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Environmental performance of bio-based and biodegradable plastics: the road ahead

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Future plastic materials will be very different from those that are used today. The increasing importance of sustainability promotes the development of bio-based and biodegradable polymers, sometimes misleadingly referred to as 'bioplastics'. Because both terms imply "green" sources and "clean" removal, this paper aims at critically discussing the sometimes-conflicting terminology as well as renewable sources with a special focus on the degradation of these polymers in natural environments. With regard to the former we review innovations in feedstock development (e.g. microalgae and food wastes). In terms of the latter, we highlight the effects that polymer structure, additives, and environmental variables have on plastic biodegradability. We argue that the 'biodegradable' end-product does not necessarily degrade once emitted to the environment because chemical additives used to make them fit for purpose will increase the longevity. In the future, this trend may continue as the plastics industry also is expected to be a major user of nanocomposites. Overall, there is a need to assess the performance of polymer innovations in terms of their biodegradability especially under realistic waste management and environmental conditions, to avoid the unwanted release of plastic degradation products in receiving environments.

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1 Introduction

It is probable that the plastic materials we will use in the future will be very different from those used today. The societal demand for more 'green' materials has induced innovations in the plastics industry to develop polymers derived from renewable biological resources ('bio-based') and polymers that are considered 'biodegradable'.^{1,2} The major areas for the development of biodegradable polymers are in packaging, disposable catering supplies, and agricultural films; whereas bio-based but non-biodegradable polymers could potentially be used for a wider range of applications where biodegradability is not a desired property. The idea behind producing bio-based materials is to use renewable carbon sources, such as starch, as a feedstock instead of non-renewable fossil sources. In contrast, the motivation for the development of biodegradable plastics is that they will easily disintegrate and biodegrade when (in)advertently emitted to the environment, irrespective of the carbon source they are produced from.

We recognise that plastics have brought many societal benefits. However, the problems associated with "conventional" plastic materials, such as the commodity polymers polyethylene (PE) and polystyrene (PS), from an environmental perspective come from the large volumes of plastic materials that are generated and from the fossil feedstock they consume (8% of the global crude oil and gas production is used to make synthetic polymers³). In addition, the short lifetime of most plastic products (in terms of actual use) results in the generation of waste that needs to be managed. A global analysis of the production, use, and end of life fate of all plastics ever produced came to the conclusion that synthetic polymers have outgrown most other man-made materials (besides steel and cement). Out of the 8300 million metric tons (Mt) plastics produced between 1905 and 2015, 2500 Mt are currently in use, 4900 Mt have been discarded (either in landfills or the natural environment), 800 Mt have been incinerated, and only 600 Mt have been recycled.⁴ As only 9% of the global plastics are recycled (not considering incineration as recycling), this review aims at revisiting the state of the science regarding the degradation of discarded plastics with a focus on the receiving natural environment.

Nowadays, the concept of a bio-based economy is gaining much societal, scientific, and economic momentum, and there is a considerable drive to develop strategies towards this goal. Among others, research and development increasingly focuses on waste and pollution prevention through the development of 'green materials'.⁵⁻⁷ With regards to synthetic polymers, such materials are often termed 'bioplastics'. In the public perception, 'bioplastics' are often regarded environmentally friendly as well as less persistent and toxic compared to conventional petrochemical polymers.^{2,8} This misconception comes from the inconsistent use to the terms with 'biopolymers' or 'bioplastics' which are often used interchangeably. As such, this ill-defined terminology has now come to represent a wide range of materials that are either bio-based (but not necessarily biodegradable), or petrochemical and bio-based plastics that are considered biodegradable.⁹⁻¹² To clarify, IUPAC only considers

bio-based polymers as 'bioplastics' and discourages the use of the term.¹³ Accordingly, we follow that recommendation and rather use the more specific terminology by ASTM (see Table 1).

As with conventional petrochemical polymers, bio-based and biodegradable polymers will also need chemical modifications (such as the addition of antioxidants to provide stability) to improve physical properties and make them a plastic material that is fit for purpose, potentially decreasing their biodegradability (Table 2).^{14,15} In addition, the intentional release of end-products into the environment (*e.g.* in the form of agricultural mulching films) implies that two conditions are fulfilled (i) full biodegradability and (ii) no ecotoxicological effects arise from any degradation products.¹⁶ Therefore, if bio-based and biodegradable plastics are to provide a viable alternative, their overall performance in terms of their environmental degradability needs to be demonstrated.

In this review, we explore some of the issues associated with bio-based and biodegradable plastics in terms of their environmental performance. For the sake of clarity, we will not focus in-depth on the important aspects of recycling and life cycle assessment, here the reader is directed to specialised reviews.^{3,17-20} In the next section, we discuss some of the often-overlapping terminology associated with different plastic materials from the perspective of their degradability. In the third section, we take a closer look at plastics from the following groups: non-biodegradable petrochemical and bio-based plastics, and biodegradable petrochemical and bio-based plastics. Finally, we provide an overview of emerging technologies relevant to plastics, and discuss factors affecting biodegradability and the potential environmental accumulation of degradation products.

2 Terminology: bioplastics, bio-based, (bio)degradable, and compostable

As discussed above, the term 'bioplastics' is an ill-defined umbrella term covering polymers from renewable feedstocks ('bio-based plastics') see Table 1 for definition and/or plastic types that (bio)degrade to different degrees under various conditions. This terminology is often used to describe plastics that are biodegradable, compostable, or degradable, even though the degradation pathways of these plastics are very different. The interchangeable use of these terms often leads to consumer confusion.¹² Biodegradable plastics undergo biological degradation through the actions of microorganisms "by lowering of the molar masses of macromolecules that form the substances".¹³ This is not to be confused with 'ultimate biodegradation' which is "often used to indicate complete transformation of organic compounds to either fully oxidized or reduced simple molecules such as carbon dioxide/methane, nitrate/ammonium, and water".¹³ As such the term 'biodegradable plastic' can lend itself to visions of a product, such as a plastic shopping bag or package film material, that will breakdown quickly into compounds that microorganisms can easily mineralise. The term biodegradable, however, is often and misleadingly applied to plastics that are bio-based but not necessarily biodegradable, for instance

Table 1 Classifications and definitions applied to different polymeric materials

Polymer	A large molecule composed of repeating units (monomers) typically connected by covalent bonds
Plastic	“a material that contains as an essential ingredient one or more organic polymeric substances of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or processing into finished articles, can be shaped by flow” ^{22,24}
Bioplastic	A plastic that it is “derived from the biomass or issued from monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow”. ¹³ Note that IUPAC discourages the use of the term and proposes “biobased polymer”
Bio-based plastic	A plastic “containing organic carbon of renewable origin like agricultural, plant, animal, fungi, microorganisms, marine, or forestry materials living in a natural environment in equilibrium with the atmosphere” ^{22,5}
Degradable plastic	“a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification” ^{22,4}
Biodegradable plastic	“a degradable plastic in which the degradation results from the action of naturally-occurring micro-organisms such as bacteria, fungi, and algae” ^{22,4}
Compostable plastic	“a plastic that undergoes biological degradation during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues” ^{22,4}
Hydro-degradable plastic	“a degradable plastic in which the degradation results from hydrolysis”, ^{22,4} examples include cellulose, starch, and polyesters ^{22,6}
Oxidatively degradable plastic	“a degradable plastic in which the degradation results from oxidation” ^{22,4}
Oxo-degradable plastics	These plastics break down into small fragments over time thanks to special additives but are not considered biodegradable since they do not meet the degradation rate or the residual-free content specified in the ASTM D6400 standards ^{22,3}
Photodegradable plastic	“a degradable plastic in which the degradation results from the action of natural daylight” ^{22,4}

