.g., methyl lactate, ethyl lactate, and propyl lactate) in presence of a catalyst such as $Zn(Et)_2$ and $Zn(Pr)_2$ [118,119]. Such lactate esters are high added value products, and they are produced through alcoholysis at high yields and with high purity. Moreover, alkyl lactates can be converted into lactide, which could then be polymerized into PLA, thus creating a truly circular economy [120].

However, the overall life cycle balance of solvolysis must also consider the cost and environmental impact of solvents, and therefore, when possible, the choice should fall on mild, non-toxic, and environmentally friendly solvents. The process temperature
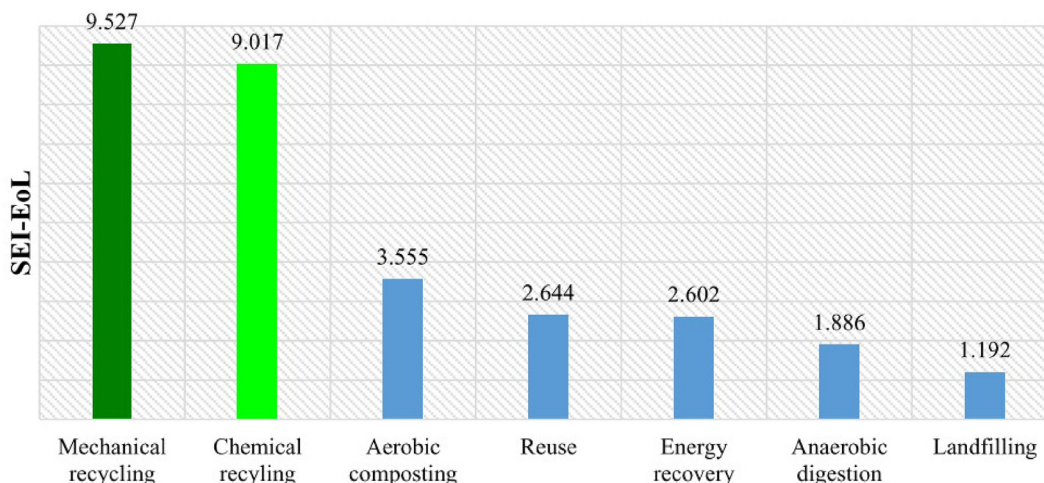

Fig. 12. Ranking of end-of-life (EoL) strategies for PLA-based film packaging on the basis of a socio-economic indicator (SEI) (reprinted with permission from Ref. [116]).

should be high enough to increase depolymerization kinetics but not excessive not to produce undesired side products. For example, patent JP2009029757 A (Teijin Fibers Ltd, 2009) discloses a method to depolymerize PLA in methanol at 60–100 °C in presence of zinc compound catalysts [22].

4.2. Recycling of PHAs

Although PHAs are not as widely diffused as PLA, they are a very interesting class of biobased and biodegradable polymers and their production capacity is expected to triple in the next five years [21]. Therefore, their increased commercialization should occur in parallel with the establishment of efficient recycling pathways. Such pathways, as pointed out by Vu et al. in a recent review [23], have yet to be well investigated, and the few studies on the mechanical, chemical and biological recycling of PHAs focus on the most diffused members of this polymer family, i.e., PHB and PHBV.

4.2.1. Mechanical recycling of PHAs

Since PHB is quite brittle and expensive, it is generally blended with other polymers [26], which explains why the studies on pure PHB recycling are so few. In one of these studies [121], the recyclability of PHB was evaluated through multiple processing cycles via extrusion and compression molding and, after each cycle, the thermal and mechanical properties were evaluated and related to the resulting polymer structure. However, these properties were significantly reduced after only two processing cycles, where the tensile strength was more than halved and the crystallinity degree increased due to chemi-crystallization by chain scission. Although these results were not very encouraging, other studies [122] pointed out that recycled and degraded PHB could be used as a plasticizer for PLA. To evaluate this hypothesis, PHB was thermally degraded at 220 °C for 45 min, which resulted in PHB oligomers with crotonate end-groups, and these oligomers were covalently bonded onto PLA chains by melt processing. A fraction of PHB oligomers of 20 wt% considerably improved the ductility of PLA, with a 66-fold increase in the strain at break.

PHBV shows a higher recycling potential than PHB. For example, after five processing cycles of extrusion and injection molding, the decrease in tensile strength was found to be only 7% [123] and the impact toughness did not decrease significantly. The recyclability of PHBV was also investigated in blend with PLA, and the blend was proven even more stable to thermomechanical degradation, as tensile and impact strength and strain at break were only marginally decreased even after six reprocessing cycles.

