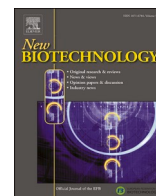




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Review Article

Renewable polymers and plastics: Performance beyond the green

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ABSTRACT

Renewable bio-based polymers are one of the effective answers that the bioeconomy offers to solve the environmental emergency connected to plastics and more specifically fossil-based plastics. Previous studies have shown that more than 70 % of the natural capital cost associated with plastic derives from the extraction and processing of fossil raw materials and that the price of fossil plastic would be on average 44 % higher if such impact was fully paid by businesses. The disclosure of the hidden costs of plastics will contribute to dispelling the myth of the expensiveness of renewable polymers. Nevertheless, the adoption of bio-based plastics in the market must be motivated by their functional properties and not merely by their green credentials. This article highlights some successful examples of synergies between chemistry and biotechnology in achieving a new generation of bio-based monomers and polymers. Their success is justified by the combination of scientific advances with positive environmental and social fallouts.

Introduction: Sustainable and performing plastics, the future is now

The use of renewable feedstock and biomass for production of plastics is not a new subject in the chemistry scenario. During the 19th and 20th centuries, manufacturing industry benefitted from a wide array of bio-based materials obtained by processing cellulose [1], plant oil [2] and proteins [3]. Some of them, such as CellophaneTM, polyamide-11, and ViscoseTM, successfully resisted the take-off of the petrochemical industry, thanks to their competitiveness in terms of technological properties and economic viability. When not designed for short-term applications such as packaging, plastics are expected to substitute for wood, glass and other heavy materials, while displaying good mechanical and thermal properties, stability and durability. The huge advantage that boosted the surge of fossil-based plastics resides in the broad variety of monomers available from petrochemistry, which can be combined through various chemical routes to obtain architectures that meet

specific technological demands and functional performances.

In the last decade, the bioeconomy, through a new synergy between biotechnologies and the bio-based chemical industry, has delivered polymeric products based on renewable feedstock. Bio-based polymers represent an important part of the bioeconomy and in 2019 the total production volume of bio-based polymers reached 3.8 Mt (million tonnes), corresponding to 1% of the production volume of petrochemical polymers, without including natural rubber and cellulosic fibres [4]. The increasing interest in bio-based plastics is motivated primarily by the fact that they may contribute to a more efficient use of natural resources, which is a pre-requisite for the development of a more sustainable and resilient economy. Nowadays, this extremely active field of research and innovation is mature for delivery of new polymeric products and solutions, which are competitive in terms of performance beyond being sustainable. Both these claims must be justified through technical data, certifications and standards that make the value of bio-based plastics evident while providing transparent information on

Abbreviations: CEN, European Committee for Standardization; DFF, 2,5-diformylfuran; EG, ethylene glycol; FDCA, 2,5-furandicarboxylic acid; FFCA, 5-formyl-2-furancarboxylic acid; GHG, greenhouse gases; HMF, 5-hydroxymethyl-furfural; HMFCFA, 5-hydroxymethyl-2-furancarboxylic acid; IA, itaconic acid; Mt, million tonnes; PBAT, poly(1,4-butylene adipate-co-1,4-butylene terephthalate); PBS, poly(1,4-butylene succinate); PE, polyethylene; PEF, poly(ethylene fuanoate); PET, poly(ethylene terephthalate); PHA, poly(hydroxyalkanoates); PIA, poly(itaconic acid); PLA, poly(L-lactide); PP, polypropylene; PTT, poly(trimethylene terephthalate); PVC, polyvinyl chloride; TA, terephthalic acid; UNEP, United Nations Environment Programme.

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their environmental benefits.

Tackling plastic impact calls for systemic solutions

The global production of plastics reached ~360 Mt in 2018 [5]. Plastic is responsible for around 10 % of generated total waste and comprises 60–90 % of marine litter, mostly through food and beverage packaging, cigarette butts and bags. According to the United Nations Environment Programme (UNEP), 8 Mt of plastic are poured into the oceans each year, an equivalent to a full truckload every minute [6][7]. Marine species and humans are being harmed since the plastic waste enters the human food chain through fish consumption [8], while the rapid spread of microplastics has made this problem even more alarming [9]. Because it is not effective to remove plastic waste and microplastics once they have entered the sea, plastic pollution needs to be tackled at its source [10].

Collecting and recycling plastics represents an answer to the problem and a study by the Ellen MacArthur Foundation showed that “replacing just 20 % of single-use plastic packagings with reusable alternatives offers opportunities for economic development worth at least \$10B” [11]. Notably, in Europe, 32.5 % of the 29.1 Mt of waste plastics collected in 2018 was recycled, while 24.9 % ended up in landfills and the rest was incinerated [5]. However, it must be underlined that plastics made from fossil fuels account for about 20 % of the total fossil oil consumption [11], causing considerable greenhouse gases (GHG) emissions. Analyses indicate that if plastic continues to be produced from fossil carbon sources, it will be responsible for 15 % of the maximum annual global carbon budget needed to limit global warming to 2 °C in 2050 [12]. Therefore, in a long-term perspective, it is necessary to boost a transition to plastics obtained from non-fossil feedstock.

The hidden natural capital cost of fossil-based plastics in numbers

A clear understanding of the environmental degradation and resource depletion connected to plastics must rely on a quantitative and transparent accounting of their impact on natural capital. The term “natural capital” [13] describes “Earth’s natural assets, including soil, air, water, and living things, existing as complex ecosystems, as well as the related ecosystem services that human societies need in order to survive and thrive”. Economic activities depend on these resources and services; however, the latter are often not factored into corporate accounting, and national accounts currently do not take their contribution fully into consideration. Establishing a sound method for natural capital accounting, with a strong focus on ecosystems and their services, is a key objective of the EU Environment Action Programme and of the EU Biodiversity Strategy to 2020 [13]. Through natural capital accounting, it becomes possible to highlight the economic values of natural capital, establishing the monetary value of goods and services provided by ecosystems.

In 2014, UNEP published a study focused on the evaluation of the natural capital costs of plastics, namely the environmental and social impacts caused by the use of plastic expressed in monetary terms to reflect the scale of the damage caused [6]. The study converted physical quantities of plastic into monetary values, using environmental or natural capital valuation techniques [14]. These estimate the value of environmental goods or services in the absence of a market price and aggregate them into a single figure. As an example, by calculating the amount of GHG caused by plastics production it is possible to ascribe a monetary value to each tonne of GHG in relation to its impact on climate change. Similarly, plastic waste incineration is associated with air pollution, which can be expressed in monetary terms, thus reflecting the scale of damage caused. On this basis, the UNEP study estimated that the total natural capital cost of the plastic used in the consumer goods industry is over \$75B per year. Such an approach translates physical impacts into a monetary figure, which expresses the potential value that

companies would have to internalise if they were held accountable for their impacts.

Fig. 1 shows the total capital cost for some of the most relevant industrial sectors contributing to the plastic problem. The calculated costs arise from the accounting of the tonnage of plastic used in the selected key consumer goods sector (based on its expenditure), which gave the plastic intensity, namely the tonnes per \$1 M revenue. The natural capital cost for a certain sector is the natural capital intensity multiplied by the aggregate revenues and expresses “the dependency of a certain sector on the natural capital” [6]. The plastic intensity in each sector reflects different contributions of the three main categories of plastic usage: i) plastic used in products; ii) plastic used as packaging; iii) plastic used by suppliers (such as bags containing fertilizer used by farmers supplying the food sector). It must be noted that, for the plastic used by suppliers, the natural capital costs were not calculated, even though the corresponding volumes were determined in order to put the first two categories into perspective [6]. This methodological approach made it evident that, for the food, soft drinks, retail and personal products sectors, the whole contribution comes from the packaging. When considering that most types of plastic are petroleum-based products, one significant outcome of the UNEP analysis is that, across all sectors, over 75 % of the known and quantifiable impacts associated with plastic usage are located in the upstream portion of the supply chain, as shown in Fig. 1. ‘Upstream’ refers to “impacts generated from the extraction of raw materials to the manufacturing of plastic feedstock”, whereas ‘downstream’ refers to “impacts generated once the consumer has discarded the product” [6]. The approach applied to the UNEP analysis faced some limitations, as discussed by the authors [6], as downstream impacts and plastic waste littering of the oceans are likely to be underestimated due to the absence of robust scientific data.

The environmental impacts associated with plastic use were calculated using lifecycle analysis techniques (LCA), using official databases as the US Toxic Release Inventory [15] and Plastics Europe eco-profiles [16]. The impact of additives leachate from plastics was also accounted, since there is a growing concern for their impacts on human health and the environment [17,18]. Additives are added to plastic during their manufacture to improve their mechanical and thermal properties and

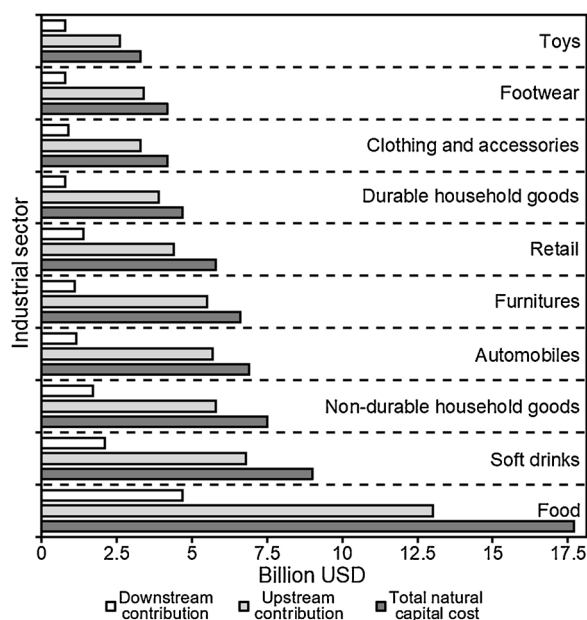


Fig. 1. Contribution to the natural capital cost of plastics from selected industrial sectors per year. Data taken from reference [6].

the study calculated the amount of additives per type of plastic based on a report of the Organisation for Economic Co-operation and Development (OECD) [19]. According to the same report, the annual leaching rate of additives is 0.16 % per year, which means that it would take 625 years for 100 % of the additives to be released from the plastics. Overall, the disclosure of the natural capital costs of plastics highlighted “the urgent need for businesses to measure, manage and disclose information on their annual use and disposal of plastic, as many companies already do with carbon emissions” [6].

Definitions and standards for sustainable plastics

When analysing the potential and limitations of plastics produced from renewable feedstock, it is crucial to start from some definitions. Acknowledging the need for common standards for bioplastics, the EC issued a mandate to CEN (European Committee for Standardization) [20] for the Development of European Standards for Bio-Polymers and Bio-Lubricants in Relation to Bio-Based Product Aspects, which resulted in a series of technical specifications and standards covering products and sectors. The resulting CEN document EN 17228:2019 [21] discusses the main aspects of bio-based polymers and plastics, referring to the corresponding fundamental standards developed on these topics. It states that the terms “biopolymers” and “bioplastics” are commonly used to identify polymers and plastics that are either bio-based, biodegradable, or feature both properties. This definition is also reported by European Bioplastics, the association representing the interests of the bioplastics industry in Europe [22]. While these definitions are quite widespread and used by industry, it is recognized that they are susceptible to misunderstanding and thus inappropriate for standardization purposes. When associated with plastics, the prefix “bio” can be perceived by consumers as an indication of biodegradability or of full natural origin. However, polymers and plastics derived from biomass can be either biodegradable or non-biodegradable whereas there are different fossil-based plastics that are biodegradable according to the relevant standards (e.g. polycaprolactone). On the other hand, the market also offers plastics made from bio-based materials which are highly resistant to biodegradation due to the chemical nature of their structure, such as polyethylene (PE) derived from biomass. To avoid misleading information and confusion across the supply chain and especially for the final consumers, the CEN document EN 17228:2019 [21] recommends that, when referring to the origin of the feedstock, the terms bio-based polymer/plastics/plastics product must be used instead of biopolymer/bioplastics/bioplastics product. The European standard EN 16575:2014 [23] specifies that the term “bio-based” means “derived from biomass” and that bio-based products (e.g. bottles, chemical intermediates, materials, etc.) are products which are wholly or partly derived from biomass. Conversely, it is important to characterize the amount of renewable carbon contained in the product by following the recognized methodologies specified in the relevant EN documents [24–26].

