Recycling of bioplastics, their blends and biocomposites: A review

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This review presents scientific findings concerning the recycling of bioplastics, their blends and thermoplastic biocomposites, with special focus on mechanical recycling of bio-based materials. The paper does not include bio-based commodity plastics such as bio-derived polyolefins that are identical to their petroleum-based counterparts and that can be recycled in the same way. During the past few years, recycling of biopolymers and their blends has been studied using both mechanical and chemical methods, whereas in biocomposites, the focus has been on mechanical recycling. This review goes through the findings on the recyclability of various materials, the strengths and weaknesses of applied methods, as well as the potential strategies and opportunities for future improvements. There are still many blends that have not been investigated for their recyclability. Information about commercially available blends containing bioplastics is summarised in the Appendix because of the importance of their possible effects on the conventional plastic recycling streams.

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0014-3057/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2013.07.025
0. Preface

Sustainable use of carbon sources, regardless of whether they are bio-based or fossil, must involve production of recyclable plastics. Both petro- and bio-based plastics will coexist in the production of sustainable and cost-effective materials for a long time to come. Thus, the increased use of bioplastics and biocomposites may have serious implications for the recycled plastics industry in the near future. Where it is cost effective to recycle, conventional plastics recycling operations are already well established and driven by industry. However, the introduction of 'green' plastics to the market has created a number of issues that need to be addressed. One important question concerns the potential risk of contamination of the collected conventional plastics. In addition, there are concerns about the cost of separation, and about increased contamination, yield loss and impact on recycled materials quality and processing. Another important issue is to develop technologically viable, effective, efficient and economical recovery systems and end markets for post-consumer bio-based materials without jeopardizing the existing recycling systems. This review paper succinctly summarises the current state of knowledge of the topics related to manufacture and recycling of bio-based plastic materials.

1. Introduction

Sustainable bio-based eco-products are products with commercial and environmental acceptability that are derived from renewable resources, and have recycling capabilities and/or triggered biodegradability [1]. As a result of new legislation on the development of environmentally and economically viable manufacturing as well as reuse and recycling of materials [2], the market for biopolymers and biocomposites is growing rapidly. According to European Bioplastics, the production capacity for bioplastics is predicted to increase from approximately 700,000 tons in 2010, to 1.7 Mtons by 2015 [3]. Most important, however, will be the expected continuation of high crude oil and natural gas prices, which will allow bioplastics to become more cost-competitive with petroleum-based resins. The terminology used in this field is sometimes misleading. The term bioplastic means a plastic produced from a biological source (short carbon cycle) while the term biodegradable refers to a material that can be degraded relatively rapidly by microbes in a bio-active environment under suitable conditions. All (bio- and petroleum-based) plastics are theoretically biodegradable; however, most materials degrade at such slow rates that they are considered non-biodegradable or durable.

Biodegradable plastics were introduced in the 1980s to find ways to produce non-petroleum-based plastics, as well as to reduce the environmental effects because of the increased landfill [4]. Biodegradable plastics have dominated the bioplastics market with a roughly 90% share. However, durable plastics based on renewable resources are forecasted to increase their market share from 10% in 2010 to about 50% by 2018. One important reason is legislation, e.g., from 2015, the regulation according to the EU ELV (end-of-life vehicles). Directive allows an incineration quota of only 5% for discarded cars. This has applied to composite materials in particular, because the recycling and reuse of traditional materials has been technically and economically questionable [2]. In particular, the automotive industry has made great efforts to shift from thermosetting composites to thermoplastic natural-fibre-reinforced composites [5]. Another example is a Japanese government directive that requires 20% of all plastics used in Japan to be bio-derived by 2020 [6]. This directive has already encouraged development of partly bio-based resins, alloys or blends of bio- and petrochemical-based materials (called hybrid bioplastics). Most durable bioplastics are being blended today with petrochemical-based polymers such as polycarbonate (PC), polypropylene (PP), acrylonitrile–butadiene–styrene (ABS), high-impact polystyrene (HIPS), poly(ethylene terephthalate) (PET) and poly(methyl methacrylate) (PMMA).

Bio-based and biodegradable polymers have a wide range of applications, such as in the biomedical, packaging and agricultural fields. The most common of the biodegradable materials are blends of thermoplastic starch (TPS) and aliphatic/aromatic polyesters, such as poly(lactic acid) or polylactides (PLA), polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and poly-hydroxybutyrate (PHB) [7]. PLA, which benefits both from coming from renewable resources and being biodegradable in the compost environment, has attracted much attention. It has become an economically viable commodity plastic in industry and is employed to produce common-use articles and packaging materials such as trays, bottles or films for the food packaging industry [8–10]. This polymer has good mechanical properties and processability and good thermal properties, but also has limited environmental impact according to life cycle assessment (LCA) [11]. PLA is a thermoplastic aliphatic polyester obtained from the ring-opening polymerisation of lactide, which may be derived from the fermentation of sugar feedstock at competitive prices [12]. PLA, like most thermoplastics, can be moulded into bottles, containers and so on by injection moulding, blow moulding, etc., or be extruded into fibres, films and sheets.

Natural bio-fibre composites are emerging as a viable alternative to glass-fibre reinforced plastics, especially in automotive applications. Thermoplastic biocomposites, composed of PP, PE, PS or biopolymers such as PLA and reinforced with natural fibres have especially attracted great attention during the past few years. Such thermoplastic biocomposites, compared with those made using a thermoset matrix, can be processed into different shapes and have the potential to be mechanically recycled. Eureka, a European research and development organisation, announced the completion of a research project in 2007 to produce new recyclable compounds for consumer products and audio components [13] that involves the combination of natural fibres such as flax, wood, jute and hemp with thermoplastics. Biocomposites, composed of natural fibres and bio-resins, have also been introduced into the market because of the increasing demand for advantageous mechanical properties per weight, important for environmental adaptation of products as well as improving prod-
uct performance [14,15]. Biocomposites with a biopolymer matrix are the future of ‘green composites’ and their recycling makes it possible to retain the whole carbon content and save primary resources [16]; furthermore, they offer reductions in weight and cost, and give less reliance on foreign oil resources [17]. Biocomposites are currently used mainly in the automotive, construction, furniture and packaging industries, where renewable products are attracting great attention because of the driving force of increasing environmental awareness and depletion of fossil resources [18].

The key measurement tool to assess a product’s environmental impact is LCA. Through LCA it is possible to account for all of the environmental impacts associated with a product, covering all stages in a product’s life, from the extraction of resources to waste disposal. However, using renewable feedstock does not guarantee that a plastic is environmentally friendly over its entire life cycle. The sustainability benefits of using renewable feedstock may not be sufficient if the material cannot be recycled. To study the recyclability of the polymeric materials including bioplastics and their derivatives, it is a well-tried practice to simulate the mechanical recycling by doing multiple extrusions and to find the durability or service life by accelerated thermal and hydrothermal ageing. These methods make it possible to assess the effects of thermal, hydrothermal and thermomechanical degradation [19,20]. The current review will present the research findings on the recyclability of bioplastics, their blends and thermoplastic biocomposites. The strengths and weaknesses of materials and applied recycling methods, as well as the potential challenges and opportunities for future improvements, are also presented.

2. Mechanical recycling of neat PLA

Mechanical recycling as a favourable recycling method has been under attention for bioplastics such as PLA. For LCAs, cradle-to-gate and cradle-to-grave, Piemonte [21] showed, for both PLA and starch-based bioplastics and using four different recycling methods, that compared with the mechanical recycling process, the other methods, viz., incineration, composting and anaerobic digestion processes, are clearly underperforming from the environmental point of view.

PLA is one of the most studied bioplastics regarding recyclability. PLA can biodegrade under certain conditions, such as the presence of oxygen and moisture [22]. Although PLA is biodegradable, which significantly reduces the negative environmental impact of PLA waste, the material recycling and investigation of changes in the properties of PLA upon its multiple processing are important. The first reason for this is that the generation of industrial waste is inevitable in various industrial processes where an online grinding of the offcuts and blending with neat polymer is integrated [23]; the second reason is the possibility to reuse the post-production (used) PLA waste because it would be advisable to extend their service lives before finally discarding them to bio-disposal facilities such as composting plants [24,25]. Finally, the low environmental impact of PLA would be compromised if the recycling of industrial wastes cannot be achieved [23].