Table 2 Plastic materials are a mixture of the representative polymer(s) and additive compounds

Polymers	Examples of additive compounds and their function
Petrochemical based polymers	Plasticisers to make the material pliable
• Non-biodegradable	Flame retardants to reduce flammability
• Biodegradable	Cross-linking additives to links together polymer chains
Biological based polymers	Stabilisers (<i>e.g.</i> antioxidants and antimicrobial agents) to increases durability
• Non-biodegradable	
• Biodegradable	
Blends (mixtures of the above)	Surfactants that are used to modify surface properties
	Inorganic fillers (<i>e.g.</i> carbon black) to reinforce the material
	Nanomaterials for improved functionality
	Micro & nano-encapsulated healing agents for improved longevity

materials that have a similar molecular structure to petrochemical polymers but are made from renewable feedstock.¹³ This is very different from a material that is fully biodegradable, for example 100% bio-based polyethylene (bio-PE) and bio-based polyethylene terephthalate (bio-PET) are not biodegradable,

whereas 100% petrochemical based polybutylene adipate-*co*-terephthalate (PBAT) and polycaprolactone (PCL) are considered to be biodegradable.⁹ Therefore, the biodegradability of a plastic material depends on its chemical structure and not the carbon source of the polymer (Section 5.1).²¹

Plastic materials that are considered either degradable or compostable are not necessarily biodegradable under ambient environmental conditions (Table 1). The term ‘degradable’ if not used correctly can lead to confusion and claims that a plastic is completely biodegradable when it is only photodegradable or hydrodegradable. Photo- and hydro-degradable plastics will not readily undergo mineralisation, but through the action of sunlight and water will breakdown into small particles that are more easily dispersed.^{22,23} These processes led to the fragmentation of the plastic material resulting in the environmental dispersion of numerous plastic particles, so-called secondary microplastics. In comparison, composting is the aerobic microbial treatment of compostable materials under controlled conditions.²⁴ Some bio-based polymers are considered compostable, however they many require conditions only available in industrial-scale composting facilities.^{12,17,19} The compostability of a plastic material not only depends on the material’s properties (polymer type, crystallinity, and additives), but also on the operational conditions (*i.e.* temperature, pH, moisture, and microbial inoculum) of the processing plant.^{25,26} Temperatures in industrial composting facilities range between 50 and 60 °C, but need to

remain above 60 °C for one week to eliminate pathogenic microorganisms.²⁷ Therefore, a plastic labelled as compostable, in theory, will undergo biological decomposition within industrial composting sites, where adequate conditions are provided. In contrast, a compostable plastic will not necessarily undergo biological decomposition under ambient environmental temperatures or in a household composting pile, mainly because the temperatures are too low. Accordingly, a recent life cycle assessment of bio-based polymers indicates that while their composting has some benefits compared to landfilling, there are also negative impacts compared to recycling (*e.g.* global warming impact by increased methane production).¹⁷ Ultimately, as highlighted by Klemchuk²² the composting of suitable plastics is of interest where recycling is not a practical option as it would permit their combination with other biological materials for useful soil-improving materials.

Overall, it is recommended not to use the term bioplastic when describing materials that are biodegradable, bio-based, compostable, or degradable and the correct terminology is to be used and clearly defined. Vert *et al.*¹³ provide a more in-depth overview of terminology for bio-related polymers. In addition, the biodegradability of end-products will also depend on the amount and types of additives used in the manufacturing process (discussed further in Section 5.2). It is also important to keep in mind that many plastic products are required not to be biodegradable (see Section 4.4), but may still be bio-based as the drive towards a bio-based economy increases.

3 Plastic (bio)degradability and the environment

The (bio)degradability of a specific plastic material is affected by the polymer structure, the additives used in the production of the plastic material, and the exposure conditions (Box 1). Exposure conditions can broadly mean the environment, waste treatment processes such as composting, or laboratory studies that investigate a plastic's degradability or stability when exposed to stressors such as ultra-violet (UV) light, water, heat, microorganisms, or a combination of these. In this section, the (bio)degradability of selected petrochemical and bio-based

polymers is described with reference to the different studied exposure conditions.

3.1 Petrochemical plastics

3.1.1 Polyethylene (PE) as a non-biodegradable polymer.

PE consists of short repeating monomer units that have strong inter-chain hydrogen bonding making a highly hydrophobic polymer that limits enzyme susceptibility,²⁸ so that only the polymer surface with a limited number of free chain ends is available to microbial action.^{29,30} Even so, the biodegradability of PE has been studied extensively. Examples include the following:

- (i) a 10 year soil incubation (25 °C) study under controlled conditions using ¹⁴C-labelled low-density PE film samples (20 µm thick), where the degree of biodegradation was estimated by the yield of ¹⁴CO₂ and showed <0.5% CO₂ evolution for pre UV-irradiated samples and <0.2% CO₂ evolution for non-irradiated samples;³¹
- (ii) PE samples buried for an estimated 32 years under a garden soil in Japan that showed only partial degradation using Fourier transform infrared (FTIR) microscopy and differential scanning calorimetry (DSC) techniques;³²
- (iii) a 120 day laboratory soil burial study in which PE was incubated at 28 °C and showed minimal biodegradation;³³
- (iv) linear low-density PE (LLDPE) mulching films with pro-oxidants buried under field conditions for 8.5 years were recovered intact even though undergoing a continuous slow abiotic degradation in soil;³⁴
- (v) LLDPE mulching films (20 µm thick) with pro-oxidants that were degraded artificially and then buried in soil for 6 years and 10 months were gradually transformed into micro-fragments in the soil;³⁵
- (vi) PE samples buried in compost for 125 days were described as unchanged by Vieyra *et al.*;³⁶ and
- (vii) maximum weight loss of 1.5 mm thick samples was 1.5–2.5% and 0.5–0.8% for low density PE and high density PE, respectively, after 6 months immersed in the bay of Bengal, India.³⁷

Overall, the bio-fragmentation of PE is initiated through photo-degradation, and can be enhanced with biodegradable additives, photo-initiators, and through copolymerisation.^{35,38–42} Then a combination of abiotic and biotic degradation process

Box 1: Factors affecting plastic degradation

Environmental factors

- Abiotic factors include temperature, pH, moisture, sunlight intensity (UV radiation), humidity, salinity, and abrasion
- Biotic factors include the density and diversity of microbial populations in a particular environment