In order to provide more complete information on the environmental impact and sustainability of bio-based products, the European Standard EN 16760:2015 [27] specifies LCA criteria. Moreover, EN 16751:2016 [28] reports sustainability criteria by addressing environmental, social and economic aspects and EN 16848:2016 [29] reports a template for the transfer of information, including recovery and disposal options of bio-based products, across the industrial chain.

Concerning the end-of-life of plastics and their biodegradability, Table 1 reports a schematic overview of the relevant standards and definitions as published by European Bioplastics [22]. Since biodegradation does not depend on the resource basis of a material, the misuse of bio-based plastics might lead to downstream environmental impacts [30], which must be prevented through adequate and clear labelling. In that respect, EN 16935:2017 [31] specifies the requirements for transparent and non-misleading business-to-consumer communication of characteristics of bio-based products by means of labelling and claims

Table 1

Definitions regarding the concepts of bio-based polymers and biodegradability. Rearranged from [22].

Bio-based (material or product)	Fully or partly derived from biomass (plants). Bio-based carbon content is the variable describing the amount of bio-based carbon (in relation to fossil-based carbon) contained in a material or product and is measured via the ^{14}C method [24–26].
Biodegradation	Chemical process during which microorganisms available in the environment convert materials into natural substances such as water, CO_2 , and compost (artificial additives are not needed to accelerate degradation). This process depends on the surrounding environmental conditions (e.g. location or temperature), on the material and on the application.
Biodegradable plastic	Bio-based or oil-based plastics that meet standards for biodegradability and compostability. If a material or product is advertised to be biodegradable, further information about the timeframe, the level of biodegradation, and the required surrounding conditions should be provided and a timeframe for biodegradation must be set in order to make claims measurable and comparable. This is regulated in the applicable standards.
Compostable plastic	Bioplastic that has proven its compostability according to international standards and can be treated in industrial composting plants (see details above). Plastic products can provide proof of their compostability by successfully meeting the harmonised European standards (ISO 17088, EN 13432 / 14995 or ASTM 6400 or 6868), a certification, and an according label (seedling label via Vinçotte or DIN CERTCO, OK compost label via Vinçotte).
Degradable or oxo-degradable plastics	Plastics to which additives have been added to enhance the degradation, but do not meet biodegradability and compostability standards. Oxo-biodegradable plastic do not fulfil the requirements of EN 13432 on industrial compostability, and are therefore not allowed to carry the seedling label.
Bio-based, non-biodegradable technical/performance polymers	Polymers such as bio-based polyamides (PA), polyesters (e.g. PTT, PBT), polyurethanes (PUR) and polyepoxides used in technical applications like textile fibers (seat covers, carpets) or automotive applications (foams for seating, casings, cables, hoses), etc. Their operating life lasts several years (durable plastics) and, therefore, biodegradability is not desired.
Bio-based, biodegradable plastics	Include starch blends made of thermo-plastically modified starch and other biodegradable polymers as well as polyesters such as polylactic acid (PLA) or polyhydroxyalkanoates (PHAs). Unlike cellulose, materials such as regenerate-cellulose or cellulose-acetate have been available on an industrial scale only for the past few years and primarily used for short-lived products. Yet this large innovative area of the plastics industry continues to grow due to the introduction of new bio-based monomers and polymers (see Tables 2–5).
Fossil-based, biodegradable plastics	Biodegradable plastics currently still made in petrochemical production processes. Mainly used in combination with starch or other bioplastics because the latter improve the biodegradability and mechanical properties. Partially bio-based versions of these materials are already being developed.

[32–34], which orient the consumer towards a correct management of the plastic waste or appropriate recycling streams.

Because biodegradation occurs at different rates in soil and in water, there is the necessity for standards which define clearly how a plastic waste must be managed in different environments. The European standard EN 13432 “Requirements for packaging recoverable through composting and biodegradation” [35] entails “at least 90 % disintegration after twelve weeks, 90 % biodegradation (CO₂ evolution) in six months, and includes tests on eco-toxicity and heavy metal content”. This is the standard for biodegradable packaging designed for treatment in industrial composting facilities and anaerobic digestion. Another standard, the ASTM D 6691 [36], offers a test method to assess biodegradation in water.

Can renewable polymers mitigate the "plastic problem"?

Bio-based polymers are widely different in terms of chemical structure and biological origin [37]. The EN 17228:2019 document distinguishes a first group of polymers synthesized by living organisms such as plants, algae (Table 2) [38–45] or microorganisms (natural or engineered) (Table 3). After extraction and purification their initial chemical structure is used as such (e.g. polyhydroxyalkanoate [46], polymalic acid [47], poly- γ -glutamic acid [48,49].) or slightly modified to obtain specific functionalities (e.g. cellulose acetates) [40]. The second group consists of materials where the chemical structure of the biomass feedstock is not maintained. For example, starch or cellulose can be hydrolysed to monomeric sugars, which are then fermented to produce monomers for the polymerization (Table 4). That is the case of lactic acid to produce poly(lactic acid) [50–52] or diacids and polyols to synthesize polyesters [53–68]. It is also possible to use low molecular weight biomass feedstock, for which the conversion of ricinoleic acid from castor oil in bio-based polyamides is the most relevant example [69–71]. All these polymers are bio-based, because the original feedstock comes from biomass, but they are non-natural polymers, i.e. they are not extracted from a plant or a bacterium.

When taking into account both the origin of the polymer (i.e. biomass or fossil feedstock) and their biodegradability, we can broadly recognize the following groups:

- 1 “fully or partly bio-based plastics that are not biodegradable, such as bio-based PE [72], polypropylene (PP) [73] and poly(ethylene terephthalate) (PET) [54–56] and bio-based technical performance polymers such as poly(trimethylene terephthalate) (PTT) [53] or thermoplastic polyester elastomers (TPC-ET)”;
- 2 “plastics that are both bio-based (partly or fully) and biodegradable, such as poly(L-lactide) (PLA) [50], poly(hydroxyalkanoates) (PHA) [46] or poly(1,4-butylene succinate) (PBS)” [57–59];
- 3 “plastics that are based on fossil resources and are biodegradable, such as poly(1,4-butylene adipate-co-1,4-butylene terephthalate) (PBAT)” [67].

Some of these are well-established commercial products, such as PLA [50], while other polymers have been developed only on demonstration scale but are already considered promising innovative replacements for some fossil-based plastics massively employed in multiple sectors and applications. For instance, polyesters deriving from bio-based 2,5-furandicarboxylic acid (FDCA) [65,66] display properties comparable to PET [52]. Many other bio-based polymers have found practical industrial applications because of their technological properties, such as the light weight of poly(methyl methacrylate) that, combined with resistance, makes this polymer of interest for the automotive sector [74,75]. The ethylene propylene diene monomer is used to produce chlorine-free alternatives to synthetic rubber in technical clothing [76], whereas applications of bio-based polyurethanes encompass paints and powder coatings as well as medical devices and biodegradable scaffolds for tissue regeneration [77–79]. Poly(furfuryl alcohol) [80] is used in the

Table 2

Naturally biosynthesized biopolymers and their chemically modified derivatives.

Chemical classification	Polymer	Properties and applications	Ref.
Polysaccharides	Polyisoprene (terpenes)	Waterproof items, engineering applications in antiseismic buildings or offshore installations for oil extraction, Component of biodegradable and biocompostable plastics. Applications in textiles, cigarette filters, surface coatings, ink additive, photographic negatives, motion picture film, microfilm, microfiche, membranes for water desalinization. Chemical modifications decrease the biodegradation of cellulose although derivatives are attacked by both aerobic and anaerobic microorganisms. Obtained from deacetylation of chitin. Biodegradable, non-toxic, bacteriostatic and fungistatic with wide application in the pharmaceutical field. Industrially applied as carrier for enzyme immobilization. Because of its aromatic and phenolic components, lignin itself is used in polymer blends as compatibilizer, plasticizer, hydrophobizing agent or as a natural antioxidant in active packaging. Employed in flame retardants, optical modifiers, stabilizers. Lignin-based polyols, reacted with diisocyanates, are used as drop-in replacement of fossil polyols in polyurethane foams for their flame-retardant properties.	[38]
	Starch based polymers; thermoplastic starch -TS		[39]
	Cellulose based polymers: Cellulose acetate Cellulose nitrate Acetylphthalylcellulose		[40,41]
Polyphenols	Chitosan		[42]
	Lignin based polymers		[43–45]

Table 3

Bio-engineered polymers bio-synthesized by microorganisms and plants.

Chemical classification	Polymer	Properties and applications	Ref.
Polyesters	Polyhydroxy alkanoates - PHAs: poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate -co-3-hydroxy-hexanoate)	Biodegradable and compostable. Chain length determines the flexibility of PHA: short chain butyrate provides rigidity, with T_m of 160 °C, whereas longer carbon chains confers T_m below 145 °C. Sensitivity to thermal degradation makes its processing challenging. Fields of application include agriculture, packaging, biomedical sector.	[46]
	Polymalic acid	Linear anionic polyester composed of L-malic acid monomers, with potential applications as drug carriers, surgical suture, and biodegradable plastics. Water-soluble, anionic, biodegradable, edible. Applications in foods, pharmaceuticals, healthcare, cosmetics, water treatment, curable adhesives.	[47]
Polyamides	Poly- γ -glutamic acid - PGA		[48, 49]

fabrication of nanoporous carbon structures for molecular sieve adsorbents and as a component for electrochemical and electronic devices, while different bio-based polymers, such as acrylonitrile butadiene styrene (ABS), are of interest for their flame-retardant properties [81, 82]. New super-adsorbent bio-based materials have been produced through the polycondensation of unsaturated monomers as acrylic [83, 84] and itaconic acids [85] and their biodegradability has been controlled by tuning the crosslinking of chains.

Bio-based polymers, referred to as 'drop-in' polymers, are made from renewable resources, but their chemical and physical properties remain identical to their fossil counterparts. This is the case for the commodity bio-based PE [72], PP [73] and PVC (polyvinyl chloride) [86] made from bio-ethanol. Drop-in polymers contribute to the reduction of the carbon footprint of plastics and can also enter the established recycling streams.

There is a debate around the environmental superiority of these polymers and on their potential impacts on biodiversity loss, water consumption and fertiliser use. Most lifecycle analyses show that bio-based plastics are better than their oil-based equivalents in aspects such as GHG emissions and fossil fuel consumption [86], but not automatically for other impacts, such as eutrophication [87]. In addition, like biofuels, some bio-based plastics require land for their production, which raises concerns over the competition with food cultivation [88]. Previous studies on the impact of biofuels showed that 92 % of all global arable land is used for food and animal feed production, 6% for industrial materials and 2% for biofuels [89]. Concerning bio-based plastics [90], recent analyses indicate that 5 Mt biomass are needed for the worldwide production of 3.6 Mt of bio-based polymers [4], corresponding to the exploitation of roughly 0.02 % of global agricultural areas [91]. According to European Bioplastics [91], the use of renewable resources is the key for increasing resource efficiency by the means of: "i) resources being cultivated on (at least) annual basis; ii) full valorisation of biomass according to a cascade use; iii) reduction of the carbon footprint and greenhouse emissions; iv) saving and substituting fossil resources step by step". Nowadays, economic viability and

Table 4

Bio-based synthetic polymers obtained from bio-based monomers or a combination of bio- and fossil-based monomers.

