Progress in Materials Science 139 (2023) 101186

Contents lists available at ScienceDirect

Progress in Materials Science

journal homepage: www.elsevier.com/locate/pmatsci

Recent advances in bio-based functional additives for polymers

Valentina Marturano [a], Angela Marotta [b], Sarai Agustin Salazar [a], Veronica Ambrogi [a,b,*], Pierfrancesco Cerruti [a,c,**]

[a] Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy
[b] Department of Chemical, Materials and Production Engineering, University of Naples "Federico II", Piazzale Tecchio, 80, 80125 Napoli, Italy
[c] Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, Via Previati 1/C, 23900, Lecco, Italy

ARTICLE INFO

Keywords:
Bio-based polymer additives
Functional additives
Antioxidants
Plasticizers
Melt stabilizers
Compatibilizers
Flame retardants

ABSTRACT

In recent decades, the strong global concern on depletion of fossil fuel and the environmental impact of oil-based compounds has pushed towards more sustainable approaches in the development of polymer-based materials. This interest is driven by the need of a more sustainable economy and a lower dependency on fossil fuels. In this frame, the replacement of synthetic additives with natural compounds in polymer commodities is progressively taking place. Additionally, according to forecasts, the production of bio-plastics will grow exponentially in the near future. However, these materials may exhibit poor physical and mechanical properties regarding

Abbreviations: ABS, Acrylonitrile-butadiene-styrene; BF, Bamboo fiber; BFR, Brominated flame retardant; BT, Natural bentonite; CAGR, Compounded Average Growth Rate; CDA, Cellulose diacetate; CNC, Cellulose nanocrystal; CNF, Cellulose nanofibril; COVID-19, Coronavirus disease; CSS, Core-shell starch; DEHP, Di(2-ethylhexyl)phthalate; DIOP, Diisooctyl phthalate; DOP, Dioctyl phthalate; DOPO, 9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide; EA, Erucamide; EBO, Epoxidized broccoli oil; EC-CMC, Eichhornia crassipes carboxylmethyl cellulose; ECA, Epoxidized citric acid; ECHA, European Chemical Agency; ECO, Epoxidized corn oil; ECP, Epoxidized cardanol oligomer; ELO, Epoxidized linseed oil; EO, Essential oil; EOD, Epoxidized oil derivatives; EPA, Environmental Protection Agency; ESeO, Epoxidised sesame oil; ESO, Epoxidized sunflower oil; ESBO, Epoxidized soybean oil; EU, European Union; EVA, Ethylene-vinyl acetate; FCM, Food contact materials; FR, Flame retardant; GM, Glucomannan; GMA, Glycidyl methacrylate; GRAS, Generally-Regarded-As-Safe; HALS, Hindered Amine Light Stabilizers; HAP, Hydroxyapatite; HCGEP, Hydrogenated cardanol glycidyl ether acetic ester containing phosphaphenanthrene groups; HPBA, Hyperbranched poly(butylene adipate); HRR, Heat Release Rate; IRR, Internal rate of return; LCA, Life Cycle Assessment; LCIA, Life Cycle Impact Assessment; LDPE, Low-density poly(ethylene); LLDPE, Linear low-density poly(ethylene); MA, Maleic anhydride; MB, Mater-Bi®; MCC, Microcrystalline cellulose; MMA, Monounsaturated amide; NP, Nanoparticle; OA, Oleamide; OIT, Oxidation Induction Time; OLA, Oligo(lactic acid); OSA, Oligo(isosorbide adipate); OSS, Oligo(isosorbide suberate); P(3,4HB), Poly(3-hydroxybutyrate-co-4-hydroxybutyrate); PA12, Polyamide-12; PAA, 3-pentadecylphenoxy acetic acid; PAc, Phytic acid; pAO, Primary antioxidants; PBA, Poly(butylene adipate); PBGA, Poly(butyleneglycol adipate); PBAT, Poly(butylene adipate-co-terephthalate); PBP, Payback period; PBS, Poly(butylene succinate); PBSA, Poly[(butylene succinate)-co-adipate]; PCL, Poly(caprolactone); PDA, Poly(dopamine); PE, Poly(ethylene); PEG, Poly(ethylene glycol); PEO, Poly(ethylene oxide); PEPQ, Sandostab PEPQ; PHA, Poly(hydroxyalkanoate); PHB, Poly(hydroxybutyrate); PHBV, Poly(hydroxybutyrate-co-valerate); PHRR, Peak heat release rate; PLA, Poly(lactic acid); PLLA, Poly-L-lactide; PMMA, Poly(methyl methacrylate); PMN, Premanufacture Notice; PP, Poly(propylene); PPC, Poly(propylene carbonate); PS, Poly(styrene); PU, Poly(urethane); PVA, Poly(vinyl alcohol); PVC, Poly(vinyl chloride); REACH, Registration, Evaluation, Authorisation and Restriction of Chemicals; sAO, Secondary antioxidants; SEP, Sepiolite; SA, Stearamide; SDH, Isosorbide dihexanoate; SP, Soy protein; TEGR, Triethylene glycol ester of gum rosin; THR, Total Heat Release; TOA, Tung oil anhydride; TPS, Thermoplastic starch; TSCA, Toxic Substances Control Act; TTI, Time to ignition.

* Corresponding author at: Department of Chemical, Materials and Production Engineering, University of Naples "Federico II", Piazzale Tecchio, 80, 80125 Napoli, Italy.

** Corresponding author at: Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy.

E-mail addresses: ambrogi@unina.it (V. Ambrogi), pierfrancesco.cerruti@cnr.it (P. Cerruti).

https://doi.org/10.1016/j.pmatsci.2023.101186
Received 24 May 2022; Received in revised form 9 May 2023; Accepted 2 September 2023
Available online 7 September 2023

Processing aids
Antimicrobials
Sustainability and safety
Economic and legislative issues

processability and end-use, which can limit their potential for applications. Therefore, academic and industrial communities are pushing their interest in fully bio-based formulations with improved performance, and tailored for specific applications, ranging from packaging to biomedicine.

This review presents the most recent advances in research and development of bio-based functional additives for polymeric materials. For each type of additive, both the scientific fundamentals and the technological aspects are encompassed, with an emphasis on the current commercially available bio-based additives and their role in market uptake of environmentally friendly products. Finally, considerations about environmental, health, regulatory, and economic issues related to the use of bio-additives in plastic materials are also addressed.

1. Introduction

For over fifty years, plastic materials have been the most practical and economical solution for both commodity and specialty applications, due to their favorable properties, such as low cost, lightweight, resistance to corrosion, ready availability, and outstanding optical, mechanical and barrier properties [1]. The diversity of polymers and the versatility of their properties are used to make a vast array of products that bring health and technological advances, energy savings and numerous other societal benefits [2]. For example, thanks to their low density and high impact resistance, plastics account for approximately 50 percent of the volume of a typical passenger car, but only 10 percent of its weight. This entails reduced fuel consumption [3] while significantly improving car safety [4]. The production of plastics has increased substantially over the last 60 years from around 0.5 million tonnes in 1950 to over 390 million tonnes in 2021. The plastics industry has a turnover of more than 400 billion euros and employs over 1.5 million people in Europe alone. In 2021, the European plastics production reached 57.2 million tonnes, and the main market sectors are packaging (39.1%), building and constructions (21.3%), automotive (8.6%), electronics (6.5%), agriculture (3.1%), the remaining is divided between consumer and household goods, furniture, sport, health and safety [5]. The performances that characterize plastic materials are typically achieved by mixing pristine polymers with functional and structural additives, so that the final formulation is customized on the requirements of each specific application [2]. The main drawbacks of plastic formulations unluckily coincide with their most appealing traits: availability and disposability. Current patterns of usage are in fact generating global waste management issues [6]. The world capacity for disposal of waste to landfill is limited, and globally space in landfills is about to be depleted [7]. Moreover, landfilling is strongly associated with environmental and economic concerns [8]. The most virtuous countries seem to have found a sustainable alternatives, such as reuse, recycle, and energy and material recovery technologies [9]. Another promising option towards sustainability relies on the exploitation of bio-based and biodegradable/compostable polymers, that are designed to provide resource efficiency and circularity [10–12]. Bio-based and biodegradable polymers are increasingly studied, and a large number of green polymer formulations are commercially available today [13–16].

To further push performances to higher standards in both commodity and specialty applications, plastic formulations require a variety of functional and structural additives [17]. For example, fibers and particles of different nature are employed to enhance mechanical, thermal and chemical resistance. Thermal and light stabilizers, as well as flame retardants (FR), are used to hinder polymer aging and to provide fire resistance, while plasticizers are introduced to reduce brittleness. However, these additives are mainly oil-based and associated with adverse health risks related to their toxicity and leaching from plastic products [18–22]. Significant examples are the recent concerns raised on phthalates largely employed in flexible poly(vinyl chloride) (PVC) items, and halogenated FRs in electronic devices. The detrimental effects of these substances have led governments to enforce regulations mostly in the European Union (EU) and North America in order to limit, or in some specific cases ban, the exposure of their citizens to them. In the case of halogenated FRs, the EU has recently prohibited their use in plastic enclosures and stands of electronic displays. The new regulation entered into force on 1 March 2021 [23,24].

The environmental and health issues related to oil-based products along with the necessity to anticipate the possible drying up of petroleum, pushed the academic and industrial world towards the development of bio-sourced equivalents to oil-based chemicals.

Bio-based materials can be wholly or partly derived from biological sources, such as plant, animal, or even fungal sources [25–27], excluding materials embedded in geological formations and fossilized [28]. Products derived from renewable feedstocks have the potential to contribute to CO_2 reduction while displaying chemical-physical properties similar to their oil-based counterparts [15,29]. Further benefits can be obtained from the valorization of bio-wastes. In particular, agri-food industry by-products are rich in nutrients and constituents that can be transformed into building blocks for plastic formulations. Exploiting the potential of wastes fulfills the milestones settled by European Commission for Circular Economy, a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops [30,31].

In light of the above considerations, the use of bio-based and natural additives represents a necessary step to meet the growing need for environmental sustainability and health protection in plastics formulations. From an academic standpoint, this is demonstrated by the remarkably increasing number of scientific papers (mostly research articles, reviews, conference papers and book chapters) dealing with this topic published in the latest years. Fig. 1 presents the number of publications of the past 10 years retrieved in the Scopus database using the query “bio-based polymer additives”. The documents regarding this subject are mainly located in the material science, chemistry, engineering and chemical engineering fields, highlighting the fact that bio-based additives are appealing not only for academic research but also for industrial applications.