Polymer chemistry

- Molecular weight, crystallinity, cross-linking, polarity, the presence/absence of hydrolysable bonds, hydrophobicity, surface chemistry
- Processing issues, for example hydroperoxides or ketones formed during polymerisation and/or processing²³⁰

Additives

- Stabilisers such as antioxidants and antimicrobial agents act to prolong the life of plastics
- Pro-oxidants act to decompose plastics in shorter time frames
- Nanoclay may provide a more favourable environment for microbial activity
- Micro-encapsulated healing agent may act as stabilising agents

Other factors

- Breakdown products that cannot be integrated into normal metabolism or are toxic to microorganisms

eventually transforms PE into increasingly smaller fragments until non-visible particles are formed.^{22,35,43}

3.1.2 Polycaprolactone (PCL) as a biodegradable polymer. PCL is a petrochemical polymer that is considered biodegradable.^{9,15} It is a polyester consisting of methylene units and ester groups, has a low melting point of 60 °C, and can be degraded by bacteria and fungi.⁴⁴ PCL undergoes hydrolytic degradation due to the presence of hydrolytically labile aliphatic ester linkages; however, the rate of degradation is rather slow (3–4 years).⁴⁴ The soil type is an important factor affecting PCL degradation: Cesar *et al.*³³ showed that PCL degraded to a greater extent in clay soils than in sandy soils, owing to the great density of microbial communities associated with the former. However, when compared to solar exposed samples, buried samples degraded at a much slower rate.⁴⁵ Chen *et al.*⁴⁶ investigated the degradation of PCL microparticles (13.4 μm diameter) and film samples, and showed that although the specific surface area of the microparticles was larger than the film there were no differences in the degradation rate. González Petit *et al.*⁴⁷ studied the degradation process of a PCL/eggshell biocomposite (50/50 w/w) for 8 weeks using a bioreactor, and noted that soil pH, heat, and an aerobic environment accelerate the degradation process, while photo-controlled, anaerobic, and moisture-saturated environments delay degradation processes.

3.2 Biobased plastics

3.2.1 Polylactic acid (PLA) as a partly compostable polymer. PLA is a bio-based thermoplastic aliphatic polyester with similar properties to PS and PET and is produced by the polymerization of lactic acid.^{15,48} The choice of PLA for this section may seem controversial as it is commonly considered biodegradable. Yet, it hardly degrades in the terrestrial and aquatic environment and is compostable under very specific conditions. The PLA monomer is a chiral molecule and exhibits two isomeric forms, D-lactic acid and L-lactic acid. On the one hand, the L-isomer of PLA is considered to be biodegradable, but the microbial communities considered capable of doing this are not widely distributed in soil.⁴⁹ On the other hand, although the D-PLA is hydrolysable in water it is considered non-biodegradable.^{50–52} The biodegradability of PLA has been studied under soil burial, composting, and in aquatic conditions. Selected examples include the following:

- (i) Soil burial studies using L-PLA over a six week time period resulted in no weight loss;⁵³
- (ii) Under composting conditions rigid film samples (0.3 mm thickness) and reported the disintegration of the samples and the formation of acidic water-soluble degradation products after 70 days (temperature up to 59 °C);⁵⁴
- (iii) PLA food utensils lost 34% weight during composting and degraded to small fragments after 7 weeks exposure at 65 °C;⁵⁵
- (iv) PLA weight loss of 2.5% was observed in a simulated marine environment over 600 days;⁵⁶
- (v) In simulated home composting experiment PLA packaging material showed no visual evidence of microbial breakdown and <5% weight loss after 180 days;⁵⁷ and

- (vi) In our laboratory, we observed negligible weight loss of rigid PLA samples degraded in aquatic medium over 112 days under conditions of constant light at 30 °C.

The difference in degradation rates between soil and aqueous media compared to composting is due to the higher temperatures of composting exposures.⁵⁸ At these elevated temperatures PLA absorbs water and undergoes significant abiotic hydrolysis,^{58,59} whereas these processes are slow or negligible in soil and water.^{53,59} However, if the compost is to be utilised as an end-product the occurrence of fragmented PLA particles needs to be evaluated given the current concerns regarding the accumulation of microplastics in environmental systems.

Neat PLA is a very brittle material and without the addition of additives has less than 10% elongation at break. This means that PLA is potentially not suitable for applications that demand a high mechanical performance unless it is modified.¹⁸ The plasticization of PLA and its copolymerization to form blends and composites are potential modifications to improve PLA characteristics such as stiffness, permeability, crystallinity, and thermal stability.^{9,60} For instance, (i) the incorporation of a chain extender/branching agent improved the thermal stability of PLA compared to neat PLA;⁴⁸ (ii) blending with PBAT improved the flexibility and toughness;⁶¹ and (iii) the use of poly(ethylene glycol) (PEG), glucosemonoesters, and partial fatty acid esters improved flexibility and impact resistance.^{62,63} The hydrolysis of PLA through the backbone ester groups is considered slow and can under conditions of ambient moisture and temperature take several years. However, it is possible to accelerate the process by subjecting PLA to temperatures above 50 °C.⁶⁴ Even so, PLA is still considered to degrade slowly compared to organic waste in commercial facilities.⁶⁵ An interesting review of PLA chemistry and various blends and composites based on PLA is provided by Sangeetha *et al.*;⁶⁶ while Karamanlioglu *et al.*⁶⁷ reviews the stability and degradation of PLA in a range of differing environments.

3.2.2 Polyhydroxyalkanoates (PHAs) as biodegradable polymers. PHAs are polyesters produced by the bacterial fermentation of sugars and lipids and are synthesised by a very wide range of microorganisms. PHAs are accumulated intra-cellularly and function as carbon and energy reserves. Microorganisms capable of accumulating PHAs include the genera *Alcaligenes*, *Bacillus*, and *Pseudomonas*, for a detailed list the reader is encouraged to see Koller *et al.*⁶⁸ In addition, a recent study has demonstrated the PHA synthesis by marine purple bacteria.⁶⁹ PHA molecules extracted from bacterial cells have a sufficiently high molecular mass which exhibit characteristics similar to PE and polypropylene (PP).⁸ The majority of PHAs are primarily linear polyesters composed of 3-hydroxy fatty acid monomers.⁷⁰ In these PHAs the carboxyl group and the hydroxyl group of neighbouring monomers form an ester bond.⁷⁰ Neat PHA polymers are considered to be directly biodegradable and can be colonised by microorganisms in the environment.^{54,71} The major focus of PHA biodegradation research has been under conditions of soil burial using thin film samples. For example:

- (i) Kunioka *et al.*⁷² used polyhydroxybutyrate (PHB) film samples (0.07 mm thick) based on polyesters of 3-hydroxybutyrate,