Polymer	Properties and applications	Ref.
Poly(L-lactide) -PLLA	Polyester. Thermoplastic. Processable by extrusion, injection molding, blow molding. Degradable by hydrolysis rather than microbial attack. Industrially compostable. Crystallinity can be controlled by co-polymerization of selected ratios of L- to D-stereoisomers of lactic acid or lactide. Mechanical, thermal and barrier properties justify applications in food packaging. Used for medical applications and drug delivery because of its biocompatibility.	[50–52]
Poly(trimethylene terephthalate) -PTT*	Polyester. Same properties as fossil-based PTT. Scarcely biodegradable. Semi crystalline thermoplastic, easily molded or thermoformed and spun into fibres. Good tensile and flexural strength, excellent flow and surface finish. Used in textiles and engineering applications (automotive parts, mobile phone housings).	[53]
Poly(ethylene terephthalate) -PET*	Polyester. Same properties as the fossil-based PET. High-performance plastic used for engineering applications, fibres, films, bottles.	[54–56]
Poly(1,4-butylene succinate) -PBS	Polyester. Biodegradable in soil and biocompostable. Its T_m of 115 °C and tensile strength of 30–35 MPa make PBS suitable for applications in packaging as an alternative to polyolefins.	[57–59]
Poly(ethylene succinate) -PES	Moderately biodegradable. Good oxygen barrier and elongation properties. Used for film applications.	[60,61]
Poly(ethylene furanoate) -PEF	Polyester. Durable, good oxygen barrier. T_m of 211 °C and T_g of 86 °C. Suitable for packaging, in the food and beverage industry.	[62,63]
Poly(trimethylene furanoate) -PTF	Polyester. Not biodegradable. T_m of 172 °C, T_g of 57 °C, good oxygen barrier properties. Employed in light weighting packaging.	[64]
Poly(butylene furanoate) -PBF	Polyester. T_m of 172 °C, T_g of 44 °C. Potential replacer of PET and PBT.	[65,66]
Poly(1,4-butylene adipate-co-1,4-butylene terephthalate) -PBAT	Polyester. Biodegradable. Used in blends with PLA and fibers due to low thermo-mechanical properties. Obtained from fossil feedstock or biotereftalic acid	[67]
Unsaturated polyester resins -UPR	Properties varies according the percentage of unsaturated diacid (e.g. itaconic acid) and the curing procedure. Applied in waterborne UV-curable coatings for wood and flooring industry.	[68]
Polyamides containing four carbons - 4C PAs: 4, 4.6 and 4.10	Not biodegradable. 4C PAs match properties of fossil-based PAs 6 and 6.6, such as thermal durability and mechanical strength, with a T_m above 250 °C. All 4C PAs have higher dielectric strength and higher retention of tensile properties as compared to PA 6.6. PA 4.10 has low moisture uptake. Applications range from water management to cable coating, food contact products and automotive.	[69,70]
Polyamides with longer chains. PAs: 6.10; 10.10; 11 and 12	Long chain carbon monomers confer flexibility to these polymers, which find application in fuel lines in cars, offshore pipelines, gas distribution piping systems, electronics, sports	[71]

(continued on next page)

Table 4 (continued)

Polymer	Properties and applications	Ref.
Polyethylene – PE* (from bio-ethanol)	equipment, furniture and automobile components. Polyolefin. Same properties of fossil-based PE. Not biodegradable, recyclable through dedicated infrastructures. Thermoplastic. High Density PE (more crystalline) finds applications in construction sector. Low Density Polyethylene is used in packaging. Ultrahigh Molecular Weight Polyethylene has applications in medical devices and bulletproof vests.	[72]
Polypropylene - PP*	Polyolefin. Same properties as the fossil PP. Not biodegradable, non-polar. Partially crystalline thermoplastic with low density. Used in a large variety of applications and in packaging.	[73]
Poly(methyl methacrylate)–PMMA	Not biodegradable. Lightweight material used as glass replacement in automotive for shatterproof and UV resistant properties.	[74,75]
Ethylene propylene diene monomer – EPDM (synthetic rubber)	Not biodegradable. Good resistance to hot water and polar solvents but poorly resistant to aromatic and aliphatic hydrocarbons. Chlorine-free synthetic rubber used for technical clothing, elastomers with shock absorption. Ozone and thermal resistant. Electrical insulation properties. Used also for automotive applications.	[76]
Polyurethanes -PURs	Produced through the reaction of a diisocyanate with a polyol. Microbial degradation depends on the chemical structure. Often blended with polyethers to increase flexibility or extensibility. Used as de-halogenated flame retardant foams, paints, powder coatings, medical devices (blood contacting applications). Biodegradable polyurethane scaffolds have been used in tissue regeneration.	[77–79]
Poly(furfuryl alcohol) - PFA	Not biodegradable. Synthesized from bio-based furfuryl alcohol (FA) deriving from sugars. Used in the fabrication of nanoporous carbons structures for molecular sieve adsorbents, membranes and as a component for electrochemical and electronic devices.	[80]
Acrylonitrile butadiene styrene - ABS	Obtained from butadiene rubber dispersed in a matrix of styrene-acrylonitrile copolymer. Not biodegradable. Thermoplastic, used to make light, rigid, moulded products such as pipes, automotive parts. Used also for its flame retardant properties.	[81,82]
Polyacrylic superabsorbent polymers - PA-SA	Its high swelling capacity is tuneable by controlling the degree of crosslinking. Its biodegradation in soil can be improved under conditions that maximize solubilisation. Find applications in personal disposable hygiene products, such as diapers and sanitary napkins.	[83,84]
Poly(itaconic acid) - PIA	Due to the presence of a vinyl moiety, itaconic acid is structurally similar to acrylic and methacrylic acid, providing a suitable bio-based alternative to poly(meth)acrylates via radical polymerization to yield poly(itaconic acid) (PIA). Applications include fibers, coatings, adhesives, thickeners, binders. As co-monomer	[85]

Table 4 (continued)

Polymer	Properties and applications	Ref.
Polyvinyl chloride – PVC*	itaconic acid gives glass-ionomer dental cement. Not biodegradable and poorly chemically degradable. Same properties as fossil-based PVC. Used in construction profile applications, bottles and non-food packaging. When made more flexible by the addition of plasticizers, it is used in electrical cable insulation, imitation leather, flooring and as rubber replacer.	[86]

environmental sustainability are boosting innovation towards second generation plastics, namely produced from agricultural by-products or residues, which do not compete with the food chain [92]. Nevertheless, the ultimate drivers for the adoption of bio-based plastics reside in their functionalities and performance.

Chemistry and biotechnology alliance towards new engineering applications of bio-based polymers

Designing and synthesizing novel polymers endowed with unprecedented properties requires a portfolio of both chemical and biotechnological tools. In many cases, the highly optimized chemical routes developed in the last century for the production of the known plastics are inadequate to tackle the new challenges because the bio-based products stem from structurally different chemical platforms. The ubiquitous presence of oxygen in lignocellulosic biomass and sugars has been considered a major drawback for the development of bio-based substitutes of the seven fundamental chemicals at the basis of the petrochemical industry, namely ethylene, propylene, butadiene (olefins), benzene, toluene, xylenes (aromatics) and methane [93]. Bio-based monomers can be chemically modified to create further chemical variety and complexity, conferring specific functional properties to the final polymeric product (Table 5). Furthermore, research in metabolic engineering has enabled the production of new bio-based monomers with tailored chemical structures at industrial scale, as for 1,4-butanediol [94].

In the case of PHAs, these linear biodegradable and biocompatible polyesters are bio-synthesized by many bacteria and archaea [92] from limited medium components, with properties tuneable by means of metabolic engineering that alter monomer composition and molecular weights [95]. Currently, PHAs with desired thermal and mechanical properties are already applied in packaging, agricultural, and medical sectors (Table 3). Moreover, the structures of the enzymes falling under the class of PHA synthases have been solved, enabling the elucidation of the polymerization mechanism and paving the way for the use of non-natural substrates [96]. Although there are still some bottlenecks for the large scale production of PHAs connected to the high costs of production, in 2019 the global estimated market of PHAs was calculated at \$57 M [97], boosted by the successful use of biorefinery and agricultural by-products and industrial wastes as fermentation feedstock that contribute to mitigate the costs [98,99]. As government regulations against single use plastics become more and more stringent, the increasing demand for biodegradable plastics is expected to boost the PHAs market up to \$98 M by 2024 [97].

New synergies between chemistry and biotechnology enable the full exploitation of the chemical complexity of biogenic feedstock, since renewable monomers are obtained through chemical transformation of natural substrates or modification of bio-based monomers produced by fermentation [100]. New monomers have been designed and developed either biotechnologically [101,102] or chemically [103–107] or by a combination of the two approaches [108–111], with the aim of

Table 5

New bio-based monomers and chemical strategies for expanding the engineering applications of bio-based polymers.

Building blocks and monomers	Structural evolution	Targeted performance	Ref.
Aromatic lignin derivatives	2,4-, 2,5-, and 2,6-pyridinedicarboxylic acid obtained by re-routing the lignin degradation pathways of <i>Rhodococcus jostii</i> RHA1	New bio-based aromatic / aliphatic polyesters obtainable via enzymatic polycondensation with Mn around 14000 Da	[101, 102]
Ricinoleic acid	Confers biocidal activity to poly(hexamethylene succinate) modified at the chain ends. Imidazolium salt was anchored on C = C bond of ricinoleic acid to improve biocidal activity.	Antimicrobial activity.	[103]
Terpenes	Pinene transformed into pinocavone, which contains a reactive exo-methylene group exploitable for radical polymerization	High molecular weight polyterpenes with excellent thermal properties (T _g > 160 °C). Polymerization of pinene would require low temperatures (−70 °C) unviable for industrial purposes. Moderation of rigidity. Increased MW. Improved mechanical properties without decreasing T _m .	[104]
Amides	Branched chains of polyamide 4. ((4,40-diyl- α -truxillic acid dimethyl ester) 4,40-diacetamido- α -truxillamide), obtained from bio-based 4-aminophenylalanine, UV coupled with cinnamic acid	High-performance biobased polyamide with T _g > 250 °C	[105]
Isosorbide	Confers rigidity	Increasing thermos and mechanical properties while preserving the biodegradability.	[106]
Modified lactides for improved PLAs	Phenyl-substituted lactide synthesized by cyclic dimerization of bio-based mandelic acid to obtain mandelide (meso stereoisomer), which is polymerized via ring opening polymerization (ROP) Norbornene-substituted lactide obtained by brominating the bio-based lactide. Elimination and Diels Alder reactions yield the norbornene lactide used in ring-opening metathesis polymerization.	Overcoming low T _g and low transparency of PLA by inserting hydrophobic bulky side chains. Polymandelide has T _g > 100 °C and is less biodegradable than PLLA.	[107]
Cyclic diols	Bio-based 1,4-cyclohexanedimethanol (CHDM) is obtainable from renewable terephthalic acid.	Polymers have T _g > 190 °C and narrow polydispersity.	[108]
Phenols	4-hydroxycinnamic acid (4HCA)	As co-monomer in polyesters of 2,5-furandicarboxylic acid-increases rigidity, confers mechanical properties comparable to PET and improves barrier properties. Its polycondensation requires temperature around 240–280 °C due to the high boiling point but such temperatures promote its decomposition. Mild enzymatic polycondensation overcomes this drawback. The aromatic ring confers liquid crystalline properties to polyesters. The bio-based liquid crystal polymers exhibits remarkable properties (strength = 63 MPa, Young's modulus = 16 GPa, maximum softening temperature = 169 °C [[109]
Succinic acid derivatives	Polyesters obtained by co-polymerization of succinic acid with furan dicarboxylic acid (FDCA)	Modifying soft properties of linear poly(succinates)s by introducing aromatic furan moieties. The corresponding polyesters poly(butylene succinate-co-butylene furandicarboxylate)s (PBSF) have Mw from 39 000 to 89 000 g/mol and display excellent thermal stability. Their structure and properties can be tuned ranging from crystalline polymers with good tensile modulus (360–1800 MPa) and strength (20–35 MPa) to nearly amorphous polymer of low T _g and high elongation (~600%), so that they may find applications in thermoplastics as well as elastomers or impact modifiers.	[110]
Furan derivatives	Nucleophilic aromatic substitution polymerization of 2,5- bis(4-fluorobenzoyl)furan (BFBF) derived from FDCA and potassium salts of aromatic bisphenols	Bio-based poly(thioether ketone) (PEEK) with T _m > 300 °C, comparable to fossil-based PEEK	[111, 112]
Itaconic acid derivatives	Functionalization of the unsaturated double bond of dimethylitaconate by thia-Michael addition reaction using 1-octanethiol. Post-polymerization modification of vinyl group of poly(itaconate) via Michael addition of primary amines. Michael additions of proline, cysteine and other S-containing nucleophiles to vinyl moiety of poly(itaconate)s. Michael addition of C-nucleophiles (acetylacetone and dimethyl malonate) to vinyl moiety of poly(itaconate)s.	Improve the stability of itaconic derivative monomers toward common conditions of polycondensation (high temperatures and metal-based catalysts) Amine-triggered degradable materials; oligoesters displaying amine functionalities for biomolecules anchoring or covalent crosslinking. Addition of pendants to polyester chain. Modifying polymer properties.	[113]
			[114]
			[115]
			[116, 117]
			[118, 119]
			[120]