Multiple extrusion of PLA up to 10 times was investigated by Zenkiewicz et al. [24] using a double-screw extruder for granulation of PLA followed by laboratory injection moulding press, for preparation of the test samples. The tensile strength values of PLA did not significantly depend on the number of extrusion cycles and they were a little different from each other, showing a slight total reduction of ca. 5.2% after 10 extrusion processes (Fig. 1). The decrease in tensile strain was also small (2.2–2.4%) and did not depend on the extrusion number. The impact strength clearly decreased with raising the number of extrusions (20.2% after 10 extrusion processes), while the melt flow rate (MFR) and water vapour and oxygen transmission rates significantly increased. The MFR value of the sample subjected to 10 extrusion processes was more than three times higher than that of the original sample. The thermal characteristics showed a slight decrease of thermal stability of PLA, lowered cold crystallization temperature and a slight reduction of the melting point with increasing number of cycles, and no effect on the glass transition temperature [24].

Another study [23] on the reprocessing of PLA (containing 92% l-lactide and 8% d-lactide) showed that only the tensile modulus remains constant with thermomechanical cycles of up to seven injection mouldings. In contrast,
stress and strain at break, modulus, hardness and rheological factors generally exhibit decreased values. The viscosity of PLA decreases greatly (from 3960 to 713 Pa s) after only one injection cycle. Zero viscosity ($\eta_0$) of PLA as a function of injection number is presented in Fig. 2. The mechanical properties of the recycled PLA had become too poor for an industrial application of the polymer.

This dramatic effect of repeated processing cycles was mainly attributed to degradation of PLA by chain scission during processing, which yields a significant decrease in the molecular weight. To understand the degradation phenomena in PLA, two stabilizers, viz., quinone (PLA-Q) and tropolone (PLA-T) were blended with PLA. Quinone was found to be an efficient stabilizer that traps free radicals and maintains PLA chain length at the processing temperatures. This confirms that the main mechanism of the degradation of PLA is through formation of free radicals and not by the hydrolysis caused by moisture [23]. A recent study by Badia et al. [25] also confirmed that during the multiple mechanical recycling of amorphous PLA (95.75 mol% of $\alpha$-lactic acid and 4.25 mol% of $\beta$-lactic acid), chain scission occurs as a result of thermomechanical degradation because, although PLA remained amorphous throughout the reprocessing cycles, a cold-crystallization during differential scanning calorimetry (DSC) and DMTA measurements occurred, with the enthalpy ($\Delta h_{cc}$) increasing with each reprocessing step. DSC data of virgin PLA (VPLA) and of reprocessed PLA (RPLA) are presented in Table 1. In a study by the same group, they simulated the thermal behaviour of virgin and multiple-injected PLA facing combustion, using multi-rate linear non-isothermal thermogravimetric experiments under oxygen. Fig. 3 represents the mass-loss profiles of VPLA and of RPLA reprocessed five times (RPLA-5) [26].

A recent accelerated hygrothermal ageing test using three-times reprocessed and virgin PLA showed that the water diffusion rate decreased with increasing number of reprocessing cycles, and increased with higher hygrothermal ageing temperatures. The degradation was confirmed to be due to the chain scission reactions promoted by temperature; however, with the presence of water in the polymer matrices, hydrolytic chain scission also occurred, which was especially noticeable for reprocessed PLA and higher temperatures. The effects of hygrothermal ageing were particularly significant at higher temperatures and for PLA reprocessed more than once [27].

It is reported that the features of processed PLA strongly depend on its stereochemistry and the impact of the proportion of L- and D-enantiomers [28]. Low amounts of the d-enantiomer (below 1.5 wt%) can accelerate the crystallization process; spherulite growth speed depends on molecular weight and increases upon decreasing the molecular weight. A remarkable level of brittleness has been observed, especially after processing via injection moulding. The proportion of L- and d-enantiomers can affect the possibility of the presence of a crystalline phase after a certain number of processing cycles that might affect the performance of PLA because of decoupling of amorphous and crystalline phases, decreasing chain mobility and modification of the mechanical properties with further processing [23,25].

A recent study on three different biodegradable bioplastics shows that poly(\(\alpha\)-lactic acid) (PLLA) and the aliphatic polyester (Mater-Bi TF01U/095R) can be mechanically recycled up to five and 10 times, respectively, with an acceptable loss in mechanical and thermal properties, whereas the used starch-based waste (Mater-Bi YI014U/C) should be destined to composting, because its recyclability is very poor [29]. PLLA is semi-crystalline and shows a high mechanical strength, whereas PLA (poly(\(\beta\)-lactic acid)) is essentially amorphous, or has a low crystallinity, because of its intrinsic structure [30]. In a study by Helfenbein [22], the processing equipment and the processing parameters were modified to suit the processing of PLA sheets directly and economically into recycled PLA pellets. These recycled PLA pellets, which can be added in 20–50% blend with virgin PLA, not only reduce the material cost, but also help to protect the environment by sending less

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_C$ (°C)</th>
<th>$T_{CC}$ (°C)</th>
<th>$T_{CC}^0$ (°C)</th>
<th>$\Delta h_{cc}$ (J g$^{-1}$)</th>
<th>$\Delta h_M$ (J g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPLA</td>
<td>57.2 ± 0.1</td>
<td>106.2 ± 1.7</td>
<td>123.5 ± 0.2</td>
<td>2.21 ± 0.01</td>
<td>2.19 ± 0.04</td>
</tr>
<tr>
<td>RPLA-1</td>
<td>56.7 ± 0.1</td>
<td>105.6 ± 0.3</td>
<td>117.3 ± 0.3</td>
<td>23.37 ± 0.14</td>
<td>23.83 ± 0.67</td>
</tr>
<tr>
<td>RPLA-2</td>
<td>56.5 ± 0.2</td>
<td>102.0 ± 0.1</td>
<td>110.2 ± 0.4</td>
<td>28.52 ± 0.34</td>
<td>29.77 ± 1.70</td>
</tr>
<tr>
<td>RPLA-3</td>
<td>56.7 ± 0.3</td>
<td>101.2 ± 0.6</td>
<td>109.1 ± 1.0</td>
<td>28.32 ± 0.60</td>
<td>27.33 ± 0.97</td>
</tr>
<tr>
<td>RPLA-4</td>
<td>56.8 ± 0.1</td>
<td>100.1 ± 0.3</td>
<td>107.3 ± 0.5</td>
<td>27.41 ± 0.51</td>
<td>26.94 ± 0.52</td>
</tr>
<tr>
<td>RPLA-5</td>
<td>56.6 ± 0.1</td>
<td>99.6 ± 0.2</td>
<td>106.4 ± 0.1</td>
<td>28.53 ± 0.73</td>
<td>28.31 ± 1.04</td>
</tr>
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</table>

**Fig. 3.** Mass-loss profiles of virgin PLA and PLA reprocessed five times. Reproduced from [26]. Copyright © 2012 Elsevier Ltd.
waste into landfill. Recently, a pilot project was started in PLA recycling by yogurt maker Stonyfield Farm, London-derry, NH, which has begun working with NatureWorks on mechanical recycling of PLA (Ingeo) trim scrap from its thermoforming/filling/sealing packaging lines [31].

3. Mechanical recycling of other neat biopolymers

Unlike PLA, there are few studies available on the mechanical recycling of other pure biopolymers. Polyhydroxyalkanoates (PHAs) have useful mechanical properties and excellent biodegradability. However, they are still expensive and polyhydroxybutyrate (PHB) in particular is quite brittle [32]. Therefore, using them in polymer blends is a better option (see Section 5). It is claimed that PHAs can be mechanically recycled with some loss of molecular weight and mechanical properties [33]. In a study by Shah et al. [34], PHB copolymer was recycled for 10 regird generations, and different blends of seven regird ratios with virgin material were also studied. For the tenth regird generation, the viscosity was reduced by 79% and the ultimate tensile strength by 10%. When using a 50:50 virgin to regird ratio, the viscosity and ultimate tensile strength were reduced by 5%.