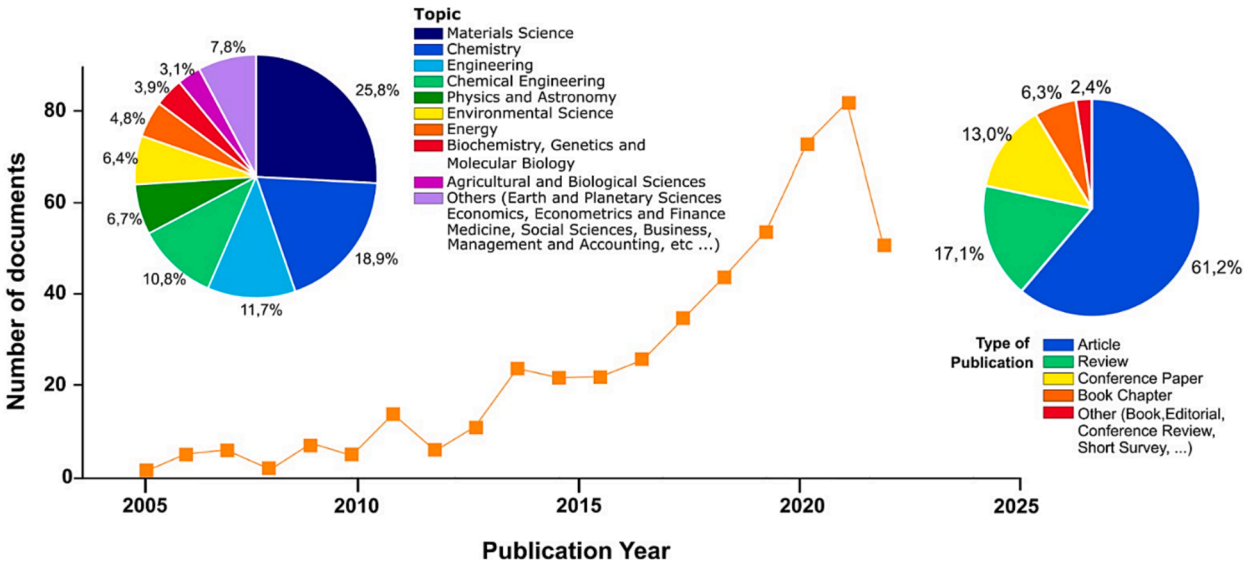


Fig. 1. Number of yearly scientific publications since 2015 regarding the topic of "bio-based polymer additives" (search performed using the Scopus database on May 7th, 2023). The pie chart on the left represents the articles distribution based on the topic (e.g. 25.8% materials science, 18.9% chemistry), the pie chart on the right reports the distribution based on publication type (e.g. reviews, research articles).

In this regard, the worldwide market for polymer bio-additives is expected to grow at a Compounded Average Growth Rate (CAGR) of approximately 5% between 2020 and 2025. As a representative example, the demand for bio-plasticizers is forecast to grow from 887 ktons in 2016 to 1900 ktons in 2025, with a corresponding increase in income of 140% [32–34]. However, such predictions are being revaluated taking into account the significant growth of single-use plastics usage, especially for personal protective products, during the coronavirus disease (COVID-19) pandemic. As a consequence, the plastic additive market is likely to expand as well, making even more crucial the shift towards eco-sustainable additives [35].

This review intends to provide a comprehensive knowledge on polymer bio-based additives, spanning from the recently published scientific research to the commercially available products. There are several articles dealing only with specific classes of polymer bio-additives [36,37]. However, to our knowledge this is the first comprehensive review on the most widely used types of functional bio-additives for both petroleum- and bio-derived polymers. More specifically, recent advances in antimicrobial, antioxidants, thermal stabilizers, processing aids, plasticizers and other polymer additives are reviewed and classified in terms of sources and polymer application. Finally, considerations about the assessment of the overall environmental and economic performance of bio-based additives by cradle-to-grave analysis, and regulatory issues related to their use in plastic materials are also discussed. Additionally, aspects related to environmental toxicity and health concerns are addressed.

2. Melt stabilizers and antioxidants

Polymer materials, like all organic compounds, deteriorate in presence of oxygen, humidity, heat or light, through specific processes such as oxidation, hydrolysis, thermolysis and photolysis [38–40]. Often these reactions occur simultaneously, generating complex degradation pathways. These degradative processes, which have a detrimental effect on the performance of polymers, are sketched and briefly described in Table 1.

In particular, oxidative degradation reactions are the major causes of failure of polymer products. Polymers experience oxidative degradation during the high-temperature processing steps (thermo-oxidation), as well as during their service life due to the exposure to the environmental agents (photo-oxidation) [41]. Thermo- and photo-oxidation consist in an oxidation process activated by high temperature and light, respectively. They are based on autocatalytic free radical chain reactions, involving initiation, propagation and termination steps [42]. Alkyl, alkoxy, peroxy and hydroxyl radicals take part in these processes, as depicted in Fig. 2.

In this frame, protecting additives must be introduced in polymer formulations, to provide resistance against degradation phenomena, which can take place in each stage of polymer life cycle, from the melt processing to the post-manufacturing storage, up to their use as end-products.

Generally, antioxidants can be classified as primary (pAO) and secondary (sAO). The former usually contain hindered phenolics, which act as radical scavengers and inhibit oxidation by donating a hydrogen atom. Their mechanism of action is highlighted in green and yellow, respectively, in Fig. 2**B**. In this way, the additive competes with the polymer substrate in the formation of peroxy radicals. sAO, typically sulfur- or phosphorous-based compounds, decompose peroxides that are intermediate products in the oxidation reactions (highlighted in pink in Fig. 2**B**). Moreover, sAO help regenerating the pAO, thus improving the thermo-oxidative stability of the polymer melt [3]. For a deeper understating of the oxidation processes of polymer substrates and their stabilization with traditional antioxidants and protective agents, we divert the readers to previous works [17,41,43]. Commercially available antioxidants and

Table 1
Degradation processes occurring in polymers [38–40].

THERMAL	Induced by heat. Includes non-oxidative depolymerization, random chain scission, and side-group elimination. Recombination processes may lead to cross-linking or cyclization
LIGHT-INDUCED	Photolysis due to visible or UV light absorption by chemical bonds present on the polymer backbone. Main mechanisms are homolytic scission (Norrish I) and intramolecular hydrogen atom transfer (Norrish II). It can lead to cross-linking or molecular weight reduction
OXIDATIVE	Induced by the presence of atmospheric oxygen. Free radicals are formed which react with oxygen-producing oxy- and peroxy- radicals, resulting in chain scission. It could be accelerated by heat (thermal oxidation) and light (photo-oxidation)
HYDROLYTIC	Hydrolysis takes place in the presence of water. Carbonyl-containing polymers, such as polyesters, polyamides and polycarbonates, can be degradedy yielding lower molecular weight oligomers. Acid and basic species accelerate degradation
BIODEGRADATION	Degradation produced by the action of naturally occurring microorganisms such as bacteria, fungi, and algae, resulting in lower molecular weight fragments. Depending on the environment, biodegradation can take place under anaerobic or aerobic conditions

protective agents for industrial polymer formulations are mostly oil-based synthetic compounds [1]. However, in the last decades environmental and health concerns [44,45] have pushed industrial and academic research towards the substitution of traditional stabilizers with their bio-based counterparts.

In the following, a survey of bio-based melt stabilizers and antioxidants used in the formulation of both oil-derived and green polymers is provided. There are two main sections: the first describes the melt stabilizers and antioxidants directly derived from plants and bio-waste (bio-based), while the second refers to compounds of natural origin additionally subjected to chemical modification (chemically modified). A further subdivision is offered on the basis of the different classes of polymers in which these additives are incorporated (for example polyolefins, biodegradable and natural polymers).

2.1. Bio-based melt stabilizers and antioxidants

Antioxidant compounds derived from plant materials have been widely studied [46,47] and recent discoveries prove that they can be efficiently employed as suitable additives in the food sector to prevent quick decay of foods and beverages and to extend their storage, and in the pharmaceutical sector to scavenge free radicals and prevent tissue lipid oxidation [48–51]. Moreover, natural antioxidants have been considered as suitable stabilizing systems also for polymer materials. Among them, natural polyphenols, vitamins, and carotenoids are effective to protect macromolecules against thermal and oxidative degradation taking place during both manufacturing and service life [52,53].

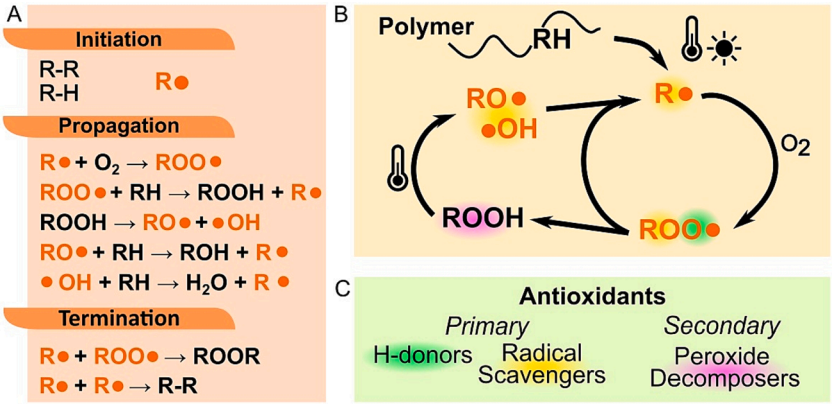


Fig. 2. (A) Basic steps of thermal- and photo-oxidation processes including initiation, propagation and termination steps, (B) thermal- and photo-oxidation cycle, and (C) classification and action mechanism (color-coded) of pAO and sAO. Adapted from [1].

2.1.1. Bio-based melt stabilizers and antioxidants for polyolefins

Polyolefins are the most abundant class of commodity thermoplastics, whose market size is estimated to reach around $270 billion by 2025, after growing at a CAGR of 6.5% during 2020–2025 [54]. Polyolefins' chemical and biological inertness and high stability make them suitable for many applications ranging from packaging and toys to appliances and disposable items. However, these materials are not exempt from degradation during processing or exposure to weathering [55,56]. Poly(ethylene) (PE), poly(propylene) (PP) and PVC are the most widespread oil-based plastic materials. Therefore, the most extensive research on bio-based additives to date has been carried out on them. One of the first examples of inclusion of natural antioxidants into synthetic polymers was reported by Mar'in et al. in 1992, who studied the effect of gossypol, a polyphenolic component of cotton-seed oil, on the oxidation retardation of PE, PP, as well as polyamide-12 (PA12) [57,58]. It was noticed that the oxygen consumption rate was lower for low gossypol concentrations, while the antioxidant efficiency was higher for PE, and lower for PA12. Following this pioneering work, a more systematic study was undertaken by Al-Malaika et al. in a series of articles published starting from 1994. They deeply investigated the antioxidant role of α-tocopherol, a phenolic constituent of vitamin E, and its behaviour and transformations during polymer processing. The authors also proposed a plausible mechanism for melt stabilization of polyolefins [59–61].

These studies *de facto* opened the pathway to future research on the stabilization of polymers with natural compounds. α-tocopherol, which is mainly extracted from olive and sunflower oils [62], is certainly the most studied natural antioxidant for polymers. Peltzer et al [63] found that a concentration of 0.3% by weight of α-tocopherol in ultra-high molecular weight poly (ethylene) (UHMWPE) had the same stabilizing efficiency of synthetic antioxidants, such as Irganox 1076. In 2010 Koontz et al [64] evaluated the performances of linear low-density poly(ethylene) (LLDPE) compounded with α-tocopherol, quercetin and their cyclodextrin inclusion complexes. Quercetin is a flavonol present in several fruits and vegetables [65]. All antioxidant additives, in particular quercetin, increased the oxidative stability of LLDPE, as indicated by Oxidation Induction Time (OIT) values. The antioxidant efficiency of quercetin was explained considering that, unlike most flavonoids, one quercetin molecule can react with two radicals [66]. Further studies on the effect of quercetin on melt stabilization of PE were conducted by Pukanszky et al. [67]. It was shown that quercetin hindered chain branching caused by the thermally induced reactions with alkyl radicals. In this respect, the efficiency of quercetin was considerably larger than that of Irganox 1010, the hindered phenolic antioxidant used as reference stabilizer (Fig. 3**A**). Moreover, quercetin acted also as an effective antioxidant. Notably, when the secondary stabilizer Sandostab PEPQ (PEPQ) was also included, OIT values of quercetin were even higher (Fig. 3**B**).