- and reported that the rate of biodegradation was enhanced by the increasing content of 4-hydroxybutyrate;
- (ii) Mergaert *et al.*⁷³ using 2 mm thick PHB samples reported a maximum weight loss of 0.64% per day for samples incubated at 40 °C;
 - (iii) Wollnough *et al.*⁷⁴ using 0.1 mm thick films reported 50% weight loss in 50 days at temperatures of up to 30 °C;
 - (iv) The extent of PHA biodegradation in aquatic reservoirs was shown to depend on the water inorganic composition, water temperature, and PHA chemical structure;⁷⁵
 - (v) Studies have demonstrated the biodegradability of PHAs under conditions of soil burial is enhanced when samples have undergone pre-UV exposure;^{76,77} and
 - (vi) In soil experiments, the microbial communities on the surface of PHA polymers were found to differ from the microbial communities of the surround soil.⁷⁸
 - (vii) The daily mass loss of PHA films and pellets was 0.04–0.33% and 0.02–0.18%, respectively, in tropical Vietnamese soils and was influenced by polymer chemical composition, specimen shape, and microbial community.⁷⁹

The biodegradability of PHA depends on the ability of degrading bacteria to secrete specific extracellular PHA depolymerases.⁷² In addition, the physicochemical properties of the polymer also influence biodegradability as PHA copolymers degrade faster than homo-polymers.^{72,80} For example, PHB/polyhydroxyvalerate (PHV) copolymers degrade to a higher degree compared to PHB under aqueous conditions, because PHB has a more crystalline structure with a high melting point.⁸¹ A similar result was also observed in a 8 week sediment burial study conducted in a tropical mangrove ecosystem at Sungai Pinang.⁸⁰ Overall, the processing of PHAs is considered challenging because of the low temperatures required for their decomposition that limits thermal stability.²¹ Properties such as toughness and processability can be improved through the addition of plasticisers that allow processing at lower temperatures and therefore avoiding thermal degradation.^{60,82} There are now a number of specialist reviews that discuss PHA synthesis, applications and environmental biodegradation including Reddy *et al.*,⁸³ Philip *et al.*,⁸⁴ Keshavarz and Roy,⁸⁵ and Laycock *et al.*⁸⁶

3.2.3 Losing biodegradable properties through modifications.

Starch and polyisoprene (natural rubber; NR) are two examples of bio-based polymers that are considered biodegradable, but lose their biodegradable properties when chemically modified to make usable materials.

3.2.3.1 Starch polymers. Starch polymers from different bio-based resources such as corn, wheat, cassava, yam, and potato have been investigated for some time, especially for agricultural and food packaging applications.^{22,87–90} Starch polymers consist of glucose, amylose, and amylopectin, with corn starch generally consisting of 20–30% amylose and 70–80% amylopectin.⁸⁸ Starches from different sources have different properties but pure starch films are brittle, absorb moisture, and are difficult to process.^{91,92} Properties can be improved through the addition of compatible plasticisers, such as glycerol or ethylene glycol,^{92,93} and further improvements can be made with the addition cross-linking agents and coating the films with a water resistant polymer.^{50,88,93}

In addition, plasticised starch can also be blended with a range of other polymers, such as PE, PCL, poly(hydroxybutyrate-*co*-valerate) (PHBV), and PLA.^{50,92,94} Starch–PE blends are not actually considered biodegradable because their degradation process is based on the biotic fragmentation initiated by the microbial break-down of the starch component. This process reduces the physical integrity of material, but the molecular weight of the remaining PE is not reduced sufficiently for microbial communities to utilise it as a food source.²² Vieyra *et al.*³⁶ concluded that starch–PE blends with 40% starch was the ideal concentration for blending with PE for an end product without additives, but 12 years would be required for complete degradation under composting conditions. The future direction for starch-based polymers seems to be in improving their functionality through the development of starch–clay nanocomposites for packaging applications. Examples include the use of nano-TiO₂ to increase hydrophobicity and UV stability of starch–TiO₂ films,⁹⁵ and starch–nano-Ag films with antimicrobial qualities.⁹⁶

3.2.3.2 Polyisoprene polymers. NR is produced by over 2000 plant species predominantly in the *cis* configuration (*cis*-1,4-isoprene), only a few plant species are known to produce polyisoprene in the *trans* configuration.⁹⁷ NR is a highly unsaturated hydrocarbon with poor dimensional stability, whereas sulphur vulcanisation transforms NR into a strong cross-linked matrix.^{97,98} Compound recipes for NR generally contain fillers, sulphur, accelerators, zinc oxides, stearic acid, softeners or extenders,⁹⁹ that make hard wearing products that are relatively resistant to biodegradation. The biodegradability of NR has been studied extensively and mainly deals with the use of concentrated microbial cultures, with the aim of assessing a particular strain's ability to degrade rubber materials. *Actinomyces* are the main group of NR degrading microbes, with *Bacillus* sp. and strains of *Nocardia* also being capable of utilizing NR as a sole carbon source.^{100–102} One of the problems that limits the biodegradability of many rubber compounds is that they include zinc oxides and zinc salts, that must be removed before successful microbial devulcanisation and subsequent metabolism can be achieved.¹⁰³ Tsuchii *et al.*¹⁰⁴ observed strips of tread cut from truck tyres were degraded only slightly when used as a sole carbon source, but degradation of the tyre was accelerated by the addition of latex glove material and unvulcanised rubber which were readily utilised by the bacteria. Overall, the biodegradability of vulcanised NR is difficult because the interlinked polymer chains reduce water absorption and permeability, and the majority of studies have focused on the *cis* configuration. Rose and Steinbuechel⁹⁷ reported that intensive attempts to demonstrate the degradation of the *trans* configuration by known rubber degrading microorganisms all failed. Yikmis and Steinbuechel¹⁰⁵ and Chengalroyen and Dabbs¹⁰⁶ provide a detailed review of the microbial degradation of natural and synthetic rubber.

3.3 Section summary

To summarise, there is broad and growing literature dealing with the (bio)degradability of various polymer types under a diverse range of conditions. The aim of biodegradation can be

viewed as twofold: from an environmental scientist's point of view, biodegradability is an attractive material property for products that have a high risk of being emitted to the environment. From a waste management perspective, biodegradable polymers are advantageous when they are digested in a composting facility. Accordingly, some materials may be industrially compostable (e.g. PLA), which does not make them necessarily fit for degradation under environmental conditions. In this sense, we need to address the two aims using different degradation protocols and international standards, which do not exist for environmental degradation at the moment. Here, cooperate initiatives, such as the one's by Cedar Grove (cedar-grove.com/compostable/compostability-testing) and Vinçotte (www.okcompost.be) may lead the path.

With many researchers from various backgrounds studying the (bio)degradation potential of pure polymers, blends, composites, and end-products specialised literature reviews focusing on individual polymer types are needed to summarise the ever-growing body of information. In addition, there is a need to identify and differentiate the degradation pathways in different media. Specifically, industrially compostable polymers are not necessarily to be considered biodegradable under ambient environmental conditions, where temperature, moisture, and carbon availability, as well as the density and diversity of micro-organism will be very different.