4.2.2. Chemical recycling of PHAs

The recyclability of PHB has been also evaluated through pyrolysis, which results mainly in crotonic acid and oligomers with crotonate end-groups [124]. Crotonic acid can be polymerized into poly(crotonic acid) and its copolymers (e.g., vinyl acetate), applicable in formulations for dental cements, plasticizers, herbicides, and cosmetic products [125]. The yield of crotonic acid is very much dependent on the physical form and purity of the PHB feedstock. For example, for purified PHB by dissolution in chloroform, the yield was found to be 60–65%, while for PHB in dried bacterial cells the yield was 20–25% [111]. In the case of PHBV, the pyrolysis produced 2-pentenoic acid and oligomers of hydroxyvalerate. Moreover, the addition of a catalyst could control the degradation rate and the relative abundance of the final pyrolysis products. For example, PHB and PHBV were thermally degraded with CaO and $Mg(OH)_2$ catalysts [125], which allowed controlled and selective degradation at a relatively low temperature (230 °C vs 290 °C). The obtained crotonic acid and 2-pentenoic acid were copolymerized into poly(crotonic acid-co-acrylic acid), which showed high glass-transition temperature and water solubility, and potential applications as hydrogels for wastewater treatment and agricultural uses.

As PHAs are also used in blends with other polymers, it is important to evaluate the chemical recyclability of their blends. For example, PE/PHBV film blends were chemically recycled through
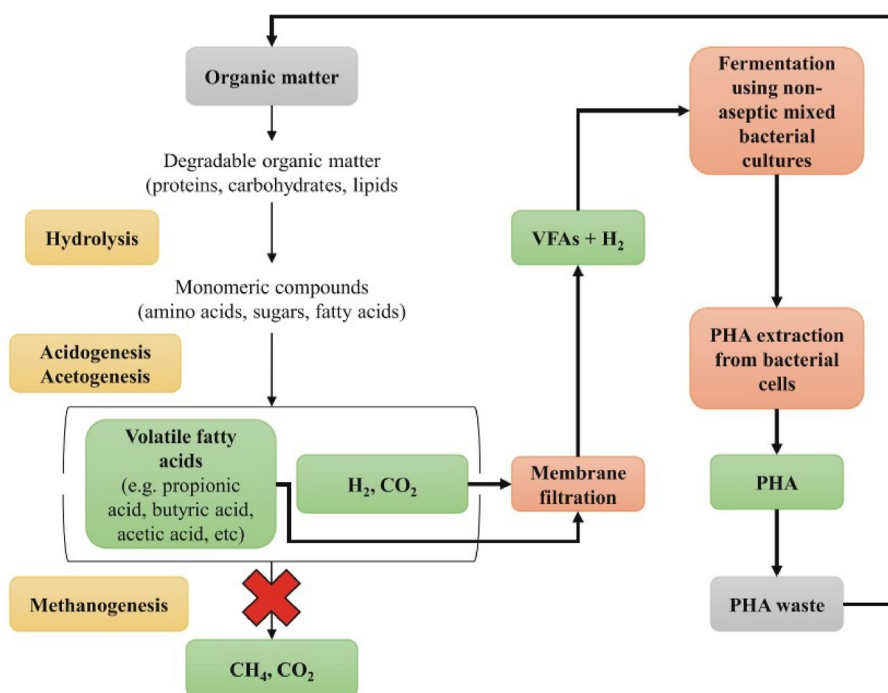

Fig. 13. Close-loop production and chemical recycling of PHAs through anaerobic digestion followed by microbial fermentation (reprinted with permission from Ref. [23]).

pyrolysis at 310 °C [111]. Since PE and PHBV degrade at different temperatures, they were separated and PHBV was converted into monomers and oligomers that were collected with high purity and without contamination by PE.

An alternative recycling route for PHB was investigated [126], based on a microwave-assisted reaction in solvents such as water, methanol, and ethanol. For example, with a reaction in methanol at 110 °C, with sodium hydroxide at 0.5%, PHB was completely degraded into crotonic acid, 3-hydroxybutanoic acid, and 3-methoxybutanoic acid in 20 min, considerably faster than other chemical recycling techniques.

4.2.3. Organic recovery

PHAs can be biologically recycled under both aerobic and anaerobic conditions, and therefore can be suitably treated both by composting and by anaerobic digestion [127,128]. The degradation can occur under the action of several bacteria and fungi through intracellular and extracellular depolymerases [129]. The time to biodegradation is influenced by several factors, such as polymer properties (e.g., molecular weight, crystallinity, functional groups, additives), product properties (e.g., size, geometry), and environmental conditions (e.g., temperature, humidity, population of micro-organisms).