Quercetin was also found to be more effective in the long-term stabilization of PP against both thermal and photo-oxidation [68], in comparison with several other phenolic compounds including chrysin (from passionfruit and acacia honey), hesperidin, naringin (from citrus fruits), and silibinin (from milk thistle). As an example, the addition of 2500 ppm silibinin in PP doubled the OIT at 210 °C, while the same amount of quercetin resulted in a ten-fold increase.

The antioxidant mechanism of quercetin was investigated by Amorati et al. [69], and two possible reaction pathways were hypothesized (Fig. 3**C**). Path A involves an electron–proton transfer (EPT) to peroxyl radicals from the catechol moiety, while Path B relies on the sequential proton loss electron transfer (SPLET = PT/ET) to water/peroxyl radicals.

The effect of other flavonoids, including rutin (from citrus plants), dihydromyricetin (from some Pinus and Cedrus species), and curcumin (from turmeric) on the thermal and oxidative stability of PE was also investigated by the group of Pukánski [70–74]. All the tested flavonoids were very efficient processing stabilizers, as they protected the polymer against degradation at contents as low as 100 ppm. In particular, the effect of rutin was comparable to that of quercetin, albeit the former partially decomposed during processing. On the other hand, at small concentrations, dihydromyricetin was even more efficient as melt stabilizer than quercetin [75]. Other flavonoids like silymarin [76] were found to be not only good natural stabilizing additives for polymers, but also natural color indicators of polymer ageing [77]. However, due to comparatively higher bond dissociation enthalpies, the stabilizing activity of silymarin was lower than that of quercetin [78]. Besides, it accelerated the depletion of the secondary stabilizer. A summary of the published results about the use of several polyphenols on the stabilization of polyolefins is provided in a recent review by Kirschweng et al., who discussed the advantages and drawbacks of this approach [79].

The interesting properties of flavonoids pushed polymer scientists to screen other herbal species with documented high content of these compounds. Interestingly, flavonoid-rich extracts of green and black tea [80] have been reported to show higher antioxidant capacity [81] than other plant extract (Lippia citriodora and Hypericum androsaemum), and their performances were even more outstanding when compared with synthetic antioxidants (Irganox 1076). Moreover, polymeric flavonoids, such as condensed tannins, have been used to successfully stabilize polymers. In particular, it was reported that condensed tannins extracted from *Pinus radiata*, larch and *Acacia mearnsii* improved thermal and UV stability of LLDPE, PP, biodegradable polyesters as well as poly(vinyl alcohol) (PVA) films [82–84]. Besides phenolic compounds, carotenoids can be used as stabilizers for polymers. Carotenoids are a class of natural pigments characterized by highly conjugated hydrocarbon backbones. Hundred species of carotenoids are available in nature, being β-carotene the most used in the field of polymers. A pioneering study on the effect of β-carotene as antioxidant for acrylonitrile–butadiene–styrene (ABS) was carried out by E.A. Abdel-Razik in 1989 [85]. Since then, other works dealt with the use of β-carotene and its effect on other polymers, such as PE. It was found that when employed in small amounts it acted as an antioxidant, while it worked as a pro-oxidant at high concentrations [75].

As already mentioned, besides PE and PP, PVC is one of the most employed polyolefins due to its high versatility, processability, and low costs. However, it suffers from poor thermal stability, as it experiences dehydrochlorination, oxidation, bond cleavage, as well as cross-linking and condensation reactions during processing and service life. For these reasons PVC must be compounded with suitable thermal stabilizers [86]. The heat stabilizers prevent degradation of PVC compounds by neutralizing hydrogen chloride, replacing weakened carbon-chlorine bonds and preventing oxidation. Typically, combinations of calcium, barium, cadmium and zinc organic salts are employed. Moreover, organotin and lead compounds, alkyl/aryl phosphites, as well as epoxy compounds are also used [87].

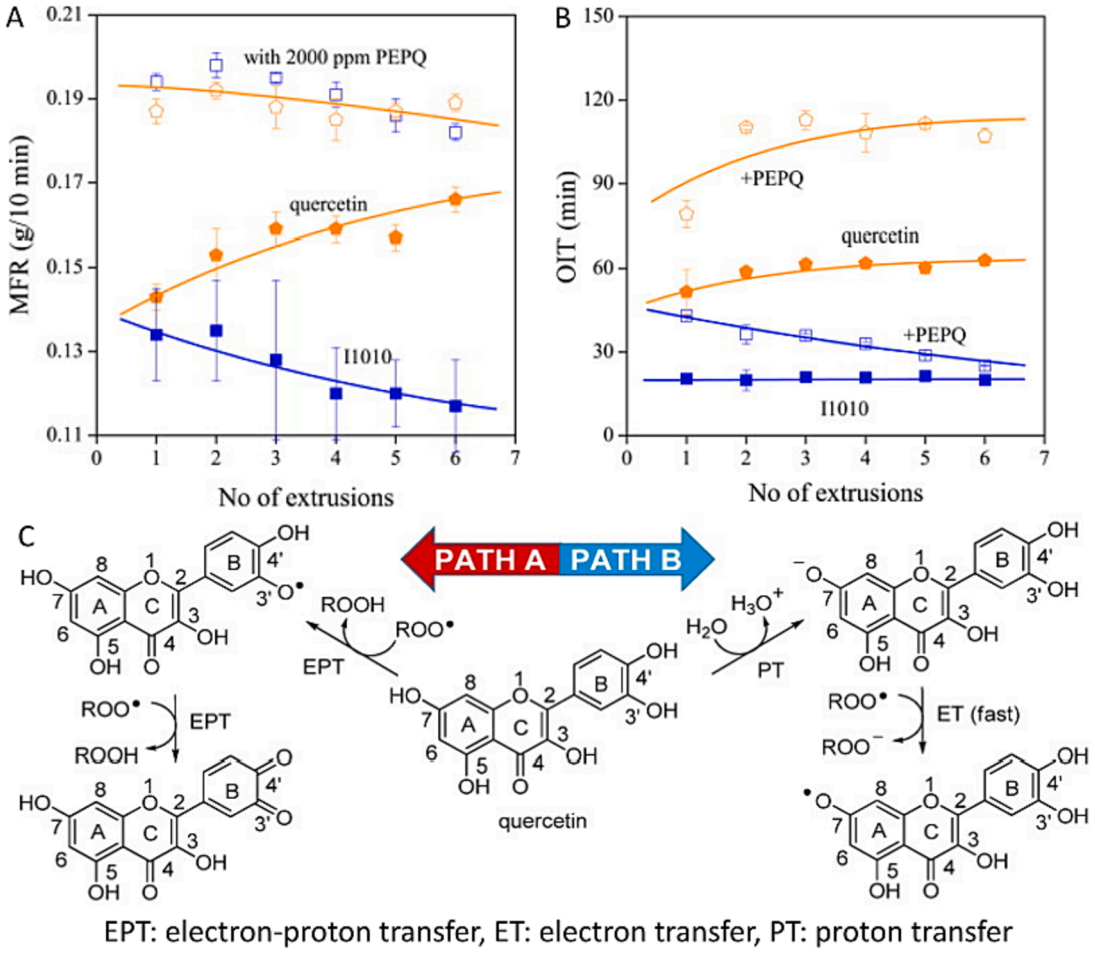


Fig. 3. (A) Change in melt flow rate (MFR), and (B) OIT as a function of the number of consecutive extrusions for PE containing 1000 ppm quercetin or Irganox 1010, or their binary mixtures with 200 ppm PEPQ, reproduced with permission from [67]; (C) Two possible reaction pathways of the action of quercetin in water, reproduced with permission from Amorati et al. [69].

However, in recent years the research has been focused on new, more sustainable additives for thermal stabilization of PVC. In their works, Hussein et al. described the synthesis and characterization of new tannin-based compounds, which were used as HCl and free radicals scavengers or as co-stabilizers in PVC products [88–90]. More recently, the stabilizing effect of rare earth complexes with curcumin on the processing of PVC was reported. It was demonstrated that for some formulations the dehydrochlorination and oxidative degradation of double bonds were inhibited due to the coordination of rare earth with Cl and unsaturation on PVC chains [91]. In another work, a combination of calcium (Ca) and zinc (Zn) salts of polycarboxylic acid derived from tung oil fatty acids was prepared and successfully tested as thermal stabilizer for PVC [92].

Light stabilizers and antioxidants are essential also for improving the weathering performances of coatings. These latter are usually acrylic based polymers and are stabilized using additives against oxidation and UV aging phenomena. Among them, benzotriazole, benzophenone and salicylate, hindered phenols (i.e commercial Irganox series), and Hindered Amine Light Stabilizers (HALS) are the most employed. However, most of these compounds can pose significant health concerns to humans [93]. Therefore, in the last years greener and safer UV-stabilizers and antioxidants have been proposed also for coatings [94,95]. Tannin-based additives are the most suitable candidates, as demonstrated by the recent literature [96–99].

A more sustainable approach to polymer stabilizers consists in the recovery of antioxidants and protective agents from agri-food industrial waste and from non-food crops and sources [100]. For example, Peltzer et al. [101] demonstrated that PP could be efficiently stabilized against thermal and thermo-oxidative degradation by hydroxytyrosol (3,4-dihydroxyphenylethanol), extracted from the solid by-product obtained during olive oil processing. Another by-product which has become an excellent source of natural antioxidants is lignin, the second most abundant natural polymer on earth after cellulose [102], predominantly obtained as waste material from paper production. Lignins vary in their chemical and physical properties depending on isolation methods and plant origin [103]. In order to be used as antioxidant, lignin must meet a few criteria, such as a relatively low molecular weight and a narrow molecular polydispersity [102]. Gregorová et al. [104] reported that the antioxidant protection of PP increased with lignin concentration up to 5 wt%. Moreover, the mixture of lignin and Irganox 1010 exhibited the highest antioxidant efficiency in both recycled and