expanding the structure and function of bio-based polymers (Table 5). Particular attention has been paid to aromatic building blocks [112–115] and, in general, to structures conferring rigidity and improved thermal and mechanical properties over polyesters. In other cases, the objective was to insert reactive chemical functionalities into the polymer chains to enable post-polymerization modifications, as with polyesters of itaconic acid (IA) [116–120]. IA is produced via fermentation of *Aspergillus terreus* [121] with a production level of 80 g L^{−1} and a worldwide industrial annual production of 80,000 tons/year and a price of about \$2 /kg [122,123]. Standard batch fermentations of *A. terreus* reported in the literature indicate a maximum volumetric productivity of 0.6 g L^{−1} h^{−1} after 100 h and an IA yield of 0.35 g per g glucose [124]. Notably, chemical synthesis by thermal decarboxylation of citric acid proved to be economically unviable, although known since 1837 [121].

IA presents two carboxylic groups and a double bond so that it can undergo both radical polymerization and also polycondensation. Its

structural similarity to acrylic and methacrylic acid makes IA a suitable bio-based alternative to these fossil-based monomers (Table 4). The synthesis of poly(itaconic acid) (PIA) is feasible, by reacting its vinyl moiety via radical polymerization of neutralized IA with quantitative yields and molar mass from 1–20 kg/mol [124]. PIAs find uses as components of cleansing agents and shampoos, or as material for drug delivery applications. Alkylated IA derivatives are polymerized to yield polymers applied as plastics, adhesives, elastomers and coatings. Some IA copolymers with acrylic acid and other unsaturated monomers find application as synthetic fibres, coatings, thickeners, binders and glass-ionomer dental cement that contains a copolymer of IA with acrylic acid. IA in concentrations of 1–5 % is utilized as a co-monomer of rubber-like resins and for the synthesis of bio-based epoxy resins. On the other hand, polyesters of IA do not yet have industrial application, because the conventional operational conditions required for chemical polycondensation (T > 150 °C) lead very easily to the cross-reactivity of the vinyl moiety (Ordel's saturation, isomerization of the C=C bond and

cross-linking) [117,120]. The radical reactions can be avoided using inhibitors whereas the prevention of Ordelt saturation appears more challenging, although mild enzymatic polycondensations [126,127] have been reported to yield pre-polymers bearing intact vinyl moieties available for post polymerization modifications (Table 5) [117,128].

The new wave of bio-based aromatic polyesters: PEF and other furan-based polymers

Poly(ethylene 2,5-furanoate), frequently abbreviated as PEF, is an aromatic polyester that can be produced by polycondensation of 2,5-furandicarboxylic acid (FDCA) and ethylene glycol (EG) (Fig. 2, A), two monomers that can be easily produced from biomass [100]. PEF has been known since the 1950s, but has gained renewed attention only recently as a potential alternative to the fossil-based PET, and in 2004 the US Department of Energy included FDCA on a list of potential substitutes for terephthalic acid (TA) [129]. Nowadays the glycol component (EG) of PET is bio-based and various technologies have been reported for the exploitation of renewable feedstock to produce bio-based TA, also starting from furfural and FDCA [130,131]. Nevertheless, PEF has the potential to become a 100 % bio-based alternative to PET, hence contributing to the replacement of the 15 Mt of PET bottles produced worldwide, which cause 440–520 PJ of NREU and 20–35 Mt of CO₂ equivalents of GHG emissions [132].

When compared with PET, FDCA-based polyesters are not only more

sustainable but also exhibit improved gas barrier properties for O₂ (10x higher) [133], CO₂ (6–19x more) [134] and water vapour (2–5x higher) [135], making them promising candidates for packaging applications such as bottles, films and food trays. PEF offers also high mechanical strength (T_g of PEF=86 °C vs T_g of PET=74 °C; T_m of PEF=235 °C vs T_m of PET = 265 °C) [136,137], suitable for applications including textiles, carpets, electronic materials and automotive parts.

Finally, in the context of a circular economy and closure of the carbon cycle, PEF has another major advantage compared to PET: its enzymatic degradability [138]. A cutinase from *Humicola insolens* was used to fully hydrolyse PEF thin films into water soluble monomers and oligomers in 72 h [139]. Indeed, when analysing the properties of PET and PEF having the same degree of crystallinity, PEF is found to be more susceptible to hydrolytic enzymatic attack and its degradability is less affected by the increase of crystallinity as compared to PET [140].

Despite all the positive environmental features and physico-chemical performance of PEF, the transition from the well-established petrol-based PET to the biomass-derived PEF appears to be less smooth than researchers would like to be. Both the conversion of biomass to FDCA and its polymerization to PEF are still challenging, although recent investigations at laboratory scale tackled these problems and achieved excellent results. A group at Ruhr University Bochum has developed a new, low-cost nickel boride-based catalyst for the conversion of 5-hydroxymethyl-furfural (HMF) to FDCA while an enzyme toolbox was developed for the synthesis of 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFA), 5-formyl-2-furancarboxylic acid (FFCA) and FDCA with good yields from HMF via selective oxidation [141]. Such a catalyst contains no rare or precious metals, and is economically affordable and readily available for the production of FDCA with yields >98 % in 30 min with negligible side products [142].

Coming to the synthesis of PEF, conventional polycondensation remains a challenge since the time-intensive reaction leads to degradation and undesirable discolouration of the reaction products. This can be easily avoided by switching from traditional chemo-catalysis to a milder, more environmentally friendly biocatalytic approach, which, however, has severe limitations due to cost and scalability of the enzymatic reaction [143,144]. These bottlenecks were overcome by synthesizing bottle-grade PEF ($M_n > 30$ kg/mol, conversion >95 %, colour-free products) via ring-opening polymerisation from cyclic PEF oligomers. The reaction led to the desired molecular masses within a few minutes without accumulation of by-products derived from FDCA degradation [145].

Novel bio-based aromatic alternatives

The industrial production of FDCA and PEF motivated the scientific community to intensify research aiming at novel bio-based aromatic polymers. Initially the studies focused attention on the substitution of the diol component of PEF (EG) with glycols and diamines having longer chain length (C₃–C₁₂) (Fig. 2A). Synthetic strategies based on traditional chemo-catalysis but also enzymatic synthesis led to polymers with various crystallization and thermal degradation behaviours [146,147]. Other strategies included the introduction of rigidity into the polymeric chain by using cyclic co-monomers such as 1,4-cyclohexanedimethanol [148], or by replacing conventional FDCA with 3,4-FDCA and 2,4-FDCA (Fig. 2B). Other studies assessed the effects of the different isomers on the final properties of polyesters [149] and explored the possible improvement of the gas barrier properties of the material by substituting FDCA with its thiophene counterpart, the 2,5-thiophenedicarboxylic acid [150].

More recently, pyridine-derived monomers were used to replace the furan ring. The 2,4-pyridinedicarboxylic and the 2,5-pyridinedicarboxylic acids (Fig. 2D) derive from lignin by rerouting the *Rhodococcus jostii* (RHA1) β -keto-adipate pathway used for the aromatic lignin breakdown [101]. A third pyridine derivative, 2,6-pyridinedicarboxylic acid, which comprises 5–15 % of the dry weight of some bacterial

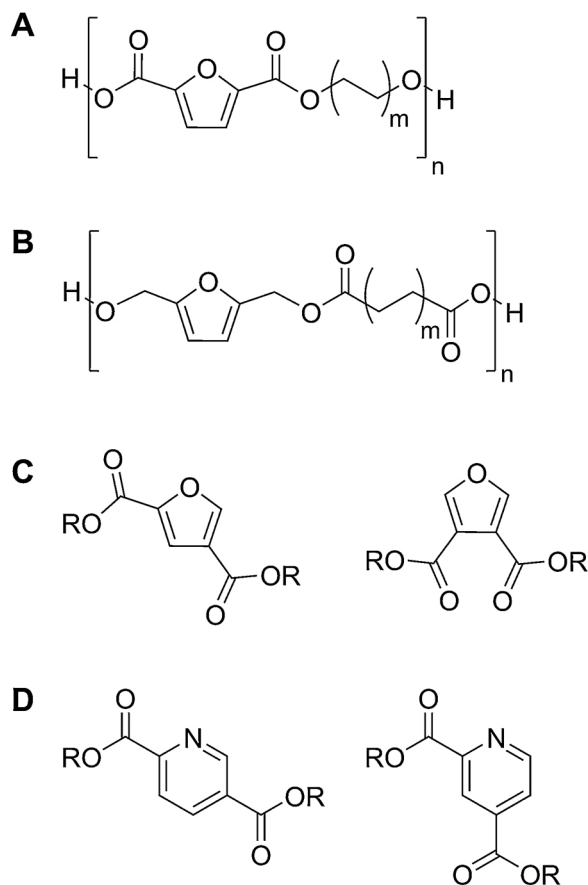


Fig. 2. Novel bio-based aromatic alternatives to FDCA for the synthesis of aromatic-aliphatic polyesters. A: polymerization of FDCA with various length diols; B: polymerization of furan diol with various length diesters; C: furan diacid derivatives (2,4- and 3,4-disubstituted furan); D: lignin-derived monomers (2,5- and 2,4-disubstituted pyridine) [142].

spores, can likewise be considered as a naturally occurring compound [152]. The use of the above-mentioned pyridine diacids in combination with aliphatic diols having a C₄–C₈ carbon chain length was investigated for the synthesis of polyesters catalysed by CalB (Lipase B from *Candida antarctica*). The similarity of the pyridinedicarboxylic acids (PDCAs) to the FDCA and TA monomers would suggest that they might offer increased rigidity if incorporated into a polymer yet retaining a potentially interesting pyridine functionality which may affect the stacking/crystallization behaviour of the final product [102]. A last relevant example of an alternative building block is the 2,5-bis(hydroxymethyl) furan, a rigid diol that was enzymatically polymerized with diesters having various carbon chain lengths (C₄–C₁₂) (Fig. 2B). The incorporation of an increasing number of methylene units into the polyester chain resulted in an enhanced degree of crystallinity, higher crystallization rate, T_m, ΔH_m and also increased thermal stability [154].

