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## Synthetic (bio)degradable polymers – when does recycling fail?

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Given the current environmental crisis caused by polymers, we have seen that it is mandatory to make changes in the way we produce, consume, and, at the downstream, dispose, and manage polymeric materials after use. For applications where recycling might not be the adequate answer, or landfilling is highly likely to occur, (bio)degradable polymers can play an important role. This appraisal acknowledges the most important synthetic (bio)degradable polymers, noticeably polyesters, and their potential for substitution of traditional persistent ones, in terms of thermal and mechanical properties and more adequate fate in controlled compostable media or instead in natural environments. Special focus is given to bio-based poly(lactic acid), poly(butylene succinate) and furan-based polyesters. Alternatively, the most recent progress and contributions to rendering fossil-based polymers such as poly(caprolactone) and poly(glycolic acid) greener are discussed.

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### Introduction

Polymers are a vast and versatile family of macromolecular organic compounds that are lightweight and durable and exhibit a vast array of physical and chemical properties allowing them to fit the purposes of countless applications, spanning from packaging and textiles to more sophisticated purposes within electronics and medicine.

In this vein, our dependency on polymeric materials is not surprising, as clearly demonstrated by their annual production, which reached 367 Mt in 2020.<sup>1</sup> The polymers with higher productions are polyolefins, namely poly(ethylene) (PE), including linear low-density (LLDPE) and high-density PE (HDPE), and poly(propylene) (PP).<sup>1</sup> The polyester poly(ethylene terephthalate) (PET) is also among the most produced ones.<sup>1</sup> All these polymers find their main applications among packaging, which represents the biggest market demand, while other sectors, such as textiles and agriculture absorb the rest of the production.<sup>1</sup> Despite their commercial relevance, the synthesis of these polymers relies on petroleum-based monomers, which are associated with greenhouse gas (GHG) emissions,<sup>2</sup> besides the fact that they do not readily (bio)degrade under common environmental conditions.<sup>3</sup> Indeed, the degradation of these polymers by microorganisms is an extremely

slow process,<sup>4</sup> with PET plastic bottles having an estimated minimum half-life of over 2500 years, whilst this value could reach 5000 years for conventional HDPE pipes.<sup>3</sup>

Recycling is often the advocated solution to manage polymers' End-of-Life (EoL), playing an unarguable role.<sup>5,6</sup> However, despite this, only around 35% of polymer waste is being recycled in the EU,<sup>1</sup> and an even smaller amount in the USA with only 9% in 2018.<sup>7</sup> Furthermore, this option is mainly applied for packaging materials,<sup>8</sup> leaving out other polymeric residues, such as textile fibres. Additionally, mechanical recycling (the most commonly used and developed approach)<sup>9</sup> fails to meet all the requirements due to polymers' molecular weight decay over repeating recycling cycles and/or the presence of additives and/or other polymer contaminations usually leading to devaluation.<sup>10</sup> Additionally, mechanical recycling is not a valid option for multilayer packaging materials where multiple polymers are present and separation is not always viable. The approach is also not an option for thermosets, which are out of the scope of this appraisal dedicated to thermoplastics.

Another topic that must not be neglected is the fact that the possibility of having efficient waste collection and appropriate recycling facilities is far from being reached globally, in particular in developing countries.<sup>11,12</sup>

Therefore, it is not surprising that the provisional data for 2020 show that over 23% of polymer waste was still being disposed in landfills in Europe, and around 75% in the USA.<sup>1,7</sup> Additionally, 42% of polymer waste was incinerated for energy recovery in Europe, while the amount in the USA was again much lower (15%). This intricate polymer scene with, on the

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one hand, their typical durability, and, on the other hand, recycling failing to promptly provide a solution to polymer waste management, urges for adequate answers.

Some synthetic polymers, able to be assimilated by the environment, or at least to be industrially compostable (ISO 17088, ISO 14855),<sup>13,14</sup> have the potential to be part of the solution. It is expected that around 5.3 Mt of (bio)degradable polymers will be produced in 2026, mainly due to the strong developments of bio-based thermoplastic polyesters, notably poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and/or partially renewable poly(butylene adipate terephthalate) (PBAT).<sup>15</sup> All these polymers are polyesters that possess in their backbone liable ester bonds prone to, for example, hydrolysis, thus triggering depolymerisation, although other polycondensates such as poly(carbonates) (PC) can also be considered due to their hydrolysable functional groups. Investigation on their use for biomedical applications has been extensively overviewed throughout the years, but these polymers have also gained both academic and commercial relevance among single use (SU) packaging, and have been applied in films in agriculture or in textile fibres.

Specifically, PLA is already among the most used polymers in the textile industry, while PBS also shows high growth potential.<sup>16</sup> Their contribution, as fibres<sup>17</sup> or as coatings and finishings,<sup>16</sup> is unequivocal for supporting an expanding textile industry, which doubled the production of synthetic polymers in the last two decades, but still more than two-thirds are going to be disposed in landfills.<sup>18,19</sup>

PBAT is a promising alternative for SU flexible polymers often used in packaging,<sup>15</sup> and for mulch films in agriculture.<sup>20–22</sup> For this application, degradability can circumvent additional costs and procedures often incurred for removing these agricultural films from the fields after use and, thus, can mitigate their environmental impact.<sup>20</sup>

These ongoing developments are motivated and supported by large-scale initiatives within the European *Green Deal* or the *United Nations Sustainable Development Goals*, which continue to contribute to a more sustainable future.<sup>23,24</sup> Furthermore,

many studies focusing on these (bio)degradable polymers advantageously follow some of the Green Chemistry principles, notably renewable origin, eco-friendly synthesis, and above all proving a more sustainable fate.

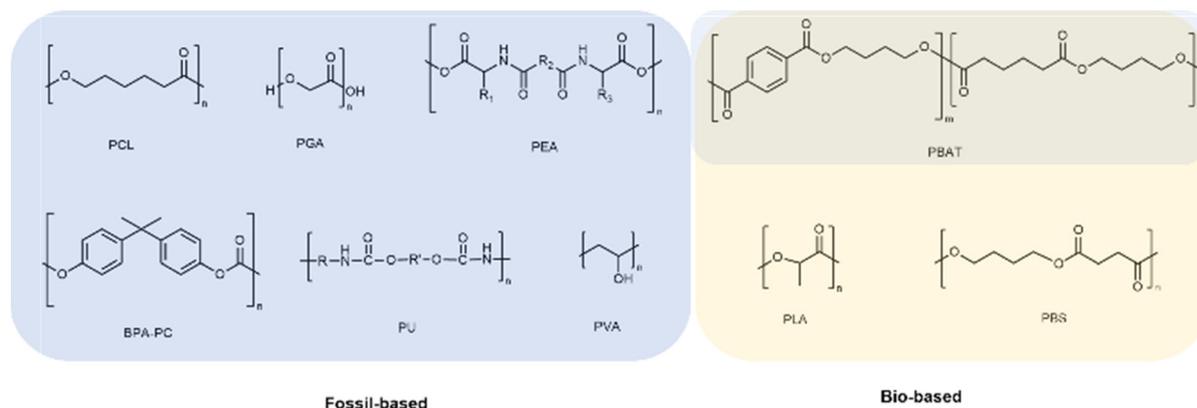
### The scope

This appraisal intends to shine a light on the ongoing research and development activities on the synthesis of (bio)degradable polymers, mainly polyesters, either fossil-based or instead renewable-based, in a quest for more sustainable alternatives.<sup>25,26</sup> Greener synthetic pathways will be preferentially overviewed. Together, characterisation and related applications are also addressed. All polymers considered for this review can be overviewed in Scheme 1.

Although naturally occurring polymers, such as thermoplastic starch and cellulose, among many others, play an important role among (bio)degradable polymers, they have been broadly overviewed before.<sup>27,28</sup> This review focuses, instead, on synthetic polymers due to their known reproducibility, versatility to fulfil specific applications' requirements,<sup>29</sup> and in many cases broad market implantation.

**(Bio)degradable polymers' definitions.** It is important, initially, and before going deeper into this review, to clarify some of the basic concepts of (bio)degradable polymers often misused. A pertinent question arises at this point: *what is a biodegradable polymer?* According to the IUPAC definition, launched in 2004 and reviewed later in 2012, biodegradable polymers are 'those susceptible to degradation by biological activity accompanied by lowering of their molar masses'.<sup>30–32</sup> The degradation mechanism results from cell activity, and ultimately will lead to mineralisation into small molecules, such as, for example, carbon dioxide, methane, nitrate, ammonium, and/or water.

It should be noted, however, that the IUPAC definition is not restricted to (bio)degradation in a natural environment, as marine or terrestrial ones, but instead the scope is broader and often leads to erroneous assumptions of safe disposal and an adequate EoL of polymers such as PLA that will not biodegrade 'easily' in the environment.<sup>33</sup> Therefore, in this review, for clarity



**Scheme 1** Overview of the fossil- and bio-based (bio)degradable synthetic polymers considered in this review. Fossil-based: poly(caprolactone) (PCL), poly(glycolic acid) (PGA), poly(ester amide) (PEA), bisphenol A poly(carbonate) (BPA-PC), poly(urethane) (PUR), poly(vinyl alcohol) (PVA); fossil- and bio-based: poly(butylene adipate terephthalate) (PBAT); bio-based: poly(lactic acid) (PLA) and poly(butylene succinate) (PBS).

reasons, whenever a polymer can be completely (bio)degraded under natural conditions, this will be unambiguously stated.

Also, for objectivity purposes, whenever a polymer (bio)degrades under very specific composting conditions, according to the international standards (e.g., EN 13432, ISO 14855, ISO 17088, ASTM D6400),<sup>13,14,34,35</sup> usually performed industrially in an aerobic or anaerobic environment or under home-composting conditions, this polymer will be referred hereinafter as compostable (according to a specific standard).

Both definitions (biodegradable and compostable polymers) lie under the more general umbrella of degradable polymers, defined, according to the IUPAC, as 'polymers in which macromolecules are able to undergo chain scissions, resulting in a decrease of molar mass'.<sup>31</sup> Degradation can be prompted by the action of different factors, such as water (hydrolytic degradation) and UV/Vis light (photodegradation), among others. Nevertheless, the relevance of this definition, without a clear indication of the (bio)degradation conditions, medium and timescale remains vague. In a circular economy approach, (bio)degradable polymers can play an effective role in efficient waste management,<sup>36</sup> in very specific situations and with adequate labelling, as already pointed out previously in this appraisal. Herein, we will disclose their uncovered potential in packaging, textiles, and film applications, thus beyond the extensively reviewed biomedical applications.

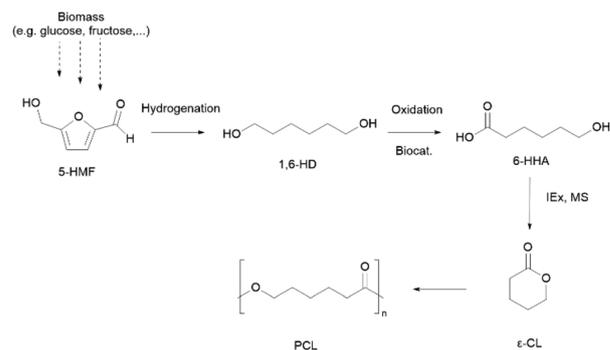
## (Bio)degradable polymers

### Overview of the main commercially available fossil-based polymers

**Poly(caprolactone) (PCL).** PCL is among the most studied and commercially applied polyesters and has been used in many different fields, such as in packaging applications. It is commercially available, for example, under the trademark Capa 6500 by Ingevity.<sup>37</sup> PCL's market implementation is undoubtedly associated with its outstanding viscoelastic and rheological properties, besides it is certified as compostable according to the European standard EN 13432.<sup>35</sup> Additionally, PCL is approved for food contact applications by the Food and Drug Administration (FDA) and European Union law (21 CFR 175.105 and EU no. 10/2011, respectively).<sup>38,39</sup>

Although PCL is derived from fossil resources, efforts to synthesise  $\epsilon$ -caprolactone ( $\epsilon$ -CL) (or similar monomers) from biomass sugars *via* the platform chemical 5-hydroxymethylfurfural (5-HMF) root (Scheme 2) or from vegetable oils have been reported.<sup>40,41</sup> However, to the best of our knowledge, none of these alternatives have reached high maturity Technology Readiness Levels (TRL).

In terms of synthesis, PCL is generally prepared through the ring-opening polymerisation (ROP) of  $\epsilon$ -CL, under relatively mild conditions leading to PCL with a low polydispersity (1.06 to 1.35).<sup>42,43</sup> Usually, metal-based catalysts, such as tin(II) 2-ethylhexanoate, are used, although there have been efforts to promote the development of greener processes using, for example, enzymes.<sup>42</sup>



**Scheme 2** An integrated microbial-chemical route to produce bio-based  $\epsilon$ -CL *via* 5-hydroxymethylfurfural (5-HMF), 1,6-hexanediol (1,6-HD) and 6-hydroxyhexanoic acid (6-HHA). Biocat: biocatalyst; IEEx: ion exchange catalyst.<sup>40</sup>

PCL is widely known for being semicrystalline, hydrophobic and soluble in most non-polar organic solvents (e.g., chloroform, benzene, toluene, *etc.*) at room temperature, and for its moderate thermal features, *viz* low melting and glass transition temperatures (60–65 °C and –60 °C, respectively).<sup>44,45</sup>

PCL also showcases enhanced barrier properties, with an oxygen (O<sub>2</sub>) permeability coefficient of 0.88, and great flexibility with a maximum elongation at break of around 1000% (LDPE has only max. elongation of 600%). When it comes to tensile strength, it also shows improvements in relation to LDPE, with maximum 785 MPa for PCL and only max. 35 MPa for LDPE. Nevertheless, some of these features are still moderate compared to its aromatic counterparts (Table 1),<sup>46</sup> although these can also be viewed as an advantage in terms of processing energy and associated costs.