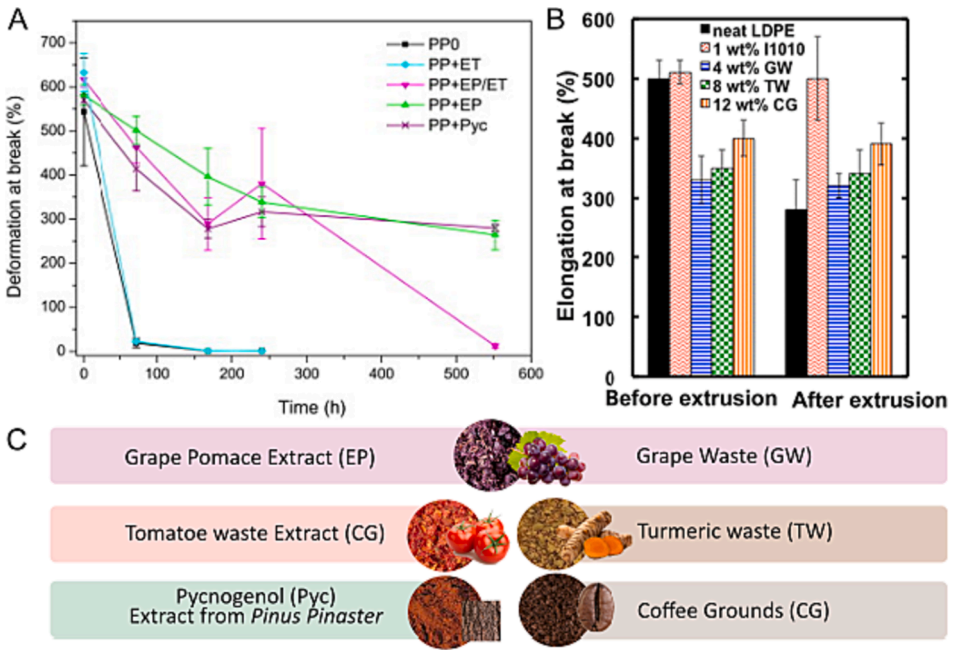


Fig. 4. (A) Deformation at break of PP loaded with different agro-waste extract, reproduced with permission from Ambrogi et al. [108]; (B) Elongation at break of LDPE loaded with different agro-waste residues, reproduced with permission from Iyer et al. [110]; (C) List of the different agro-waste antioxidants employed in the two works.

pristine PP. It was demonstrated that the use of lignin as filler can also increase the resistance toward thermo-oxidative degradation of natural rubber compounds [105] and vulcanized natural rubber [106]. Cork, another antioxidant-rich material obtained from tree bark, can also be recovered as by-product of the preparation of stoppers. Aroso et al. [107] have successfully used cork extracts, rich in suberin and lignin, as additives for the stabilization of PP. The protective effect was attributed to the ethanol soluble fraction present in the cork extractives. In a similar approach, Ambrogi et al. [108] employed Pycnogenol®, a water extract of French maritime pine bark, as stabilizer for PP. A significant increase in thermal degradation resistance was observed, although the non-homogeneous dispersion of the additive had a detrimental effect on the mechanical performance. The same group investigated other by-products of agri-food industry, among which red grape seeds [109] and red grape seed extract [108] were found effective promoters of the long-term stability of PP. In the same vein, Iyer et al. not only confirmed the positive performance of grape pomace waste as protective agent for low-density poly(ethylene) (LDPE) but also explored other antioxidant-rich agro-wastes. Grape pomace waste, turmeric shavings and waste, coffee grounds, and orange peel waste were used as-received as thermal-stabilizers for pristine and recycled LDPE [110]. The importance of this work relies in the use of raw materials which, without chemical treatment or extraction (with virtually zero expenses and zero CO_2 emission), can be transformed from waste to high-value commercial products. Ambrogi [108] and Iyer [110] evaluated how agro-waste extracts were able to preserve their effect over hours of aging and several reprocessing steps, respectively. In the first case, it was shown that PP containing Pycnogenol® and grape pomace extract samples exhibited deformation at break values up to 300% even after 552 h of oven aging (Fig. 4**A**), suggesting that these additives had effective long-term antioxidant activity. In the second report, Iyer et al. (Fig. 4**B**) found that after ten extrusion cycles LDPE containing antioxidant food wastes showed almost unchanged elongation at break values. Moreover, the elongation at break values for the LDPE/agro-waste hybrids were similar or higher than those of neat LDPE after the same treatment.

In a different study [94] spent coffee grounds have been treated with 6 M HCl. The resulting all-natural, biocompatible material successfully stabilized PE films from thermal and photo-oxidative degradation. Other groups have focused their research on high-volume agri-food by-products, such as hazelnut and cocoa kernels [111]. Results demonstrated that these extracts acted as antioxidant for PP, and showed plasticizing and reinforcement effects on the polymer matrix.

2.1.2. Bio-based melt stabilizers and antioxidants for biodegradable and natural polymers

Although polyolefins still represent the most widely employed polymer materials, in the latest years an ever-growing use of bio-based and/or biodegradable polymers has been recorded [13–15,112]. Among the most commercialized ones, poly(lactic acid) (PLA) has certainly emerged as a competitive and more sustainable alternative to its oil-based non-biodegradable counterparts in many applications such as packaging, textile, electronics and additive manufacturing [11,14]. The PLA market is projected to reach USD 1,756 million by 2025, recording a CAGR of 17.4% in terms of value [113].

Compounding of natural antioxidants with PLA and other bio-based polymers represents a challenging approach towards manufacturing of wholly bio-based polymer formulations [114–116]. In the case of PLA, phenol derivatives are typically used to enhance its oxidative stability [117,118]. Agustin-Salazar et al. [119] have reported an increased thermal and photo-oxidative stability

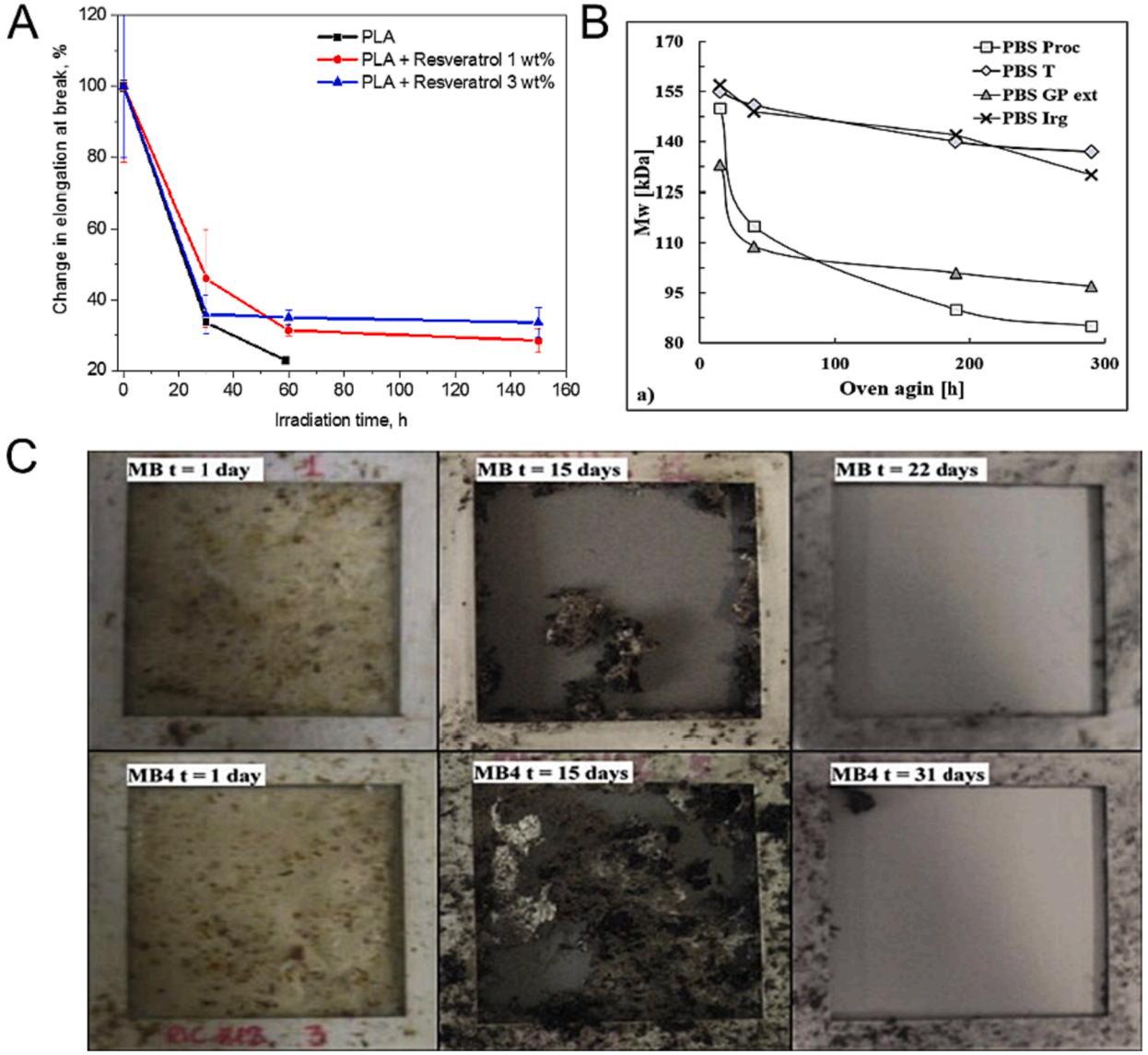


Fig. 5. (A) Percent relative changes of elongation at break of PLA films containing 1 and 3 wt% resveratrol as a function of the UV-irradiation time, reproduced with permission in an adapted form from Agustin-Salazar et al. [119]; (B) Molecular weight change of PBS-samples modified with grape pomace extract (GPext), grape seed extract (T), and Irganox 1010 as a function of oven aging time, reproduced with permission from Nanni et al. [126]: (C) Evolution of biodisintegration of MB, neat and containing 4 wt% of a winery bio-waste extract, buried under solid composting material, reproduced with permission from Cerruti et al. [135].

of PLA compounded with resveratrol (Fig. 5**A**), a naturally occurring stilbenoid commonly associated with the antioxidant potential of berries, peanuts, red wine, and grapes [120].

The effectiveness of resveratrol as protective agent relies on its ability to trap highly reactive oxygen radicals as well as on its UV screening effect. Analogously to other polymers, also in the case of PLA lignin derivatives are widely employed to enhance thermal, oxidative and UV-stability [121–123]. In their work, Park et al. fractionated lignin with different organic solvents and used some of them to develop novel lignin-grafted poly-L-lactide (PLLA) copolymers. Experimental results showed that lignin moieties in co-polymers were able to enhance UV-stability as well as tensile modulus with respect to neat PLA [124].

Other biodegradable polyesters are those including succinic acid derivatives. Due to its semi-crystalline nature, thermal stability and good processability, poly(butylene succinate) (PBS) is a promising alternative to polyolefins, especially in the field of flexible packaging applications [125]. However, despite its good tensile strength PBS suffers from a moderate oxidative resistance, thus requiring proper additives to improve its long-term stability. In this respect, naturally occurring polyphenols have been successfully used to protect PBS-based formulations [82]. Nanni et al. [126] carried out a thorough investigation on the effect of a grape seed commercial extract on PBS stabilization through oven aging and thermo-mechanical reprocessing. Interestingly, the additive helped to

preserve the molecular weight of PBS subjected to six reprocessing steps or 300 h of oven aging (Fig. 5**B**). In another work [127], a series of ferulic acid-based polyphenols were synthesized by Reano et al. and used as antioxidants for PBS. OIT and Fourier-transform infrared spectroscopy (FTIR) studies demonstrated that tris-o-dihydroferuloyl glycerol (GTF) was even more efficient than commercial Irganox 1010 for the thermo-oxidative stabilization of PBS. Polyphenol derivatives were also used for the manufacturing of PBS biocomposites. In particular, hydrotalcites intercalated with Olive Mill Wastewater (OMW) were prepared and melt blended with PBS [128]. The results demonstrated that all the OMW-modified layered double hydroxides (LDH) were effective in enhancing the thermal and oxidative stability of the polymer matrix. Moreover, the used biowaste did not require any pre-treatment, making this approach cost-effective and sustainable.