Not many studies have been performed on the degradation of PHAs under aerobic conditions (e.g., composting). For example, the degradation of PLA/PHA nonwoven mulching films was studied under simulated aging conditions at 63 °C, under UV irradiation and water spraying [130]. Under these conditions, the degradation of the PLA/PHA blend was achieved in 180 days with a reduction in molecular weight of 90%.

For biodegradation in anaerobic conditions, PHB was seen fragmenting quickly but degrading slowly in an anaerobic sludge and showed a weight loss of 23% after an incubation of 10 weeks, but the degradation rate was still higher than that of PCL, which degraded by 7.3% in the same time frame [131]. Different degradation rates but similar conclusions were found in another study [132], where the biodegradability of PHB in anaerobic digestion conditions has been compared to that of PLA, PCL, and PBS. 90% of PHB was degraded after 9 days, while PLA and PCL presented a considerably lower degradation rate (29–49% and 3–22% after 277 days, respectively) and PBS did not degrade appreciably. Even better results were obtained with a preliminary thermal alkaline treatment on PHB [133], which led to more complete digestion and higher CH_4 yields, useful for producing biogas.

More recently, another product of anaerobic digestion attracted considerable attention, i.e., volatile fatty acids (VFAs) (see Section 3.3.1.2), produced through acidogenic fermentation [134]. VFAs are considered promising for producing several valuable biochemicals and biofuels, and they also show potential as a raw material to produce PHAs, as proposed by Vu et al. [23] (see Fig. 13). This may occur via a two-stage fermentation process where acidogenic fermentation is followed by a fermentation using non-aseptic mixed bacterial cultures. This closed-loop process is expected to considerably expand thanks to the improving technology and knowledge about anaerobic digestion, biogas production, and membrane bioreactors.

5. Conclusions and future trends

Plastic materials have become essential for many everyday and industrial applications, but the non-renewable origin of most commercial plastics and the issues related to the management of an ever-growing amount of plastic waste are pressing to find more sustainable alternatives. Such an alternative can be represented by bioplastics, defined as plastics that are biodegradable and/or derived from renewable resources. Biodegradable bioplastics have alternative routes for waste disposal, thus limiting the amount of plastic waste ending up in our environment, while bioderived bioplastics allow a substantial reduction in the carbon footprint in the stage of resource extraction. However, the growing bioplastics production must be paralleled with effective end-of-life strategies of bioplastic waste.

Non-biodegradable bioplastics such as bioPET, bioPE, and bioPP can be collected and recycled in the same waste management stream as their petrochemical counterparts. On the other hand, the scenario is not as clear for biodegradable bioplastics, such as PLA and PHAs, for which biodegradation is often seen as the only acceptable end-of-life option. However, biodegradable bioplastic waste could also be suitable for other waste management routes, such as mechanical and chemical recycling, which may be better from the economic and ecological point of view. In fact, they address the issue of waste accumulation while recovering valuable materials and building blocks, thereby reducing the consumption of primary resources.

Considering one of the most diffused biodegradable bioplastics, i.e., PLA, its biodegradation in environmental and marine conditions is very slow, which may result in considerable environmental pollution if PLA-based waste is incorrectly managed. Therefore, it is important to evaluate the recyclability of PLA, which must start with finding the best strategy for PLA waste collection and the opportunity to establish an independent recycling stream, to preserve the output quality of the well-established recycling pathways of conventional plastics, such as PET. Then, the best recycling route (mechanical, chemical, enzymatic) and the recycling conditions must be chosen, which may depend on several factors such as the material quality of PLA waste. Although mechanical recycling is often designated as the best recycling option from an environmental and socio-economical point of view, it is fundamental to tackle the tendency of PLA to thermally degrade during reprocessing. This can be addressed by carefully selecting the processing parameters and by a proper compounding/additivation stage, to obtain a high-quality recycled PLA with tailored properties that can easily find a market share.

The study of the best recycling route for biodegradable and non-biodegradable plastic waste must also consider the economical convenience and the marketability of the output products of every recycling strategy. In any case, since the bioplastics production is growing and such materials will coexist with conventional plastics for decades to come, it is vital to find the best end-of-life pathways for each of the most common bioplastics, regardless of their biodegradability, to promote a concrete shift of the whole plastics value chain towards sustainability.

Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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