Although PCL's fate is not desirable to occur in natural environments, notably aquatic media, and particularly marine salty ones, if it happens it is quite important to have data beforehand on degradation in these media. In this regard, Narancic *et al.*<sup>47</sup> reported that PCL reached 80% degradation in the marine environment and a maximum 50% degradation in fresh water in 8 weeks. Also, Tsuji *et al.*<sup>48</sup> studied the behaviour of PCL and several other (bio)degradable aliphatic polyester films in static sea water (10 weeks at 25 °C), showing that the degradability of the aliphatic polyesters in controlled seawater decreased in the order PCL > poly[(R)-3-hydroxybutyrate] > poly(L-lactide) (PLLA).

Enzymatic pathways have also been explored as an effective way to degrade PCL. In this vein, Su and Wang<sup>60</sup> reported the use of *Candida antarctica* lipase B (CALB) for degrading PCL with different starting weight-average molecular weights ( $M_w$ ). The study demonstrated the rapid degradation of PCL in the first 12 h with around 85% of mass loss (phosphate-buffered saline medium at 45 °C), without the influence of the initial  $M_w$ . Another study reported the processing of PCL into micro-particles and their enzymatic degradation with lipases (although the authors have not specified which lipase was used).<sup>61</sup>

**Table 1** Overview of the essential mechanical, thermal and barrier properties of the synthetic polymers mentioned in this review

Category	Polymer	Mechanical properties				Thermal properties				Barrier properties			Ref.
		Elongation at break (%)	Elongation at yield (%)	Young's modulus/GPa	Tensile strength/MPa	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_d/^\circ\text{C}$	$\text{O}_2$ permeability coefficient	$\text{CO}_2$ permeability coefficient			
Fossil-based persistent	LDPE	100–1000	5–425	100–200	7–35	–100	98–218						49–51
	PET	30–300	4–6	1700	48–72	69–125	245–280				0.03–0.04	0.12–0.23	46 and 51
Fossil-based (bio) degradable	PCL	20–1000		0.2–0.4	4–785	–65 to –60	58–64	350			0.88	14.3	51 and 52
	PGA	15–35			339–394	36–45	210–230	254			0.01	0.05	52
	PBAT	500–800			21–40	–30	110–125						51 and 53
	PVA	225–445		37–45	24–110	58–85	180–265				0.02	0.09	51, 52 and 54
Bio-based (bio) degradable	PC	10–138			62	150	250–343				1.05	6	50 and 52
	PUR	2–950	3–50	11–540	8–39	–34 to –15	46–48	108–160					55 and 56
	PLA	2–240	1.8–3.7	3.98	28–53	40–70	130–180	235–255					51, 52 and 57
Blends (bio) degradable	PEFL					25–76	120	289–384					52
	PBAF	307–748		0.02–0.12	9–42	–53–23	27–156	417–430					58
	PBS	379		320	27	–44	109	400					59
	Mater-Bi®	780–886		180–185	25–30		160						49

Low density poly(ethylene) (LDPE), poly(ethylene terephthalate) (PET), poly(caprolactone) (PCL), poly(glycolic acid) (PGA), poly(butylene adipate terephthalate) (PBAT), poly(vinyl alcohol) (PVA), poly(carbonate) (PC), poly(urethane) (PUR), poly(lactic acid) (PLA), poly(ethylene 2,5-furandicarboxylate-co-poly(l-lactic acid)) (PEFL), poly(butylene adipate-co-butylene 2,5-furandicarboxylate) (PBAF), poly(butylene succinate) (PBS), Mater-Bi®(starch/PCL blend).

Besides, in 2012, a PCL-degrading *Bacillus* strain, namely *B. pumilus* was reported.<sup>62</sup> In this study, the ability of the microorganism to degrade PCL films during soil burial tests (35% moisture and 40 °C) was studied and it was demonstrated that degradation can be seen on the surface of PCL films in just 20 days of incubation.

One of PCL's most highlighted properties is undoubtedly its compostability, especially when recycling is not adopted. Narancic *et al.*<sup>47</sup> evaluated PCL degradation under industrial (ISO 14855)<sup>14</sup> and home composting conditions through net gaseous CO<sub>2</sub> production measurements. The authors found that for the former, complete degradation was achieved in just 45 days, whereas in home composting (28 °C) it took 88 days to reach full degradation. Rutkowska *et al.*<sup>63</sup> compared PCL's degradation in different environments and under different conditions, namely in compost with activated sludge. PCL's degradation was the quickest with the activated sludge (compared to liquid medium), with complete disintegration observed just after 7 weeks of incubation.

Blending and copolymerisation have both been used to circumvent the described PCL's moderate thermal and mechanical properties, with the additional possibility of incorporating bio-based materials, and therefore increasing the renewable content.<sup>64,65</sup> In this vein, Mater-Bi®, commercialised by Novamont (Italy), is a very interesting example of a blend of PCL and starch.<sup>66</sup> This blend is certified compostable according to the European standard EN 13432<sup>35</sup> and is mostly used to produce carrier bags, cutlery, and food packaging, among others.<sup>20</sup>

In some studies, the addition of starch to improve PCL's Young's modulus is reported in order to make the films less ductile, which also means a decrease in tensile strength and elongation at break.<sup>65</sup> PCL/starch blends have comparable mechanical performance to well established LDPE. They exhibit greater elongation at break (780–886% *vs.* 150–600% for LDPE) and comparable Young's modulus and tensile strength (Table 1).<sup>49,66</sup>

PCL films modified with a 10% ethylene butyl acrylate copolymer were studied for their degradation in aqueous environments, revealing that the seawater medium gave improved results with complete degradation after 7 weeks.<sup>63</sup> Along the same line, PLA and PCL blends and copolymers have been reported in the literature,<sup>67–72</sup> showing that PCL enhances PLA's degradability, but this topic will be discussed in detail in a later section of this review. Additionally, due to the non-degradability of commonly used PET, a PET/PCL reactive blend has been used to attempt accelerating degradability.<sup>73–75</sup>

**Poly(glycolic acid) (PGA).** PGA is another fossil-based polyester, currently in the market with the tradename Kuredux™ from Kureha Corporation (Japan).<sup>76</sup> It has enhanced thermal and barrier properties, especially compared to PCL. Furthermore, as a (bio)degradable polymer, similarly to PCL, it satisfies the composting certifications of ISO 14855, ASTM D6400 and EN 13432.<sup>14,34,35</sup> A valuable asset of properties makes PGA suitable for food packaging, and also for textiles and agriculture. Nevertheless, the excessive production cost of

the PGA precursor (glycolide) still limits its wider market penetration, besides the fact that its synthesis is, generally speaking, not *green!*

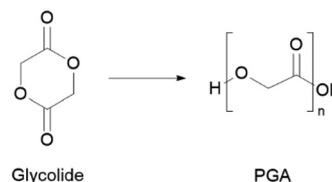
Currently, glycolide is predominantly produced from the carbonylation of formaldehyde, a toxic compound, requiring high temperature and pressure.<sup>77</sup> This monomer can also be produced *via* hydrolysis of chloroacetic acid (also known to be toxic and corrosive).<sup>77</sup> Partially greener alternatives include formaldehyde conversion into glycolonitrile, which is then converted into high-purity glycolide *via* chemoenzymatic processes.<sup>78,79</sup> More recently, there have also been attempts to synthesise glycolic acid from biomass derived sugars.<sup>80</sup> As for PGA production, it is mainly synthesised by ROP using glycolide lactone (Scheme 3).

When it comes to its general properties, in Table 1, it is possible to note PGA's high melting point ( $T_m = 220\text{--}230$  °C), especially when compared to PCL, associated with its linear close packing aliphatic chains, and a high degree of crystallinity (45–55%). Additionally, it also has excellent barrier properties of extreme importance for food and beverage packaging, with an O<sub>2</sub> and CO<sub>2</sub> permeability coefficient of 0.014 and 0.052, respectively.<sup>77</sup>

Typically, PGA easily undergoes hydrolytic degradation, even in the absence of enzymes.<sup>77</sup> Shawe *et al.*<sup>81</sup> studied the degradation of PGA films with different thicknesses (at 37 °C in phosphate-buffered saline) and their weight loss variation throughout 24 days. By the end of this study, the thinner film (0.06 mm) had 60% mass loss compared to 35% weight loss for the thicker ones (0.3 mm).

Despite these features, PGA's high hydrophilicity, rapid degradation, and brittleness have limited its broader practical application, yet they gave its copolymers and blends a lot of importance. Glycolic acid has been often copolymerised with lactic acid forming the well-known poly(lactic-*co*-glycolic acid) (PLGA)<sup>82</sup> or with  $\epsilon$ -caprolactone to produce poly(glycolic acid-*co*- $\epsilon$ -caprolactone) (PGC).<sup>83,84</sup> Cai *et al.*<sup>83</sup> performed tensile mechanical tests indicating that PGC could withstand an extension of 250% without cracking, which was much higher than that previously reported for PLGA (10–15%) or PGA (15–35%). Degradation studies (in phosphate-buffered saline at 37 °C) showed good degradability, with PGC having 50% mass loss in just 6 weeks.

With regard to other blends, Vieira *et al.*<sup>68</sup> studied the degradation of some aliphatic polyesters processed as fibres, namely PGA and a PGA/PCL blend. The fibres obtained from the PGA/PCL blend were the most prone to degradation after



**Scheme 3** PGA conventional synthesis *via* ROP.

12 weeks with over 80% weight loss (in phosphate-buffered saline at 37 °C). Although PCL has a lower degradation rate than PGA, the combination of the two results in less crystalline copolyesters accelerated the degradation process.

**Poly(butylene adipate terephthalate) (PBAT).** PBAT is an aromatic-aliphatic thermoplastic with a partially renewable content assigned to the incorporation of 1,4-butanediol. PBAT has both stiff butylene terephthalate and soft butylene adipate units. The presence of aromatic groups contributes to both enhanced thermal and mechanical properties and resistance to degradation, whereas the incorporation of aliphatic moieties in the polymer chain allows for degradability behaviour. PBAT is commercialised by BASF under the tradename Ecoflex, and by Novamont, BIOTECH and KINGFA, being certified as compostable under industrial conditions (EN 13432).<sup>35,85</sup> It is mainly used in packaging applications, more specifically as compostable bags and cutlery.<sup>53</sup> In the agricultural industry, PBAT also plays an important role in the development of agricultural mulch films.<sup>53</sup>

PBAT is one of the most produced polyesters nowadays with almost 20% of global production capacity of bio-based and (bio)degradable polymers.<sup>15</sup> It is typically synthesised by the conventional two-stage bulk polyesterification<sup>86</sup> of fossil-based terephthalic acid (TPA), adipic acid (AA) and 1,4-butanediol (BD) (Scheme 4), although there are several reports on the synthesis of bio-based AA.<sup>87,88</sup> In this regard, bio-based AA can be obtained from the direct fermentation of biomass into AA or fermentation to muconic or glucaric acids, followed by chemical hydrogenation.<sup>89</sup>

PBAT conventional synthesis requires harsh conditions, such as high temperature, vacuum, long reaction times, and metal-based catalysts.<sup>53</sup> To our knowledge, efforts to render this synthesis greener have not yet been a focus of scientific interest.

Although PBAT's general mechanical properties depend on the TPA/AA monomer composition and polymers' molecular weight, they are quite similar to LDPE<sup>53</sup> which makes PBAT a promising partially bio-based and *greener* alternative. Also, typically, the  $T_m$  varies between 110 and 125 °C and the  $T_g$  is

around  $-30$  °C;<sup>90</sup> while the elongation at break is around 500–800% and the tensile strength is in the range of 21–40 MPa (compared to LDPE 7–35 MPa, Table 1).<sup>53</sup>

When it comes to PBAT's copolyester degradation, Witt *et al.*<sup>91,92</sup> published a couple of studies on this topic. First, in 1995 they reported the influence of TPA and AA ratios in the degradation process (in aerated mineral liquid medium at 30 °C and soil burial), concluding that for a TPA molar fraction >0.3 (including neat PBT), no degradation could be observed in liquid medium. However, for soil burial tests, for copolyesters with 0.39 and 0.43 (mol/mol) of TPA units a relevant weight loss (around 20%) was observed at the end of 3 months.<sup>91,92</sup>

More recently, Kijchavengkul *et al.*<sup>93</sup> studied the composting degradation (ASTM D5338 at 58 °C)<sup>94</sup> of PBAT films, by monitoring their conversion into CO<sub>2</sub>. The authors observed a total degradation of films in manure compost after 45 days.

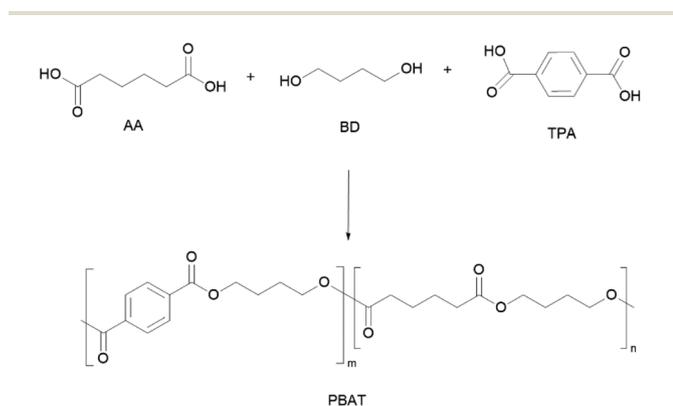
Another important sustainability aspect approached by Witt *et al.*<sup>95</sup> is the ecotoxicity of degradation intermediates. They found that no toxic effects from composting PBAT could be detected, which can be considered a great advantage for its fate after use.<sup>95</sup> When it comes to blending, there are several reports on PBAT blends with bio-based PLA in order to improve PLA's degradability, but that will be discussed in the PLA section below.<sup>96–98</sup>

**Poly(ester amide)s (PEAs).** PEAs are a group of broadly investigated polymers, obtained by condensation reactions leading to the formation of both ester and amide groups in their polymeric backbone, imparting tailor-made thermo-mechanical properties and the ability to degrade. The first commercially available PEAs were trademarked as BAK from Bayer AG.<sup>99</sup> They were based on caprolactam, BD and AA or on 1,6-hexamethylene diamine (HMDA), BD, AA and diethylene glycol. They were sold from 1997 to 2001, mainly for agriculture mulch films, SU cutlery and biowaste bags, but abandoned thereafter due to their high costs.<sup>100</sup> Nevertheless they remain an object of interest mainly in the biomedical field (such as in drug carriers and resin matrices for biomedical scaffolds).