Another relevant study on the use of biowaste as multifunctional additive for PBS was recently published by Domínguez-Robles et al., who successfully prepared lignin/PBS composites exhibiting antimicrobial and antioxidant properties. Notably, a reduction of 2,2-diphenyl-1-picrylhydroxyl (DPPH) concentration up to 80% in less than 5 h was observed. Moreover, a remarkable antibiofilm activity against the nosocomial pathogen *Staphylococcus aureus* was demonstrated, as bacterial adhesion was reduced by 90% compared to pristine PBS [129].

The above-mentioned biodegradable polymers are typically obtained through synthetic processes based on the use of oil- or bio-based monomers. Other biodegradable polymers are produced by plants, animals and microorganisms [14]. These polymers can be successfully employed as commodity products due to their renewability and biodegradability combined with good processing and mechanical properties. Among them, poly(hydroxyalkanoate)s (PHAs) and polysaccharides are the most representative ones.

PHAs are a class of polyesters obtained from microbial fermentation. They are biodegradable in various environments including sea water [19]. Due to their thermal processability and biocompatibility, PHAs have found applications in many fields, ranging from packaging to biomedical [15,16]. In order to improve the polymer oxidative stability polyphenolic compounds have been added to PHA. In their work, Masek et al. compounded rutin and hesperidin with poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3,4HB)), a copolymer belonging to the family of PHAs. Both flavonoid derivatives efficiently increased the oxidative stability of P(3,4HB). Interestingly, the progress of the oxidation could be monitored through the color change caused by the reaction between hydroxyl groups of the additives and the macromolecular chains [130]. In a more recent paper, with the aim of getting further insights on the effect of natural stabilizing agents on green polymer formulations, the same authors studied the effect of different natural antioxidants, namely flavone, *trans*-chalcone and lignin, against solar aging and thermal oxidation of a PLA/P(3,4HB) blend [131]. It was demonstrated that all the natural additives were able to retard the oxidative degradation. Moreover, while lignin and *trans*-chalcone caused a color change upon aging, potentially acting as aging indicators, flavone prevented discoloration, thus being a good candidate as yellowing retardant. Another interesting class of natural antioxidants for PHAs is represented by tannins and their derivatives [132,133]. In their work, Grisby et al. [82,134] used different tannin esters of varying ester chain length as stabilizing agents for PHAs and other biodegradable polyesters. Through color analysis tests they were able to demonstrate that the additives inhibited UV penetration in the bulk polymer, acting as sacrificial agents. The effect was enhanced using tannin esters with longer chain due to their higher compatibility with the polymer matrix.

Polysaccharides are made of carbohydrate monomer units linked together by O-glycosidic bonds. The most abundant polysaccharides are cellulose, starch, and chitin [11] Polysaccharides have been employed in several applications ranging from packaging to biomedical, depending on monosaccharide composition, degree of polymerization, linkage nature. Starch is the most used in the field of food packaging. The properties of this polymer can be controlled by the addition of properly selected natural compounds. In their work, Cerruti et al. used winery bio-waste polyphenolic extract to tailor the properties of a starch-based polymer (Mater-Bi®, MB). It was found that the additive retarded crosslinking, which occurred upon thermo-oxidative aging. The extract also acted as processing aid decreasing melt viscosity and slowed down bio-disintegration rate of MB films (Fig. 5**C**) [135].

In another study, MB was compounded with α-tocopherol and quercetin and its photooxidation behavior was compared with the polymer modified with a synthetic antioxidant and a light stabilizer [136]. The results inferred from mechanical tests and spectroscopic analysis carried out on samples aged at different times showed that quercetin was able to protect the MB films against thermal and photo-oxidative degradation. The additive hindered the hydrogen abstraction from polymer chains and inhibited the formation of the photooxidation products.

Only few examples on the addition of natural antioxidants/stabilizers to cellulose-based systems are reported in literature [137,138]. In these papers, organosolv lignins were incorporated in carboxymethyl- and nitro-cellulose matrices, acting as effective thermal stabilizers.

2.2. Chemically modified melt stabilizers and antioxidants

One of the pillars of “green” innovation in the field of polymer additives is the use of bio-based building blocks for the design of sustainable and performing compounds, exploiting the benefits of plentiful, renewable feedstocks while magnifying their intrinsic value *via* chemical modification [139,140]. For example, even though p-hydroxycinnamic acids (p-coumaric acid, ferulic acid, and sinapic acid) and their esters possess a very interesting antioxidant activity [141,142], their use as antioxidant additives in a polymer is relatively restricted due to their low thermal stability and leaching issues from polymer matrix. Reano et al. [143] synthesized a series of p-hydroxycinnamic acid-based bis- and triphenols and evaluated their antioxidant activity in comparison with commercial compound Irganox 1010. Interestingly, the novel compounds displayed a comparable antiradical activity and a decreased tendency to leach, with the main advantage of being 100% bio-based and prepared by an eco-friendly, chemo-enzymatic pathway. The same group reported a facile biocatalytic access to obtain linear polyphenolic polymers with bisguaiacol-type moieties with promising antioxidant properties [144]. Caffeic acid methyl ester, another member of the family of hydroxycinnamic acids, modified with horseradish

peroxidase via oxidative polymerization, was also used as stabilizer for PE [145]. Evidence suggested that this novel bio-inspired phenolic polymer possesses antioxidant activity, primarily scavenging high reactive oxygen radicals and repairing free radical damage to LLDPE by efficient H-atom transfer (Fig. 6**A**).

Scientists have also been inspired by our very own skin protective agent, melanin. There is growing evidence to suggest that cellular melanin displays an antioxidant activity in the body. Indeed, melanin is able to scavenge free radicals, deactivate electronically excited oxidizing species, sequester redox active metal ions, such as iron and copper, and scavenge intermediate radicals, such as peroxyl and alkoxyl [146]. Shanmuganathan et al. [147] investigated the stabilizing effect of natural and synthetic melanin against thermo-oxidation of different commercial polymers. Their findings show that synthetic, and in lesser extent natural melanin provide good stabilization to poly(methyl methacrylate) (PMMA).

One of the main drawbacks related to the incorporation in polyolefins of natural compounds, especially polyphenols, is their poor compatibility due to the highly hydrophilic groups in the hydrophobic polymer matrix. Synthetic approaches to overcome this problem consist in chemical modification of the additive, such as esterification and etherification [148–151], butylation [152] or the introduction of block or graft co-polymers to enhance the interfacial compatibility between the additive and the polymer matrix [83]. An interesting approach was proposed by Xin et al. [153] to improve the dispersion of gallic acid, a powerful antioxidant [154], in PP. The synthesized gallate derivatives, bearing alkyl chains of different length, were found to have an improved compatibility with the PP matrix, preventing physical loss and enhancing the polymer stability (Fig. 6**B**). Pasanphan et al. [155] have reported on the modification of chitosan, an extract of crustaceans' shells, with deoxycholic acid and gallic acid, and use of the bio-derived compound as antioxidant for LDPE. The additive exhibited good radical scavenging activity as well as good compatibility with the polymer matrix, opening the way to the research on polyphenol-chitosan conjugates [156]. In another work, Rodrigues et al. synthesized poly (β-pinene) through controlled polymerization, and blended it with chitosan to develop antimicrobial and antioxidant bio-based films [157].

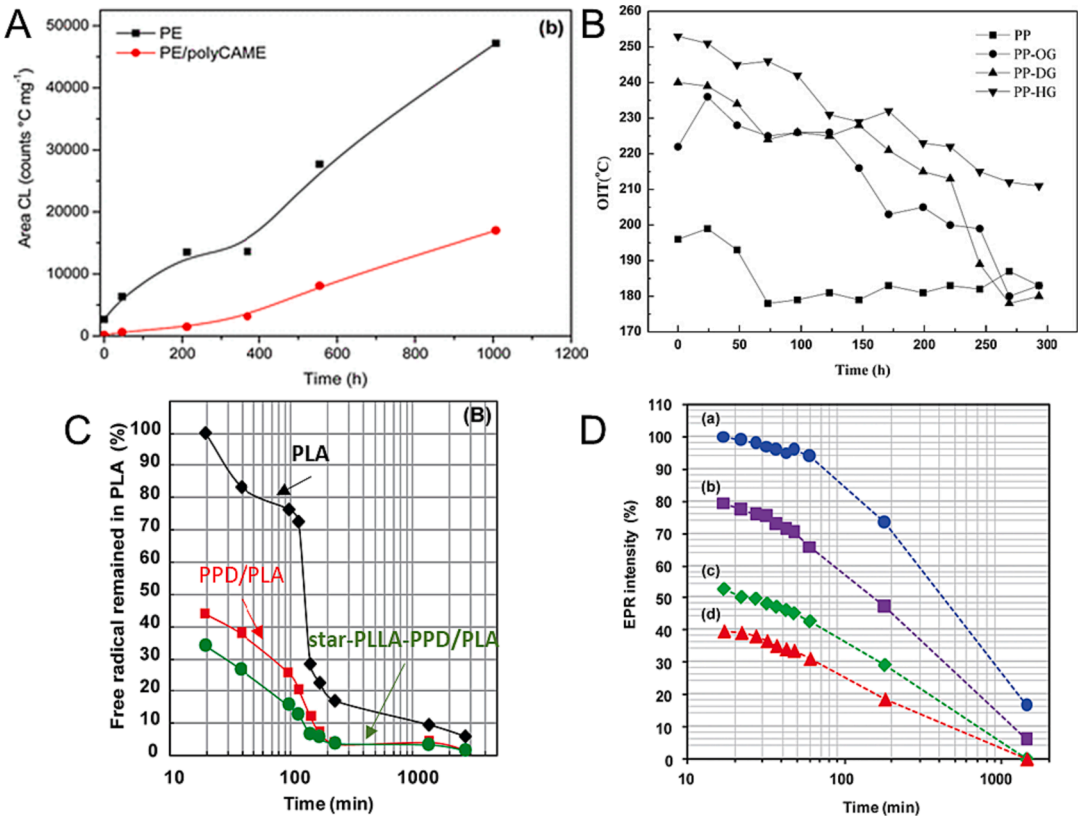


Fig. 6. (A) Evolution of the area under the chemiluminescence (CL) emission curve (corresponding to the relative concentration of peroxides accumulated at different irradiation times), of PE and its blend with a biocompatible phenolic polymer of caffeic acid methyl ester (polyCAME) PE/polyCAME, reprinted with permission from Ambrogi et al. [145]; (B) OIT of PP, PP-octyl gallate (PP-OG), PP- dodecyl gallate (PP-DG), and PP-hexadecyl gallate (PP-HG), at increased aging times, reproduced with permission from Xin et al. [153]; (C) percentages of the remaining free radicals of neat PLA, PPD/PLA and star-PLLA-PPD/PLA after different post-irradiation times (irradiation dose of 10 kGy), reproduced with permission from Haema et al. [160]; (D) Electron paramagnetic resonance intensities of PLA free radicals in neat PLA (a), PLA blended with 2 wt% of chitosan (b), PLA blended with 2 wt% of stearylate chitosan—PPD NPs (SMA-CS0-PPD) (c), and PLA blended with 2 wt% of irradiated stearylate chitosan—PPD NPs (SMA-CS40-PPD) (d), reproduced with permission from Rattanawongwiboon et al. [161]

A further interesting approach is based on the use of polymers chemically modified with naturally derived molecular units exhibiting antioxidant activity, to develop intrinsically active, bio-based materials. This strategy has been undertaken for both PLA and acrylic polymers, and it was found to be effective in protecting polymers against oxidative aging [158,159]. An example has been reported by Haema et al., who synthesized a 4-arm star-shaped PLA conjugated with a piperidine substituent, which was proposed as a PLA-based antioxidant additive for PLA bioplastics (Fig. 6**C**) [160]. The same piperidine stabilizer has been also grafted to stearyl-modified chitosan (SMA-CS) nanoparticles (NPs), and the resulting product showed good compatibility with PLA, while efficiently scavenged free radicals produced in the PLA blend upon gamma-ray irradiation (Fig. 6**D**) [161].