4 Beyond biodegradation

Biodegradability is not the only variable to consider in the designing of plastic materials, and it may only come to be a principle one for single use materials (e.g. food packaging materials) and those that are designed to be intentionally released to the environment (e.g. agricultural films). Bio-based polymers are generally divided into three categories: (i) those derived through the modification of naturally occurring polymer (often agricultural resources), (ii) polymers obtained from

microbial production, and (iii) polymers from precursors synthesised from biological feedstocks (Box 2).^{107,108} Regarding the latter two categories polymer feedstock may be derived from a wide variety of innovative biological sources. These sources include CO₂ (direct incorporation in polycarbonates), terpenes and terpenoids from pine trees, lemon peel or mint (to make polycarbonates and thermoplastic elastomers), triglycerides from vegetable oils (for polyesters and self-healing elastomers), and plant-derived carbohydrates, including starch and sucrose to make PLA, PBS, and PEF and glucose directly converted to PHA by microbes.¹⁰⁹ Up to date information on bio-based polyesters is provided by Zia *et al.*¹¹⁰ For further in-depth information the reader is directed to Patel *et al.*,¹¹¹ Babu *et al.*,¹¹² Mohanty *et al.*,¹¹³ Isikgor and Becer,¹¹⁴ and Brodin *et al.*¹¹⁵ Rather the objective here is to present specific examples and to ultimately look beyond biodegradation.

4.1 Bio-based innovations

PLA in particular has previously been used to make Walkman casings, battery packaging, computer body parts,¹¹⁶ disposable cups, and in 3D printing; while PHA production is between pilot plant and commercial stage.^{117,118} One of the major hurdles inhibiting both PLA and PHA market penetration are its high production costs.^{85,119,120} Up to date accounts on the recent progress to lower PHA production costs and future developments are provided by Wang *et al.*¹²¹ and Możejko-Ciesielska and Kiewisz.¹²² In addition, the replacement of petrochemical PET with bio-based PET has been described with regard to its applications in fibres and drinks bottles.¹²³

Companies that have shown interest in manufacturing bio-based plastics include: (i) the Coca-Cola Company who introduced a 30% plant-based PET bottle in 2011, and have recently announced a 100% plant-based PET bottle;¹²⁴ (ii) the beer manufacturer Carlsberg showcased a prototype wood-fibre based bottle as part of a program for designing cradle-to-cradle packaging materials;¹²⁵ and (iii) in the late 2016 Tetra Pak announced the launch of a new packaging manufactured

Box 2: Petrochemical and biobased polymer sources and their classification, based on information given in Vieira *et al.*¹⁰⁸ and Reddy *et al.*⁹

Petrochemical sources – biodegradable examples

- Polycaprolactones (PCL), polyesteramides (PEA), polybutylene succinate (PBS), polybutylene adipate-*co*-terephthalate (PBAT), and polyvinyl alcohol (PVOH)

Petrochemical sources – non-biodegradable examples

- Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC)

Biobased sources – from agricultural resources

- Polysaccharides (e.g. starches)
- Cellulosics (e.g. wood, straw, pectins, chitosan)

Biobased sources – from microbial production

- Polyhydroxyalkanoates (PHA) including poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV)

Biobased sources – from chemically synthesized using monomers obtained from agro-resources

- Polylactic acid (PLA)
- Bio-PET
- Bio-PE

Biobased sources – future carbon sources

- Polymers derived from food wastes (e.g. citrus peels, whey, used coffee grounds)
- Polymers derived from microalgae (e.g. *Chlorella vulgaris*)
- Polymers derived from engineered yeasts (e.g. *Candida tropicalis*)

from a bio-based plastic film and cap in combination with cardboard.¹²⁶ Beverage containers are an interesting packaging material because they need to have excellent mechanical, barrier, and UV resistant properties. These properties are often achieved using multi-layered film materials to limit oxygen diffusion and increase shelf life. Innovations in the field of material science on the one hand are very positive, while on the other hand their biodegradability and/or recyclability will need to be suitably evaluated if cradle-to-cradle is to be achieved.

4.2 Development of future bio-based feedstocks

The extent to which new innovations compete with resources needed for food production (water, land, fertilisers *etc.*), issues related to the regular supply of feedstocks, and other environmental and societal effects is often unclear.³ For instance, plastic bottles made from bio-PET have a 21% lower global warming potential compared to petroleum-based PET but perform worse in terms ecotoxicity and ozone depletion.¹²⁷ This has led to the development of so-called third generation bio strategies (Table 3), in particularly the biofuels industry is developing feedstock from microalgae.¹²⁸ Microalgae are a fast-growing diverse group of single-celled organisms that grow in a wide range of freshwater and salt-water environments, and algae-derived chemicals can also be used for producing bio-based polyesters^{110,129} A number of species have been found to naturally contain high levels of oil and protein.¹²⁸ For example, the microalga *Chlorella vulgaris* and the cyanobacterium *Spirulina maxima* have protein contents of 51–58% and 60–71%, respectively, based on dry biomass.¹²⁸ However, Zeller *et al.*¹³⁰ showed that an algae based polymer made from 100% *Chlorella* is brittle, but when plasticised showed better structural properties that reduced the on-set of degradation. Other microalgae species with the potential for biotechnology innovations include the diatom *Phaeodactylum tricornutum*,¹³¹ the freshwater microalga *Neochloris oleabundans*, and the marine microalga *Nannochloropsis* sp.¹³² The two main approaches for using algae in plastic composites are as fillers and as reinforcing fibres.¹³³ The challenge of making plastics from algae is currently addressed by the EU-funded research project SPLASH

(Sustainable PoLymers from Algae Sugars and Hydrocarbons, www.eu-splash.eu). The aim of this project is to develop an “industrial platform that uses microalgae as a raw material for the sustainable production and recovery of hydrocarbons and exopolysaccharides from algae, as well as their further conversion into renewable polymers.”

Other innovations for bio-based polymers include the development of engineered yeast species and the use of food wastes to produce hydrocarbons for plastics production. Recent research has focused on the diploid yeast *Candida tropicalis* and its transformation of fatty acids into commercially viable omega-hydroxy fatty acids that have the potential for synthesising PE-like polymers.¹³⁴ Food wastes, specifically citrus oil, are also under investigation. Citrus peels are a source of D-limonene that is produced by more than 300 plants and in oranges it makes up ~95% of the peel. The process of combining limonene oxide with CO₂ to produce the polymer polylimonene carbonate is described by Byrne *et al.*¹³⁵ Further to this, researchers from the University of York (UK), the University of Sao Paulo (Brazil), and the University of Cordabo (Spain) have formed a partnership with the intention of making a prototype bio-refinery.¹³⁶ The technique uses high-powered microwaves that transform the orange peel waste into volatile gases that are then distilled into liquid.¹³⁷ The limonene can then be turned into an epoxide and combined with CO₂ through the use of zinc based catalyst to create a polymer structure.¹³⁵ The limonene-based polycarbonate can further be modified to produce several other polymers. According to Hauenstein *et al.*¹³⁸ it “is the perfect green platform polymer, from which many functional materials can be derived.” Besides these two examples legumes have also been noted as a potential feedstock for the production of lactic acid.⁶

Bio-based innovations for filler materials include other food waste products such as eggshells and used coffee grounds. Chicken eggshells have been investigated as a potential bio-filler for PP,¹³⁹ PCL,⁴⁷ and PE bio-composites.^{140,141} Whereas, used coffee grounds have been investigated as a potential bio-filler for PP,¹⁴² and PBAT,¹⁴³ as well as a feedstock for PHA production.^{144,145} Indeed, the use of used coffee grounds as a