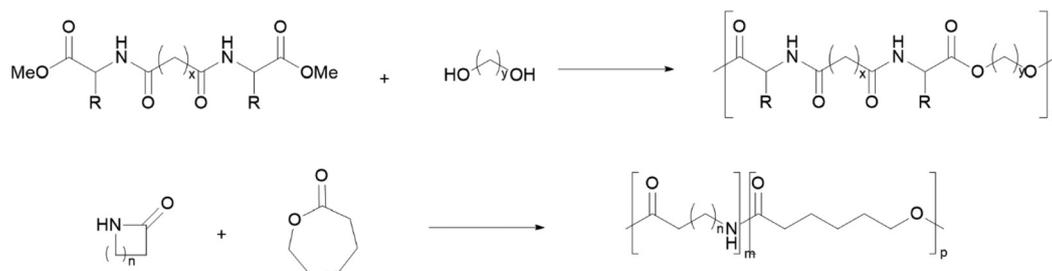
PEAs are mainly composed of fossil-based monomers, such as the above-mentioned HMDA or caprolactam (CLM), although there is currently a trend to replace them with their renewable counterparts, such as, for example, biobased HMDA obtained from HMF or adiponitrile by hydrogenation.<sup>101</sup> In this regard, some progress has been made with PEAs derived from BD and AA,<sup>102</sup> amino acids<sup>103,104</sup> or sebacic acid,<sup>105</sup> or other natural products such as carbohydrates.<sup>106</sup>

PEAs can be synthesised *via* polycondensation of linear monomers (Scheme 5, top), usually performed under reduced pressure, high temperatures and using transesterification catalysts.<sup>102,107</sup> Alternatively, greener strategies based on the ROP of cyclic monomers have also been used (Scheme 5, bottom), which can be associated with high  $M_w$  PEAs, low dispersity<sup>108</sup> and without any volatile by-products. This approach is also associated with increased atom economy.

In terms of properties, PEAs are a very adaptable family of polymers prompted by varying the structural nature of the



**Scheme 4** Synthesis of PBAT with fossil-based TPA and AA and renewable-based BD.



**Scheme 5** Examples of PEA synthesis through polycondensation of a diamine diester and an alkyldiol (top) and ROP of lactams and lactones (bottom).<sup>102,107,108</sup>

starting monomers and of course their relative proportion.<sup>109</sup> As an example, Ge *et al.*<sup>110</sup> studied PEAs with the incorporation of 11-aminoundecanoic acid into the PLA chain to obtain improved thermal properties. The ensuing polymer showed enhanced thermal degradation compared to neat PLA (252 to 214 °C, respectively).

When it comes to PEA degradability, Gonsalves *et al.*<sup>111</sup> and Chen *et al.*<sup>112</sup> reported the hydrolytic degradation of two types of PEA copolymers, one based on ε-caprolactone and ε-caprolactam and the other on 1,6-hexanediol, HMDA and adipoyl chloride. In aqueous media, these copolymers had a maximum weight loss of 59% in 19 days, under mild conditions (phosphate-buffered saline at 37 °C). However, only the hydrolysis of ester groups and no breakdown of amide bonds were detected, which is expected based on the nature of each group.

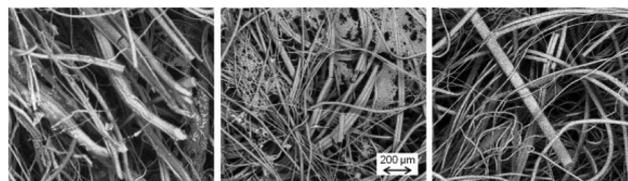
Similar observations were made by Zhiyong *et al.*<sup>113</sup> with PEAs based on lactic and 1,10-aminoundecanoic acids. The lowest hydrolytic degradation rate was associated with the highest amide content and crystallinity (phosphate-buffered saline at 37 °C).

Some more PEA degradation studies were performed in basic and acidic aqueous media.<sup>114–116</sup> Across the literature, it is clear that PEAs are more prone to alkaline hydrolysis than neutral hydrolysis, with the degradation mechanism occurring primarily on ester bonds. Some authors also pointed out the inability of lipase from *C. cylindracea* to prompt enzymatic degradation compared with proteases.<sup>117</sup>

More recently, Novotný *et al.*<sup>118</sup> studied the performance of the bacterium *Pseudomonas aeruginosa*, yeast *C. guilliermondii* and micromycete *Aspergillus fumigatus* in a six week degradation trial at 28 °C of PEA fibres based on ε-caprolactone and ε-caprolactam (Fig. 1).

The morphological changes observed in SEM images lead to mass losses between 5 and 10% in both biotic experiments and an abiotic control, demonstrating that the microorganisms' contributions are not relevant. However, the culture supernatants that contained polymer degradation products exhibited significant biological toxicity. This topic needs to be further investigated to provide adequate EoL management.<sup>118</sup>

**Poly(vinyl alcohol) (PVA).** PVA is a water-soluble synthetic polymer widely known for being the only polymer bearing only carbon atoms in the main chain that is considered (bio)



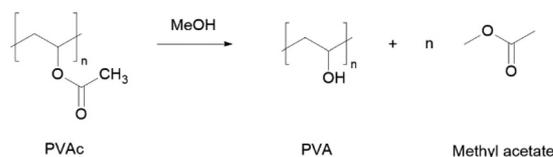
**Fig. 1** SEM images of PEA fibres based on ε-caprolactone and ε-caprolactam after degradation with: *Aspergillus fumigatus* (left), *C. guilliermondii* (middle), and the abiotic control (right). Adapted with permission from ref. 118 Copyright 2014, with permission from Elsevier.

degradable under both aerobic and anaerobic conditions.<sup>119,120</sup> PVA is commercialised by Kuraray<sup>121</sup> and Sekisui,<sup>122</sup> under the trademark names Poval and Selvol, respectively. It is commonly used for adhesives or paper coating, but increasingly used in packaging applications, and agriculture, among others.<sup>123</sup>

The repeating unit of PVA is vinyl alcohol, which is, in principle, unstable and cannot be isolated or obtained in high concentrations.<sup>124</sup> Because of that, the most common method to synthesize PVA is through the alcoholysis or hydrolysis of poly(vinyl acetate) (PVAc) (Scheme 6). To the best of our knowledge, there are no reports of efforts on PVA green synthesis.

Although its properties depend on the degree of alcoholysis (and thus  $M_w$ ), PVA is resistant to oil, grease, and organic solvents,<sup>124</sup> and has excellent barrier properties, such as a low O<sub>2</sub> permeability (0.02 vs. 0.03–0.04 for PET, Table 1) due to its relatively high degree of crystallinity and strong intermolecular forces arising from the hydroxyl groups in its repeating unit.<sup>125</sup>

Regarding degradability, Chiellini's group performed several studies on PVA degradation.<sup>126–129</sup> In a comparative study, through composting, soil burial and aquatic degradation tests, they managed to identify an active PVA-degrading



**Scheme 6** PVA synthesis by methanolysis of PVAc.

bacterial mixed culture starting from sewage sludge of a paper mill as an inoculum.<sup>126</sup> They found the most significant degradation level within a short incubation time in liquid cultures (13% degradation in 21 days) in comparison with soil or compost samples where they found limited mineralisation. Additionally, PVA with different molecular weights was studied and no influence of molecular weight on bacterial degradation was observed.<sup>128</sup>

In an effort to endow PVA based materials with an increased renewable content, and also to modulate their properties, some authors followed a trend already observed for previously discussed polymers, that is to prepare blends with natural polymers and other biobased mixtures/compounds, such as protein wastes, collagen hydrolysate, and glycerol.<sup>130</sup> This latter PVA blend was degraded by a mixed culture from water treatment after an approximately 10-day lag phase. This combination was proved to be a good option since the added protein hydrolysate and glycerol in PVA increased the (bio)degradability (activated sludge at 25 °C) more than expected from the proportional representation of the individual components, with increased CO<sub>2</sub> production (up to approx. 94%).

Azahari *et al.*<sup>131</sup> reported the addition of corn-starch to a PVA matrix in an attempt to increase its degradation rate. In this case, a 30/70 (in %) PVA/starch blend had a 92.5% weight loss for enzymatic degradation after just 60 hours, and up to 85% in both the soil and compost for 8 weeks (while pure PVA had only 60 and 20% degradation, respectively). However, the results from mechanical testing showed that as the starch content increased, the tensile and elongation at break decreased, whereas the modulus increased (Fig. 2).

To overcome these disadvantages, Guohua *et al.*<sup>132</sup> reported the preparation of PVA blends with methylated corn-starch (MCS). The obtained films had higher water resistance and both tensile strength and percent elongation at break of the MCS/PVA film were improved as the degree of substitution of MCS increased. In soil burial experiments, the MCS/PVA film showed rapid degradation in the initial 45 days (around 60%

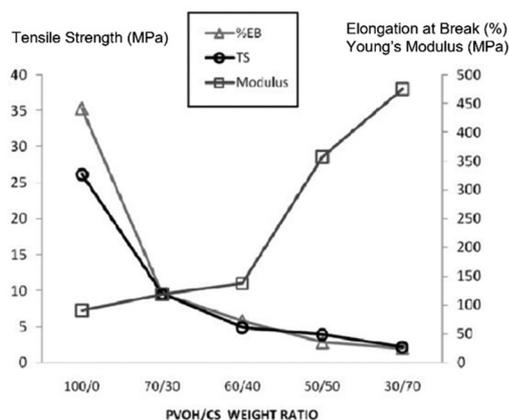


Fig. 2 Effect of the variation of PVA/starch blend content on the tensile strength, elongation at break and Young's modulus. Adapted from ref. 130 Copyright 2011, with permission from USM Press.

weight loss) followed by a slow degradation until the end of the experiment (maximum 70% in 180 days). Still, the blend showed improved degradation when compared to pure PVA, that could only reach a maximum of 20% weight loss.

**Polycarbonates (PCs).** PCs are polymers with hydrolysable functional groups, which have been commercially exploited (Cyrolon™, Markrolon™) for their combination of outstanding mechanical, thermal and optical properties.

PCs are conventionally synthesized by polycondensation of either highly toxic phosgene or harmful diphenyl carbonate, and with the health and environmental hazardous bisphenol A (BPA). Indeed, this compound has been identified as an endocrine disruptor with acute toxicity in the range of 1–10 μg ml<sup>-1</sup> for aquatic species.<sup>133</sup> Despite that, BPA-PCs (PCs containing BPA) are sold under a number of trade names, including the above cited Cyrolon (Acrylite)<sup>134</sup> or Markrolon (Bayer).<sup>135</sup> Furthermore, they have been mainly used in plastic lenses for eyewear, protective gear, and even to manufacture baby bottles.

This success is clearly related to their outstanding properties. In this regard these polymers have superior mechanical properties, such as great impact resistance (850 vs. 90 J m<sup>-2</sup> in comparison with PET)<sup>52</sup> and also toughness and flexibility at room temperature. Besides they present heat resistance and superior optical properties, such as transparency.

When it comes to BPA-PC degradation, Artham *et al.*<sup>136</sup> performed relevant studies in seawater medium. BPA-PC was able to show only 9% weight loss and 5% *M<sub>n</sub>* reduction after 1 year of incubation under laboratory conditions, proving its slow degradation in the marine environment. Despite this result, the same authors, on another study, reported 9 μg ml<sup>-1</sup> of BPA and the respective oxidized products in the supernatant for seawater degradation studies.<sup>137</sup> Further investigation showed that, in fact, the amount of released BPA in 1 year was higher than the half-maximal effective concentration (EC<sub>50</sub>) for marine species. In 2003, Sajiki *et al.*<sup>138</sup> also studied the release of BPA but in different aquatic media (10 ml of water, river water, seawater at 20 °C) and BPA's behaviour afterwards under laboratory conditions. Fig. 3 shows BPA's concentration along time in these different media and at different temperatures.

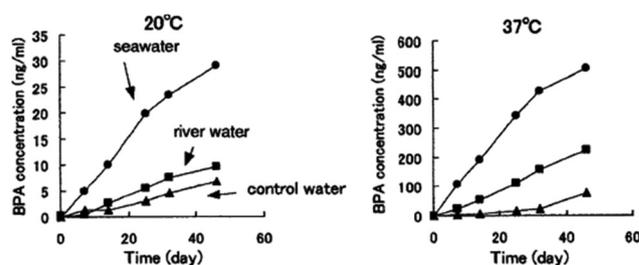


Fig. 3 Variation of the time of PBA concentration in water (20 and 37 °C) from PC's degradation at 20 °C (left) and 37 °C (right). Reprinted with permission from ref. 138 Copyright 2002, with permission from Elsevier.