Recently, a bioplastic copolymer, polyhydroxybutyrate-co-valerate (PHBV), has been mechanically recycled by Zaveri et al. [20], showing that PHBV is recyclable for up to five cycles, because the reprocessing cycles did not significantly affect the mechanical properties (tensile testing, flexural testing and impact toughness). After reprocessing, the mechanical properties (tensile, flexural and impact strength) were maintained for four cycles; however, they showed a slight decrease after the fifth cycle (7.1%). According to gel permeation chromatography (GPC) results, a slight decrease in molecular weight was observed after the third, fourth and fifth cycles (8.7%, 13.5% and 16.6%, respectively). Fourier transform infrared (FTIR) spectroscopy showed that the chemical structure of PHBV was maintained during reprocessing. PHBV is a copolymer of PHB and polyhydroxyvalerate (PHV) and is a biodegradable polyester produced by microorganisms.

4. Chemical and biological recycling of neat bioplastics

Although mechanical recycling of plastics is the most favourable technology for the industry, it still has some limitations. For example, it may be difficult to convert PLA waste into useful products considering the previously mentioned reprocessing behaviour of PLA, especially thermomechanical degradation during extrusion. Therefore, after each cycle the product quality is lower compared with the starting material and thus its market value decreases [24,35]. On the other hand, maintaining the quality of the recylcate is vital for ensuring the feasibility of the process and the market value [36]. The mentioned facts regarding the difficulty of mechanical recycling of PLA, as well as the sensitivity of this recycling method to contamination, makes it useful for researchers to investigate the possibilities of chemical recycling. In chemical recycling, the polymer chain molecules are broken down into smaller hydrocarbon molecules (e.g., monomers), which are then fed into the polymerisation process. Regarding the energy balance as well as costs, these processes stand between pure remelting and combustion [37].

Two main processes have been used for chemical recycling of PLA. The first one is hydrolysis of PLA at high temperatures to obtain lactic acid [38–41], and the second one is thermal degradation of PLA to prepare L,L-lactide, which is a cyclic dimer and can be used for polymerisation of new PLA [42–45]. The chemical recycling process that breaks down PLA into lactic acid is called hydrolysis, and requires the presence of water as well as high temperature. The obtained lactic acid has a high purity and can be polymerised to virgin PLA. This recycled PLA closes the loop and the process may be called a cradle-to-cradle process [22,40]. The recycling efficiency has been shown by Faisal et al. [40] to depend strongly on the operating conditions such as temperature, reaction time and ratio of water to sample. Table 2 shows the influence of the reaction time and temperature on the recycling efficiency. Furthermore, depending on the temperature, the predominant reaction was recycling to lactic acid (at lower temperatures) or thermal degradation into other low molecular weight carboxylic acids (at higher temperatures).

Chemical recycling has been tried for other biopolymers as well. The chemical recycling of PHAs by thermal degradation, which resulted in transformation into vinyl monomers [46], and enzymatic transformation into an oligomer [47] have been reported.

Cellulose esters prepared from the esterification of cellulose have become highly significant as biodegradable materials obtained from renewable bio-feedstock, and among them, thermoplastic cellulose acetate is the most industrially favourable derivative [48]. Reprocessing of acetate-based fibres waste goes back to the 80s, when conversion of cellulose acetate yarn and cellulose triacetate yarn to end-use products such as hand knitting yarns, knitted outerwear and non-woven fabrics was suggested [49]. However, most of the manufacturing waste and post-consumer waste of cellulose acetate has been simply sent to landfill, and still there is an unsatisfied need for a process for the recycling of manufacturing waste of cellulose acetate [50]. A patent on recycling of cellulose acetate was disclosed in 2010 in which cellulose acetate ester waste and a hydrolysing agent are added to a reactor. The waste is hydrolysed by agitation and heating the agent/waste mixture. After distilling the hydrolysing agent, the solid material is separated from the hydrolysed mixture to create a water-soluble product.

### Table 2

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>Recycling efficiency (%)</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>11.9</td>
</tr>
<tr>
<td>8</td>
<td>35.2</td>
</tr>
<tr>
<td>10</td>
<td>61.7</td>
</tr>
<tr>
<td>15</td>
<td>85.5</td>
</tr>
<tr>
<td>20</td>
<td>–</td>
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<td>30</td>
<td>–</td>
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(Received 23 July 2013; accepted 23 October 2013)
stream. This stream includes monosaccharides, polysaccharides, partially hydrolysed cellulose, acetic acid or combinations thereof. Finally, the water-soluble product stream is collected \[50\]. Recently, blending and functionalization of cellulose acetate through reactive melt processing has been achieved to produce more environmentally friendly products and to improve the biodegradation aspects of these cellulosic derivatives \[48\].

Biological recycling is another alternative option. The recycled material forms a biomass that binds carbon for a longer period than mechanical recycling or incineration. Biological recycling is usually considered as composting, where microorganisms degrade the organic waste and the degradation products are returned to the natural carbon cycle \[51\]. This belief is fairly common, but unfortunately not correct. The CEN standard for biodegradable polymeric materials stipulates that they must be substantially (>90%) converted to carbon dioxide in a compost environment within six months \[52\]. This means that compostable materials do not bind carbon for a longer period. Instead, carbon dioxide is formed as in incineration but without energy recovery and brings no benefit to the environment (authors’ remark).

A recent method explored the preparation of biomonomers from the degradation residuals of bioplastics. According to Accinelli et al. \[53\], a variety of microbial isolates can use the starch-based bioplastic (in their study called Mater-Bi) as a source of carbon, which suggests a new alternative method of recycling the carrier bags made of this material. After deterioration of the bags in the soil, starchy residues from bags were fermented by the fungus *Rhizopus oryzae* to produce up to 35 mg of lactic acid per g of bag residues. In a review on conversion of biomass to selected chemical products, it is reported that biopolymers can be depolymerised/fermented into molecules that can be used for synthesis of chemicals. Conversion of biopolymers (not bioplastics) such as polysaccharides (cellulose, hemicellulose, starch, inulin and chitin) or other biopolymers (lignin, proteins) to different small molecules or chemicals has been discussed \[54\].

### 5. Mechanical recycling of blends containing bioplastics

Similar to pure bioplastics, the recycling of bioplastic blends has been investigated using both mechanical and chemical recycling methods. Hybrid bioplastics, which refer to blends of bio-based and petro-based polymers, are regarded as more sustainable than pure synthetic polymers because of substituting a part of the petro-based resin by polymers from renewable resources. Apart from the environmental aspects, another advantage of this type of blend is that the limitations in the properties of neat bioplastics are overcome. For example, pure PLA has some drawbacks, such as poor toughness, low impact resistance and poor crystallization behaviour, that limit its current use in food packaging \[55\]. Another drawback of PLA is related to its processing in the molten state, and its tendency to undergo thermal degradation. Degradation during processing is related to the processing temperature, the residence time in the extruder and hot runner, and in some cases to the moisture content of the granules \[56\]. These drawbacks affect also the recyclability of PLA. To overcome the drawbacks of pure PLA, an economically viable strategy is blending PLA with other polymers, because other improvement methods such as copolymerisation of lactic acid with other monomers have not been really successful or commercially viable \[57\]. Another example is thermoplastic starch (TPS) with typical drawbacks such as low moisture and low temperature resistance as well as starch recrystallization over time leading to embrittlement and plasticizer migration. To partly overcome such problems, TPS is blended into a hydrophobic polymer matrix, and different blends of TPS with biodegradable and non-biodegradable polymers have been studied \[55,58,59\]. Starch blends in polymer applications already have a good position in world markets \[60\]. PHAs as another family of bioplastics are still expensive, and, for example, PHB is quite brittle. Thus, blends of PHAs offer biodegradable materials with better economy and good mechanical properties. Miscible blends of PHAs with appropriate polymers can be formed through hydrogen bonding and/or donor–acceptor interactions. Immiscible blends of PHA show a better apparent biodegradability compared with miscible blends.
An economically sustainable measure to decrease the greenhouse gas emissions (GHG) is by using polymer blends with TPS. These hybrid bioplastics replace a part of the petro-based polymers with TPS while maintaining properties, reducing the cost and helping the environment. Furthermore, it is claimed that such blends can be recycled with very little loss in properties, and some of them are available as fully biodegradable blends [64].

Reprocessing of a biodegradable starch-based system, mainly composed of starch and PCL (Mater-Bi series Z from Novamont), has been investigated by La Mantia et al. [65]. The rheological and mechanical properties of reprocessed samples by extrusion indicated that, in the adopted processing conditions, the properties are preserved. After five extrusions, only a slight decrease of these properties was observed. An investigation on the thermomechanical degradation of this blend in a mixer showed that during melt processing, two processes take place simultaneously: degradation because of the breaking of polymer chains (mostly in the PCL phase) and the formation of some cross-linked structures in the starch phase. The degradation was due mostly to the thermal stress; however, the mechanical stress could strongly increase the degradation as well.