Table 3 Biological strategies for the development of bioplastics

Feedstock generation	Issues
First generation: the first generation of bio strategies for the production of bioplastics, such as PLA, cellulose acetate, and thermoplastic starch, used natural feedstocks based on the carbohydrate biomass of crops such as starch and cellulose from corn. Another strategy was use natural proteins from soybean and sunflower crops ^{130,227}	These strategies have been criticised as they compete for resources with food production and use large amounts of irrigation water and fertilisers ^{2,68,71,130,228}
Second generation: this generation of bio strategies were developed based on non-edible waste materials (<i>e.g.</i> agricultural wastes) to avoid the issues associated with first-generation bio strategies ^{68,229}	This strategy can be problematic as the seasonal availability affects the quantities of feedstock materials required for them to compete conventional petrochemical feedstocks. ¹³⁰ For instance, surplus whey from dairy industries is available in large amounts in Europe and North America and considered a suitable feedstock for the production of PHAs. ⁶⁸ The production of PHAs from used coffee grounds has also been investigated ¹⁴⁴
Third generation: currently refers mainly to algae biomass that has a higher growth yield than first and second-generation feedstock	Industrial scale production will require large volumes of water and potentially fertilisers

bio-filler for PLA enhances the biodegradability of PLA compared to neat PLA during soil incubation.¹⁴⁶

4.3 Plastics and nanotechnologies

The next important development for the plastics industry is the utilisation of nanoscale materials that are the foundation for nanotechnology. Nanotechnologies are generally defined as the understanding and control of matter at dimensions between 1 and 100 nm. There are two main classes of products: nanomaterials (NMs) that are fixed to a substrate and free nanoparticles (NPs).¹⁴⁷ At the nanoscale, the physical and chemical properties of a material differ from the properties of the bulk matter counterpart. This creates the potential to exploit these new properties, for example (i) weight reduction through the use of nanofillers (nanoclay) and nanosilica, (ii) improved mechanical strength by including carbon nanotubes, and (iii) antimicrobial activity of plastic food packaging materials through nano-Ag. The plastic industry is considered to be a major area for the use of nanoscale materials, with an estimated 7% share of nanocomposites among plastics in the USA by 2020.¹⁴⁸ Food packaging materials are a principal application for the introduction of NMs because they have the potential to provide improved mechanical, barrier and antimicrobial properties, together with nano-sensors for tracing and monitoring the condition of food during transport and storage.^{149,150} The unique property of NPs is their very high surface to volume ratio. For example, in polymer-nanoclay composites each layered sheet of montmorillonite (MMT) nanoclay platelets has a thickness 1 nm, surface dimensions of 100 to 2000 nm, and a surface area of 750 m² g⁻¹.¹⁵¹ This means that it is possible for the entire polymer matrix of a nanoclay-composite to be in contact with the nano-component. In this case the nanoclay component provides a favourable environment for microorganisms that can utilise the polymer matrix as a food source and has been reported to promote microbial growth by stabilizing pH in the polymer matrix.¹⁵²

As the physical properties of the nanoparticles are considered superior to those of the polymer, the properties of the nanocomposite material will be influenced more by those of the NM. The question is what does the introduction of NMs mean for plastic biodegradability? Researchers have started to investigate the stability of various plastic nanocomposites under various conditions. In the case of nano-clay composites, the rate of photooxidative degradation in PE-MMT and PP-MMT was accelerated when compared to pure PE and PP, respectively.^{153,154} An enhanced compostability of PLA-MMT films has also been observed.¹⁵⁵ However, the opposite was found by Spiridon *et al.*¹⁵⁶ who studied the enzymatic degradation of nanoclay-starch-polyvinyl alcohol (PVOH) composite films and concluded that NPs hindered the biodegradation, and biodegradation rates depended on both NP type and content. In the case of inorganic nanocomposites, Tang *et al.*¹⁵⁷ studied the biodegradability of nano-SiO₂ reinforced starch-PVOH nanocomposite films with 5% nano-SiO₂ in a soil burial test at 25 °C for 120 days. Weight loss of the bulk sample was up to 60% and was similar for starch-PVOH with and without nano-SiO₂. This indicates that NPs had no significant influence on biodegradability of the film samples. However, Topolniak *et al.*¹⁵⁸ investigated ethylene vinyl alcohol

(EVOH) nanocomposites based on zeolite NPs and found that these accelerated the photochemical oxidation of EVOH, attributed to iron impurities in the zeolite particles. Nano-TiO₂ incorporated into PHB films has been shown to slow the degradation under conditions of sediment burial,⁸⁰ whereas PLA/TiO₂ nanocomposites subjected to hydrolytic degradation at 37 °C and pH 7.4 accelerated the degradation through a catalytic effect of the TiO₂ particles.¹⁵⁹ In addition, fullerene (C₆₀) positively influences the thermal stability of various polymers including poly(methyl methacrylate) and PS,¹⁶⁰ PP,¹⁶¹ and HDPE,^{162,163} by acting as a free radical scavenger suppressing chain scission. This all indicates that degradation processes will depend on the polymer type, the NM used, and the exposure conditions. Another important question is how the inclusion of engineered NM will affect the impact of the polymer on human and environmental health (see Bouwmeester *et al.*¹⁶⁴ for lessons learned from nanotoxicology). In the absence of empirical data, we can speculate that inclusion of NM in plastic products will have the following impacts: (i) the degradation behaviour of the plastic composite will be different compared to a non-composite polymer. This will change the release of plastic fragments in the environment. Whether more or less micro- and nanoplastics will be generated remains so far unclear. (ii) The composite polymer will release EN during and after use to a certain extent. This may result in an additional contamination of the packed good (*e.g.* foodstuff) or the environment. So far, the release and migration rates of NM from the polymer matrix are unknown and will depend on the specific formulation of the material. In addition, no toxicity data are available for polymer composite leachates. While it is currently impossible to evaluate potential health impacts of these new materials, health and environmental safety should be the key principles guiding the development of nano-enhanced polymers. The same is also true for self-healing polymers.

4.4 Self-healing plastics

The major innovation for the plastics industry where durability is a sought-after property is in what are termed 'self-healing plastics'. Conceptually, self-healing plastics have a built-in capacity to recover their structural function after damage in the form of cracks that would otherwise lead to mechanical breakdown compromising structural integrity.^{165,166} White *et al.*¹⁶⁶ developed a micro-encapsulated healing agent containing a catalyst that is embedded in the polymer matrix. As cracks form, the micro-capsule is ruptured and the healing agent is released into the crack plane where the catalyst triggers the polymerization that closes the crack.¹⁶⁶ Further innovations include the development of submicron and nano capsules with diameters of 220 nm seemingly achievable.¹⁶⁷ The idea is that reduced capsule size will increase the responsive self-healing properties, making micrometre cracks healable.^{167,168} Applications for polymers with self-healing properties are likely in transportation, sporting goods, civil engineering, and electronics.¹⁶⁵ In addition, advances in capsule size reduction will open up applications for self-healing thin films, coatings, and adhesives.¹⁶⁷ Recent reviews focusing on this area of innovation include Thakur and Kessler,¹⁶⁹

Wang *et al.*,¹⁷⁰ and Yang and Urban.¹⁷¹ A further direction for this area of research is its development towards use in bio-based non-biodegradable materials with a focus on, for example, PLA and vulcanised NR to prolong the use phase of such materials.