They found that BPA's leaching rate in seawater was the fastest for both tested temperatures, with BPA's rapid increase at  $11 \text{ ng day}^{-1}$  at  $37 \text{ }^\circ\text{C}$ . This resulted in the highest concentration of BPA, around  $500 \text{ ng ml}^{-1}$ , after 45 days. This value corresponds to approximately half of the minimum concentration for acute toxicity for aquatic species.<sup>133</sup>

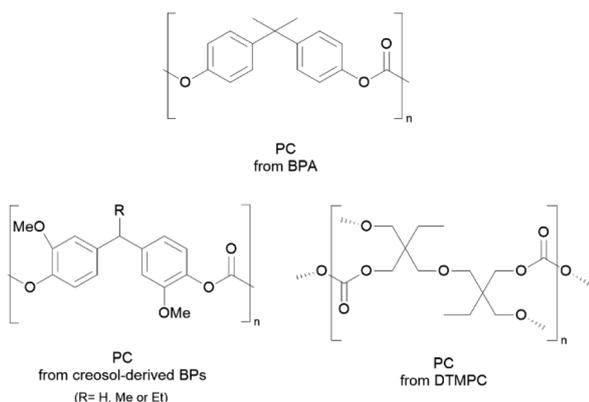
Nevertheless, BPA-free and more sustainable PCs are being increasingly studied,<sup>139,140</sup> with some alternatives in the market such as Kostrate® PC by the Plastic Selection Group.<sup>141</sup> Other alternatives to prepare BPA-free PCs can be seen in Scheme 7, with for example PCs synthesised from creosol-derivatives, which are simultaneously non-estrogenic and bio-based.<sup>139</sup>

These creosol-derived BPA-free PCs show a good thermal performance with high thermal stabilities, with a decomposition temperature ( $T_{d5\%}$ ) up to  $383 \text{ }^\circ\text{C}$ .<sup>139</sup> In that work no degradability tests were carried out, despite their relevance for anticipating future behaviour both in natural environments and under controlled composting conditions.

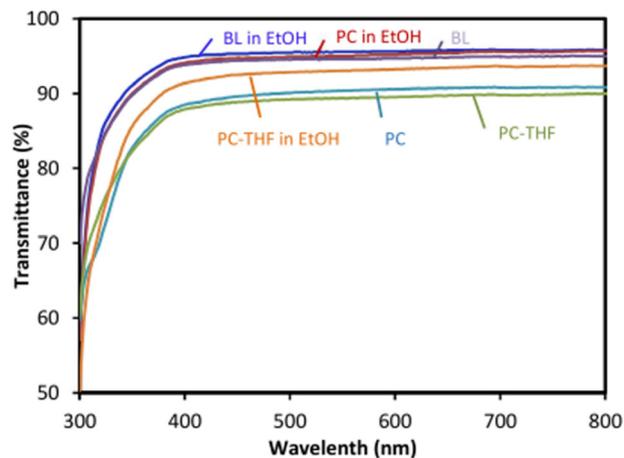
Other studies suggest the synthesis of BPA-free PCs from ditrimethylolpropane dicyclic carbonate (DTMPC) by greener ROP homopolymerisation (Scheme 1) with a metal-free organic-based catalyst system.<sup>142</sup> The ensuing PCs have shown to be highly transparent materials when compared to commercial PC sheets (Fig. 4).

The high optical transparency (with all BPA-free PCs above 85%) makes these new PCs excellent candidates for a variety of applications, such as food contacting materials in packaging. Despite the initial stages of development of these BPA-free alternatives, the existing BPA-PCs' degradation studies are of extreme importance to understand the persistence (or not) of these polymers in the environment.

**Polyurethanes (PURs).** PURs are also a vast class of polymers with interesting properties, having the ability to produce materials with either high strength and rigidity, or high flexibility and toughness.<sup>143</sup> Elastollan is the trademark named for thermoplastic PURs commercialised by BASF,<sup>144</sup> with a wide



**Scheme 7** Chemical structures of PCs derived from BPA and some alternatives derived from creosol and DTMPC.<sup>138,141</sup> Reproduced from ref. 138, 141 with permission from the Royal Society of Chemistry, copyright 2021 and 2018.



**Fig. 4** Optical transparency (% transmittance) properties of PBA-free PCs, prepared from DTMPC. BL: blank; BL in EtOH: blank in ethanol; PC in EtOH: PC in ethanol; PC-TFH: PC after being submerged in THF for 15 min; PC-TFH in EtOH: PC after being submerged in THF for 15 min in ethanol. Reproduced from ref. 141 with permission from the Royal Society of Chemistry, copyright 2018.

range of possible uses, ranging from flexible and rigid foams, adhesives, and surface coatings.

However, linear PURs are typically synthesised from hazardous and fossil-based diisocyanates with polyols. These different building blocks can be made of aromatic or aliphatic isocyanates and several types of polyols, such as polyester-, polyether-, and PC-derivatives, among others.

There is great interest today in a greener transition, and, hence, in switching to bio-based PURs, to reduce their fossil resource dependency. There are many bio-based polyols available,<sup>145</sup> mainly derived from vegetable oils, fatty acids, glycerol, crop residues and protein-based feedstocks.<sup>146</sup> PURs produced with bio-based polyols and fossil-based isocyanates have been reported.<sup>147</sup>

In order to obtain a completely bio-based PUR, alternatives for isocyanate substitution have also been addressed. For example, Hojabri *et al.*<sup>148</sup> reported the synthesis and characterisation of unsaturated diisocyanate from oleic acids and its incorporation into a bio-based PUR with canola diol and canola polyol.

Another issue regarding the quest for more sustainable PURs is the fact that typically diisocyanates have high toxicity for humans. In this regard, in 2020, the EU agency of Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) published restrictions on the use of diisocyanates.<sup>149</sup> Additionally, the release of diisocyanates in the EoL of PURs is of serious concern and brings about an enormous disadvantage for their use. Nevertheless, as reported by Kim *et al.*<sup>150</sup> PURs do suffer from composting degradation, the extent of which depends on the different chemical structures. In this work, the diisocyanates used were 4,4'-diphenylmethane diisocyanate and 1,6-hexane diisocyanate with a variety of polyols. PURs' weight losses ranged from 5 to 43% at

the end of 45 days of composting (ASTM D 5338).<sup>94</sup> When the polyol used was poly(1,6-hexamethylene adipate)diol or PCL-diols, the maximum degradation was achieved when compared to poly(1,10-decamethylene adipate) diol or poly(ethylene adipate)diol, for example.

Therefore, diisocyanate substitution is of extreme relevance when it comes to the EoL, with extreme priority for non-toxic alternatives. In that perspective, there are precisely several efforts being made to produce alternative isocyanate-free PURs.<sup>151–153</sup> Besse *et al.*<sup>154</sup> reported the use of isosorbide dicyclocarbonates, instead of diisocyanates, in the preparation of bio-based PURs (Scheme 8). The above-mentioned alternative isosorbide-based PUR<sup>154</sup> had no alcohol or alkene by-products being formed during thermal degradation ( $T < 500$  °C), and the only degradation products were CO<sub>2</sub> and secondary amines. Further hydrolytic degradation studies, but specially composting tests due to their relevance to waste management, should be performed to understand their environmental impact in-depth.

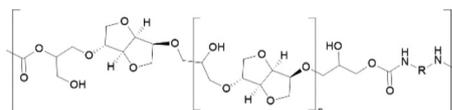
### Overview of the main commercially available bio-based polymers

In the last two decades an unprecedented quest for renewable-based chemicals, monomers and polymers thereof started,<sup>155–157</sup> mainly motivated by expert predictions about the depletion of fossil reserves, and the prevailing worrisome concern about the geopolitical situation of these dwindling resources.<sup>158</sup>

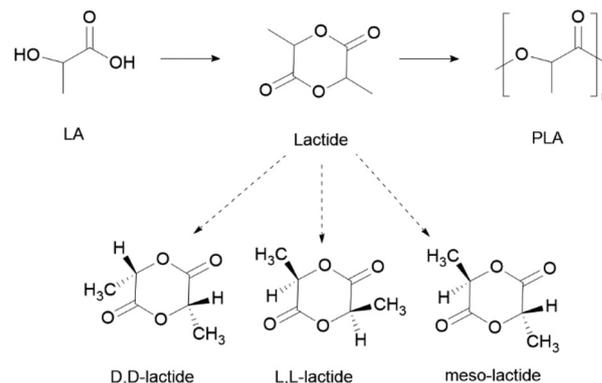
Research and innovation initiatives have been implemented ubiquitously both by academia and industrial sectors. Biomass became an inexhaustible source of building-block monomers suitable for increasing the renewable content of polymers such as the case of PBAT, mentioned previously, or instead to prepare a variety of fully bio-based thermoplastic polyesters, described subsequently, a few of which are already at the market (*e.g.*, PLA, PBS).

**Poly(lactic acid) (PLA).** PLA is well-established as the first synthetic thermoplastic polymer entirely based on renewable raw materials to be commercialised at a large scale.<sup>33</sup> Ingeo, Purac and Renew, for example, are some of the commercial names for PLA materials (mainly PLLA)<sup>159</sup> manufactured by NatureWorks, Corbion and Futerra, respectively.<sup>160–162</sup> A set of interesting properties, including compostability, has dictated its main use in food and beverage packaging, cutlery, and even as 3D printing feedstock.

PLA can be obtained from the lactic acid (LA) monomer, although the related lactide dimer is more commonly used *via* ROP (Scheme 9). Because of the chirality of the lactyl unit,



**Scheme 8** Example of an isocyanate-free PUR synthesized from a carbonated oligoisorbide and 1,10-diaminododecane.<sup>154</sup>

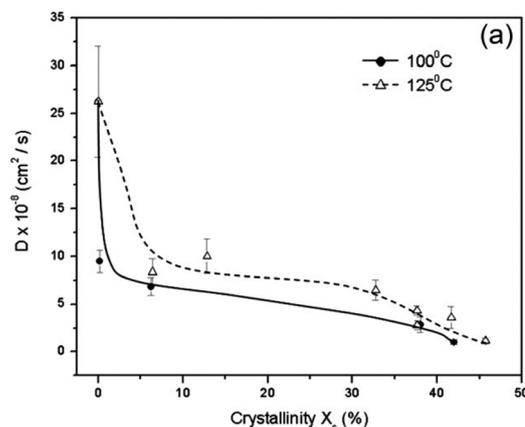


**Scheme 9** General process of PLA synthesis, through ROP, and respective stereoisomeric forms of the lactide monomer.

lactide exists in three diastereoisomeric forms: *l*-lactide, *d*-lactide and *meso*-lactide (Scheme 9).<sup>163</sup> The polymer thereof can be obtained as the enantiomerically pure form poly(*d*-lactide) (PDLA) and poly(*l*-lactide) (PLLA), or as the racemic poly-(DL-lactide) (PDLLA) form.

PLA's renewable origin is, without a doubt, one of the most attractive features. However, its mechanical properties, when compared to, for example, fossil-based PCL can limit its widespread use (lower tensile strength, elongation at break and yield, as observed in Table 1. PLA possesses an intrinsic low crystallisation rate and limited barrier properties compared to its oil-based counterparts, like PET (3.5–15 vs. 1–5 O<sub>2</sub> permeability coefficient).<sup>164</sup> As can be seen in Fig. 5, diffusivity decreases as the crystallinity increases.<sup>164</sup> Furthermore, PLA samples annealed at 125 °C have a higher diffusivity than those annealed at a lower temperature, but with the same level of crystallinity.

Studies on PLA hydrolytic degradation in aquatic environments, where temperatures are usually very low, revealed low degradation under these media. In this vein, Bagheri *et al.*<sup>165</sup>



**Fig. 5** Effect of crystallinity on the O<sub>2</sub> diffusion coefficient for PLA samples annealed at 100 and 125 °C. Reprinted with permission from ref. 164. Copyright © 2009 Wiley Periodicals, Inc.

performed a comparative degradation study of PLA with several (bio)degradable polymers, namely PCL, in fresh water and seawater. PLA showed no significant weight variation for one year period in both aquatic media, and the same result was obtained for PCL. In static seawater (25 °C), Tsuji *et al.*<sup>48</sup> also studied the comparative degradation of PLLA and PCL. While the latter showed a 25% weight loss at the end of 10 weeks, PLLA showed no significant changes during that period. The relevant work of the Scott and Suh group highlights precisely the same trend, even showing that the specific surface degradation rate of PLA and the well-established non-degradable HDPE are similar in the marine environment.<sup>3</sup>

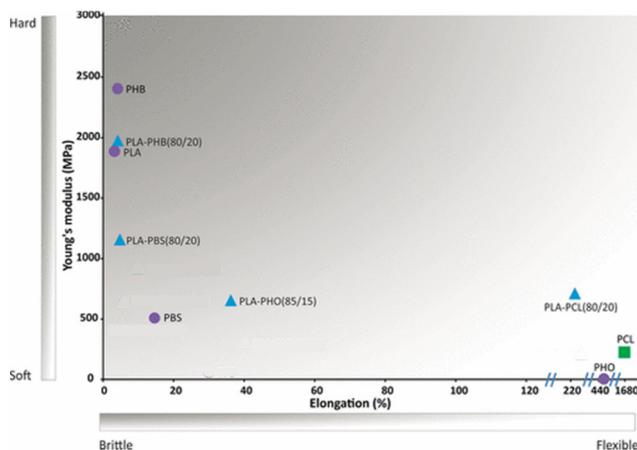
Despite the non-degradability of PLA in aquatic media, and the probable persistence in the case of ending up in these environments, if suitable composting facilities are instead used, following well-defined international standards (*e.g.*, EN 13432, ISO 14855, ISO 17088, ASTM D6400),<sup>13,14,34,35</sup> PLA will have an adequate EoL. As an example, Kale *et al.*<sup>166</sup> studied the industrial composting (60 °C) of PLA bottles reporting complete degradation in just 30 days. Despite that, PLA's degradation at ambient temperatures (*e.g.*, home composting conditions) becomes much slower due to the lower temperatures and most probable different biota. Rudnik *et al.*<sup>33</sup> reported the degradation of PLA fibres and films in soil and compost at ambient temperatures. The first significant changes started to occur only after 7 months, and sample disintegration could only be clearly observed at the end of 11 months.

PLA's previously mentioned poor mechanical properties can be circumvented, as pointed out for other polymers, by copolymerisation or by blending PLA and polymers with enhanced mechanical properties like PCL.<sup>47</sup> In fact, blending PLA with a relatively low loading of PCL (<20% w/w) leads to a substantial reduction of the Young's modulus and increase of the elongation at break when compared to pristine PLA, resulting, thus, in more flexible materials (Fig. 6).<sup>47</sup>

The same study reported other PLA blends (Fig. 6), showcasing for example, the incorporation of poly(hydroxyoctanoate) (PHO) to improve PLA's flexibility, with the PLA/PHO (85/15) blend having 35% elongation at break.