Blends containing TPS can also be made using recycled petro-based polymers. Blends of mechanically recycled petro-based polymers such as low-density polyethylene (LDPE) with corn starch can not only substitute the virgin synthetic polymer with post-consumer materials and also renewable material, but also the product may become biodegradable and cheap, as is claimed by Pedroso and Rosa [66]. However, the biodegradability of such material is questionable because of the recalcitrance of PE to biological attack related to its hydrophobicity, hydrorepellency and high molecular weight. Consequently, if the PE part of the material is not modified to facilitate its disintegration and the subsequent biodegradation, only the starch part of the blend will biodegrade with fragmentation of the material as a result (authors’ remark).

An example of this type of blend is packaging bottles made of TPS and recycled PE, which contain both recycled and bio-based content and could reduce the GHG by 75% compared with neat PE. To maintain the performance, applying strategies such as multilayer construction has allowed 25% TPS in two of the three layers of bottles without compromising the performance of the bottle [67]. Blends of soy protein–corn-starch plastics have been prepared and tested for recycling by Ralston and Osswald [68]. Among different formulations tried in the injection moulding, the soy protein-to-corn-starch ratio of 2:3 showed the best overall tensile properties (tensile strength of 4.8 MPa, modulus of 154 MPa and elongation at break of 120%) and a titanate coupling agent also improved the tensile properties. After recycling this plastic, the tensile properties were slightly decreased. Higher relative humidity substantially decreased the strength, modulus and elongation, and led to gel formation.

There are still many bioplastic blends whose recyclability has not been studied. The commercially available bioplastic-containing blends are collected in the Appendix at the end of this paper. It is important to be aware of such blends because of their coming effects on the conventional
plastic waste streams. When preparing this Appendix, the main focus was on listing the available durable bioplastic hybrids because they are more important for the mechanical recycling than are the biodegradable blends designed for composting.

6. Chemical recycling of blends containing bioplastics

Chemical recycling of bioplastic blends has also been investigated because of the limitations of the mechanical recycling method, especially the required sorting, thermomechanical degradation of polymers and sensitivity to material impurities. For example, PLA and PET cannot be easily or cheaply sorted by sight or by separation methods based on density, which are not efficient enough because of the similar densities of the polymers [69]. On the other hand, industry is concerned about the potential contamination of the PET recycling stream by water bottles made of PLA. It is believed that PLA at even very low contents (any level >0.1% in a PET recycling stream) can act as contamination and seriously affect the properties of the recycled PET. Therefore, PLA needs to be separated from PET before the recycling process starts [70]. It was shown by NatureWorks LLC that near infrared (NIR) technology can separate 93 of every 100 PLA bottles out of a PET recycling stream, and that the remaining level of contamination would not create a significant haze or colour difference [70,71]. However, even when PLA is separable, it is still problematic because it can increase the cost of recycling by necessitating investment in new sorting equipment, such as NIR sensors, that requires an expensive investment [69]. Furthermore, it is shown that sorting by this method is not always effective. According to a research report from WRAP in UK [72], NIR sorting systems have difficulty in identifying black polymers, or those with special structures such as laminated trays or cups. Therefore, alternative solutions to waste treatment (such as selective chemical recycling) need to be evaluated. On the other hand, another report by NatureWorks claims that PLA is a neutral component in the recycling stream and can be effectively sorted out using available detection technologies, because PLA can be sorted from other plastics in the recycle stream at approximately 98% accuracy, using NIR detection technology, which is the same sorting equipment used today to remove plastics other than #1 and #2 plastics [73]. Plastics designated #1, made from PET, are the easiest and most common plastics to recycle (used in, e.g., soda and water bottles), whereas plastics #2 are products use as, e.g., milk and shampoo containers made of high-density polyethylene (HDPE) [74].

A recently published paper by La Mantia et al. [75] confirms that the presence of small amounts of PLA in the PET waste can significantly affect the rheological properties under non-isothermal elongational flow. The mechanical properties were considerably affected only in some circumstances while thermal stability was not significantly affected. PET is largely used in processing operations where the elongational flow, especially a non-isothermal elongational flow (e.g., spinning and blow moulding), is applied. Therefore, a rheological characterisation under non-isothermal elongational flow (melt strength and breaking–stretching ratio) was performed to investigate the potential use of PLA-contaminated PET for the same applications as for pure PET. Melt strengths of some samples are presented in Fig. 5.

A selective recycling of mixed PLA and PET was studied by depolymerising PLA into a liquid and recovering the unreacted solid PET by filtration. Among three different catalysts tried for the glycolysis of post-consumer PET waste, zinc acetate was the most soluble and effective. Furthermore, for alcoholysis of PLA, zinc acetate could yield an effective depolymerisation of waste PLA (in methanol or ethanol) giving lactate esters, whereas PET remained as an unreacted solid under the same reaction conditions. This is a promising process for the chemical recycling of both neat PLA and mixed PLA/PET, as the separation is facilitated via converting PLA to a liquid monomer from which the solid PET can be filtered. Different routes and the alcoholysis reaction of PLA are presented in Figs. 6 and 7, respectively [35].

To clarify the influences of other types of plastics as contaminants during chemical recycling, some specific polymer blends were studied. It was found that linear LDPE and PS had no effect on the chemical recycling of PLLA [76].
Developing a selective chemical recycling process, blends of PLLA/PE [76] and PLLA/poly(butylene succinate) (PBS) [76,77] were studied, to be degraded into each of the repolymerisable oligomers using catalysts and enzymes. Two procedures for the selective chemical recycling of PLLA/PE and PLLA/PBS blends were investigated by Tsuneizumi et al. [77]. The first route was the direct separation of PLLA and PE from the PLLA/PE blend by their solubility in toluene, and then the chemical recycling of PLLA. The second route was the selective degradation of PLLA in PLLA/PE blend forming the lactic acid oligomer. The isolated PBS was degraded into cyclic butylene succinate (BS) oligomer using lipase (triacylglycerol hydrolase + carboxylesterase), and PLLA was degraded into lactic acid (LA) oligomer using montmorillonite (MK5). Both BS and LA oligomers were repolymerisable to polymers. The repolymerised PLLA was obtained with molecular weight, $M_w$, greater than 100,000 g/mol. The PE remained unchanged and was quantitatively recovered. Fig. 8 shows the routes to selective recycling of PLLA/PE blend.

Jarerat et al. [78] developed an efficient method for production of PLA degrading enzymes. They speculate that biological recycling of PLA from plastic wastes containing PLA, using the enzymes, will be more economically competitive compared to other methods.
7. Recycling of bio-based PA, PUR and PC

High-performance engineering plastics are being extensively used, especially in automotive and electrical applications. Currently, high-performance plastics are produced from fossil raw materials; however, there is a rapid development towards bio-based engineering plastics. Biotechnology and biorefinery processes are now being developed to supply renewable components, which are polymerised in effective conventional melt- or gas-phase polymerisation processes. The resulting bio-based polymers combine the advantages of a low carbon footprint, because of renewable feedstocks, with the recycling capability and energy effectiveness of the polymerisation processes. There are, for instance, several possible biological routes for producing intermediates towards PA manufacture, such as routes involving bio-based adipic acid, hexamethylenediamine (HMDA) and caprolactam. The most important source is currently castor oil, obtained from the seed of the castor oil plant. The key ingredient in castor oil for PA use is sebacic acid, also known as decanedioic acid. More than 70% of the global sebacic acid demand is for PA 10:10 and 6:10, according to an industry source. In 2010, global demand for sebacic acid was 58,700 tonnes [80]. PA is a thermoplastic and can be reground to pellet size and reprocessed. The main issues with mechanical recycling of PA are the fact that there are so many different materials: PA 6, PA 6:6, PA 6:12, PA 11, PA 12 and so on. There are few examples of recycling of bio-PA. One example is the bio-based PA 11 derived from castor beans, produced by French-based chemical company Arkema. This polymer has good compatibility with PA 6:6, and at the end of a carpet’s useful life, the TruBlend carpet fibre is recyclable using PA 6:6 recycling methods to convert it back into polymer for fibre [81].