Performance and sustainability in practice: bio-based composite membranes and mulching films for agriculture

A special case of biodegradable plastics are those designed for an in-soil final destination. This is the case of fibre-reinforced composites, geomembranes and biodegradable mulching films (Table 6). The field performance of such materials is equivalent to that of traditional plastics films and composites but, in contrast to their non-biodegradable alternatives, they can be incorporated in the environment at the end of their usage. In Europe, the agricultural plastic films market size reaches approximately over 780 Ktons per year [155]. Mulch films represent about 80 Ktons/year and are used on the main vegetable crops (zucchini, tomatoes, peppers, lettuce, etc.). Traditional plastic mulch films are made of LDPE (low density polyethylene) and need to be removed and properly disposed of at the end of their use, to prevent dispersion of plastic into the environment. These operations represent costs, which are highly dependent on the type of crop, soil, and agronomical technique, use of the film in open fields or greenhouses and the thickness of the film. Conventional mulch films are generally recognized to have significant agronomical advantages including: i) increasing the yield and improving the quality of crops; ii) weed control; iii) reduction in use of irrigation water (up to 30 %, compared to bare soil) and pesticides; iv) enhancing early crop production; v) increasing the temperature and moisture in the soil [156]. Collecting the used plastic films and recycling them at the end of their use is challenging because mulch films are highly contaminated with soil, sand, and organic material, which can reach up to 50–75 % of the initial weight, making the mechanical recycling difficult and economically unviable [156]. Fig. 3 shows the

collection rate in percentage of the overall quantity of plastic films used in the European agricultural market. According to the data from the European Organization for Agricultural Plastic Environment, in 2014 only about 32 % of the used agricultural plastic was properly collected and disposed of (Fig. 3) [5].

Occasionally, in some areas where plastic films are not properly collected and recycled, it may happen that they are disposed of by burning directly in the field or in uncontrolled landfills leading to environmental concerns [157]. Ineffective management practices of the plastic waste cause hazards linked to the plastic residues remaining in the soil which, due to their accumulation year after year, can lead to changes in the characteristics of the soil and, conversely, to a reduction in crop yields [158]. Studies carried out in China, especially in the Xinjiang Autonomous Region, revealed the effect of residuals of plastic mulch films in the soil, evaluating their impact on soil fertility and on agronomical activities. The plastic residues appeared to be responsible of the damage of the soil structure and the decrease of its ventilation, resulting in poor moisture retention and limited migration of water in the soil, with a consequent general decrease of the soil quality [30,159]. In that respect, biodegradable materials for agriculture, such as biodegradable mulch films, but also silage films, pots, threads, can prevent the production of waste and/or enter the recovery stream for bio-waste to yield compost that brings organic matter to the soil, closing the carbon cycle.

Biodegradable mulch films have been commercially available on the market since the early 2000s and have been tested in fields and successfully used by growers. They proved to have agronomical performance similar to traditional materials in terms of quantity and quality of crop yields for the main vegetal crops, as well as the same level of weeding effect and they can be placed in the field by the same type of machines used for conventional plastic mulches. Furthermore, biodegradable mulches can be used for some crops where plastic mulches cannot generally be employed, mainly due to the impossibility of removing them fully at the end of the crop cycle (e.g. for new vine plantations, or cotton) or when the mechanical harvesting is not feasible (e.g. processing tomatoes). Technical results have been widely published, and some examples are reported in the following bibliography [160,161].

The market share of biodegradable mulch film accounts for about 5% of the total for plastic mulches [162], with Italy, France, Germany, Benelux and Spain as the primary users. This estimate does not take into account fragmentable mulches (both oxo and/or photo), which do not meet the requirements of the international standards on compostability and biodegradability of plastic materials (see Table 1). At the beginning of 2018, CEN published the European standard EN 17033: 2018 for biodegradable mulches [163], which constitutes the European reference for the definition of the characteristics of biodegradation, non-ecotoxicity, mechanical and optical performance of biodegradable sheets and constituents. Thus, it represents a key document to differentiate the actually biodegradable materials from the oxo-photo-degradable ones, such as the non-biodegradable polyethylene, regardless it is bio-based or derives from fossil feedstock. The EN 17033 standard specifies the methods of analysis and the criteria relating to biodegradation, ecotoxicology, tensile and optical properties that biodegradable sheets must have. The CEN TC / 249 / WG7 working group (relating to plastics) referred to both the pre-existing "OK Biodegradable Soil" program (Vincotte, now TUV) and the most recent Italian UNI 11495 standard to develop the biodegradation criteria in soil. Accordingly, sheets must have a minimum biodegradation of 90 %, within 24 months, measured as the release of CO₂ followed by a biodegradation test conducted in soil at room temperature according to the standard ISO 17556 method. At present, biodegradable mulch films represent the main application of biodegradable polymers in the agricultural sector.

Table 6

End-bioproductions for agricultural and forest applications registered in GreenPla (Japan BioPlastics Association, JBPA 2016; www.jbpaweb.net, modified by the authors).

Product Type	Bioplastic Material	Share (%)
Mulching film	PBAT, PBSA, PBS, BS-LA copolymer, PBLDA, TP Starch, PCL, PLA	51
Film for fumigation	PBAT	3
Sheet/Forestry films	PBAT, PCL	12
Band, Tapes, Ties	PBAT, PBSA, PBS, PLA	12
Floating cover	PLA	1
Nets	PBA, PLA	4
Yarn, Rope	PBS, PBA, PLA,	3
Pots/Planters	PBSA, PBS, PBLDA	7
Other products (e.g. clips)	PBSA, PBS, BS-LA, PLA	10

PBLDA: Co-polymer of butanediol with long chain dicarboxylic acids; PBAT : Polybutylene adipate/terephthalate; PBSA :Polybutylene succinate adipate; PBS :Polybutylene succinate; BS-LA copolymer: Butyl succinate/polylactic acid; PBS: Poly(1,4-butylene succinate; PCL: polycaprolactone; PLA: polylactic acid; TP starch: thermoplastic starch.

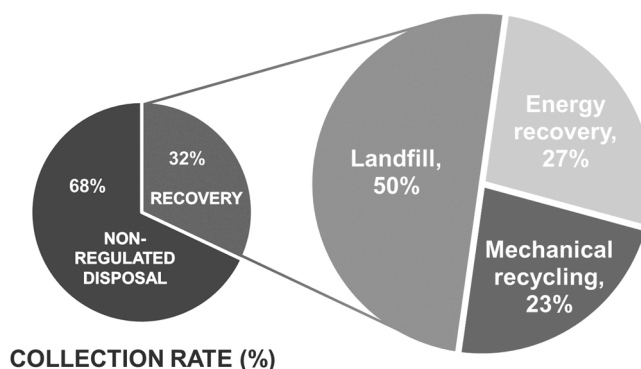


Fig. 3. Disposal of used agricultural plastic in EU. Adapted from <http://www.plastiques-agricoles.com/apc-europe-missions/agricultural-plastics-european-regulation>.

Conclusions

Environmental and sustainability motivations boosted the development of a first wave of renewable polymers and plastics that in some cases found their position in the market with difficulties because they had to compete with highly optimized and standardized fossil-based products. Looking beyond the so called “drop-in” renewable polymers, there is a wealth of chemical and biotechnological knowledge that is fertilizing the polymer sector while boosting the delivery of a new generation of advanced engineered polymers obtainable from renewable feedstock. Being aware that in Europe more than 1.45 million people are working in 62,000 (mainly) small and medium sized companies creating an annual turnover above €350B [7], innovating the polymer sectors appears as both an obligation and an opportunity for economic and social development. The bioeconomy, through the integration of biotechnology, chemistry, and bio-based industry, enables the decoupling of plastic production from fossil feedstock. This transition will be accelerated not only by supporting research and innovation but also by dispelling the myth of the high costs of renewable and bio-based polymers, through the disclosure and open discussion of the real costs and impact of fossil plastics.

Declaration of Competing Interest

The authors report no declarations of interest.

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References

- [1] Haskell VC, Owens DK. A structural comparison of films regenerated from cellulose acetate and viscose. *Text Res J* 1960;30:993–8. <https://doi.org/10.1177/004051756003001213>.
- [2] Martino L, Basilissi L, Farina H, Ortenzi MA, Zini E, Di Silvestro G, et al. Bio-based polyamide 11: synthesis, rheology and solid-state properties of star structures. *Eur Polym J* 2014;59:69–77. <https://doi.org/10.1016/j.eurpolymj.2014.07.012>.
- [3] Casein; its preparation and technical utilisation : Scherer, Robert : Free Download, Borrow, and Streaming : Internet Archive n.d. <https://archive.org/details/caseinitsprepara00scherich/page/n6/mode/2up> (accessed April 28, 2020).
- [4] Skoczinski P., Chinthapalli R., Carus M., Baltus W., de Guzman D., Käh H., Raschka A., Ravenstijn J. Bio-based Building Blocks and Polymers – Global Capacities and Trends 2019–2024. <http://bio-based.eu/downloads/bio-based-building-blocks-and-polymers-global-capacities-production-and-trends-2019-2024/> (accessed September 14, 2020).
- [5] Plastics-the Facts. An analysis of European plastics production, demand and waste data. 2019 (accessed April 28, 2020), https://www.plasticseurope.org/application/files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.pdf.
- [6] Raynaud J. Valuing Plastics: The Business Case for Measuring, Managing and Disclosing Plastic Use in the Consumer Goods Industry. United Nations Environment Programme (UNEP) 2014. <https://www.oceanrecov.org/pdf/valuing-plastic-report.html>.
- [7] Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, et al. Plastic waste inputs from land into the ocean. *Science* 2015;347:768–71. <https://doi.org/10.1126/science.1260352>.
- [8] Smith M, Love DC, Rochman CM, Neff RA. Microplastics in seafood and the implications for human health. *Curr Environ Heal Reports* 2018;5:375–86. <https://doi.org/10.1007/s40572-018-0206-z>.
- [9] <https://www.unenvironment.org/news-and-stories/story/plastic-planet-how-tiny-plastic-particles-are-polluting-our-soil> (website visited on April 28th 2020).
- [10] https://ecostandard.org/news_events/tackling-microplastic-pollution-at-its-source-the-example-of-pellets/ (accessed April 28, 2020).
- [11] http://www3.weforum.org/docs/WEF_The_New_Plastics_Economy.pdf (accessed April 28, 2020).
- [12] <https://www.trucost.com/publication/scaling-sustainable-plastics/> (website visited on April 28th 2020).
- [13] Natural capital accounting: overview and progress in the European Union. Publications Office of the European Union 2019. doi:10.2779/819449.
- [14] Caparrós A, Oviedo JL, Álvarez A, Campos P. Simulated exchange values and ecosystem accounting: theory and application to free access recreation. *Ecol Econ* 2017;139:140–9. <https://doi.org/10.1016/j.ecolecon.2017.04.011>.
- [15] Toxics Release Inventory (TRI) Program. US EPA. <https://www.epa.gov/toxics-release-inventory-tri-program> (accessed April 28, 2020).
- [16] Eco-profiles: PlasticsEurope. <https://www.plasticseurope.org/en/resources/eco-profiles> (accessed April 28, 2020).
- [17] Wegener Sleeswijk A, Heijungs R. GLOBOX: a spatially differentiated global fate, intake and effect model for toxicity assessment in LCA. *Sci Total Environ* 2010;408:2817–32. <https://doi.org/10.1016/j.scitotenv.2010.02.044>.
- [18] Van Zelm R, Huijbregts MAJ, Van De Meent D. USES-LCA 2.0-A global nested multi-media fate, exposure, and effects model. *Int J Life Cycle Assess* 2009;14:282–4. <https://doi.org/10.1007/s11367-009-0066-8>.
- [19] Environment Directorate Joint Meeting Of The Chemicals Committee And The Working Party On Chemicals, Pesticides And Biotechnology. Series on Emission Scenario Documents No. 38 JT03447969, 2019. <https://www.cen.eu/Pages/default.aspx> (accessed April 28, 2020).
- [20] EN 17228:2019 - European Standards. <https://www.en-standard.eu/search/?q=EN+17228%3A2019> (accessed April 28, 2020).
- [21] EN 16575 - European Standards. <https://www.en-standard.eu/search/?q=EN+16575> (accessed April 28, 2020).
- [22] EN 16640:2017 - European Standards. <https://www.en-standard.eu/search/?q=EN+16640%3A2017> (accessed April 28, 2020).
- [23] EN 16785-1:2015 - European Standards. <https://www.en-standard.eu/search/?q=EN+16785-1%3A2015> (accessed April 28, 2020).
- [24] EN 16785-2 - European Standards. <https://www.en-standard.eu/search/?q=EN+16785-2> (accessed April 28, 2020).