Logically, PLA's blends and copolymers have also been studied in the attempt to improve its degradation under mild conditions. When PLA is blended with fossil-based PCL, besides improving mechanical properties, it also becomes home compostable (180 days at ambient temperature), which is of extreme importance.<sup>47</sup> In this study a PLA/PCL blend with a ratio of 80/20 was able to degrade under simulated home composting conditions (ISO 14855 at 28 °C)<sup>14</sup> in 260 days, unlike PLA alone.<sup>47</sup> However, this PLA/PCL blend was not able to pass other degradation tests according to the ISO and ASTM standards, so it would not be able to degrade in marine, fresh water, or soil environments.

Following this trend, Fukushima *et al.*<sup>71</sup> also tested a blend of poly(DL-lactide) and PCL (PDLA/PCL = 80/20 (in %)). The addition of PCL also showed improvements in PDLA's composting behaviour that was generally higher in compost after



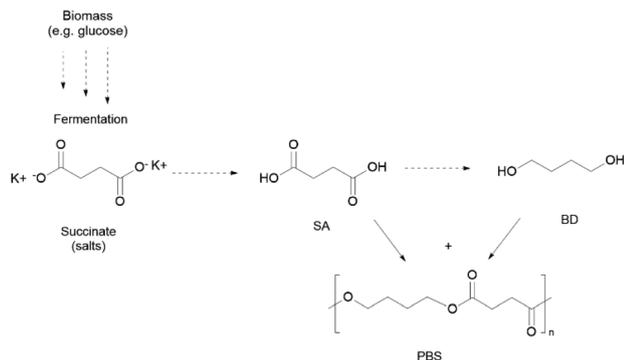
**Fig. 6** Mechanical properties of biobased polymers (purple circles) and fossil-based PCL (green square) and their blends (blue triangles). Adapted with permission from ref. 47. Copyright 2018 American Chemical Society.

just 84 days at 37 °C. Other attempts for improving PLA's degradation with alternative blends, such as PLA/PBAT, can also be found in the specialised literature.<sup>96,97</sup> However, it was found that the expectation of accelerating PLA degradation in soil by blending with PBAT was not achieved, since PLA and PBAT individual controls degraded faster than the blend thereof.

When it comes to copolymers, the incorporation of the glycolic moiety is able to enhance the degradation, with the copolymer poly(lactic-*co*-glycolic acid) (PLGA) (lactide/glycolide molar feed ratio of 50/50), known to be the most common bioresorbable copolymer, showing the best results of Bagheri's seawater study (25 °C) with complete degradation after 270 days.<sup>165</sup>

**Poly(butylene succinate) (PBS).** PBS is another aliphatic polyester synthesised *via* the polycondensation of succinic acid (SA) and BD. Although, commercially, SA is still mostly manufactured by the hydrogenation of fossil-based maleic anhydride to succinic anhydride, followed by hydrolysis, in the foreseeable future it is expected to shift its production to the fermentation route based on renewable sugar feedstocks, like starch, glucose, and xylose, as exemplified in Scheme 10.<sup>167,168</sup> Furthermore, BD can also be of renewable origin, providing, thus, the potential to have entirely biobased PBS. Currently, PBS is commercialised by Mitsubishi Chemical Corporation under the trade name of BioPBS™, with certifications for food contact applications (EU10/2011) and compostability (EN13432).<sup>169</sup> Therefore its main applications are in flexible packaging such as, for example, in coated papers, agriculture mulch films and sports equipment.

PBS is a highly crystalline polyester with a melting point at around 115 °C.<sup>170</sup> When compared to well-established PLA (Table 1), it has a lower  $T_m$  (115 °C *vs.* 160 °C), but it reveals a higher flexibility, with an elongation at break of 379% (maximum 240% for PLA). These characteristics make PBS a

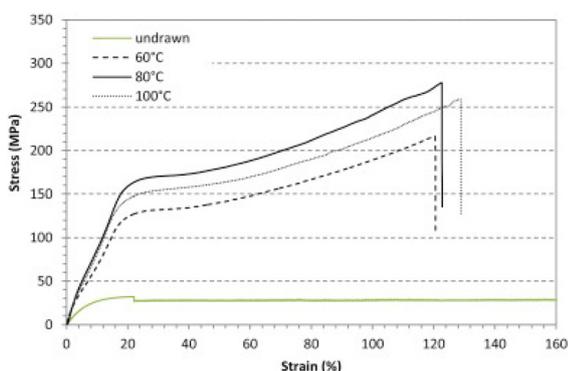


**Scheme 10** PBS production via polycondensation of succinic acid (SA) and 1,4-butanediol (BD).

viable option to replace, for example, fossil-based PP in fishing gear.

In this vein, Deroiné *et al.*<sup>171</sup> reported a resistant monofilament based on PBS as an alternative for fishing gear. The monofilaments were prepared by melt-processing using a single-screw extruder and by controlling the processing temperature they managed to improve the tensile behaviour of PBS monofilaments (Fig. 7).

The monofilaments' tensile behaviour was improved in comparison with undrawn PBS. However, in this study degradation studies in aquatic environments (at least hydrolytic degradation) of PBS monofilaments are missing, despite their particular relevance for target fishing gear application. Nevertheless, other authors studied the hydrolytic degradation of PBS pieces ( $5 \times 6 \times 0.2 \text{ mm}^3$ ) at ambient temperatures in phosphate-buffered saline.<sup>172</sup> The samples started losing weight slowly, with only 10% after 9 weeks, but they reached 65% weight loss at the end of 15 weeks. When it comes to microbial degradation, Zhao *et al.*<sup>173</sup> isolated and identified different microbial strains from the compost of PBS degradation, and *Aspergillus versicolor* revealed to be the best PBS-degrading microorganism.



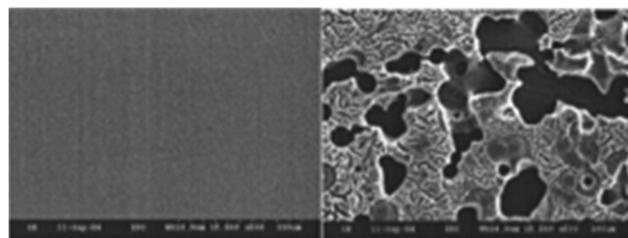
**Fig. 7** Evolution of the tensile behaviour of PBS monofilaments drawn at different temperatures. Adapted with permission from ref. 171. Copyright 2018, with permission from Elsevier.

When it comes to controlled composting studies (ISO 14855, 58 °C),<sup>14</sup> Zhao *et al.*<sup>173</sup> studied PBS degradation in different forms (powder, granulate, and films). The maximum composting degradation was achieved, as one could anticipate, with powdered samples with maximum 72% after 90 days. The SEM analysis allows the observation of the changes in the PBS surface, thus confirming its degradation in compost (Fig. 8).

Some copolymers and blends with PBS have also been reported as a strategy to tailor degradation. In a comparative study, Tsutsumi *et al.*<sup>174</sup> studied both the enzymatic (lipases in phosphate-buffered solution at 37 °C) and oxidative degradation (sodium hydroxide solution at 37 °C) of PBSA and a PBS/PCL blend and compared them with PBS. They found that PBSA was readily degraded by various lipases, with a maximum weight loss of 96% after just 10 days by AK lipase from *Pseudomonas* sp. The degradation rate of PBSA by the same lipase was 16 times faster than that by the tested oxidative degradation. Also, for the same enzyme, the PBS/PCL blend reached a *ca.* 56% weight loss while PBS reached only 14%.

Zhu *et al.*<sup>175</sup> described the microbial degradation of poly(butylene succinate-co-adipate) (PBSA) and poly(butylene-co-hexylene succinate) (PBHS) copolymers carried out with *Penicillium chrysogenum* (37 °C), whereas Wang and co-workers<sup>176</sup> used *Aspergillus versicolor* fungi (30 °C) instead. For the former, the copolyesters reached over the course of 52 days, a maximum weight loss of only *ca.* 7% (PBSA), although this result is higher than that observed for pristine PBS. Hence, in the case of *Penicillium chrysogenum*-mediated degradation (as well as soil burial tests) the copolymerisation strategy was not enough to make a noticeable impact on the overall degradation process. Oppositely, in the case of *Aspergillus versicolor* mediated microbial degradation of PBSA, more than 90% of the copolymer was assimilated within 25 days.<sup>176</sup> At the early stage of PBSA microbial degradation, the decrease in molecular weight is mostly attributed to the random non-enzymatic hydrolysis of the polymer chains. Once the molecular weight decreases to a point where microbial attack can proceed, the biotic hydrolysis is accelerated.

**Furan-based polymers.** The intense quest of both scientific and industrial communities to produce new high-performance bio-based polymers, which typically is not accessible with pure



**Fig. 8** SEM images of the surface changes of PBS films before composting (left) and after composting (right) for 90 days. Adapted with permission from ref. 173. Copyright © 2005 Wiley Periodicals, Inc.

aliphatic polymers, has spotlighted furan-based ones amongst the most interesting in terms of properties and future applications. Notably bio-based poly(ethylene 2,5-furandicarboxylate) (PEF) has the potential to phase out the widely used PET, mainly in packaging applications due to a set of properties including superior barrier performance and a more favourable degradation profile.<sup>177–182</sup> Avantium N.V., a technology company in the field of renewable chemistry, leads PEF developments towards market introduction.<sup>183</sup>

PEF is synthesized from bio-based 2,5-furandicarboxylic acid (FDCA) as opposed to fossil-based TPA, and ethylene glycol through a typical two-step melt polycondensation procedure (Scheme 11) applying high temperature (>200 °C), vacuum, and long reaction times and using metal-based catalysts.<sup>184,185</sup> Nevertheless, greener synthesis has been proposed, either using ROP in less than 30 min,<sup>186,187</sup> or using ionic liquids or non-metal catalysts.<sup>188,189</sup>

PEF is expected to reach several markets, with applications in packaging, mainly in the form of bottles for soft drinks (being 31 times less permeable to CO<sub>2</sub> than PET); other potential applications comprise textiles and as films.<sup>178,190</sup> The unique set of properties of PEF include thermal properties such as high melting (200–215 °C) and glass transition (75–80 °C) temperatures, together with high thermal stability (up to 350 °C).<sup>177</sup> Furthermore, this polyester is a highly stiff material with a Young's modulus of approximately 2450 MPa and maximum stress equal to 35 MPa.<sup>184</sup>

In terms of composting experiments, Avantium reported the degradation of PEF under accelerated (58 °C) industrial composting conditions by Organic Waste System (OWS).<sup>182,191</sup> In these tests, it was observed that in just 9 months PEF reached 90% degradation based on the amount of CO<sub>2</sub> released (*vs.* only 10% for PET). Nevertheless, further studies under natural conditions (such as typical aquatic and soil degradation) are required to provide a more realistic scenario of PEF behaviour.

Furan-based polymers include many others, besides PEF, namely furanic–aliphatic (co)polyesters with potential enhanced degradability compared to PEF, and in this regard, with multiple EoL options. In this vein, Sousa *et al.*<sup>192</sup> introduced the synthesis of this family of polymers with poly(ethylene 2,5-furandicarboxylate-*co*-poly(L-lactic acid))s (PEFLs). The authors reported an overall trend of improved thermal stability of PEFLs when compared with the PLLA precursor (>300 °C *vs.*

257 °C, respectively). Also, the *T<sub>g</sub>* was higher due to an increase in stiffness prompted by the furanic moieties. The incorporation of just 8 mol% of lactyl units was enough to increase the enzymatic degradability of the copolyester in phosphate-buffered saline medium (37 °C), while not compromising the thermal properties, as can be seen in Table 1. Nevertheless, the highest weight loss was achieved with 74% lactyl units, reaching almost 60% total weight loss over the course of 12 weeks. Later, in 2015, Wu *et al.* complemented the previous study with PEFL degradation tests in garden soil at 35 °C, for 55 days.<sup>193</sup> As observed for the phosphate-buffered saline incubation tests performed by Sousa *et al.*,<sup>192</sup> a maximum weight loss was achieved for the copolymer incorporating 80% of lactyl units.

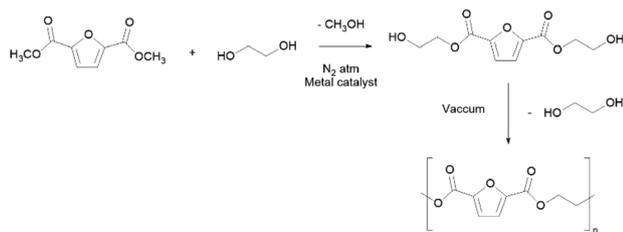
Efforts on this family of polymers have also turned to furanic replacements of previously described fossil-based TPA in PBAT, that is poly(butylene adipate-*co*-butylene 2,5-furandicarboxylate)s (PBAFs).<sup>58,194,195</sup> These copolyesters possess the excellent thermal stability of furan-based polyesters (*T<sub>d,5%</sub>* > 340 °C).<sup>58</sup> PBAFs with a lower furanic content (<50%) also exhibited high-elastic deformation and rebound resilience, but the Young's modulus ranged between 18 and 122 MPa and the tensile strength was 9–17 MPa.<sup>58</sup> PBAF with 40% of butylene 2,5-furanoate moieties has the lowest tensile modulus and strength due to the weakest ability to crystallise (also associated with statistic factors). With increasing furanic content, the stress hardening becomes more obvious, and the tensile modulus and strength of PBAF increase, but the elongation at break follows a downward trend.