Thermoplastic polyurethanes (TPUs) consist of linear segmented block copolymers composed of hard and soft segments. TPUs are formed by the reaction of diisocyanates with short-chain diols (so-called chain extenders) and diisocyanates with long-chain difunctional diols (known as polyols). The number of possible combinations is almost unlimited by varying the structure and/or molecular weight of the three reaction compounds, which makes it possible to design the structure of the polymer in many different ways. The currently available TPUs can be divided mainly into two groups, based on soft segment chemistry, viz., polyester-based TPUs (mainly derived from adipic acid esters) and polyether-based TPUs (mainly based on tetrahydrofuran (THF) ethers). For the present, bio-based polyurethanes (PURs) are creating a lot of attention to replace their petroleum-based counterparts. Because isocyanates, so far, have not been made using the bio-based approach, the development work is mainly concentrated on replacing fossil polyols with bio-polyols. The most important source of bio-polyols is castor oil, but soybean oil is also commonly used. However, lower mechanical properties of soy PURs and the necessity to reinforce the material with glass fibres or hemp fibres have been reported [82].

Novel bio-based plastics can also be derived from citrus fruits and carbon dioxide using limonene oils that can be produced by extraction of orange peel in an industrial process. The oils can then be used to form mono- and difunctional epoxides by oxidation, followed by subsequent catalytic copolymerisation of limonene monoxide with carbon dioxide. The result is thermoplastic poly(limonene carbonates) with properties similar to polystyrene (PS). Copolymerisation of limonene monoxide with dicarboxylic acid anhydrides, such as succinic anhydride, yields limonene-based polysters. Limonene dioxide can also be used to produce limonene dicarbonates, which can be cross-linked with polyfunctional amines, such as citric aminoamides, to produce a wide variety of cross-linked terpene-based bio-PURs without use of isocyanates [83].

Like other plastics, PUR can be recycled either by mechanical or by chemical recycling. However, the recycling of PUR has always posed unique challenges because of its wide variety of applications. Mechanical regrinding is the oldest method in PUR waste recycling and the regrind wastes are used as filler in the new formulations. For instance, flexible PUR foam can be recycled using pieces of chopped material and a binder to create carpet underlay, sports mats, cushioning and similar products. PUR parts from various applications, such as automobile parts, refrigerators and industrial trim can be granulated and blended either with a powerful binder or polyurethane systems, then formed into boards or mouldings under heat and pressure. The resulting products are used in sound-proofing applications, furniture and flooring [84]. Chemical recycling of PUR includes techniques such as glycolysis, hydrolysis, pyrolysis and hydrogenation, but it is for the most part considered economically uncompetitive compared with formulating with virgin raw materials.

Polycarbonate (PC) is one of the most important engineering thermoplastics because of its favourable properties, such as impact resistance, transparency, heat resistance and dimensional stability. Unlike most thermoplastics, PC can undergo large plastic deformations without cracking or breaking. As a result, it can be processed and formed at room temperature using sheet metal techniques, such as bending on a brake. There is a lot of interest in replacing petroleum-based PC with bio-based PC in conformity with other polymers. Because the conventional PC is synthesised from bisphenol A and phosgene (BPA-PC), there is an additional driving force to replace both phosgene, which is a toxic gas, and BPA, which exhibits hormone-like properties that raise concerns about its suitability in consumer products. Recently, several new alternative synthesis pathways have been developed: Enantiomerically pure functional PC was synthesised from...
a novel seven-membered cyclic carbonate monomer derived from naturally occurring L-tartaric acid. The monomer was synthesised in three steps and screened for polymerisation with four commercially available lipases from different sources at 80 °C, in bulk [85]. A novel type of glycerol-derived, water-soluble PC with pendant, primary hydroxyl groups was prepared from 2-(2-benzoyloxyethoxy)trimethylene carbonate [86]. A PC has also been synthesised successfully from terpene diphenol and diphenyl carbonate by melt polymerisation without using any catalysts [87].

PC can be processed by all of the methods typical for thermoplastics, but it is a difficult polymer to process. Its processing temperature is high (about 300 °C at injection) because of the low heat conductivity. In the melted state, PC shows strong adhesion to metals, which makes the processing considerably more difficult and its high viscosity requires high injection power. Furthermore, the advantageous properties of PC, such as impact resistance, become impaired when additives such as coloured pigments, fillers or flame retardants are used in the compound. Because the recycling steps reduce the mechanical performance of PC, the use of impact modifiers can be necessary in recycled PC to reach the desired level of performance. Another possibility when recycling PC residues is to increase the molecular weight to a sufficient level for the projected new use.

It is well known that during reprocessing, condensation thermoplastics such as PET, PBT, PA, BPA-PC and TPU, as well as their blends, degrade via hydrolysis, alcoholysis, thermal cleavage, etc. The main reason is that condensation thermoplastics are processed at very high temperatures (around 300 °C) where the rate of these degradation reactions is very fast, leading to a decrease in molecular weight and severe loss of mechanical and thermal properties. These conditions constitute an obstacle for reprocessing large amounts of post-industrial polycarbonate waste into demanding engineering applications. To overcome this obstacle it is sometimes necessary to increase the molecular weight of the polymers. One process for increasing the molecular weight of decomposed low-molecular weight polycarbonates is by using reactive chain lengtheners [88]. These chain lengtheners react in the plastic melt, e.g., in an extruder, with the functional chain ends of the polymer under conventional compounding conditions.

8. Recycling of biocomposites

There are several definitions for biocomposites; the most accepted definition is by Mohanty et al. [89], stating that biocomposites are composite materials in which at least one of the constituents is derived from natural resources. This corresponds well with the definition stated in the CEN standard. Such a definition offers countless possibilities for the design of the composite formulations, ranging from petroleum-based to bio-based polymer matrices, from glass fibre to natural fibre reinforcement and from virgin to recycled polymers. Important for all biocomposites, is that their susceptibility to abiotic degradation, water absorption and biodegradation processes must be considered to guarantee their structural and functional stability during their service life. Biocomposites cannot easily be called sustainable materials. According to Vilaplana et al. [90], a sustainable biocomposite should fulfill several requirements: (1) be manufactured from renewable and/or recycled resources; (2) the synthetic, modification and processing operations should be energy effective and favourable; (3) all the stages of their life cycle should be free of any hazardous environmental or toxicological effects; and (4) have implemented waste management options. Developing biocomposites with a thermoplastic rather than thermoset matrix has been of great interest, mainly because of their recyclability [91]. It is shown that using natural fibres in synthetic thermoplastic-reinforced biocomposites may offer a protective effect against photo-oxidation. The photo-oxidation promoted by ultraviolet radiation results in chain scission in the thermoplastic matrix and the formation of surface cracks in the composites [92,93]. However, the propagation of such cracks can be controlled by increasing fibre load [98] and by improving adhesion between fibres and matrix [117], either by fibre treatment or by the addition of compatibilizers [90].

When natural fibres and biopolymer matrix are mixed together, each component originates from renewable resources and such biocomposites may be compostable, making them attractive alternatives to glass–fibre-reinforced petrochemical polymers. Besides biodegradation, recycling of biocomposites makes them even more interesting, extending their life cycle and reducing the global impact on the environment by lowering consumption of raw materials and saving carbon for a longer time. Biocomposites based on PLA and flax fibre have been recycled by mechanical processing [94–96]. Compostable flax/PLLA has been shown to have similar mechanical properties to those of glass fibre/PP and superior properties to hemp/PP and sisal/PP composites. After mechanical recycling, as shown in Fig. 9, the tensile properties of biocomposites containing flax fibres at different fibre contents (20% and 30% by weight) are conserved until the third

Fig. 9. Evolution of tensile strength at yield for PLLA/flax fibre biocomposites containing 20% fibre (BC-20%) and 30% fibre (BC-30%) as a function of injection cycles. Reproduced from [96]. Copyright © 2008 Published by Elsevier Ltd.
injection cycle. In general, reprocessing resulted in lower molecular weight, reduction of fibre length and separation of fibre bundles. However, the biocomposite properties after three cycles (with no added virgin polymer) were promising regarding the recyclability of this material. Scanning electron microscopy (SEM) images in Fig. 10 show the tensile fracture surfaces, which give qualitative information about dispersion and orientation of fibres. After the first injection cycle, many bundles of fibres can be noted (Fig. 10a), whereas after six injection cycles a more homogeneous fracture surface is observed (Fig. 10b) [96]. PLA/flax composites have their main application in the automotive industry. The mechanical recycling of PLA/flax has led to a decrease in the tensile strength (23%), impact strength (8%) and E-modulus (5%), as well as a corresponding decrease in the PLA molar mass. Although the effect of a decrease in the fibre length was not investigated, it was suggested to be an important factor in the observed deterioration of mechanical properties [100, 98].