4.5 Section summary

The development of microalgae and food waste feedstocks is part of a wider drive for bio-based strategies promoting the development of bio-based polymers.^{132,172} However, such strategies requires a sound knowledge of sustainable biomass availability and bio-refinery technological improvements.^{10,173} Likewise, solutions are needed to integrate new bio-based polymers in existing recycling systems.¹⁷⁴ Importantly, ecological and societal implications are key aspects to be considered. For nanocomposites, a detailed understanding of degradation mechanisms and the extent to which NPs act to catalyse or retard degradation processes is needed. Overall, if new bio-based resources are to be used to produce materials that are intentionally released to the environment or recommended for composting, there is a need to ensure their biodegradability. In addition, there is a need to clarify the environmental effects of nanomaterials associated with bio-based nanocomposites. To achieve this, we need to understand the microbial processes involved and thoroughly analyse the degradation products to demonstrate the absence of toxic residues. In addition, design decisions must account for application-specific requirements and consider environmental impacts concurrently with material deterioration.¹⁷⁵ In the case of NMs used in the production of plastics that are to be labelled as biodegradable a structured investigation into how these materials affect biodegradation is needed. For applications, which require longevity research and development in self-healing plastics are a possible future direction.

5 Polymer composition and the environment

Bio-based and biodegradable plastic face many challenges because end-products could potentially be blends of biodegradable and non-biodegradable polymers.^{9,15} Moreover, polymers in their pure states are not generally usable as a commercially viable material, as such end-products are compounded with chemical additives to improve relevant properties and to expand their application range.^{15,176–178} In this section, the effects of polymer structure and chemical modifications on biodegradability are discussed alongside some of the ecotoxicological challenges compostable and biodegradable plastics in particular need to overcome. For a detailed discussion on how additives effect recyclability see La Mantia.¹⁷⁹

5.1 Polymer structure

Structural characteristics have an important impact on the potential for biodegradation to occur. The molecular features generally considered to facilitate biodegradation include ester linkages,^{180,181} oxygen atoms in the form of hydroxyl, aldehyde, or carboxylic acid groups, and ketones.⁵ The enzymatic

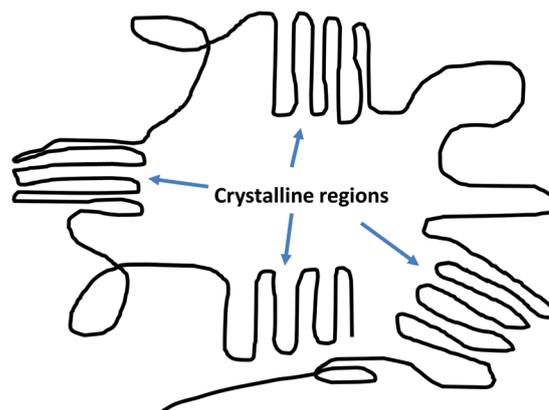


Fig. 1 Crystalline regions within a polymer matrix.

hydrolysis of ester groups is possible the most reported of these because esterase enzymes tend to have broad substrate specificity. In addition, most chemicals already containing an oxygen atom biodegrade more readily than chemicals that do not.⁵ The molecular composition of a plastic material will also affect the hydrophobicity of the outer surface, which in turn affects how easily microorganisms can attach themselves.¹⁸⁰ Molecular characteristics that generally increase resistance to biodegradation are the complexity of the polymer structure and use of structural features that are not easy to biodegrade. Here, crystallinity is an important property because the crystalline region consists of more ordered and tightly structured polymer chains. Crystallinity affects physical properties such as density and permeability (Fig. 1).¹⁸² This in turn affects their hydration and swelling behaviour, which affects accessibility of sorption sites. For example, Chen *et al.*⁴⁶ and Gorrasi and Pantani¹⁸³ showed that for PCL and PLA the degree of crystallinity increased with degradation time showing the preferential degradation in the amorphous region of the polymer. However, the degree of PHA crystallinity was shown not to change (*i.e.* the levels of degradation of both the amorphous and crystalline phases were almost the same) after 140 day submergence at a marine site in the South China Sea.¹⁸⁴ In addition, cross-linked polymers, such as vulcanised NR, have a more highly ordered structure that inhibits the accessibility to excreted enzymes (Section 3.2.3). Other examples include Kaczmarek and Bajer¹⁸⁵ who noted that the inefficient biodegradation of plasticised polyvinyl chloride (PVC) samples containing cellulose was the result of the polymer's partial cross-linking that impeded the accessibility by enzymes. Cinelli *et al.*¹⁸⁶ characterised the compostability of PVOH, starch, and lignocellulosic films with and without a cross-linking agent, and showed that for both neat PVOH and PVOH blends the cross-linking slowed degradation rate compared to uncross-linked samples. Finally, Awadhya *et al.*¹⁸⁷ showed that the cross-linking of agarose, a polysaccharide polymer material, with citric acid increased thermal stability, decreased water absorption, and slowed the degradation rate.

5.2 Chemical modifications

Plasticisers are generally liquids with high boiling points and are one of the most discussed performance enhancing polymer

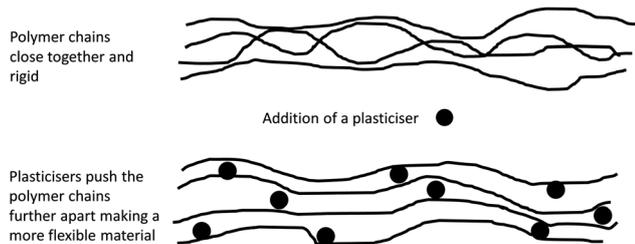


Fig. 2 Plasticisers within a polymer matrix.

modifications used to improve flexibility and processability. The low molecular weight of plasticizers makes them occupy the intermolecular spaces between polymer chains acting as molecular lubricants and affecting the organisation of the polymer chains (Fig. 2).⁸⁹ The compatibility between polymer and plasticizer depends molecular weight, chemical composition, and functional groups of a specific system. These properties will influence the plasticiser's migration in the surrounding compartment, *e.g.* environmental matrices or foodstuffs. This leaching in turn influence the extent to which a plasticiser enhances the properties and lifetime of a material.