Data concerning the most significant bio-based and bio-synthetic additives discussed in this chapter are summarized in Table 2. To guide the reader in the selection of bio-based melt-stabilizers and antioxidants, for each bio-active molecule its chemical structure, its source (which vegetal it is extracted from) and its use in polymeric formulation are reported.

3. Plasticizers

The council of the International Union of Pure and Applied Chemistry (IUPAC) defined a plasticizer as "a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility'' [162].

Plasticizers can be classified as internal or external, see Fig. 7**A** [163]. The principle of internal plasticization relies on the copolymerization with monomers able to lower polymer glass transition temperature. The soft segments can be included either in the main chain or as side groups. Being chemically bonded, the rigid and the flexible segments cannot be separated, avoiding the release of plasticizer. However, the technique is usually limited, as flexibility and dimensional stability are strongly dependent on temperatures, and occasionally the use of external plasticizer is also required.

External plasticizers are non-volatile compounds physically added to the polymer matrix. Their use represents the most frequent plasticizing method. The additive amount can be regulated to achieve the proper flexibility, and virtually there is no upper limit to its uptake. The main concern is related to the loss of the additive from the plasticized material by migration, evaporation, or extraction phenomena. Loss of plasticizer can lead to reduced flexibility, embrittlement, and cracking [164,165].

There are numerous cases of polymer matrices requiring the use of plasticizing additives. This is mostly the case of PVC, but also of other petro-derived polymers, such as polyolefins, polyacrylates and polyamides. Therefore, the variety of plasticizers is huge, as they can range from low- to high- molecular weight systems, with specific chemical composition.

In the case of PVC, the most widely used external plasticizers mainly consist of phthalate esters, aliphatic dibasic acid esters, benzoate esters, trimellitate esters and citrates [166,167]. In particular, di(2-ethylhexyl)phthalate (DEHP), also known as dioctyl phthalate (DOP), was introduced in 1930, and has been since then the most widely used plasticizer worldwide. However, in the early 1980 s, concerns have been raised regarding the use DOP and phthalates, due to the strong tendence to migrate outside the polymer matrix combined to their high toxicity to humans and environment [168,169]. These concerns have pushed governments to impose new and restrictive regulations regarding the use of phthalates in flexible PVC products [170–172]. In addition, alternative plasticizers and mixtures with low migration levels and toxicity have been widely used in the last decades to overcome these problems [173]. Among them, fatty acid esters, benzoates, tartrates and chlorinated hydrocarbons, esters of citric, adipic, azelaic and sebacic acid have been employed [20,167]. Although these additives have lower impact on environment and human health, additive migration is still a challenge.

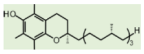
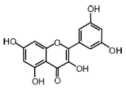
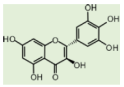
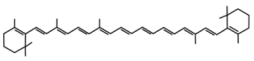
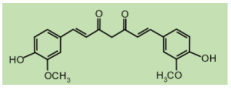
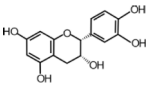
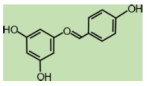
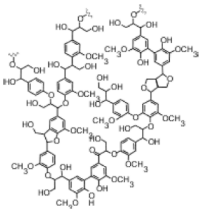
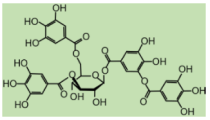
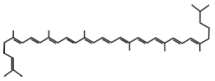
A different approach to address this issue is based on blending PVC with polymeric plasticizers, including biopolymers such as poly (caprolactone) (PCL), poly(1,3-butyleneglycol adipate) (PBGA) In particular, hyperbranched polymers can exhibit lower values of migration in comparison with the linear homologues, as demonstrated in the case of poly(butylene adipate) (PBA) [174].

3.1. Bio-based plasticizers

As the bio-based plastic market expands, the demand for environmentally friendly plasticizers is becoming increasingly higher. Bio-based plasticizers provide the dual advantage of being effective alternatives to phthalates, as well as limiting the use of oil-based feedstock [33,175]. In a comprehensive review, Bocqué et al. described a huge number of plasticizers that can be obtained from agricultural biomasses and their wastes [176]. Several of these bio-plasticizers are available on the market, being the epoxidized oils from different sources (including coconut, sunflower, castor, linseed and soybean oils) the most adopted [177,178]. Moreover, bio-based esters, such as sebacates, adipates, succinates and citrates, as well as other naturally occurring low-molecular weight compounds, such as glycerol, sugars, cardanol and even water, are regarded as suitable substitutes for traditional plasticizers. This holds true in particular in toys, food packaging, medical devices, and personal care products, as phthalates are banned by different government in these commodities. Global bio-plasticizers market is expected to reach an estimated $ 2.4 billion by 2026 with a CAGR of 10% from 2020 to 2026 [179]. So far, high pricing of bio plasticizers has limited their market diffusion. However, continuous innovation in bio-based compounds is projected to favor the growth of the bio plasticizers market.

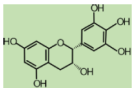
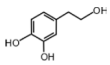
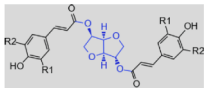
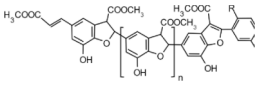
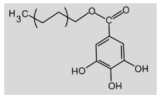
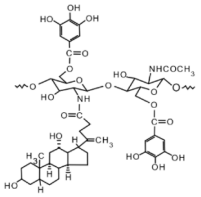
Water is the most common example of a ready-to-use plasticizer for biopolymers, and its application has been widely reported in the literature [180]. Its plasticizing effect is based on its ability to increase the free volume reducing T_g especially in the case of hydrophilic biopolymers [181], such as polysaccharides and proteins [182]. Water was also proved to impart a synergic effect in the plasticizing activity of a bio-based additive on hydrophobic biopolymers [183]. In this respect [184], it was observed that the presence of absorbed water in the 50% RH-conditioned poly(hydroxybutyrate) (PHB) samples further enhanced the plasticizing activity of pomace extract, a bio-waste of winery industry.

Table 2
Summary of mentioned bio-based melt stabilizers and antioxidants from plant and bio-waste (name, chemical composition, chemical structure, natural derivation and polymer formulation composition as reported in literature) or bio-synthetic melt stabilizers and antioxidants (description of the chemical modification, chemical structure and polymer formulation composition as reported in literature).

Bio-based melt stabilizers and antioxidants from plants and bio-waste			
Compound name and structure		Source	Formulation in polymer
α-tocopherol (vitamin E)		Weat germ oil Sunflower oil	0,3 wt% in UHMWPE [63] 0,28 wt% in LLDPE [64] 0,1–0,5 wt% in MB [134]
Quercetin (flavonol)		Radish Red onion Radicchio	0,20 wt% in LLDPE [64] 0,25 wt% in PP [68] 0,025 wt% in PE [71] 0,1–0,5 wt% in MB [133]
Dihydromyricetin (flavanonol)		Hovenia dulcis Pinus/Cedrus species	0,05 wt% in PE [74]
β-carotene (terpenoids)		Carrots Pumpkin	0,1 wt% in PE [75]
Curcumin (phenol)		Turmeric	up to 0.1 wt% in PE [73]
Pycnogenol®		French maritime pine bark	1 wt% in PP [108]
Resveratrol (stilbenoid)		Berries Grapes Peanuts	3 wt% in PLA [119]
Lignin (phenolic polymer)		Paper processing by-product	5 wt% in PP [104] 13 wt% in Rubber [105]
Cork extract		Stoppers production by-product	1,5 wt% in PP [107]
Red grape seed extract (tannins)		Winery industry waste	1 wt% in PP [108,109] 4 wt% in LDPE [110] 1 phr in PBS [126]
Tomato waste extract (lycopene)		Tomato industry by-products	1 wt% in PP [108]

(*continued on next page*)

Table 2 (*continued*)

Bio-based melt stabilizers and antioxidants from plants and bio-waste			
Compound name and structure	Source		Formulation in polymer
Spent coffee grounds (gallocathechin) 	Coffee by-products		12 wt% in LDPE [110]
Hydroxytyrosol 	Olive processing solid by-product		0,1 wt% in PP [101]
Black/green tea extract (Various compounds)	Tea extract		0,05 wt% in PP [81]
Chemically modified bio-based melt stabilizers and antioxidants			
Type of modification	Structure		Formulation in polymer
Bio-trisphenols derived from p-hydroxycinnamic acids and bio-based diols/triols			1 wt% in PE [143]
Caffeic acid methyl ester (family of hydrocycinnamic acids) modified with horseradish peroxidase			1 wt% in PE [145]
Gallate derivatives (octyl, dodecyl and hexadecyl gallate)			0,4 wt% in PP [153]
Modification of chitosan with deoxycholic acid and gallic acid			2 wt% in LDPE [155]

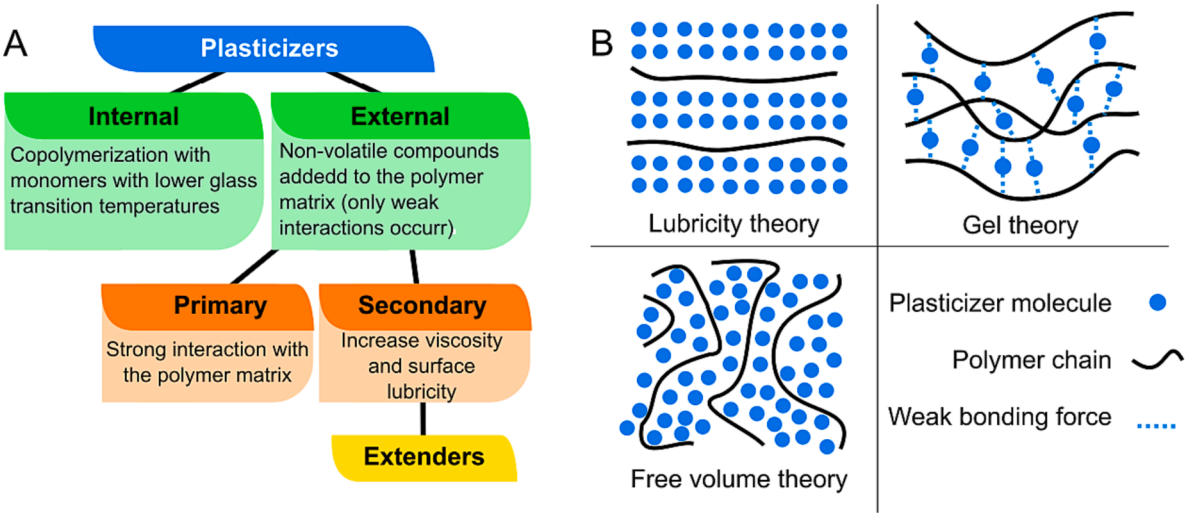


Fig. 7. (A) Classification of plasticizers, and (B) depiction of three theories regarding the mechanism of plasticization.