The recycling ability of biodegradable polymer matrices and their cellulose-reinforced composites has been investigated by Lopez et al. [29]. Three different biodegradable matrices, viz., PLLA, aliphatic polyester and starch-based matrices were reinforced with chemothermomechanical pulp (CTMP)-fibres. CTMP-fibres acted mainly as filler in PLLA composites, but reinforced TPS-based composites presented enhanced recyclability and mechanical properties. A study on highly functional PLA composites by Inoue et al. [97] reports that a kenaf-fibre-reinforced PLA has high impact strength, high heat resistance and good mouldability, and has been used in PC parts and mobile phone housings since 2004 and 2006, respectively. A thermoreversibly cross-linked PLA has excellent shape memory and recyclability, for example, in rewritable shape memory.

Bourmaud et al. [98–100] have shown that composites of PP and vegetal fibres are recyclable following the European directive 2000/53/EC, which imposes the reusing/recycling of at least 95% of a worn vehicle weight before 2015. The mechanical and thermophysical behaviour of PP/hemp or sisal composite after seven injection cycles showed a small decrease in tensile strength and modulus of the seventh-time recycled composite, which could be compensated by adding extra fibres/polymers in proportion to the recycled materials. This could retain the mechanical properties of the material. To analyse rigidity after recycling, the experimental tensile test values were applied in micromechanical models, taking the aspect ratio changes into account, to estimate the stiffness of the PP/vegetal fibre-injected composites before and after recycling [100]. Although mechanical properties were well conserved with the reprocessing of PP/vegetal fibre composites, the adhesion between the fibres and PP without any treatment was poor [98]. In a study by Rao et al. [101], the sisal–PP composite sheets were mechanically recycled using an extruder. The effects of recycling on crystallinity, fibre length, mechanical properties and stress relaxation were evaluated. According to Srebrenkoska et al. [102,103], the recycling of PP-based composites reinforced with rice hulls or kenaf fibres is promising because their properties remain almost unchanged after the recycling processes. Furthermore, the recycled composites have potential use as construction materials for indoor applications because the flexural strength and modulus of these materials are comparable to those of conventional formaldehyde wood medium-density fibreboards. Furthermore, PP-based composites were less sensitive to processing cycles than PLA-based composites.

Recycling of thermoplastic composites with wood fibres has also been studied [104,105]. Wood-fibre-reinforced PP with a maleated polypropylene (MAPP) as coupling agent was recycled/reprocessed up to eight cycles and showed a decrease in both tensile strength and Young’s modulus, but an increase in the elongation at break because of the decreased average fibre length. Thermal stability and moisture resistance of composites improved with recycling because of the improvement of interfacial bonding between fibre and matrix [105]. For PVC/wood–fibre composites, the influence of the vegetable fibres on the thermomechanical degradation of the composite material was studied after several processing cycles. The different behaviours between the composite and the pure PVC was due to the effect of the fibres, which accelerated the PVC degradation by dehydrochlorination followed by cross-linking reactions [106]. Composite materials containing PE and rice hulls, wood flour or bagasse fibres and 2% compatibilizer were recycled up to five times by regrinding and reprocessing. The recycled composites had considerably lower water absorption and thickness swellings than those
of the original composites, reflecting changes in physical and chemical properties under the recycling process [107].

Grinding a biocomposite and then using it as reinforcement is another method of recycling. Grozdanov et al. [108] have recycled biocomposites of PLA reinforced with rice husks and kenaf fibres, as a means of reuse as reinforcement. Recycling–reuse facilities to transfer solid polymer composite waste into polymer mortars and concrete structures for the low–cost building industry have been designed and presented. To prepare polymer mortars, milled recycled biocomposites (milled size of 0.050 mm) and foundry sand were mixed in unsaturated polyester resin as a binder (commercially available o-phthalic liquid polyester with 35% monomer content). The mix proportions were 20/40/40 wt%, respectively.

Generally, it is expected that biopolymer-reinforced composites have less recyclability than their neat thermoplastic matrix, because composites are more sensitive to thermomechanical degradation. That is why composting is supposed to be the main waste management route for such materials; however, as mentioned before, attempts to recycle composites have been tried, such as compostable flax/PLLA [90,96]. In general, the recyclability of natural-filler-reinforced biocomposites (based on either a synthetic or a biopolymeric thermoplastic matrix) is usually guaranteed up to several reprocessing cycles to have preserved mechanical properties. Multiple processing may even enhance the interfacial adhesion between fillers and matrix, resulting in a reported increase in thermal stability in the reprocessed biocomposites. However, different degradation effects can happen because of repeated recycling of biocomposites, such as fibre length reduction and chain scission in the synthetic thermoplastic matrix, which leads to a decrease in the molecular weight and an increase in crystallinity [90].

Considering the achievements in the processing of biocomposites, there are different potential strategies to improve the properties of recycled biocomposites as well. For example, it is reported that high-energy radiation (gamma irradiation) can improve the interfacial adhesion between fibre and matrix in jute-fibre-reinforced PCL [109] and short sisal-fibre-reinforced natural rubber biocomposites [110,111]. This can consequently improve the mechanical properties and slow down the degradation rates in weathering, water exposure and soil burial testing. Gamma radiation treatment may be used in special products to tailor the properties, because this method is expected to increase the production cost [90].

Nanobiocomposites made of biopolymers and nanoparticles (cellulose or lignin) are another class of novel biocomposites; however, there is a lack of knowledge about potential toxicity issues of nanoparticles in regard to recycling, composting or incineration, because nanofibres are obtained by the Kraft process and hazardous chemicals are used to improve their performance [112].

9. Limitations, challenges and opportunities

In general, plastic recycling issues are complex. Some general important aspects, such as the need to revise collection and reprocessing infrastructures, the ‘eco-design’ approach to products, and life cycle analysis of ‘cradle-to-grave’ use [113] are important in bioplastic recycling as well. A study in 2012 by Álvarez-Chávez et al. [114] provides insight into the health and environmental impacts of bio-based plastics, and analysis found that none of the bio-based plastics currently in commercial use or under development is fully sustainable.

A study in 2007 reported that to be mechanically recyclable, a polymer should have a critical mass; therefore, biopolymers must be either completely substitutable with existing recycled resins, or be available in sufficiently large quantities to achieve the needed critical mass. However, to date, biopolymer volume has not been encouraging. The recycling of plastics mixed with bioplastics is also challenging. For example, although some bioplastics may have little performance or economic effect on recycled HDPE at low contents, they have been shown to be incompatible with PET, resulting in performance and economic limitations at even very low concentrations [115]. Mechanical recycling provides an effective and easy way of reusing the material, but recycled polymers are often contaminated, resulting in inferior mechanical properties to created feedstock. The increased use of bioplastics and biocomposites may have further serious implications for the recycled plastics industry, as it could potentially lead to the contamination of collected conventional plastics by bioplastics, affecting the quality and physical integrity of the resulting materials [116]. Investment may be needed in sorting technology to deal with this challenge. Another barrier could be the compatibility with existing manufacturing equipment and end-of-life management systems.