- [27] EN 16760:2015 - CEN/TC 411 - Bio-based products. https://standards.cen.eu/dyn/www/f?p=204:110:0:::FSP_PROJECT:39303&cs=1379CA21646C94EFCDB785629FC62F8F3 (accessed April 28, 2020).
- [28] EN 16751:2016 - CEN/TC 411 - Bio-based products. https://standards.cen.eu/dyn/www/f?p=204:110:0:::FSP_PROJECT,FSP_ORG_ID:39302,874780&cs=1C217387307361732C25B757AE322E2EA (accessed April 28, 2020).
- [29] EN 16848 - European Standards. <https://www.en-standard.eu/search/?q=EN+16848> (accessed April 28, 2020).
- [30] Song JH, Murphy RJ, Narayan R, Davies GBH. Biodegradable and compostable alternatives to conventional plastics. *Philos Trans R Soc B Biol Sci* 2009;364:2127–39. <https://doi.org/10.1098/rstb.2008.0289>.
- [31] EN 16935 - European Standards. <https://www.en-standard.eu/search/?q=EN+16935> (accessed April 28, 2020).
- [32] EN ISO 14020 - European Standards <https://www.en-standard.eu/search/?q=EN+ISO+14020> (accessed April 28, 2020).
- [33] ISO 16620-2:2015 - European Standards. <https://www.en-standard.eu/search/?q=ISO+16620-2%3A2015> (accessed April 28, 2020).
- [34] ISO 16620-4 - European Standards. <https://www.en-standard.eu/search/?q=ISO+16620-4> (accessed April 28, 2020).
- [35] EN 13432 - European Standards. <https://www.en-standard.eu/search/?q=EN+13432> (accessed April 28, 2020).
- [36] ASTM D. 6691 - European Standards. <https://www.en-standard.eu/search/?q=ASTM+D+6691> (accessed April 28, 2020).
- [37] Nakajima H, Dijkstra P, Loos K. The recent developments in biobased polymers toward general and engineering applications: polymers that are upgraded from biodegradable polymers, analogous to petroleum-derived polymers, and newly developed. *Polymers (Basel)* 2017;9:523. <https://doi.org/10.3390/polym9100523>.
- [38] Kurian T, Mathew NM. Natural Rubber: Production, Properties and Applications. Biopolymers, Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2011, p. 403–436. <https://doi.org/10.1002/9781118164792.ch14>.
- [39] Mohanty AK, Misra M, Hinrichsen G. Biofibres, biodegradable polymers and biocomposites: an overview. *Macromol Mater Eng* 2000;276–277:1–24. [https://doi.org/10.1002/\(SICI\)1439-2054\(20000301\)276:1<1::AID-MAME1>3.0.CO;2-W](https://doi.org/10.1002/(SICI)1439-2054(20000301)276:1<1::AID-MAME1>3.0.CO;2-W).
- [40] Candido RG, Godoy GG, Gonçalves A. Characterization and application of cellulose acetate synthesized from sugarcane bagasse. *Carbohydr Polym* 2017;167:280–9. <https://doi.org/10.1016/j.carbpol.2017.03.057>.
- [41] Sharma A, Sundaram ST, Zhang YZ, Brodman BW. Nitrocellulose degradation by a coculture of *Sclerotium rolfsii* and *Fusarium solani*. *J Ind Microbiol* 1995;15:1–4. <https://doi.org/10.1007/BF01570005>.
- [42] MNVR Kumar, Muzzarelli RAA, Muzzarelli C, Sashiwa H, Domb AJ. Chitosan chemistry and pharmaceutical perspectives. *Chem Rev* 2004;104:6017–84. <https://doi.org/10.1021/cr030441b>.
- [43] Yang J, Ching YC, Chuah CH. Applications of lignocellulosic fibers and lignin in bioplastics: a review. *Polymers (Basel)* 2019;11:751. <https://doi.org/10.3390/polym11050751>.
- [44] Graupner N. Application of lignin as natural adhesion promoter in cotton fibre-reinforced poly(lactic acid) (PLA) composites. *J Mater Sci* 2008;43:5222–9. <https://doi.org/10.1007/s10853-008-2762-3>.
- [45] Réti C, Casetta M, Duquesne S, Bourbigot S, Delobel R. Flammability properties of intumescent PLA including starch and lignin. *Polym Adv Technol* 2008;19:628–35. <https://doi.org/10.1002/pat.1130>.
- [46] Chen GQ. A microbial polyhydroxyalkanoates (PHA) based bio- and materials industry. *Chem Soc Rev* 2009;38:2434–46. <https://doi.org/10.1039/b812677c>.
- [47] Zou X, Cheng C, Feng J, Song X, Lin M, Yang ST. Biosynthesis of polymalic acid in fermentation: advances and prospects for industrial application. *Crit Rev Biotechnol* 2019;39:408–21. <https://doi.org/10.1080/07388551.2019.1571008>.
- [48] Bajaj I, Singhal R. Poly (glutamic acid) - an emerging biopolymer of commercial interest. *Bioresour Technol* 2011;102:5551–61. <https://doi.org/10.1016/j.biortech.2011.02.047>.
- [49] Richard A, Margaritis A. Poly(glutamic acid) for biomedical applications. *Crit Rev Biotechnol* 2001;21:219–32. <https://doi.org/10.1080/07388550108984171>.
- [50] Garlotta D. A literature review of poly(lactic acid). *J Polym Environ* 2001;9:63–84. <https://doi.org/10.1023/A:1020200822435>.
- [51] Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. *Macromol Biosci* 2004;4:835–64. <https://doi.org/10.1002/mabi.200400043>.
- [52] Hamad K, Kaseem M, Yang HW, Deri F, Ko YG. Properties and medical applications of polylactic acid: a review. *Express Polym Lett* 2015;9:435–55. <https://doi.org/10.3144/expresspolymlett.2015.42>.
- [53] Kaku M. Poly(trimethylene terephthalate, PTT. 1st ed. Tokyo: CMC Publishing Co. Ltd.; 2013.
- [54] Colonna M, Berti C, Fiorini M, Binassi E, Mazzacurati M, Vannini M, et al. Synthesis and radiocarbon evidence of terephthalate polyesters completely prepared from renewable resources. *Green Chem* 2011;13:2543–8. <https://doi.org/10.1039/c1gc15400a>.
- [55] Shiramizu M, Toste FD. On the diels-alder approach to solely biomass-derived polyethylene terephthalate (PET): conversion of 2,5-Dimethylfuran and acrolein into p-Xylene. *Chem - A Eur J* 2011;17:12452–7. <https://doi.org/10.1002/chem.201101580>.
- [56] Tachibana Y, Kimura S, Kasuya KI. Synthesis and verification of biobased terephthalic acid from furfural. *Sci Rep* 2015;5. <https://doi.org/10.1038/srep08249>.
- [57] Siracusa V, Lotti N, Munari A, Dalla Rosa M. Poly(butylene succinate) and poly (butylene succinate-co-adipate) for food packaging applications: gas barrier properties after stressed treatments. *Polym Degrad Stab* 2015;119:35–45. <https://doi.org/10.1016/j.polymdegradstab.2015.04.026>.
- [58] Xu J, Guo B-H-H. Poly(butylene succinate) and its copolymers: research, development and industrialization. *Biotechnol J* 2010;5:1149–63. <https://doi.org/10.1002/biot.201000136>.
- [59] Luo S, Li F, Yu J, Cao A. Synthesis of poly(butylene succinate-co-butylene terephthalate) (PBST) copolymers with high molecular weights via direct esterification and polycondensation. *J Appl Polym Sci* 2010;115:2203–11. <https://doi.org/10.1002/app.31346>.
- [60] Niaounakis M. Biopolymers: applications and trends. Elsevier Inc. 2015. <https://doi.org/10.1016/c2014-0-00936-7>.
- [61] Gan Z, Abe H, Doi Y. Biodegradable poly(ethylene succinate) (PES). 2. Crystal morphology of melt-crystallized ultrathin film and its change after enzymatic degradation. *Biomacromolecules* 2000;1:713–20. <https://doi.org/10.1021/bm00055t>.
- [62] Burgess SK, Karvan O, Johnson JR, Kriegl RM, Koros WJ. Oxygen sorption and transport in amorphous poly(ethylene furanoate). *Polymer (Guildf)* 2014;55:4748–56. <https://doi.org/10.1016/j.polymer.2014.07.041>.
- [63] Burgess SK, Leisen JE, Kraftschik BE, Mubarak CR, Kriegl RM, Koros WJ. Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate). *Macromolecules* 2014;47:1383–91. <https://doi.org/10.1021/ma5000199>.
- [64] Klonos PA, Papadopoulos L, Tzetzis D, Kyritsis A, Papageorgiou GZ, Bikiaris DN. Thermal, nanoindentation and dielectric study of nanocomposites based on poly (propylene furanoate) and various inclusions. *Mater Today Commun* 2019;20:100585. <https://doi.org/10.1016/j.mtcomm.2019.100585>.
- [65] Soccio M, Costa M, Lotti N, Gazzano M, Siracusa V, Salatelli E, et al. Novel fully biobased poly(butylene 2,5-furanoate/diglycolate) copolymers containing ether linkages: structure-property relationships. *Eur Polym J* 2016;81:397–412. <https://doi.org/10.1016/j.eurpolymj.2016.06.022>.
- [66] Gigli M, Quartarello F, Soccio M, Pellis A, Lotti N, Guebitz GM, et al. Enzymatic hydrolysis of poly(1,4-butylene 2,5-thiophenedicarboxylate) (PBTF) and poly (1,4-butylene 2,5-furandicarboxylate) (PBF) films: a comparison of mechanisms. *Environ Int* 2019;130. <https://doi.org/10.1016/j.envint.2019.05.046>.
- [67] Ferreira FV, Cividanes LS, Gouveia RF, Lona LMF. An overview on properties and applications of poly(butylene adipate-co-terephthalate)-PBAT based composites. *Polym Eng Sci* 2019;59:E7–15. <https://doi.org/10.1002/pen.24770>.
- [68] Fidanovski BZ, Spasojevic PM, Panic VV, Seslija SI, Spasojevic JP, Popovic IG. Synthesis and characterization of fully bio-based unsaturated polyester resins. *J Mater Sci* 2018;53:4635–44. <https://doi.org/10.1007/s10853-017-1822-y>.
- [69] Winnacker M, Rieger B. Biobased Polyamides: Recent Advances in Basic and Applied Research. *Macromol Rapid Commun* 2016;37:1391–413. <https://doi.org/10.1002/marc.201600181>.
- [70] Tokiwa Y, Calabria BP, Ugwu CU, Aiba S. Biodegradability of plastics. *Int J Mol Sci* 2009;10:3722–42. <https://doi.org/10.3390/ijms10093722>.
- [71] Moran CS, Barthelon A, Pearsall A, Mittal V, Dorgan JR. Biorenewable blends of polyamide-4,10 and polyamide-6,10. *J Appl Polym Sci* 2016;133. <https://doi.org/10.1002/app.43626>.
- [72] Morschbacker A. Bio-ethanol based ethylene. *Polym Rev (Phila Pa)* 2009;49:79–84. <https://doi.org/10.1080/15583720902834791>.
- [73] Cacciari I, Quatrini P, Zirlotta G, Mincione E, Vinciguerra V, Lupattelli P, et al. Isotactic polypropylene biodegradation by a microbial community: physicochemical characterization of metabolites produced. *Appl Environ Microbiol* 1993;59:3695–700.
- [74] Samuel C, Raquez JM, Dubois P. PLLA/PMMA blends: A shear-induced miscibility with tunable morphologies and properties? *Polymer (Guildf)* 2013;54:3931–9. <https://doi.org/10.1016/j.polymer.2013.05.021>.
- [75] Chakrabarti R, Das M, Chakraborty D. Physical, mechanical, and thermal properties of PVC/PMMA blends in relation to their morphologies. *J Appl Polym Sci* 2004;93:2721–30. <https://doi.org/10.1002/app.20621>.
- [76] Sang JS, Park EY, Lim SW, Park S, Oh KW. Performance of bio-ethylene propylene diene monomer (bio-EPDM) foam with mixed chemical and encapsulated blowing agents. *Fash Text* 2019;6. <https://doi.org/10.1186/s40691-019-0178-0>.
- [77] Kurańska M, Cabulis U, Auguścik M, Prociak A, Ryszkowska J, Kirpluks M. Bio-based polyurethane-polyisocyanurate composites with an intumescent flame retardant. *Polym Degrad Stab* 2016;127:11–9. <https://doi.org/10.1016/j.polymdegradstab.2016.02.005>.
- [78] Gamerith C, Herrero Acero E, Pellis A, Ortner A, Vielnascher R, Luschig D, et al. Improving enzymatic polyurethane hydrolysis by tuning enzyme sorption. *Polym Degrad Stab* 2016;132. <https://doi.org/10.1016/j.polymdegradstab.2016.02.025>.
- [79] Howard GT. Biodegradation of polyurethane: a review. *Int Biodeterior. Biodegrad* 2002;49:245–52. [https://doi.org/10.1016/S0964-8305\(02\)00051-3](https://doi.org/10.1016/S0964-8305(02)00051-3).
- [80] Wang H, Yao J. Use of poly(furfuryl alcohol) in the fabrication of nanostructured carbons and nanocomposites. *Ind Eng Chem Res* 2006;45:6393–404. <https://doi.org/10.1021/ie0602660>.
- [81] Costes L, Laoutid F, Brohez S, Dubois P. Bio-based flame retardants: when nature meets fire protection. *Mater Sci Eng R Rep* 2017;117:1–25. <https://doi.org/10.1016/j.mser.2017.04.001>.
- [82] Li Y, Shimizu H. Co-continuous polyamide 6 (PA6)/acrylonitrile-butadiene-Styrene (ABS) nanocomposites. *Macromol Rapid Commun* 2005;26:710–5. <https://doi.org/10.1002/marc.200400654>.