Glycerol is the second most common plasticizers for bio-based and biodegradable polymers, including whey protein [185], and polysaccharides, such as chitosan [186], and starch [187]. Even if glycerol is typically fossil-sourced, its production as a derivative of bio-refinery processes is preferable [188]. In the following, further details on other bio-based plasticizers produced from vegetable oils, cardanol, and sugars are provided.

3.1.1. Biobased plasticizers from vegetable oils

Vegetable oil derivatives are the most widely used natural product type plasticizers. They have the advantage of being readily available, environment friendly, non-toxic, biodegradable and cheap [189]. They are composed of different triacylglycerols, esters of glycerol and fatty acids that vary depending on crop and growing conditions [190]. The properties of vegetable oils mainly depend on the chemical structure of fatty acids, i.e. the number and position of double bonds, and the chain length. Usually, the latter is between C12 and C20, with oleic acid (C18 and 1 double bond), linoleic acid (C18 and 2 double bonds) and linolenic acid (C18 and 3 double bonds) being the most common [21,191]. Vegetable oils used as plasticizers may contain different fatty acid units bonded to glycerol, characterized by different lengths and variable number of double bonds. As an example, soybean oil has roughly 4.5 double bonds per molecule [192,193]. Thanks to their unsaturated chains, fatty acids have the ability to intercalate between the host polymer chains, improving their mobility. On the other hand, ester groups can effectively interact with the polymer functional sites, enhancing the mutual compatibility with the matrix. Moreover, the presence of carboxylic groups and double bonds in the fatty acid residues make vegetable oils prone to be epoxidized, acetylated and esterified, leading to additives with enhanced plasticizing performances [194,195]. For these reasons, the use of modified vegetable oils has become a trending paradigm in both academic studies and industrial applications [196].

Epoxidation represents the most employed chemical modification route to vegetable oil-based plasticizers. Thanks to the incorporation of epoxy groups on the main chain, the additives are able to scavenge HCl formed upon thermal degradation of PVC [197,198], as well as to enhance their compatibility with the polymer, thus mitigating plasticizer migration [199]. Among them, epoxidized soybean oil (ESBO) is the most used bio-based plasticizer for PVC, especially in food contact applications, such as coatings, gaskets and wraps [200,201]. Along with other epoxidized oils, it has been tested also in other polymeric matrixes, such as PLA [202–205] and its composites [206,207]. New trends in the field involve the investigation of other vegetable oils, including jojoba [208], broccoli [209], cottonseed [210], sunflower [211,212], linseed [213], karanja [214], and olive oil [215–217]. Promising results have been obtained in the case of rice fatty acids derivatives, where polyesterification stands as the most successful technique for the synthesis of bio-based plasticizers, preferably with high molecular mass [218,219]. On the other hand, the use of low molecular mass compounds remains limited, owing to their low performance and high migration rates [220]. Recently, the effect of epoxidized cardoon oil as plasticizer for biodegradable film blends based on PLA and corn thermoplastic starch (TPS) has been evaluated, demonstrating that its incorporation also improved barrier properties and surface wettability [221].

Palm oil is also considered a good plasticizing agent, having been tested in both pristine [222] and epoxidized form [223–226] in PP, PVC and PLA matrices. Moreover, with a net zero carbon footprints and 30–40% less energy consumption, palm oil fronds have been proposed as biomass for the production of bio-succinic acid [227], a commonly used precursor for PVC plasticizers [228,229]. However, the sustainability of palm oil has been recently argued at a global level. Studies have shown that deforestation associating with palm oil production can result in significant secondary external impacts, such as air and water pollution, and soil erosion [230,231]. Even though a more responsible model for the use of this natural resource has been proposed [232], parallel research studies are investigating waste materials as a potential resource of plasticizers. Among them, cooking oils are mostly investigated [233–237].

A mechanism of action of vegetable oil based plasticizers was offered by Arrieta et al: [213] epoxidized linseed oil (ELO) was used in PVC together with triethylene glycol ester of gum rosin (TEGR) as natural viscosity increasing agent. As shown in Fig. 8**A and B**, the elastic modulus of the formulations was directly proportional to the TEGR content, and inversely with respect to ELO concentration. The higher mechanical resistance revealed by PVC-ELO10-TEGR40 confirmed that ELO was necessary to obtain good mechanical performance, acting not only as plasticizer but also as a compatibilizer between PVC and TEGR. ELO was able to increase the free volume among PVC chains, imparting great flexibility to PVC macromolecular structure, thus allowing a better dispersion of TEGR in the formulation.

Another vegetable oil, epoxidized broccoli oil (EBO), was employed as a plasticizer for PHA by Audic et al. [209]. In Fig. 8**C**, the variations in the elastic modulus and the elongation at break of PHA as a function of the EBO content (from 0 to 15% w/w) are reported. The brittleness of commercial PHAs (elastic modulus = 2800 MPa, elongation at break = 1.38%) was mitigated with the addition of EBO: the elastic modulus dropped to about 2200 MPa for only 5% w/w EBO, reaching values lower than 1900 MPa for 15% w/w EBO. The inverse trend is visible for the deformation at break, which increases with higher EBO concentrations. These findings proved the effectiveness of EBO as a plasticizer for PHAs.

3.1.2. Bio-based plasticizers from sugars

In the range of bio-based plasticizers, extensive scientific research also revolves around sugar-based biorefinery. The main sources are starch, extracted from rice, wheat, maize and potatoes, and cellulose obtained from straws and cotton fibers. These polysaccharides are processed to provide sugars, such as glucose or mannose that, in turn, are modified to produce sugar alcohols and isosorbide [238–243]. The latter is considered a valuable product from biomass, since it is synthesized by dehydration of sorbitol. Yin et al. reported on the synthesis of three oligomeric isosorbide esters, and performed a comparison between their efficiency as plasticizers for PVC [244]. The films plasticized by oligo(isosorbide adipate) (OSA) and oligo(isosorbide suberate) (OSS) showed better performances when compared to isosorbide dihexanoate (SDH) or diisooctyl phthalate (DIOP) plasticized films (Fig. 9**A**). Interestingly, isosorbide

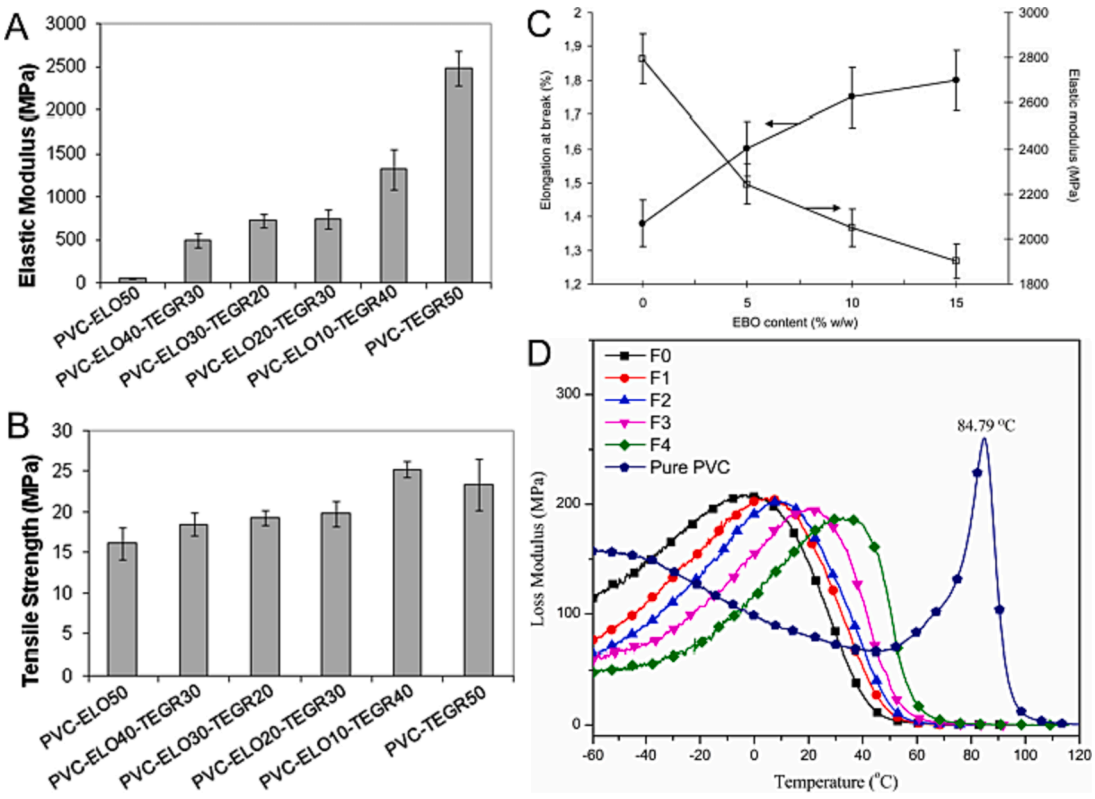


Fig. 8. (A) Elastic modulus, and (B) elongation at break of PVC-ELO-TEGR formulations, reproduced with permission from Arrieta et al. [213]; (C) Elongation at break and elastic modulus of PHA containing increasing concentration of EBO as plasticizer, reproduced with permission from Audic et al. [209]; (D) DMA loss modulus for PVC films loaded with cardanol-derived plasticizer and/or commercial plasticizer DOP, reproduced with permission from Chen et al. [262].

esters were also used as plasticizers for PLA matrix. In particular, Isosorbide dioctoate displayed better miscibility with PLA than DIOP, providing high transparency even at high loading [245].

Among other sugar derivatives, glucose, sucrose, and furan-based esters have been proposed as green substitutes for phthalate esters in PVC [246,247]. In particular, Yu et al. employed 2,5-furandicarboxylate esters, prepared through the dehydration and cyclization of monosaccharides or polysaccharides (Fig. 9**B**) revealing a significant effect on melt flow index of PVC plasticized with different amounts of dibutylfuran-2,5-dicarboxylate (DBF), diisoamylfuran-2,5-dicarboxylate (DIAF) and di(2-ethylhexyl)furan-2,5-dicarboxylate (DEHF) [248]. More recently, furandicarboxylic acid derivatives synthesized by a one-pot multistep reaction between bioalcohol and galactaric acid from marine-biomass and studied their effect on PVC properties [249]. Finally, Howel et al. [250] synthesized and characterized a series of esters derived from bio-based 2,5-bis(hydroxymethyl)furan, demonstrating that these compounds had good compatibility with PVC and low migration tendency. Moreover, they provided good flexibility to the polymer matrix without affecting its thermal stability.

Sugars have been also employed to plasticize polysaccharide-based polymers [251–253], and also to improve the flexibility of biodegradable plastics based on PLA [254]. In this regard, PLA and its blends have been successfully plasticized with sorbitol and glycerol (Fig. 9**D,E**) [255,256], as well as glucose hexanoate esters (GHs) [257].