Degradation experiments in phosphate-buffered saline medium (37 °C), simulated seawater (5–10 °C) and CALB enzymatic incubation revealed PBAFs' tendency to degrade, especially for higher percentages of adipic acid,<sup>194</sup> as already observed for the PBAT counterparts.<sup>196</sup>

In other similar studies, PBSFs prepared from FDCA, succinic acid and 1,4-butanediol were also mentioned,<sup>58,197,198</sup> but many others could also be included as those made of poly(ethylene glycol) segments<sup>199,200</sup> or from long chain alkanoids and alkane diols.<sup>201,202</sup>

## Criteria and opportunities for (bio)degradable polymers

(Bio)degradable polymers can play a role in polymer waste management or, at least, in mitigating their accumulation in natural environments, and, thus, prompting a more adequate EoL for polymer articles. This review shows that there is not a *one size fits all* solution, as would be expected for a complex problem as polymer waste, instead it requires a series of varied efforts, starting from social behavioural ones, along with adequate legal frameworks, to, at the downstream, stronger collection, sorting and better recycling technologies.<sup>203</sup> However, it is undeniable that in certain circumstances compostable or fully (bio)degradable polymers can attenuate the persistent polymers' environmental impact. Anticipating the need for a



**Scheme 11** General route for the synthesis of PEF *via* two-step polycondensation.

judicious replacement of traditional persistent polymers with compostable ones, the European Bioplastics Association (EUBP) has set forth a group of recommendation criteria for considering such substitution:<sup>204</sup>

(i) alternative reusable solutions cannot be redesigned, highlighting the need to reuse polymeric objects;

(ii) contamination with food waste occurs and cleaning is not feasible;

(iii) they provide potential to reduce biowaste contamination;

(iv) only when mechanical recycling fails to effectively recycle polymers and likely they will end up in the organic waste collection, (bio)degradable options should be considered.

Besides the need to reuse before performing a substitution, polymer separation from organic waste might be challenging and cross-contamination might be a serious problem.<sup>205</sup> It is not uncommon for polymer articles made of non-degradable polymers to coexist with food residues in a collection stream. Here, they act as cross-contaminants to each other, limiting both their EoL solutions, namely recycling and composting, respectively. Precisely, several studies indicate that approximately 4 to 5 wt% of biowaste streams are contaminated with non-(bio)degradable polymers, with the majority being plastic bags and packaging films typically made from PE and PP, or even PET.<sup>206,207</sup> Other products that fall under similar EoL issues are, for example, tea bags and fruit stickers.<sup>204</sup> In these situations, the most probable fate of these contaminated polymers is either landfills or incinerators.<sup>208</sup> From a general point of view, the advantage of using compostable polymers is evident when there is a risk of cross-contamination, and recycling fails.

Furthermore, collection is often associated to several issues, being not cost-effective, rather incomplete, or even impossible due to causes as diverse as the countries' underdeveloped collecting/separation system,<sup>209</sup> not practiced by the users as is the case of agriculture mulch films from LDPE, and of the fishing gear's dolly rope, commercially manufactured from persistent PP. All of these open up great opportunities for compostable polymers, such as PBAT or PLA, as well as to innovative recycling technologies.

Additionally, there may be advantages of using biodegradable polymers in situations where separation is an impossible task, for example when small polymer pieces are unavoidably mixed with sewage and likely to escape to the environment.<sup>205</sup> For example, microbeads with typically less than 1 mm in diameter present in exfoliants are small plastic pieces.<sup>210</sup> Recently, there have been further reports on the environmental impact of microplastics in cosmetics', stressing the urgent need for global legislation.<sup>211,212</sup>

To conclude, following the previously mentioned criteria, a series of products can be identified as potential for being produced from compostable polymeric materials, although this path also brings technological challenges. Nevertheless, Fig. 9 illustrates some of those products based on how commonly they are found in compost and how rarely they are recycled. In this regard tailor-made synthetic (bio)degradable polymers are a very promising solution for a sustainable development.

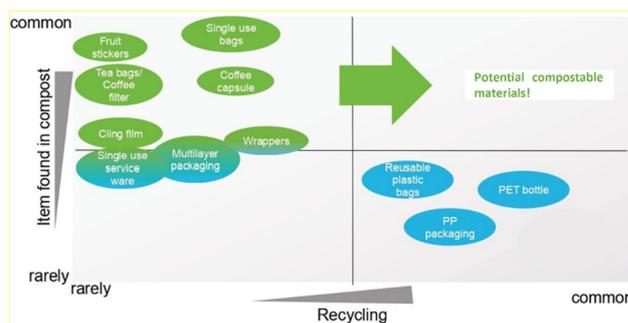


Fig. 9 Several products and their potential compostable materials based on how often they are found in compost and their recyclability. Reproduced from ref. 203 with permission from European Bioplastics e. V., 2022.

## Conclusions

In summary, there are a variety of promising synthetic (bio) degradable polymers, either fossil-based or, even better, bio-based ones. PCL, PGA, PBAT, PLA, PBS and furan-based polymers are some of the materials judiciously selected to be reviewed in this appraisal due to their properties and related (potential) commercial relevance for packaging, textile fibres or films. They were in-depth overviewed from three main aspects: green efforts to render their composition and/or synthesis greener, properties and applications, and (bio)degradation behaviour in natural environments and under controlled composting conditions.

We have also discussed a very pertinent point for a conscientious transition from persistent polymers to (bio)degradable ones – the criteria and the specific situations where they are beneficial for a sustainable development. For example, in cases where reuse is not possible, cross-contamination and separation are not cost-effective or mostly incomplete, and recycling fails.

## Author contributions

AFS – conceptualisation, supervision, and writing – original draft and review & editing. BA – data curation and writing – review & editing. AJDS and JC – writing – original draft and review & editing.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 Plastics Europe - Association of Plastic Manufacturers (Organization), *Plastics - the Facts 2021*, 2021.
- 2 R. A. Sheldon and M. Norton, *Green Chem.*, 2020, **22**, 6310–6322.
- 3 A. Chamas, H. Moon, J. Zheng, Y. Qiu, T. Tabassum, J. H. Jang, M. Abu-Omar, S. L. Scott and S. Suh, *ACS Sustainable Chem. Eng.*, 2020, **8**, 3511.
- 4 J. D. Gu, *Int. Biodeterior. Biodegrad.*, 2003, **52**, 69–91.
- 5 B. Agostinho, A. J. D. Silvestre and A. F. Sousa, *Green Chem.*, 2022, **24**, 3115–3119.
- 6 I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes and B. M. Weckhuysen, *Angew. Chem., Int. Ed.*, 2020, **59**, 15402–15423.
- 7 United States Environmental Protection Agency, National Overview: Facts and Figures on Materials, Wastes and Recycling, <https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials>, (accessed 10 May 2022).
- 8 European Environment Agency, Waste recycling in Europe, <https://www.eea.europa.eu/ims/waste-recycling-in-europe>, (accessed 10 May 2022).
- 9 Plastics Europe - Association of Plastic Manufacturers (Organization), Recycling technologies, <https://plasticseurope.org/sustainability/circularity/recycling/recycling-technologies/>, (accessed 21 June 2022).
- 10 I. A. Ignatyev, W. Thielemans and B. Vander Beke, *ChemSusChem*, 2014, **7**, 1579–1593.
- 11 United Nations Conference on Trade and Development, UN recognition of the least developed countries, <https://unctad.org/topic/least-developed-countries/recognition>, (accessed 19 January 2022).
- 12 J. Jambeck, B. D. Hardesty, A. L. Brooks, T. Friend, K. Teleki, J. Fabres, Y. Beaudoin, A. Bamba, J. Francis, A. J. Ribbink, T. Baleta, H. Bouwman, J. Knox and C. Wilcox, *Mar. Policy*, 2018, **96**, 256–263.
- 13 ISO - Online Browsing Platform (OBP), ISO 17088 - Plastics - Organic recycling - Specifications for compostable plastics, <https://www.iso.org/obp/ui/#iso:std:iso:17088:ed-3:v1:en>, (accessed 11 April 2022).
- 14 ISO - Online Browsing Platform (OBP), ISO 14855-2 -Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide - Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale, <https://www.iso.org/standard/72046.html>, (accessed 11 April 2022).
- 15 European Bioplastics e.V., Bioplastics market data, <https://www.european-bioplastics.org/market/>, (accessed 22 March 2022).
- 16 T. Grethe, *Tekstilec*, 2021, **64**, 32–46.
- 17 K. Twarowska-Schmidt, *Fibres Text. East. Eur.*, 2004, **12**, 17–20.
- 18 B. Younes, *J. Text. Inst.*, 2017, **108**, 674–682.
- 19 K. Shirvanimoghaddam, B. Motamed, S. Ramakrishna and M. Naebe, *Sci. Total Environ.*, 2020, **718**, 137317.
- 20 D. J. Sarkar, M. Barman, T. Bera, M. De and D. Chatterjee, in *Encyclopedia of Polymer Applications*, 2018, pp. 1–20.
- 21 S. Kasirajan and M. Ngouajio, *Agron. Sustainable Dev.*, 2012, **32**, 501–529.
- 22 S. Bandopadhyay, L. Martin-Closas, A. M. Pelacho and J. M. DeBruyn, *Front. Microbiol.*, 2018, **9**, 1–7.
- 23 European Commission, *The European Green Deal*, Brussels, 2019.
- 24 United Nations Development Programme, The SDGs Goals in Action, <https://www.undp.org/sustainable-development-goals>, (accessed 22 March 2022).
- 25 T. V. Shah and D. V. Vasava, *e-Polymers*, 2019, **19**, 385–410.
- 26 B. D. Ulery, L. S. Nair and C. T. Laurencin, *J. Polym. Sci., Part B: Polym. Phys.*, 2011, **49**, 832–864.
- 27 P. Béguin and J.-P. Aubert, *FEMS Microbiol. Rev.*, 1994, **13**, 25–58.
- 28 A. M. Nafchi, M. Moradpour, M. Saeidi and A. K. Alias, *Starch/Staerke*, 2013, **65**, 61–72.
- 29 V. Siracusa, P. Rocculi, S. Romani and M. D. Rosa, *Trends Food Sci. Technol.*, 2008, **19**, 634–643.
- 30 IUPAC, *Compendium of Chemical Terminology*, Blackwell Scientific Publications, Oxford, 2nd edn, 1997.
- 31 M. Vert, Y. Doi, K. H. Hellwich, M. Hess, P. Hodge, P. Kubisa, M. Rinaudo and F. Schué, *Pure Appl. Chem.*, 2012, **84**, 377–410.
- 32 K. Horie, M. Barón, R. B. Fox, J. He, M. Hess, J. Kahovec, T. Kitayama, P. Kubisa, E. Maréchal, W. Mormann, R. F. T. Stepto, D. Tabak, J. Vohlídal, E. S. Wilks and W. J. Work, *Pure Appl. Chem.*, 2004, **76**, 889–906.
- 33 E. Rudnik and D. Briassoulis, *Ind. Crops Prod.*, 2011, **33**, 648–658.
- 34 ASTM International, Standard Specification for Labeling of End Items that Incorporate Plastics and Polymers as Coatings or Additives with Paper and Other Substrates Designed to be Aerobically Composted in Municipal or Industrial Facilities, <https://www.astm.org/Standards/D6868.htm>, (accessed 22 April 2021).
- 35 Comité Européen de Normalisation (CEN), 2005.
- 36 J. G. Rosenboom, R. Langer and G. Traverso, *Nat. Rev. Mater.*, 2022, **7**, 117–137.