- [83] Mullen B, Rodwogin M, Stollmaier F, Yontz D, Leibig C. New bio-derived superabsorbents from nature. *Int J Green Nanotechnol Mater Sci Eng* 2013;1: 186–90. <https://doi.org/10.1680/jgmt.12.00018>.
- [84] Stahl JD, Cameron MD, Haselbach J, Aust SD. Biodegradation of superabsorbent polymers in soil. *Environ Sci Pollut Res* 2000;7:83–8. <https://doi.org/10.1065/espr199912.014>.
- [85] Delidovich I, Hausoul PJC, Deng L, Pfützenreuter R, Rose M, Palkovits R. Alternative monomers based on lignocellulose and their use for polymer production. *Chem Rev* 2016;116:1540–99. <https://doi.org/10.1021/acs.chemrev.5b00354>.
- [86] Alvarenga RA, Dewulf J, De Meester S, Wathet A, Villers J, Thommeret R, et al. Life cycle assessment of bioethanol-based PVC. *Biofuels, Bioprod Biorefining* 2013;7:396–405. <https://doi.org/10.1002/bbb.1398>.
- [87] Hann S, Ettlinger S, Gibbs A, Hogg D. The impact of the use of oxo-degradable. Plastic on the Environment. 2016. <https://doi.org/10.2779/992559>.
- [88] OECD iLibrary | Policies for Bioplastics in the Context of a Bioeconomy. https://www.oecd-ilibrary.org/science-and-technology/policies-for-bioplastics-in-the-context-of-a-bioeconomy_5k3xp9rww6d-en (accessed April 28, 2020).
- [89] Zhang Z, Lohr L, Escalante C, Wetzstein M. Food versus fuel: what do prices tell us? *Energy Policy* 2010;38:445–51. <https://doi.org/10.1016/j.enpol.2009.09.034>.
- [90] Aeschelmann F, Carus M. Biobased building blocks and polymers in the world: capacities, production, and applications—status quo and trends towards 2020. *Ind Biotechnol (New Rochelle N Y)* 2015;(11):154–9. <https://doi.org/10.1089/ind.2015.28999.fae>.
- [91] <https://www.european-bioplastics.org/bioplastics/feedstock/> (accessed September 14, 2020).
- [92] Koller M, Marsálek L, de Sousa Dias MM, Braunneg G. Producing microbial polyhydroxyalkanoate (PHA) biopolyesters in a sustainable manner. *N Biotechnol* 2017;37:24–38. <https://doi.org/10.1016/j.nbt.2016.05.001>.
- [93] Koutinas AA, Vlysidis A, Pleissner D, Kopsahelis N, Lopez Garcia I, Kookos IK, et al. Valorization of industrial waste and by-product streams via fermentation for the production of chemicals and biopolymers. *Chem Soc Rev* 2014;43:2587–627. <https://doi.org/10.1039/c3cs60293a>.
- [94] Yim H, Haselbeck R, Niu W, Pujol-Baxley C, Burgard A, Boldt J, et al. Metabolic engineering of *Escherichia coli* for direct production of 1,4-butanediol. *Nat Chem Biol* 2011;7:445–52. <https://doi.org/10.1038/nchembio.580>.
- [95] Chen GQ. A microbial polyhydroxyalkanoates (PHA) based bio- and materials industry. *Chem Soc Rev* 2009;38:2434–46. <https://doi.org/10.1039/b812677c>.
- [96] Zou H, Shi M, Zhang T, Li L, Li L, Xian M. Natural and engineered polyhydroxyalkanoate (PHA) synthase: key enzyme in biopolyester production. *Appl Microbiol Biotechnol* 2017;101:7417–26. <https://doi.org/10.1007/s00253-017-8485-0>.
- [97] Polyhydroxyalkanoate (PHA) Market Analysis | Recent Market Developments | Industry Forecast to 2019–2024 | MarketsandMarketsTM n.d. <https://www.marketsandmarkets.com/Market-Reports/pha-market-395.html> (accessed April 28, 2020).
- [98] Gahlawat G. Challenges in PHAs production at mass scale. Cham: Springer; 2019. p. 25–30. https://doi.org/10.1007/978-3-030-33897-8_3.
- [99] Poltronieri P, Kumar P. Polyhydroxyalkanoates (PHAs) in industrial applications. *Handb. Ecomater. Springer International Publishing*; 2017. p. 1–30. https://doi.org/10.1007/978-3-319-48281-1_70-1.
- [100] Pellis A, Herrero Acero E, Gardossi L, Ferrario V, Guebitz GM. Renewable building blocks for sustainable polyesters: new biotechnological routes for greener plastics. *Polym Int* 2016;65. <https://doi.org/10.1002/pi.5087>.
- [101] Mycroft Z, Gomis M, Mines P, Law P, Bugg TDH. Biocatalytic conversion of lignin to aromatic dicarboxylic acids in *Rhodococcus* justii RHA1 by re-routing aromatic degradation pathways. *Green Chem* 2015;17:4974–9. <https://doi.org/10.1039/C5GC01347J>.
- [102] Pellis A, Comerford JW, Weinberger S, Guebitz GM, Clark JH, Farmer TJ. Enzymatic synthesis of lignin derivable pyridine based polyesters for the substitution of petroleum derived plastics. *Nat Commun* 2019;10. <https://doi.org/10.1038/s41467-019-09817-3>.
- [103] Totaro G, Cruciani L, Vannini M, Mazzola G, Di Gioia D, Celli A, et al. Synthesis of castor oil-derived polyesters with antimicrobial activity. *Eur Polym J* 2014;56: 174–84. <https://doi.org/10.1016/j.eurpolymj.2014.04.018>.
- [104] Miyaji H, Satoh K, Kamigaito M. Bio-based polyketones by selective ring-opening radical polymerization of α -Pinene-Derived pinocarvone. *Angew Chemie Int Ed* 2016;55:1372–6. <https://doi.org/10.1002/anie.201509379>.
- [105] Kawasaki N, Nakayama A, Yamano N, Takeda S, Kawata Y, Yamamoto N, et al. Synthesis, thermal and mechanical properties and biodegradation of branched polyamide 4. *Polymer (Guildf)* 2005;46:9987–93. <https://doi.org/10.1016/j.polymer.2005.06.092>.
- [106] Tateyama S, Masuo S, Suvannasara P, Oka Y, Miyazato A, Yasaki K, et al. Ultrastrong, transparent polytruxillamides derived from microbial photodimers. *Macromolecules* 2016;49:3336–42. <https://doi.org/10.1021/acs.macromol.6b00220>.
- [107] Dussenne C, Delaunay T, Wiatz V, Wyart H, Suisse I, Sauthier M. Synthesis of isosorbide: an overview of challenging reactions. *Green Chem* 2017;19:5332–44. <https://doi.org/10.1039/c7gc01912b>.
- [108] Liu T, Simmons TL, Bohnsack DA, Mackay ME, Smith MR, Baker GL. Synthesis of polymandelide: a degradable polylactide derivative with polystyrene-like properties. *Macromolecules* 2007;40:6040–7. <https://doi.org/10.1021/ma061839n>.
- [109] Jing F, Hillmyer MA. A bifunctional monomer derived from lactide for toughening polylactide. *J Am Chem Soc* 2008;130:13826–7. <https://doi.org/10.1021/ja804357u>.
- [110] Corici L, Pellis A, Ferrario V, Ebert C, Cantone S, Gardossi L. Understanding potentials and restrictions of solvent-free enzymatic polycondensation of itaconic acid: an experimental and computational analysis. *Adv Synth Catal* 2015;357. <https://doi.org/10.1002/adsc.201500182>.
- [111] Kaneko T, Matsusaki M, Hang TT, Akashi M. Thermotropic liquid-crystalline polymer derived from natural cinnamoyl biomonomers. *Macromol Rapid Commun* 2004;25:673–7. <https://doi.org/10.1002/marc.200300143>.
- [112] Kaneko T, Thi TH, Shi DJ, Akashi M. Environmentally degradable, high-performance thermoplastics from phenolic phytomonomers. *Nat Mater* 2006;5: 966–70. <https://doi.org/10.1038/nmat1778>.
- [113] Wu L, Mincheva R, Xu Y, Raquez J-M-M, Dubois P. High Molecular Weight Poly (butylene succinate- co -butylene furandicarboxylate) Copolyesters: From Catalyzed Polycondensation Reaction to Thermomechanical Properties. *Biomacromolecules* 2012;13:2973–81. <https://doi.org/10.1021/bm301044f>.
- [114] Kanetaka Y, Yamazaki S, Kimura K. Preparation of poly(ether ketone)s derived from 2,5-furandicarboxylic acid via nucleophilic aromatic substitution polymerization. *J Polym Sci Part A: Polym Chem* 2016;54:3094–101. <https://doi.org/10.1002/pola.28193>.
- [115] Giacobazzi G, Gioia C, Colonna M, Celli A. Thia-michael reaction for a thermostable itaconic-based monomer and the synthesis of functionalized biopolyesters. *ACS Sustain Chem Eng* 2019;7:5553–9. <https://doi.org/10.1021/acscuschemeng.9b00063>.
- [116] Cesugli M, Lotterio S, Navarini L, Lonzarich V, Del Terra L, Vita F, et al. Rice husk as an inexpensive renewable immobilization carrier for biocatalysts employed in the food, cosmetic and polymer sectors. *Catalysts* 2018;8:471–93. <https://doi.org/10.3390/catal8100471>.
- [117] Guarnieri A, Cutifani V, Cesugli M, Pellis A, Vassallo R, Asaro F, Ebert C, Gardossi L. Functionalization of enzymatically synthesized rigid poly(itaconate)s via post-polymerization aza-michael addition of primary amines. *Adv Synth Catal* 2019;361. <https://doi.org/10.1002/adsc.201900055>.
- [118] Chanda S, Ramakrishnan S. Poly(alkylene itaconate)s - An interesting class of polyesters with periodically located exo-chain double bonds susceptible to Michael addition. *Polym Chem* 2015;6:2108–14. <https://doi.org/10.1039/c4py01613k>.
- [119] Farmer TJ, Clark JH, Macquarrie DJ, Ogunjobi JK, Castle RL. Post-polymerisation modification of bio-derived unsaturated polyester resins via Michael additions of 1,3-dicarbonyls. *Polym Chem* 2016;7:1650–8. <https://doi.org/10.1039/c5py01729g>.
- [120] Pellis A, Hanson PA, Comerford JW, Clark JH, Farmer TJ. Enzymatic synthesis of unsaturated polyesters: functionalization and reversibility of the aza-Michael addition of pendants. *Polym Chem* 2019;10. <https://doi.org/10.1039/c8py01655k>.
- [121] Robert T, Friebl S. Itaconic acid-a versatile building block for renewable polyesters with enhanced functionality. *Green Chem* 2016;18:2922–34. <https://doi.org/10.1039/c6gc00605a>.
- [122] Itaconic Acid Market by Derivative & Application. Industry Forecast to 2017–2022 - MarketsandMarketsTM. https://www.marketsandmarkets.com/Market-Reports/itaconic-acid-market-35695455.html?gclid=CjwKCAjwqJ_1BRBZEiAv73uwCzIbAz5AYMM0zd-wT02IJh0e3vSAWvaBl8golWxQU-qQGHQZA59URoCPaMQAvD_BwE (accessed April 28, 2020).
- [123] Regestein L, Klement T, Grande P, Kreyenschulte D, Heyman B, Maßmann T, et al. From beech wood to itaconic acid: case study on biorefinery process integration. *Biotechnol Biofuels* 2018;11:279. <https://doi.org/10.1186/s13068-018-1273-y>.
- [124] Delidovich I, Hausoul PJC, Deng L, Pfützenreuter R, Rose M, Palkovits R. Alternative monomers based on lignocellulose and their use for polymer production. *Chem Rev* 2016;116:1540–99. <https://doi.org/10.1021/acs.chemrev.5b00354>.
- [126] Comerford JW, Byrne FP, Weinberger S, Farmer TJ, Guebitz GM, Gardossi L, et al. Thermal upgrade of enzymatically synthesized aliphatic and aromatic oligoesters. *Materials* 2020;13:368. <https://doi.org/10.3390/ma13020368>.
- [127] Pellis A, Gardossi L. Integrating computational and experimental methods for efficient biocatalytic synthesis of polyesters. In *Enzymatic polymerization*, Bruns N. And Loos K. Eds. *Methods Enzymol* 2019;627:23–55. <https://doi.org/10.1016/b.s.mie.2019.07.040>.
- [128] Farmer TJ, Comerford JW, Pellis A, Robert T. Post-polymerization modification of bio-based polymers: maximizing the high functionality of polymers derived from biomass. *Polym Int* 2018;67. <https://doi.org/10.1002/pi.5573>.
- [129] U.S. Department of Energy. Annual Report | Department of Energy. 2004 <https://www.energy.gov/management/office-management/operational-management/freedom-information-act/documents/annual-reports>.
- [130] Tachibana Y, Kimura S, Kasuya KI. Synthesis and verification of biobased terephthalic acid from furfural. *Sci Rep* 2015;5. <https://doi.org/10.1038/srep08249>.
- [131] Ogunjobi JK, Farmer TJ, McElroy CR, Breeden SW, Macquarrie DJ, Thornthwaite D, et al. Synthesis of biobased diethyl terephthalate via diels-alder addition of ethylene to 2,5-Furandicarboxylic acid diethyl ester: an alternative route to 100% biobased poly(ethylene terephthalate). *ACS Sustain Chem Eng* 2019;7:8183–94. <https://doi.org/10.1021/acscuschemeng.8b06196>.