Another challenge with mechanical recycling is the inherent thermomechanical degradation during reprocessing that may change the polymeric structure [117] and finally result in deterioration of the properties of the recycled products [26,118]. In fact, during mechanical recycling, polymers are affected by degrading agents such as shear stress, heat, oxygen, UV light, catalyst residue and water. Consequently, this leads to changes in chemical and physical properties that alter the recycled polymers’ stability, functional quality and long-term properties during their life cycle (synthesis-processing-service life-discarding-recovery). Thus, extruded recycled products of high quality are difficult to obtain. High quality is especially crucial in some applications such as thin films. The mentioned degradation may reduce the molecular weight of a polymer and change the thermal behaviour, and viscoelastic and mechanical properties of recycled bioplastics and petroleum-based polymers [25,36,119–121]. The degradation under processing takes place not only in polymers sensitive to such factors, such as PLA, but also in polymers that are relatively resistant to degradation, for instance, PE. Furthermore, synthetic polymers may show different behaviour upon recycling. These factors should be considered when recycling the blends of bioplastics and petroleum-based polymers. For instance, in the case of PE, after multiple processing, both degradation and cross-linking occurs, which increases the melt viscosity, whereas using antioxidants significantly hinders an increase in the melt flow rate [122–124]. In contrast, the multiple extru-
sion of PP and its copolymers results in a decrease in the molecular weight and the viscosity of the polymer in the plasticized state, and as a result, the tensile strength at break decreases [125–129]. The degradation in biocomposites may be even more complicated than in pure bioplastics or blends, as both polymer matrix and fibre may degrade under high processing temperature and shear forces. Furthermore, the mechanical processing reduces the reinforcing-fibre lengths, resulting in decreased overall mechanical strength of the recycled composite [101,105,130]. The sensitivity to moisture uptake and hydrothermal degradation is also a well-known weakness of many bioplastics. Water absorption can also affect biocomposites manufacture by impairing the interfacial strength between the reinforcement and the resin in the final composites. It is not yet fully understood how interactions between different components in bio-composites affect thermal stability and the formation of degradation products during processing [131,132].

Where the limitations of mechanical recycling reduce the economic viability, other alternatives are used. Galactic in Belgium has started the first pilot unit to chemically recycle PLA (called Loopla) [133]. However, chemical recycling has its own drawbacks, for example, being costly because of high energy consumption, having a complicated process, and being applicable in only some biopolymers [134]. In the case of PLA, because thermal degradation and hydrothermal depolymerisation generally require a temperature above 200 °C, it requires a high amount of energy and often causes isomerization [77,134]. Mechanical and chemical recycling can be difficult in some cases. For example, in biocomposites, because of the sensitivity of the bio-based matrix and/or the reinforcing fibre to thermal processing, composting appears to be a possible alternative, if the matrix is biodegradable. The composting process must be performed at an industrial level to control the environmental factors such as temperature, pH and moisture [90]. Although the quality of the recycled materials and the cost of recycling are key issues in the recycling of composites, it is shown that the natural-fibre-reinforced thermoplastics can be economically recycled, but reproducibility still needs improvement [135]. The valorization technologies, such as pyrolysis and combustion, can be a viable solution to waste management of bio-based recycled plastics, if no better method can be found [136]. Incineration as the final option can partially recover the energy value of the bioplastics and biocomposites [90]. Combustion has been pointed out as appropriate for the energy recycling of reprocessed PLA submitted to more than three successive injection cycles [26]. All four different recycling methods of mechanical, chemical, composting and incineration have their own negative and positive characteristics.

Mechanical recycling is still the most preferred and viable recycling method. There are many factors that can be considered to facilitate and improve the mechanical recycling of bio-based materials. For instance, additives can play an important role in improving bioplastics for durable uses by providing cost reduction, reinforcement, inhibiting degradability, increasing thermal resistance, reducing brittleness and increasing crystallization rate [137–139]. When recycling the blends of bioplastics, because a polymer mixture is generally immiscible and incompatible, it is necessary to develop new methods to improve the interfacial adhesion, such as using adequate compatibilizers, other additives, or electron irradiation [140]. A promising method is by using γ-irradiation, as a recent article in press shows. Blends of TPS/PC were γ-irradiated in the range 0–150 kGy, which resulted in numerous radicals remaining trapped in the materials after irradiation, even after a long time, enabling reactions between starch and PC. A relatively good affinity between the two components after blending in a microextruder was observed and the irradiated blends exhibited higher thermal stability than non-irradiated blends [141]. In the case of recycling biocomposites, it is expected that the factors influencing the performance of biocomposites can affect the performance of the recycled biocomposites as well. For example, higher as-

### Appendix A

Commercially available blends containing biopolymers (RC = renewable content).

<table>
<thead>
<tr>
<th>Bio-blend</th>
<th>Features, other information</th>
<th>Application</th>
<th>Product code</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch/LLDPE up to 30/70 wt%</td>
<td>Hybrid, RC, TP&lt;sup&gt;a&lt;/sup&gt;, granulate</td>
<td>Blown film</td>
<td>Terraloy (TM) BP-10000A</td>
<td>Teknor Apex</td>
</tr>
<tr>
<td>Starch/PP up to 30/70 wt%</td>
<td>Hybrid, RC, TP, granulate</td>
<td>Extrusion</td>
<td>Terraloy (TM) BP-13000A</td>
<td>Teknor Apex</td>
</tr>
<tr>
<td>Starch/HIPS up to 30/70 wt%</td>
<td>Hybrid, RC, TP, granulate</td>
<td>Injection moulding</td>
<td>Terraloy (TM) BP-18003A</td>
<td>Teknor Apex</td>
</tr>
<tr>
<td>Starch/LLDPE up to 50/50 wt%</td>
<td>Hybrid, RC, MB&lt;sup&gt;b&lt;/sup&gt;, granulate</td>
<td>Blown film</td>
<td>Terraloy (TM) MB-10000A</td>
<td>Teknor Apex</td>
</tr>
<tr>
<td>Starch/PP up to 50/50 wt%</td>
<td>Hybrid, RC, MB, granulate</td>
<td>Injection moulding</td>
<td>Terraloy (TM) MB-13000A</td>
<td>Teknor Apex</td>
</tr>
<tr>
<td>Starch/HIPS up to 50/50 wt%</td>
<td>Hybrid, RC, MB, granulate</td>
<td>Injection moulding</td>
<td>Terraloy (TM) MB-18003A</td>
<td>Teknor Apex</td>
</tr>
<tr>
<td>Bio-blend</td>
<td>Features, other information</td>
<td>Application</td>
<td>Product code</td>
<td>Manufacturer</td>
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</tr>
<tr>
<td>Ethylene–methyl acrylate copolymer/starch</td>
<td>Hybrid, RC, durability, flexibility and toughness. TP, granulate</td>
<td>Extrusion, injection moulding: consumer goods, footwear, handbags, wire and cable insulation, tubes and hoses</td>
<td>Hybrid 651D</td>
<td>Cereplast</td>
</tr>
<tr>
<td>PP–PE copolymer/starch (30–55%)</td>
<td>Hybrid, RC, TP, granulate</td>
<td>Injection moulding: durable applications, consumer goods, interior automotive parts, furniture, packaging</td>
<td>Hybrid 101, 102D, 105D, 106D</td>
<td>Cereplast</td>
</tr>
<tr>
<td>TPE/starch (20–50%)</td>
<td>Hybrid, RC, stretch with some recovery TPE, granulate</td>
<td>Injection moulding: handles for bicycles and tools, packaging, housewares, household appliances, footwear and automotive applications</td>
<td>Hybrid 111D, Hybrid 112D</td>
<td>Cereplast</td>
</tr>
<tr>
<td>PP–PE copolymer/starch (30%)</td>
<td>TP, granulate</td>
<td>Thin-wall injection moulding such as packaging and paint cans</td>
<td>Biopropylene®</td>
<td>Cereplast</td>
</tr>
<tr>
<td>PC/PLA (25 or 40%)</td>
<td>Hybrid, RC. Does not readily decompose TP, granulate</td>
<td>Injection moulding: for mobile phones, electronics, furniture, sporting goods, toys, auto interiors and housings/enclosures</td>
<td>MAKROBLEND BC250 and BC400</td>
<td>Bayer MaterialScience</td>
</tr>
<tr>
<td>Different blends of thermoplastics with PLA, PHB, PHBV or biopolymers</td>
<td>Hybrid, RC, temperature, impact and cost performance TP, granulate</td>
<td>Consumer durable goods, electronics equipment, medical devices and equipment, interior automotive components</td>
<td>reSound™ Biopolymer</td>
<td>PolyOne</td>
</tr>
<tr>
<td>PLA/PMMA</td>
<td>Hybrid, bio-based acrylic resin, TP</td>
<td>Transparent disposable medical devices: diagnostics, lab ware, fluid suction, reservoir and fluid collection apparatus</td>
<td>Plexiglas® Rnew</td>
<td>Arkema Inc.</td>
</tr>
<tr>
<td>PC/PLA (31%)</td>
<td>Hybrid, RC, TP, granulate</td>
<td>Injection moulding</td>
<td>RTP 2099 X 121235 D RTP 2099 X 126213</td>
<td>RTP</td>
</tr>
<tr>
<td>PC/PLA (32%)</td>
<td>Hybrid, RC, TP, granulate</td>
<td>Injection moulding</td>
<td>RTP 2099 X 126210</td>
<td>RTP</td>
</tr>
<tr>
<td>PC/PLA (32%)</td>
<td>Hybrid, RC, TP, 50% post-consumer PC, black only</td>
<td>Injection moulding</td>
<td>RTP 2099 X 127618 R</td>
<td>RTP</td>
</tr>
<tr>
<td>PC/PLA (20%)</td>
<td>Hybrid, RC, TP, flame retardant/halogen-free</td>
<td>Injection moulding</td>
<td>RTP 2099 X 121241 B</td>
<td>RTP</td>
</tr>
<tr>
<td>PC/PLA (26%)</td>
<td>Hybrid, RC, TP, permanently antistatic</td>
<td>Injection moulding</td>
<td>RTP 2099 X 115382 C RTP 2099 X 115375 C</td>
<td>RTP</td>
</tr>
<tr>
<td>HDPE/PLA (39%)</td>
<td>Hybrid, RC, TP, granulate</td>
<td>Injection moulding</td>
<td>RTP 2099 X 115382 C RTP 2099 X 115375 C</td>
<td>RTP</td>
</tr>
<tr>
<td>PMMA/PLA (39%)</td>
<td>Hybrid, RC, TP, transparent</td>
<td>Injection moulding</td>
<td>RTP 2099 X 115375 B</td>
<td>RTP</td>
</tr>
<tr>
<td>PMMA/PLA (39%)</td>
<td>Hybrid, RC, TP, impact modified-opaque</td>
<td>Injection moulding</td>
<td>RTP 2099 X 115375 B</td>
<td>RTP</td>
</tr>
</tbody>
</table>