- 37 Ingevity, Capa® 6500, <https://www.ingevity.com/products/capa-6500/>, (accessed 13 April 2022).
- 38 U.S. Food & Drug Administration (FDA), CFR - Code of Federal Regulations Title 21, <https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/cfrsearch.cfm?fr=175.105>, (accessed 6 June 2022).
- 39 EUR-Lex (European Union law), Commission Regulation (EU) No 10/2011, <https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32011R0010>, (accessed 6 June 2022).
- 40 S. H. Pyo, J. H. Park, V. Srebny and R. Hatti-Kaul, *Green Chem.*, 2020, **22**, 4450–4455.
- 41 G. Acik, *J. Polym. Environ.*, 2020, **28**, 668–675.
- 42 M. Labet and W. Thielemans, *Chem. Soc. Rev.*, 2009, **38**, 3484–3504.
- 43 T. L. Yu, C. C. Wu, C. C. Chen, B. H. Huang, J. Wu and C. C. Lin, *Polymer*, 2005, **46**, 5909–5917.
- 44 I. Vroman and L. Tighzert, *Materials*, 2009, **2**, 307–344.
- 45 V. Guarino, G. Gentile, L. Sorrentino and L. Ambrosio, in *Encyclopedia of Polymer Science and Technology*, 2017, pp. 1–36.
- 46 A. F. Sousa, R. Patrício, Z. Terzopoulou, D. N. Bikiaris, T. Stern, J. Wenger, K. Loos, N. Lotti, V. Siracusa, A. Szymczyk, S. Paszkiewicz, K. S. Triantafyllidis, A. Zamboulis, M. S. Nikolic, P. Spasojevic, S. Thiyagarajan, D. S. Van Es and N. Guigo, *Green Chem.*, 2021, **23**, 8795–8820.
- 47 T. Narancic, S. Verstichel, S. Reddy Chaganti, L. Morales-Gamez, S. T. Kenny, B. De Wilde, R. Babu Padamati and K. E. O'Connor, *Environ. Sci. Technol.*, 2018, **52**, 10441–10452.
- 48 H. Tsuji and K. Suzuyoshi, *Polym. Degrad. Stab.*, 2002, **75**, 347–355.
- 49 C. Bastioli, *Polym. Degrad. Stab.*, 1998, **59**, 263–272.
- 50 M. LLc, Matweb - Material Property Data, <https://www.matweb.com/search/DataSheet.aspx?MatGUID=501acbb63cbcf4748faa7490884cdbcac&ckck=1>, (accessed 19 April 2022).
- 51 P. A. M. Lips and P. J. Dijkstra, *Biodegradable Polymers for Industrial Applications*, Woodhead Publishing Limited, 2005.
- 52 J. E. Mark, *Polymer Data Handbook*, Oxford University Press, New York, 1999.
- 53 J. Jian, Z. Xiangbin and H. Xianbo, *Adv. Ind. Eng. Polym. Res.*, 2020, **3**, 19–26.
- 54 L. K. Massey, *Permeability Properties of Plastics and Elastomers - A Guide to Packaging and Barrier Materials*, 2nd edn, 2003, vol. 92.
- 55 A. Eceiza, K. de la Caba, G. Kortaberria, N. Gabilondo, M. Corcuera and I. Mondragon, *Polym. Eng. Sci.*, 2008, **48**, 297–306.
- 56 A. Boubakri, N. Haddar, K. Elleuch and Y. Bienvenu, *Mater. Des.*, 2010, **31**, 4194–4201.
- 57 V. C. Pinto, T. Ramos, S. Alves, J. Xavier, P. Tavares, P. M. G. P. Moreira and R. M. Guedes, *Procedia Eng.*, 2015, **114**, 635–642.
- 58 B. Wu, Y. Xu, Z. Bu, L. Wu, B. G. Li and P. Dubois, *Polymer*, 2014, **55**, 3648–3655.
- 59 T. M. Crizel, T. M. H. Costa, A. O. Rios and S. H. Flôres, *Ind. Crops Prod.*, 2016, **87**, 218–228.
- 60 Q. Ma, K. Shi, T. Su and Z. Wang, *J. Polym. Environ.*, 2020, **28**, 2947–2955.
- 61 D. R. Chen, J. Z. Bei and S. G. Wang, *Polym. Degrad. Stab.*, 2000, **67**, 455–459.
- 62 M. J. Motiwalla, P. P. Punyarthi, M. K. Mehta and V. Kelkar-mane, *J. Environ. Biol.*, 2013, **34**, 43–49.
- 63 M. Rutkowska, K. Krasowska, A. Heimowska, H. Janik, J. Haponiuk and S. Karlsson, *Pol. J. Environ. Stud.*, 2002, **11**, 413–420.
- 64 M. E. F. César, P. D. S. C. Mariani, L. H. Innocentini-Mei and E. J. B. N. Cardoso, *Polym. Test.*, 2009, **28**, 680–687.
- 65 H. Yavuz and C. Babaç, *J. Polym. Environ.*, 2003, **11**, 107–113.
- 66 Novamont S.p.A., Mater-Bi, <https://www.novamont.com/eng/mater-bi>, (accessed 28 February 2022).
- 67 A. Ostafinska, I. Fortelny, M. Nevalova, J. Hodan, J. Kredatusova and M. Slouf, *RSC Adv.*, 2015, **5**, 98971–98982.
- 68 A. C. Vieira, J. C. Vieira, R. M. Guedes and A. T. Marques, *Mater. Sci. Forum*, 2010, **636–637**, 825–832.
- 69 N. T. T. Thao, S. Lee, G. R. Shin, Y. Kang, S. Choi and M. S. Kim, *Pharmaceutics*, 2021, **13**, 253.
- 70 A. Richert and G. B. Dąbrowska, *Int. J. Biol. Macromol.*, 2021, **176**, 226–232.
- 71 K. Fukushima, J. L. Feijoo and M. C. Yang, *Eur. Polym. J.*, 2013, **49**, 706–717.
- 72 N. K. Kalita, S. M. Bhasney, C. Mudenur, A. Kalamdhad and V. Katiyar, *Chemosphere*, 2020, **247**, 125875.
- 73 K. Y. Lim, B. C. Kim and K. J. Yoon, *J. Appl. Polym. Sci.*, 2003, **88**, 131–138.
- 74 K. Y. Lim, B. C. Kim and K. J. Yoon, *J. Polym. Sci., Part B: Polym. Phys.*, 2002, **40**, 2552–2560.
- 75 E. Chiellini, *J. Environ. Polym. Degrad.*, 1996, **4**, 37–50.
- 76 Kureha Corporation, Kuredux, <https://www.kureha.co.jp/en/business/material/kuredux.html>, (accessed 13 April 2022).
- 77 P. K. Samantaray, A. Little, D. M. Haddleton, T. McNally, B. Tan, Z. Sun, W. Huang, Y. Ji and C. Wan, *Green Chem.*, 2020, **22**, 4055–4081.
- 78 A. Panova, L. J. Mersinger, Q. Liu, T. Foo, D. C. Roe, W. L. Spillan, A. E. Sigmund, A. Ben-Bassat, L. W. Wagner, D. P. O'Keefe, S. Wu, K. L. Petrillo, M. S. Payne, S. T. Breske, F. G. Gallagher and R. Dicosimo, *Adv. Synth. Catal.*, 2007, **349**, 1462–1474.
- 79 S. Wu, A. J. Fogiel, K. L. Petrillo, R. E. Jackson, K. N. Parker, R. DiCosimo, A. Ben-Bassat, D. P. O'Keefe and M. S. Payne, *Biotechnol. Bioeng.*, 2008, **99**, 717–720.
- 80 C. Lachaux, C. J. R. Frazao, F. Krauß, N. Morin, T. Walther and J. M. François, *Front. Bioeng. Biotechnol.*, 2019, **7**, 359.
- 81 S. Shawe, F. Buchanan, E. Harkin-Jones and D. Farrar, *J. Mater. Sci.*, 2006, **41**, 4832–4838.
- 82 R. S. Bezwada, D. D. Jamiolkowski, I. Y. Lee, V. Agarwal, J. Persivale, S. Trenka-Benthin, M. Erneta, J. Suryadevara, A. Yang and S. Liu, *Biomaterials*, 1995, **16**, 1141–1148.

- 83 Q. Cai, J. Bei and S. Wang, *Polymer*, 2002, **43**, 3585–3591.
- 84 S. H. Lee, B. S. Kim, S. H. Kim, S. W. Choi, S. I. Jeong, I. K. Kwon, S. W. Kang, J. Nikolovski, D. J. Mooney, Y. K. Han and Y. H. Kim, *J. Biomed. Mater. Res., Part A*, 2003, **66**, 29–37.
- 85 BASF SE, Ecoflex® (PBAT): The Original since 1998 – Certified Compostable Plastic, [https://plastics-rubber.basf.com/global/en/performance\\_polymers/products/ecoflex.html](https://plastics-rubber.basf.com/global/en/performance_polymers/products/ecoflex.html), (accessed 24 February 2022).
- 86 Q. Zhiguo, Y. Jilei, Q. Yi, Z. Langhui, S. Jie, G. Xueshan, Z. Chaoshan, S. Yuzeng, M. Yuebo, F. Buxue, L. Wei, W. Li, X. L. Xianfeng, W. Haiqiang, C. Liang, T. Shuai, C. Jinbo, H. Yongning and Y. Chuanzhong, CN105237750A, 2015.
- 87 S. Unlu, W. Niu, Y. Yas, Y. Demirel, S. Unlu, W. Niu and Y. Demirel, *Biofuels, Bioprod. Biorefin.*, 2020, **14**, 794–807.
- 88 T. Beardslee and S. Picataggio, *Lipid Technol.*, 2012, **24**, 223–225.
- 89 E. Skoog, J. H. Shin, V. Saez-Jimenez, V. Mapelli and L. Olsson, *Biotechnol. Adv.*, 2018, **36**, 2248–2263.
- 90 Y. Deng, C. Yu, P. Wongwiwattana and N. L. Thomas, *J. Polym. Environ.*, 2018, **26**, 3802–3816.
- 91 U. Witt, R.-J. Müller and W.-D. Deckwer, *Chem. Ing. Tech.*, 1995, **67**, 904–907.
- 92 U. Witt, R. J. Müller and W.-D. Deckwer, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 1995, **32**, 851–856.
- 93 T. Kijchavengkul, R. Auras, M. Rubino, S. Selke, M. Ngouajio and R. T. Fernandez, *Polym. Degrad. Stab.*, 2010, **95**, 2641–2647.
- 94 ASTM International, Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures, <https://www.astm.org/d5338-15r21.html>, (accessed 12 July 2022).
- 95 U. Witt, T. Einig, M. Yamamoto, I. Kleeberg, W. D. Deckwer and R. J. Müller, *Chemosphere*, 2001, **44**, 289–299.
- 96 P. A. Palsikowski, C. N. Kuchnier, I. F. Pinheiro and A. R. Morales, *J. Polym. Environ.*, 2018, **26**, 330–341.
- 97 Y. X. Weng, Y. J. Jin, Q. Y. Meng, L. Wang, M. Zhang and Y. Z. Wang, *Polym. Test.*, 2013, **32**, 918–926.
- 98 Y. Han, J. Shi, L. Mao, Z. Wang and L. Zhang, *Ind. Eng. Chem. Res.*, 2020, **59**, 21779–21790.
- 99 E. Grigat, R. Koch and R. Timmermann, *Polym. Degrad. Stab.*, 1998, **59**, 223–226.
- 100 S. Mecking, *Angew. Chem., Int. Ed.*, 2004, **43**, 1078–1085.
- 101 J. Lee, Y. Lee, S. Kim, E. E. Kwon and K. Y. A. Lin, *Korean J. Chem. Eng.*, 2021, **38**, 1079–1086.
- 102 M. Winnacker and B. Rieger, *Polym. Chem.*, 2016, **7**, 7039–7046.
- 103 H. Sun, F. Meng, A. A. Dias, M. Hendriks, J. Feijen and Z. Zhong, *Biomacromolecules*, 2011, **12**, 1937–1955.
- 104 C. C. Chu, *J. Fiber Bioeng. Inform.*, 2012, **5**, 1–31.
- 105 L. J. del Valle, M. Roa, A. Díaz, M. T. Casas, J. Puiggali and A. Rodríguez-Galán, *J. Polym. Res.*, 2012, **19**, 9792.
- 106 M. B. Martínez, I. M. Pinilla, F. Z. Mata and J. A. G. Ferez, *Macromolecules*, 1997, **30**, 3197–3203.
- 107 A. Rodriguez-Galan, L. Franco and J. Puiggali, *Polymers*, 2011, **3**, 65–99.
- 108 L. Wen, S. Zhang, Y. Xiao, J. He, S. Zhu, J. Zhang, Z. Wu and M. Lang, *Macromolecules*, 2020, **53**, 5096–5104.
- 109 K. Guo and C. C. Chu, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 1595–1606.
- 110 Y. P. Ge, D. Yuan, Z. L. Luo and B. B. Wang, *EXPRESS Polym. Lett.*, 2014, **8**, 50–54.
- 111 K. E. Gonsalves, X. Chen and J. A. Cameron, *Macromolecules*, 1992, **25**, 3309–3312.
- 112 X. Chen, K. E. Gonsalves and J. A. Cameron, *J. Appl. Polym. Sci.*, 1993, **50**, 1999–2006.
- 113 Q. Zhiyong, L. Sai, Z. Hailian and L. Xiaobo, *Colloid Polym. Sci.*, 2003, **281**, 869–875.
- 114 Z. Qian, S. Li, Y. He, H. Zhang and X. Liu, *Biomaterials*, 2004, **25**, 1975–1981.
- 115 H. Zhang, Y. He, S. Li and X. Liu, *Polym. Degrad. Stab.*, 2005, **88**, 309–316.
- 116 Y. He, Z. Qian, H. Zhang and X. Liu, *Colloid Polym. Sci.*, 2004, **282**, 972–978.
- 117 Y. Fan, M. Kobayashi and H. Kise, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 1318–1328.
- 118 Č. Novotný, P. Erbanová, H. Sezimová, K. Malachová, Z. Rybková, L. Malinová, I. Prokopová and J. Brožek, *Int. Biodeterior. Biodegrad.*, 2015, **97**, 25–30.
- 119 R. A. Gross and B. Kalra, *Science*, 2002, **297**, 803–807.
- 120 N. B. Halima, *RSC Adv.*, 2016, **6**, 39823–39832.
- 121 Kuraray Europe GmbH, Polyvinyl alcohol, PVA, PVOH - Kuraray Poval™, <https://www.kuraray-poval.com/>, (accessed 21 June 2022).
- 122 Sekisui Specialty Chemicals, Selvol™ Polyvinyl Alcohol Product Information, <https://www.sekisui-sc.com/products/polyvinyl-alcohol/>, (accessed 21 June 2022).
- 123 P. Alexy, D. Káčhová, M. Kršiak, D. Bakoš and B. Šimková, *Polym. Degrad. Stab.*, 2002, **78**, 413–421.
- 124 O. Olabisi and K. Adewale, *Handbook of Thermoplastics*, Taylor & Francis Group, LLC, 2nd edn, 2016.
- 125 M. Lim, H. Kwon, D. Kim, J. Seo, H. Han and S. B. Khan, *Prog. Org. Coat.*, 2015, **85**, 68–75.
- 126 E. Chiellini, A. Corti and R. Solaro, *Polym. Degrad. Stab.*, 1999, **64**, 305–312.
- 127 R. Solaro, A. Corti and E. Chiellini, *Polym. Adv. Technol.*, 2000, **11**, 873–878.
- 128 A. Corti, R. Solaro and E. Chiellini, *Polym. Degrad. Stab.*, 2002, **75**, 447–458.
- 129 E. Chiellini, A. Corti, G. Del Sarto and S. D'Antone, *Polym. Degrad. Stab.*, 2006, **91**, 3397–3406.
- 130 J. Hoffmann, I. Řezníčková, J. Kozáková, J. Růžička, P. Alexy, D. Bakoš and L. Precnerová, *Polym. Degrad. Stab.*, 2003, **79**, 511–519.
- 131 N. A. Azahari, N. Othman and H. Ismail, *J. Phys. Sci.*, 2011, **22**, 15–31.
- 132 Z. Guohua, L. Ya, F. Cuilan, Z. Min, Z. Caiqiong and C. Zongdao, *Polym. Degrad. Stab.*, 2006, **91**, 703–711.