- [132] AJJE Eerhart, Faaij APC, Patel MK. Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. *Energy Environ Sci* 2012;5:6407–22. <https://doi.org/10.1039/c2ee02480b>.
- [133] Burgess SK, Karvan O, Johnson JR, Kriegel RM, Koros WJ. Oxygen sorption and transport in amorphous poly(ethylene furanoate). *Polymer (Guildf)* 2014;55:4748–56. <https://doi.org/10.1016/j.polymer.2014.07.041>.
- [134] Burgess SK, Kriegel RM, Koros WJ. Carbon dioxide sorption and transport in amorphous poly(ethylene furanoate). *Macromolecules* 2015;48:2184–93. <https://doi.org/10.1021/acs.macromol.5b00333>.
- [135] Burgess SK, Mikkilineni DS, Yu DB, Kim DJ, Mubarak CR, Kriegel RM, et al. Water sorption in poly(ethylene furanoate) compared to poly(ethylene terephthalate). Part 2: kinetic sorption. *Polymer (Guildf)* 2014;55:6870–82. <https://doi.org/10.1016/j.polymer.2014.10.065>.
- [136] Burgess SK, Leisen JE, Kraftschik BE, Mubarak CR, Kriegel RM, Koros WJ. Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate). *Macromolecules* 2014;47:1383–91. <https://doi.org/10.1021/ma5000199>.
- [137] Papageorgiou GZ, Tsanakis V, Bikiaris DN. Synthesis of poly(ethylene furandicarboxylate) polyester using monomers derived from renewable resources: Thermal behavior comparison with PET and PEN. *Phys Chem Chem Phys* 2014;16:7946–58. <https://doi.org/10.1039/c4cp00518j>.
- [138] Pellis A, Haernvall K, Pichler CM, Ghazaryan G, Breinbauer R, Guebitz GM. Enzymatic hydrolysis of poly(ethylene furanoate). *J Biotechnol* 2016;235:47–53. <https://doi.org/10.1016/j.jbiotec.2016.02.006>.
- [139] Weinberger S, Canadell J, Quartinello F, Yeniad B, Arias A, Pellis A, et al. Enzymatic degradation of poly(Ethylene 2,5-furanoate) powders and amorphous films. *Catalysts* 2017;7. <https://doi.org/10.3390/catal7110318>.
- [140] Weinberger S, Haernvall K, Scaini D, Ghazaryan G, Zumstein MT, Sander M, et al. Enzymatic surface hydrolysis of poly(ethylene furanoate) thin films of various crystallinities. *Green Chem* 2017;19. <https://doi.org/10.1039/c7gc02905e>.
- [141] Qin YZ, Li YM, Zong MH, Wu H, Li N. Enzyme-catalyzed selective oxidation of 5-hydroxymethylfurfural (HMF) and separation of HMF and 2,5-diformylfuran using deep eutectic solvents. *Green Chem* 2015;17:3718–22. <https://doi.org/10.1039/c5gc00788g>.
- [142] Barwe S, Weidner J, Cychy S, Morales DM, Dieckhöfer S, Hiltrop D, et al. Electrocatalytic oxidation of 5-(Hydroxymethyl)furfural using high-surface-Area nickel boride. *Angew Chemie Int Ed* 2018;57:11460–4. <https://doi.org/10.1002/anie.201806298>.
- [143] Pellis A, Corici L, Sinigoi L, D'Amelio N, Fattor D, Ferrario V, et al. Towards feasible and scalable solvent-free enzymatic polycondensations: integrating robust biocatalysts with thin film reactions. *Green Chem* 2015;17:1756–66. <https://doi.org/10.1039/C4GC02289K>.
- [144] Pellis A, Ferrario V, Cesugli M, Corici L, Guarneri A, Zartl B, et al. Fully renewable polyesters via polycondensation catalyzed by Thermobifida cellulolytica cutinase 1: an integrated approach. *Green Chem* 2017;19:490–502. <https://doi.org/10.1039/c6gc02142e>.
- [145] Rosenboom JG, Hohl DK, Fleckenstein P, Storti G, Morbidelli M. Bottle-grade polyethylene furanoate from ring-opening polymerisation of cyclic oligomers. *Nat Commun* 2018;9. <https://doi.org/10.1038/s41467-018-05147-y>.
- [146] Papageorgiou GZ, Tsanakis V, Papageorgiou DG, Chrissafis K, Exarhopoulos S, Bikiaris DN. Furan-based polyesters from renewable resources: crystallization and thermal degradation behavior of poly(hexamethylene 2,5-furan-dicarboxylate). *Eur Polym J* 2015;67:383–96. <https://doi.org/10.1016/j.eurpolymj.2014.08.031>.
- [147] Jiang Y, Woortman AJJ, Alberda Van Ekenstein GOR, Loos K. A biocatalytic approach towards sustainable furanic-aliphatic polyesters. *Polym Chem* 2015;6:5198–211. <https://doi.org/10.1039/c5py00629e>.
- [148] Skoczinski P, Espinoza Cangahuala MK, Maniar D, Albach RW, Bittner N, Loos K. Biocatalytic synthesis of furan-based oligomer diols with enhanced end-group fidelity. *ACS Sustain Chem Eng* 2020;8:1068–86. <https://doi.org/10.1021/acssuschemeng.9b05874>.
- [149] Thiagarajan S, Vogelzang W, Knoop JI, Frissen R, et al. Biobased furandicarboxylic acids (FDCA): effects of isomeric substitution on polyester synthesis and properties. *Green Chem* 2014;16:1957–66. <https://doi.org/10.1039/c3gc42184h>.
- [150] Guidotti G, Gigli M, Soccio M, Lotti N, Salatelli E, Gazzano M, et al. Tailoring poly(butylene 2,5-thiophenedicarboxylate) features by the introduction of adipic acid co-units: biobased and biodegradable aliphatic/aromatic polyesters. *Polymer (Guildf)* 2018;145:11–20. <https://doi.org/10.1016/j.polymer.2018.04.063>.
- [152] McClintock MK, Fahnhorst GW, Hoyer TR, Zhang K. Engineering the production of dipicolinic acid in *E. Coli*. *Metab Eng* 2018;48:208–17. <https://doi.org/10.1016/j.mbsen.2018.05.009>.
- [154] Jiang Y, Woortman AJJ, Alberda Van Ekenstein GOR, Petrović DM, Loos K. Enzymatic synthesis of biobased polyesters using 2,5-Bis(hydroxymethyl)furan as the building block. *Biomacromolecules* 2014;15:2482–93. <https://doi.org/10.1021/bm500340w>.
- [155] AMI Conferences - Network with your colleagues in the global plastics industry. <https://www.ami.international/events> (accessed March 30, 2020).
- [156] Martín-Closas L, Pelacho AM, Picuno P, Rodríguez D. Properties of new biodegradable plastics for mulching, and characterization of their degradation in the laboratory and in the field. *Acta Hort.*, vol. 801 PART 1. International Society for Horticultural Science 2008. <https://doi.org/10.17660/ActaHortic.2008.801.27>. p. 275–82.
- [157] Plasticulture Magazine – 2016 – N° 135 – Plasticulture Magazine n.d. <http://ci-pa-plasticulture.com/plasticulture-magazine/en/produit/plasticulture-magazine-2016-n-135/> (accessed March 30, 2020).
- [158] Fu-guang L, Jin-jie C. Study of agricultural tri-dimension pollution on ecological system in Cotton Field and its control tactics. 2005.
- [159] What is White Pollution, IGI Global. <https://www.igi-global.com/dictionary/white-pollution/76530> (accessed March 30, 2020).
- [160] American Society of Plasticulture n.d. https://www.pubhort.org/asp/35/35_4.htm (accessed March 30, 2020).
- [161] Martín-Closas L, Pelacho AM. Agronomic potential of biopolymer films. *Biopolym. - new mater. Sustain. Film. Coatings*. Chichester, UK: John Wiley & Sons, Ltd; 2011. p. 277–99. <https://doi.org/10.1002/9781119994312.ch13>.
- [162] Kyrikou I, Briassoulis D. Biodegradation of agricultural plastic films: a critical review. *J Polym Environ* 2007;15:125–50. <https://doi.org/10.1007/s10924-007-0053-8>.
- [163] New EU standard for biodegradable mulch films in agriculture published – European Bioplastics. <https://www.european-bioplastics.org/new-eu-standard-for-biodegradable-mulch-films-in-agriculture-published/> (accessed March 30, 2020).