(continued on next page)
## Appendix A (continued)

<table>
<thead>
<tr>
<th>Bio-blend</th>
<th>Features, other information</th>
<th>Application</th>
<th>Product code</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS/PLA (40%)</td>
<td>Hybrid, RC, competitive with HIPS</td>
<td>Injection moulding</td>
<td>RTP 2099 X 121236 A</td>
<td>RTP</td>
</tr>
<tr>
<td>Bio-PA (31% bio-content)</td>
<td>Hybrid, RC, TP, permanently antistatic</td>
<td>Injection moulding</td>
<td>RTP 2099 X 121825 E</td>
<td>RTP</td>
</tr>
<tr>
<td>Compounds based on PLA</td>
<td>Main part RC, higher heat resistance, faster injection moulding than pure PLA, TP</td>
<td>Film, sheet, fibre, non-woven, resin, etc.</td>
<td>TERRAMAC</td>
<td>Unitika</td>
</tr>
<tr>
<td>PUR/starch (60%)</td>
<td>NA</td>
<td>NA</td>
<td>BioPar TPU BIOP</td>
<td>BIOP</td>
</tr>
<tr>
<td>TPS/polyolefins</td>
<td>Hybrid, RC, TP, granulates</td>
<td>Injection moulding and extrusion, cutlery, toothbrushes, combs, tubes and rods, pipes, caps and closures</td>
<td>Cardia Biohybrid⁶</td>
<td>Cardia Bioplastics</td>
</tr>
<tr>
<td>Blends of PLA and other plastics</td>
<td>Hybrid, RC, high stiffness, heat-shrinkable film</td>
<td>Heat-shrinkable film for tight seal around the closure of bottles and caps with labels</td>
<td>PLABIO</td>
<td>Mitsubishi Plastics</td>
</tr>
<tr>
<td>PLA/PBS polymers</td>
<td>Renewable, stronger, more flexible</td>
<td>–</td>
<td>Patented No. 5,883,199</td>
<td>Metabolix, Inc.</td>
</tr>
<tr>
<td>Based on PHA/additives</td>
<td>Biodegradable, not in landfill TP, granulate</td>
<td>Thermoforming</td>
<td>Mirel 3000 Series</td>
<td>Metabolix, Inc.</td>
</tr>
<tr>
<td>PLA-L/lignin/fatty acid/wax</td>
<td>Biodegradable, good mechanical properties similar to ABS, TP</td>
<td>Furniture, toy, mechanical engineering, medical, food and textile industry. Replacement of PET</td>
<td>Bio-Flex A 4100 CL</td>
<td>FKuR</td>
</tr>
<tr>
<td>PLA/biodegradable copolyester</td>
<td>Main part RC, biodegradable, mechanical properties similar to PE and PP depending on grade, TP</td>
<td>Blown film; co-extrusion as the middle layer between two skins of Bio-Flex A 4100 CL</td>
<td>Bio-Flex F 2201 CL</td>
<td>FKuR</td>
</tr>
<tr>
<td>Blend based on PLA; PLA &gt;75%</td>
<td>Biodegradable, mechanical properties similar to PE and PP depending on grade, TP</td>
<td>Blown film extrusion, moulded parts</td>
<td>Bio-Flex A 4100 CL</td>
<td>FKuR</td>
</tr>
<tr>
<td>Modified PBS</td>
<td>Biodegradable, feels like PP or PVC, TP, made with bio-succinic acid</td>
<td>Food contact, personal care, cosmetics/medical, electronics and business equipment, automotive components</td>
<td>–</td>
<td>BioAmber Inc.</td>
</tr>
<tr>
<td>PLA/PBS</td>
<td>Biodegradable, TP</td>
<td>Specifically designed for food service ware</td>
<td>–</td>
<td>BioAmber Inc.</td>
</tr>
<tr>
<td>Blends of PLA and PBS or PBSA</td>
<td>Biodegradable, TP, opaque, off-white materials</td>
<td>Sheet extrusion/ thermoforming: for foodservice ware</td>
<td>Ingeo AW 240D</td>
<td>NatureWorks</td>
</tr>
<tr>
<td>Blends of PLA and PBS or PBSA</td>
<td>Biodegradable, TP, opaque, off-white materials</td>
<td>Injection moulding: for hot foods and drinks</td>
<td>Ingeo AW 300D</td>
<td>NatureWorks</td>
</tr>
</tbody>
</table>
pect ratios of fibres result in a greater reinforcement. The ‘aspect ratio’ is a measure of the relation between the length and diameter of a fibre. However, keeping a high fibre aspect ratio under the manufacturing process is difficult, and in some finished products the fibre length is shortened and the fibre acts as filler only, which does little to impart true reinforcement to the composite. Other factors affecting the performance of biocomposites are the alignment of the reinforcing fibres within the matrix, degradation of fibre under high processing temperature and possible volatile emissions [18,130].

Separation methods are still not efficient. An example is media density as the fundamental for separation and/or preconcentration in the recycling of plastics, but the current use of static media processes limits the capacity and size of material that can be treated commercially. To improve the commercial recovery of recyclable plastics, Gent et al. [69] in 2009 reviewed cylindro-conical and cylindrical cyclone-type media separators (such as those used for processing coal) and suggested their use as a potential substitute. Another example that was explained in detail in Section 4 regarding the recycling of PET mixed with PLA, is the limitations of NIR sorting systems, not only their difficulty in identifying polymers with special colours or structures, but also their high cost. Finally, the introduction of LCA and systems analysis throughout the design, use and recycling of bioplastics and biocomposites makes it necessary ultimately to guarantee their sustainability as suitable alternatives to traditional plastics and composites. To maximise the effective use of ‘green’ plastics, it is important to prepare for their recycling through a suitable labelling system and initiatives to increase public awareness and education about different types of plastics [114].

As a general short final conclusion, research on the recycling of bio-based materials, especially bio-blends and biocomposites, is still at a preliminary stage and lacks a deep understanding of the different factors affecting the performance, economy and sustainability of recycled bioplastics.

Role of the funding source

Mistra is an independent research foundation in Sweden.

Acknowledgement

The authors are grateful to The Swedish Foundation for Strategic Environmental Research, Mistra, for financial support.

References

La Carrubba V, Carfi Pavia F, Brucato V, Piccarolo S. PLLA/PLA biocomposites.


Lunt J. Introduction to bioplastics, Seminar 20 February, Orlando, Florida; 2012.


[70] Jerepey M; 2009. <plasticsnews.com>


[90] Plackett David, Södergrå A. Natural fibers, biopolymers, and biocomposites. Polylactide-Based Biocompo, New York; 2005. [Chapter 17].