- 133 H. C. Alexander, D. C. Dill, L. W. Smith, P. D. Guiney and P. Dorn, *Environ. Toxicol.*, 1988, **7**, 19–26.
- 134 Acrylite, Cyrolon® Polycarbonate, <https://www.acrylite.co/products/our-brands/cyrolon/polycarbonate>, (accessed 22 June 2022).
- 135 Covestro, Makrolon® resists heat and attracts innovators, <https://solutions.covestro.com/en/brands/makrolon>, (accessed 22 June 2022).
- 136 T. Artham and M. Doble, *J. Polym. Environ.*, 2009, **17**, 170–180.
- 137 T. Artham and M. Doble, *Environ. Chem. Lett.*, 2012, **10**, 29–34.
- 138 J. Sajiki and J. Yonekubo, *Chemosphere*, 2003, **51**, 55–62.
- 139 M. D. Garrison, P. J. Storch, W. S. Eck, V. H. Adams, P. W. Fedick and B. G. Harvey, *Green Chem.*, 2021, **23**, 8016–8029.
- 140 P. Wang, J. H. Park, M. Sayed, T.-S. Chang, A. Moran, S. Chen and S.-H. Pyo, *Polym. Chem.*, 2018, **9**, 3798–3807.
- 141 Plastic Selection Group Inc., Plastic Selection Group Products, <https://www.go2psg.com/clear-thermoplastic-resin-products>, (accessed 4 March 2022).
- 142 P. Wang, J. H. Park, M. Sayed, T. S. Chang, A. Moran, S. Chen and S. H. Pyo, *Polym. Chem.*, 2018, **9**, 3798–3807.
- 143 V. S. Bonab and I. Manas-Zloczower, *J. Polym. Sci., Part B: Polym. Phys.*, 2017, **55**, 1553–1564.
- 144 BASF SE, Think, create, Elastollan® (TPU), [https://plastics-rubber.basf.com/emea/en/performance\\_polymers/products/elastollan.html?at\\_medium=sl&at\\_campaign=PM\\_BAW\\_EMEA\\_EN\\_Elastollan\\_TRA\\_CROSS&at\\_term=tpuplastic&at\\_creation=Search\\_Google\\_SERP\\_Elastollan-General-EMEA-EN&at\\_platform=google&at\\_variant](https://plastics-rubber.basf.com/emea/en/performance_polymers/products/elastollan.html?at_medium=sl&at_campaign=PM_BAW_EMEA_EN_Elastollan_TRA_CROSS&at_term=tpuplastic&at_creation=Search_Google_SERP_Elastollan-General-EMEA-EN&at_platform=google&at_variant), (accessed 23 June 2022).
- 145 I. Singh, S. K. Samal, S. Mohanty and S. K. Nayak, *Eur. J. Lipid Sci. Technol.*, 2020, **122**, 1900225.
- 146 Y. Li, X. Luo and S. Hu, *Bio-based Polyols and Polyurethanes*, Springer International Publishing, Cham, 2015.
- 147 R. Mort, K. Vorst, G. Curtzwiler and S. Jiang, *RSC Adv.*, 2021, **11**, 4375–4394.
- 148 L. Hojabri, X. Kong and S. S. Narine, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 3302–3310.
- 149 Isopa (European Diisocyanate & Polyol Producers Association), *A guide to the REACH Restriction applying to diisocyanates*, 2021.
- 150 Y. D. Kim and S. C. Kim, *Polym. Degrad. Stab.*, 1998, **62**, 343–352.
- 151 B. Quienne, N. Kasmi, R. Dieden, S. Caillol and Y. Habibi, *Biomacromolecules*, 2020, **21**, 1943–1951.
- 152 M. Włoch and K. Błazek, *ACS Symp. Ser.*, 2021, **1380**, 107–166.
- 153 L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau and H. Cramail, *Chem. Rev.*, 2015, **115**, 12407–12439.
- 154 V. Besse, R. Auvergne, S. Carlotti, G. Boutevin, B. Otazaghine, S. Caillol, J. P. Pascault and B. Boutevin, *React. Funct. Polym.*, 2013, **73**, 588–594.
- 155 A. F. Sousa, C. Vilela, A. C. Fonseca, M. Matos, C. S. R. Freire, G. J. M. Gruter, J. F. J. Coelho and A. J. D. Silvestre, *Polym. Chem.*, 2015, **6**, 5961–5983.
- 156 A. F. Sousa and A. J. D. Silvestre, *Curr. Opin. Green Sustain. Chem.*, 2022, **33**, 100557.
- 157 M. Brodin, M. Vallejos, M. T. Opedal, M. C. Area and G. Chinga-Carrasco, *J. Cleaner Prod.*, 2017, **162**, 646–664.
- 158 I. Capellán-Pérez, I. Arto, J. M. Polanco-Martínez, M. González-Eguino and M. B. Neumann, *Energy Environ. Sci.*, 2016, **9**, 2482–2496.
- 159 R. Datta and M. Henry, *J. Chem. Technol. Biotechnol.*, 2006, **81**, 1119–1129.
- 160 NatureWorks, Ingeo, <https://www.natureworkslc.com/>, (accessed 12 April 2022).
- 161 Corbion, PURAC®, <https://www.corbion.com/biochemicals/pharma/brands/purac>, (accessed 12 April 2022).
- 162 Futerro, Renew, <https://www.futerro.com/>, (accessed 12 April 2022).
- 163 J. Ahmed, J.-X. Zhang, Z. Song and S. K. Varshney, *J. Therm. Anal. Calorim.*, 2009, **95**, 957–964.
- 164 M. Drieskens, R. Peeters, J. Mullens, D. Franco, P. J. Lemstra and D. G. Hristova-Bogaerds, *J. Polym. Sci., Part B: Polym. Phys.*, 2009, **47**, 2247–2258.
- 165 A. R. Bagheri, C. Laforsch, A. Greiner and S. Agarwal, *Global Challenges*, 2017, **1**, 1700048.
- 166 G. Kale, R. Auras, S. P. Singh and R. Narayan, *Polym. Test.*, 2007, **26**, 1049–1061.
- 167 H. Song and S. Y. Lee, *Enzyme Microb. Technol.*, 2006, **39**, 352–361.
- 168 C. Delhomme, D. Weuster-Botz and F. E. Kühn, *Green Chem.*, 2009, **11**, 13–26.
- 169 Mitsubishi Chemical Corporation, BioPBS™, <https://www.mcpp-global.com/en/mcpp-europe/products/brand/biopbsTM/>, (accessed 12 April 2022).
- 170 J. Xu and B. H. Guo, *Biotechnol. J.*, 2010, **5**, 1149–1163.
- 171 M. Deroiné, I. Pillin, G. Le Maguer, M. Chauvel and Y. Grohens, *Polym. Test.*, 2019, **74**, 163–169.
- 172 H. Li, J. Chang, A. Cao and J. Wang, *Macromol. Biosci.*, 2005, **5**, 433–440.
- 173 J. H. Zhao, X. Q. Wang, J. Zeng, G. Yang, F. H. Shi and Q. Yan, *J. Appl. Polym. Sci.*, 2005, **97**, 2273–2278.
- 174 C. Tsutsumi, N. Hayase, K. Nakagawa, S. Tanaka and Y. Miyahara, *Macromol. Symp.*, 2003, **197**, 431–442.
- 175 C. Zhu, Z. Zhang, Q. Liu, Z. Wang and J. Jin, *J. Appl. Polym. Sci.*, 2003, **90**, 982–990.
- 176 J. H. Zhao, X. Q. Wang, J. Zeng, G. Yang, F. H. Shi and Q. Yan, *Polym. Degrad. Stab.*, 2005, **90**, 173–179.
- 177 K. Loos, R. Zhang, I. Pereira, B. Agostinho, H. Hu, D. Maniar, N. Sbirrazzuoli, A. J. D. Silvestre, N. Guigo and A. F. Sousa, *Front. Chem.*, 2020, **8**, 1–18.
- 178 S. K. Burgess, R. M. Kriegel and W. J. Koros, *Macromolecules*, 2015, **48**, 2184–2193.
- 179 S. K. Burgess, O. Karvan, J. R. Johnson, R. M. Kriegel and W. J. Koros, *Polymer*, 2014, **55**, 4748–4756.
- 180 S. K. Burgess, R. M. Kriegel and W. J. Koros, *Macromolecules*, 2015, **48**, 2184–2193.
- 181 X. Fei, X. Fei, X. Fei, J. Wang, J. Wang, J. Zhu, J. Zhu, X. Wang, X. Liu and X. Liu, *ACS Sustainable Chem. Eng.*, 2020, **8**, 8471–8485.

- 182 G. Gruter, *Technology & Markets Day Path to the Future*, [https://www.avantium.com/wp-content/uploads/2019/06/20190606-Technology-Day\\_CTO\\_Gert-Jan\\_Gruter\\_break-out\\_final\\_.pdf](https://www.avantium.com/wp-content/uploads/2019/06/20190606-Technology-Day_CTO_Gert-Jan_Gruter_break-out_final_.pdf), (accessed 29 November 2020).
- 183 Avantium, Avantium and Carlsberg sign offtake agreement on PEF, <https://www.avantium.com/press-releases/avantium-and-carlsberg-sign-offtake-agreement-on-pef/>, (accessed 13 July 2022).
- 184 R. J. I. Knoop, W. Vogelzang, J. Van Haveren and D. S. Van Es, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4191–4199.
- 185 L. Papadopoulos, A. Zamboulis, N. Kasmi, M. Wahbi, C. Nannou, D. A. Lambropoulou, M. Kostoglou, G. Z. Papageorgiou and D. N. Bikiaris, *Green Chem.*, 2021, **23**, 2507–2524.
- 186 J. G. Rosenboom, D. K. Hohl, P. Fleckenstein, G. Storti and M. Morbidelli, *Nat. Commun.*, 2018, **9**, 1–7.
- 187 J. C. Morales-Huerta, A. M. Ilduya and S. Muñoz-Guerra, *Polymer*, 2016, **87**, 148–158.
- 188 X. L. Qu, M. Jiang, B. Wang, J. Deng, R. Wang, Q. Zhang, G.-Y. Zhou and J. Tang, *ChemSusChem*, 2019, **12**, 4927–4935.
- 189 J. Wu, H. Xie, L. Wu, B. G. Li and P. Dubois, *RSC Adv.*, 2016, **6**, 101578–101586.
- 190 V. Haas, J. Wenger, L. Ranacher, N. Guigo, A. Sousa and T. Stern, *Sustain. Prod. Consum.*, 2022, **31**, 370–383.
- 191 E. de Jong, H. A. Visser, A. S. Dias, C. Harvey and G.-J. M. Gruter, *Polymers*, 2022, **14**, 943.
- 192 M. Matos, A. F. Sousa, A. C. Fonseca, C. S. R. Freire, J. F. J. Coelho and A. J. D. Silvestre, *Macromol. Chem. Phys.*, 2014, **215**, 2175–2184.
- 193 H. Wu, B. Wen, H. Zhou, J. Zhou, Z. Yu, L. Cui, T. Huang and F. Cao, *Polym. Degrad. Stab.*, 2015, **121**, 100–104.
- 194 H. Hu, J. Li, S. Luo, Y. Tian, J. Wang, Y. L. Zhao, R. Zhang and J. Zhu, *J. Hazard. Mater.*, 2022, **425**, 127752.
- 195 A. K. Moeller, K. Molawi and M. Yamamoto, US010189989B2, 2019, 2.
- 196 U. Witt, R. J. Müller and W. D. Deckwer, *J. Environ. Polym. Degrad.*, 1996, **4**, 9–20.
- 197 S. Peng, L. Wu, B. G. Li and P. Dubois, *Polym. Degrad. Stab.*, 2017, **146**, 223–228.
- 198 N. Jacquel, R. Saint-Loup, J. P. Pascault, A. Rousseau and F. Fenouillot, *Polymer*, 2015, **59**, 234–242.
- 199 H. Hu, R. Zhang, Z. Kong, K. Wang, W. B. Ying, J. Wang and J. Zhu, *Adv. Ind. Eng. Polym. Res.*, 2019, **2**, 167–177.
- 200 A. F. Sousa, J. F. J. Coelho and A. J. D. Silvestre, *Polymer*, 2016, **98**, 129–135.
- 201 Z. Jia, J. Wang, L. Sun, J. Zhu and X. Liu, *J. Appl. Polym. Sci.*, 2018, **135**, 1–11.
- 202 M. J. Soares, P. K. Dannecker, C. Vilela, J. Bastos, M. A. R. Meier and A. F. Sousa, *Eur. Polym. J.*, 2017, **90**, 301–311.
- 203 L. Filiciotto and G. Rothenberg, *ChemSusChem*, 2021, **14**, 56–72.
- 204 European Bioplastics e.V., EUBP proposes criteria and product examples for preferable use of compostable plastics, <https://www.european-bioplastics.org/eubp-proposes-criteria-and-product-examples-for-preferable-use-of-compostable-plastics/>, (accessed 18 April 2022).
- 205 Science Advice for Policy by European Academies, *Biodegradability of Plastics in the Open Environment*, 2020.
- 206 Environmental Protection Agency, *Household Waste Characterisation Campaign Final Report*, 2018.
- 207 CIC - Italian Composting and Biogas Association, *Annual Report on Biowaste Recycling November*, Rome, 2017.
- 208 F. D. Innocenti and T. Breton, *ACS Sustainable Chem. Eng.*, 2020, **8**, 9239–9249.
- 209 O. O. Ayeleru, S. Dlova, O. J. Akinribide, F. Ntuli, W. K. Kupolati, P. F. Marina, A. Blencowe and P. A. Olubambi, *Waste Manage.*, 2020, **110**, 24–42.
- 210 H. A. Leslie, *Review of Microplastics in Cosmetics – Scientific background on a potential source of plastic particulate marine litter to support decision-making*, 2014, vol. 476.
- 211 C. Guerranti, T. Martellini, G. Perra, C. Scopetani and A. Cincinelli, *Environ. Toxicol. Pharmacol.*, 2019, **68**, 75–79.
- 212 L. Anagnosti, A. Varvaressou, P. Pavlou, E. Protopapa and V. Carayanni, *Mar. Pollut. Bull.*, 2021, **162**, 111883.