Colourants are interesting additives and many plastics have their colour added during the manufacturing process to produce a homogeneously coloured melt that is then moulded into the finished product.^{177,188} Generally, colourants are either pigments or dyes, and can often influence the final thermal and UV stability of a plastic material.¹⁸⁹ A common colorant is titanium dioxide that has properties that can improve the impact strength and UV stability of a material. Indeed, nano-TiO₂ is used in sunscreen products to provide protection from UV light.^{190,191} Fillers are also acquiring increasing importance as reinforcing materials in composites because of their low cost and low density.¹⁴² Fillers, such as carbon black, and pigments are widely used to influence a plastics characteristics to suit a particular application.¹⁹² Here lignocellulosic fibres are of interest because they are bio-based. However, these materials are highly hydrophilic compared to most hydrophobic polymers resulting in a low compatibility, and the need for chemical compatibiliser agents.^{142,143}

Overall, additives are an important component of the chemical makeup of plastics with many modifications achieved through the incorporation of additives derived from petrochemical sources (Table 1). Other examples include stabilising systems that depend on the action of UV absorbers, excited-state quenchers, peroxide decomposers, free radical scavengers,^{192,193} antioxidants and antimicrobial agents that act to prolong the life of plastics.^{43,194,195} Additives such as pro-oxidants, often transition metal catalysts, act to decompose the plastic in shorter time frames.^{22,29,196} However, many additives intended to promote biodegradation are ineffective according to a study on PE and PET degradation under compost, anaerobic digestion, and soil burial conditions.¹⁹⁷ In addition, such novel additives may compromise the recyclability of polymers and pose a challenge to the recycling sector. Accordingly, Design of Recycling principles need to cover not only the polymers but also the additives from a systemic perspective.¹⁹⁸

If additives, such as the ones mentioned above, can also be based on renewable resources a plastic material from 100% bio-based compounds could be feasible,¹⁵ and for biodegradable polymers the additives should preferably also be biodegradable.¹⁹⁹ In addition, additives should preferably be non-volatile, non-toxic, and exhibits minimal leaching or migration during ageing.⁶⁰ Review articles focusing on plasticiser modifications for bio-based and biodegradable plastics include Vieira *et al.*,¹⁰⁸ Altenhofen da Silva *et al.*,²⁰⁰ and Mekonnen *et al.*²¹

5.3 Environmental considerations

Biodegradability is a desired property for many single use plastic materials that are difficult or uneconomical to recycle. However, designing plastics to be biodegradable is not easy as modifications such as blends, composites, and the use of additives to maximise functionality and to expand the range of application may render an otherwise biodegradable polymer into one that is not. Therefore, the biodegradability of end-products claiming to be biodegradable need to be rigorously tested. This can be determined according to specific guidelines, such as those published by the American Society of Testing and Materials (ASTM) and the International Standards Organisations (ISO). Examples include ASTM D5988-12²⁰¹ and ISO 17088²⁰² for aerobic biodegradation in soil (*i.e.* biodegradability), and ASTM D6400-12²⁰³ under composting conditions. In theory, a biodegradable plastic must undergo biological degradation when exposed to real environmental conditions.

The limitations of ASTM D5988-12²⁰¹ and ISO 17088²⁰² for biodegradable plastics intended for agricultural use have recently been point out by Brodhagen *et al.*²⁰⁴ The authors note that testing standards are intended for optimal laboratory conditions that do not account of the diverse soil and weather conditions encountered in field situations that may slow biodegradation rates. An example can be found in a field study that investigated the biodegradability of commercially available agricultural films labelled as biodegradable and compostable. The films were first pre-used during a growing season and then buried under field conditions for 6 months and displayed minimal degradation.²⁰⁵ Therefore, any given plastic material's biodegradation is tied to a specific environment and the time that it spends in that environment. For example, soil type is an important factor because clay soil will support a greater density of microbial communities than sandy soils,³³ whereas in ocean environments biodegradation is considered minimal because of the low temperatures and reduced density of microbial communities.²⁰⁶ In addition, recent studies have demonstrated that earthworms and collembolan species facilitated the transportation of plastic particles from the soil surface down through the soil profile, highlighting potential exposure to other soil biota.^{207,208}

The results of laboratory biodegradation tests will depend on the specifications of the plastic material under investigation, and the dynamics of the microbial populations used that are in-turn influenced by the test conditions as well as the inoculate source. Such laboratory experiments do not simulate realistic exposure conditions or mimic the complex microbial

communities that influence a material's biodegradability.²⁰⁹ Inoculates sourced from different wastewater treatment plants can also give different results as far as biodegradability, because of differences in inoculum quality that can vary according to place and season of sampling.²¹⁰

The environmental safety of degradation products formed from the breakdown of plastics thought to be biodegradable has been highlighted previously.^{22,211} There is now a great deal of interest in the environmental effects of microscopic plastic fragments,^{43,212–216} and the toxicity of leachates from weathered plastics.^{217–220} This literature indicates that the fate of microscopic plastic fragments, as well as other chemical degradation products, and their long-term impact to the environment has not been established yet. In addition, there are now many reviews that focus on the use and biodegradation of agricultural plastic films.^{22,204,221–223} A topic of particular concern is that many biodegradable plastics used in agriculture are only biodegradable, hydrodegradable, photodegradable, or only partially biodegradable,^{204,222} and there is a lack of knowledge regarding the ecological consequences of degradation products. Indeed, a full assessment of their persistence, bioaccumulation, and toxicity is needed to avoid the unwanted accumulation of plastic derived chemicals in receiving environments.

5.4 Section summary

Overall, properties such as biodegradability and compostability depend on chemical structure rather than the carbon source. Like their traditional counterparts these polymers will be compounded with additives to improve the functional properties of the finished product and to expand the range of application. However, because different manufacturers will add different additives at various concentrations, materials made from the same polymer should not be considered chemically identical. This puts an increasing emphasis on proving the biodegradability, compostability, or preferably recyclability of end-products rather than solely relying on data relating to the pure polymer. Compostable plastics used for products such as disposable kitchen-ware require clearer labelling for consumers to indicate whether the material is suitable for home composting or not.

6 Conclusion

The aim of this work was to explore some of the issues associated with bio-based and biodegradable plastics in terms of their environmental performance. The long-term stability of plastics is an important property for many applications that conflicts with a desired and "safe" breakdown in the environment. The use of bio-based or biodegradable plastics promoting the latter is often justified by claims that they biodegrade faster than their conventional petrochemical counterparts. However, the biodegradability of a particular plastic material depends on its chemical structure, the types and amounts of additive compounds used in their formulation, and not the carbon source of the polymer. Additives such as stabilisers, anti-oxidants, and anti-microbial agents will act to

improve the material's durability, and extend the environmental residence times. Accordingly, while the polymer that the plastic material is based on may be biodegradable, the plastic material itself may actually degrade only slowly. In addition, the degradation of end-products under realistic conditions in receiving environments remains largely unknown.

In the future, new polymer types and additives will enter the production cycle due to technological innovations. The challenge will be for society to decide what it wants from these new materials: will the emphasis be on biobased or biodegradable plastics, or will the preferred direction depend on the application? From a sustainability perspective, biobased polymers are preferably as-long-as the societal and environmental impacts of feedstock production are minimised. From a waste management perspective, biodegradable polymers should only be used in applications in which an emission to the environment is unavoidable not to promote littering. Finally, when plastics are developed that are both biobased and biodegradable, the issue of potentially toxic degradation products needs to be properly addressed.

Conflicts of interest

There are no conflicts to declare.

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