3.1.3. Bio-based plasticizers from other sources

In the frame of the exploitation of biowaste feedstock, cardanol, a cheap and abundant by-product of the cashew nut industry [258], and its derivatives have also been vastly tested as plasticizers for PVC. For example, Yang et al. [259] have developed a click reaction to covalently bind cardanol to PVC, thereby significantly reducing PVC glass transition temperature and migration rates, while increasing thermal stability. Greco et al. [260] studied the effect of the epoxidation conditions on the properties of cardanol-derived plasticizers when compared to both phthalates and other bio-plasticizers. Interestingly, higher yield of epoxidation reduced plasticizer leaching. The same group also attempted the scaling up of the process to a medium scale (about 100 g of plasticizers) performing the epoxidation without the use of solvents and/or toxic reagents [261].

An interesting approach involves the chemical synthesis of bio-based compounds with multiple functionalities, potentially able to serve as multi-purpose additives for polymers. In this frame, Chen et al. [262] have synthesized hydrogenated cardanol glycidyl ether acetic ester containing phosphaphenanthrene groups (HCGEP). DMA loss module of the PVC-DOP-HCGEP formulations is reported in

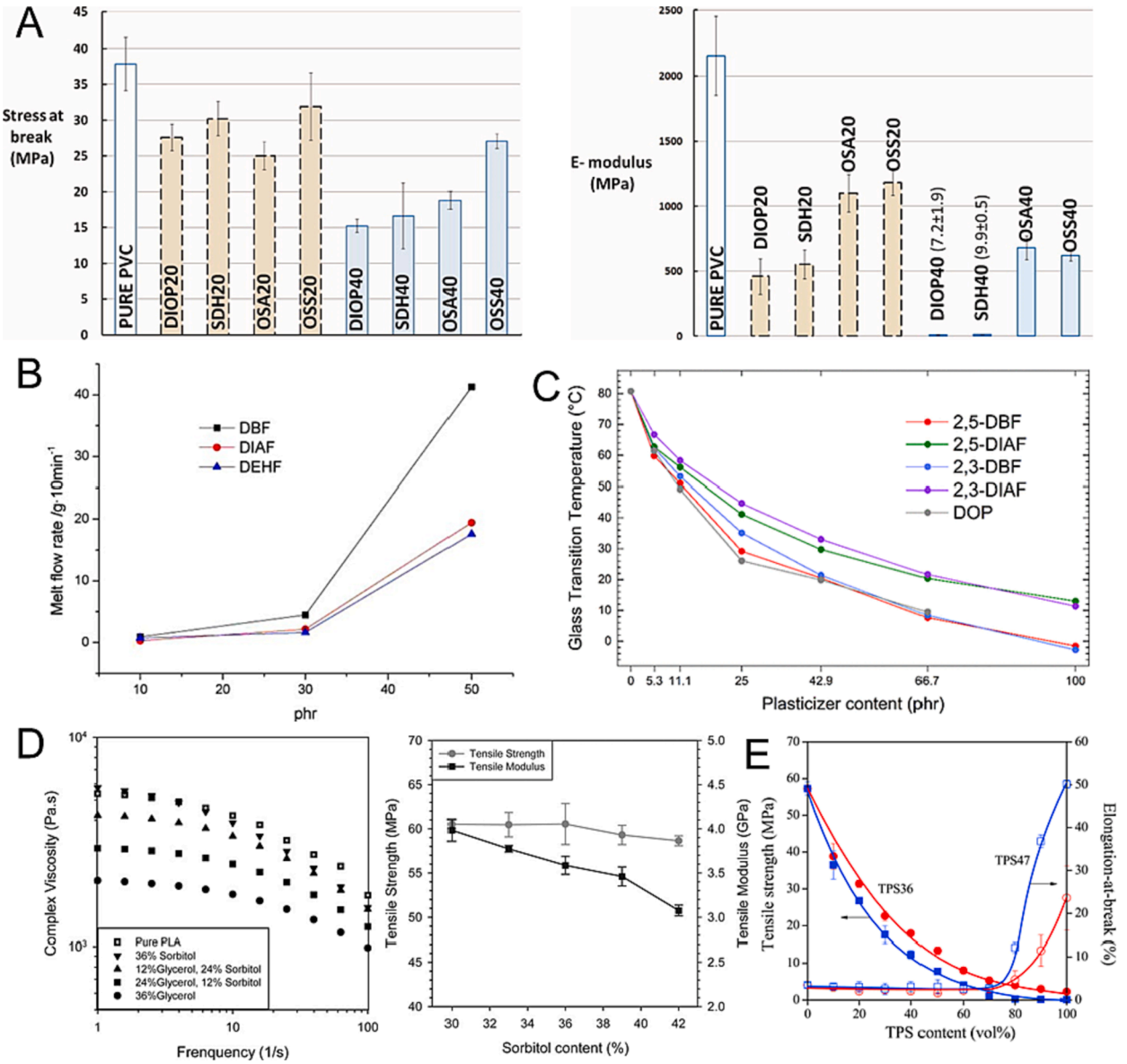


Fig. 9. (A) Strain at break and elastic modulus of PVC films containing 20 or 40 wt% of the different plasticizers, DIOP, SDH, OSA, and OSS, reproduced with permission from Yin et al. [244]; (B) Melt flow index of PVC plasticized with different amounts of dibutylfuran-2,5-dicarboxylate (DBF), diisoamylfuran-2,5-dicarboxylate (DIAF) and di(2-ethylhexyl)furan-2,5-dicarboxylate (DEHF), reproduced with permission from Yu et al. [248]; (C) glass transition temperature of PVC plasticized with different amounts of di-n-butyl furan-2,3-dicarboxylate (2,3-DBF), di-n-butyl furan-2,5-dicarboxylate (2,5-DBF), diisoamyl furan-2,3-dicarboxylate (2,3-DIAF), and diisoamyl furan-2,5-dicarboxylate (2,5-DIAF), reproduced with permission from Nguyen at al. [249]; (D) Variation of complex viscosity of TPS/PLA blends with the addition of different sorbitol/glycerol ratios, and the effect of the sorbitol content on the tensile modulus and strength of TPS/PLA blends, reproduced with permission from Li et al. [255]; (E) Tensile strength and elongation at break of PLA blended with TPS containing 36 wt% (TPS36) or 47 wt% (TPS47) glycerol as a function of TPS content, reproduced with permission from Müller et al. [256].

Fig. 8**D**. The authors found that 10–20 phr of HCGEP (indicated as F1 and F2, respectively) provided a plasticizing effect on PVC comparable to commercial DOP. The same work showed that the addition of HCGEP enhanced thermal stability and FR activity. Similar results were obtained with epoxidized cardanol glycidyl ether (ECGE) [263]. Cardanol derivatives provide efficient plasticization effect also in cellulose. Toyama and coworkers [264] modified cardanol to obtain a compound, the 3-pentadecylphenoxy acetic acid (PAA), that showed increased reactivity towards thermoplastic cellulose diacetate (CDA). The PAA-bonded CDA displayed improved bending strength, elastic modulus and water resistance when compared with CDA bonded with stearic acid. Interestingly, a further enhancement of impact strength was achieved by the addition of a small amount (1–5 wt%) of polyether silicones [265].

Another advantage of the use of epoxidized cardanol based plasticizers was highlighted by a recent study, which proved that these additives exhibit a very low eco-toxicity and do not show endocrine perturbation effect [266].

Alongside cardanol, other bio-derived biodegradable plasticizers are citrate derivatives [267], which can be also retrieved from orange waste [268], and extracts of grape pomace [269]. Cerruti et al. [135] have reported that the addition of 4 wt% pomace extract, a noble by-product of winery industry, to MB resulted in a stabilizing and plasticizing effect, with an increase in elongation at break of about 14% with respect to the pristine polymer.

Due to its structure and through the functionalization of its hydroxyl groups, lignin is also considered as a suitable building block for the preparation of bioplasticizers. In a pioneering work by Baumberger et al. the effect of lignin structure on different properties of lignin-starch composites was studied. It emerged that whole pine kraft lignin was capable to increase ten times the starch elongation at break [270]. In more recent works, it has been observed that organosolv lignin increased the elongation of PLA composites around 97% with respect to neat polymer [271], while organosolv lignin fractions exhibited a plasticizing effect on PMMA [272]. Sugarcane lignin has been also surface-modified with ESBO, maleic anhydride, tributyl citrate and vinyl acetate by reactive mixing, and used as PLA thermoplasticizer [273].

Among lignin derivatives, vanillin has been studied due to its effect as plasticizer. Zhu et al. [274] have developed several formulations based on vanillin to obtain bio-based plasticizers for PVC. In their study, vanillin-based plasticizer (VA4-C1) improved up to 55% the elongation a break values of thin PVC films, in comparison to DOP. Khashayary and Aarabi [275] reported the use of vanillin to enhance the mechanical properties of gluten based films. It was found that 1 wt% vanillin resulted in a 286% increase of elongation at break compared to neat film, while when vanillin was used in combination with salicylic acid and montmorillonite, the extent of enhancement reached 1288% of the pristine film value.

Vanillin is not the only lignin-derived molecule evaluated for its plasticizing properties; very recently, homo- and cross-coupling products of 4-hydroxybenzoic acid, vanillic acid and syringic acid have been studied as PVC plasticizers. These bioderived molecules are potential substitutes to DEHP, as they are capable of lowering the T_g of PVC by about 30 °C while increasing its thermal resistance by about 10 °C [276]. Finally, valuable approaches to plasticization have been reported using oligomeric plasticizers, including oligo lactic acid (OLA) [277], and poly(ethylene glycol) (PEG) [278].

Plasticizers represent by far the most widespread bio-based polymer additives. Table 3 summarizes the most significant bio-based plasticizers discussed in this section, along with their chemical structure, source, and use in polymer formulations.

4. Compatibilizers and coupling agents

The design of novel performing plastics usually involves blending of two or more polymers, or mixing a polymer with a low molecular weight additive or with a filler. This approach is the preferred method by industry due to low cost and facile processing. Compatibilizers and coupling agents are used to promote interfacial adhesion at polymer/polymer or polymer/additive interface, respectively, resulting in improvement of polymer blend miscibility and particle dispersion and distribution [279–283]. The refinement of the blend morphology results in enhanced mechanical performance of the final materials. In the past decades, a wide variety of compatibilizers [284] and coupling agents [285] have been made available for commodity polymers and composites.

Compatibilization mechanisms are typically defined as non-reactive and reactive. In the first case, the introduction of polymers with strong physical interaction with the two components of the mixture can improve their adhesion. As schematized Fig. 10**A**, non-reactive compatibilization is usually obtained with the addition of block-copolymers to the blend, one block being miscible with one blend component, and the other with the second [286–290].

A more performing strategy involves reactive compatibilization (Fig. 10**B**), where macromolecules with functional ends [291–294], oligomers [295] or low molecular weight chemicals [296,297], are chemically bound to the blend components. A further classification takes into account the formation of a heterophase upon the incorporation of the compatibilizer.

4.1. Bio-based compatibilizers

4.1.1. Bio-based non reactive compatibilizers

As in the case of other polymer additives, also for compatibilization the ongoing research focus is directed towards the use of bio-based additives [298]. In particular, in the case of non-reactive compatibilizers, biopolymers, such as PBS and poly(hydroxybutyrate-co-valerate) (PHBV), have been employed to enhance miscibility of PLA blended with poly(butylene adipate-co-terephthalate) (PBAT), resulting in an increase in melt flow (Fig. 11**A**) [299]. A similar approach was reported by Tsuji et al. [300], who have used PLA–PCL di-block copolymer to increase compatibility and mechanical performances of PLA/PCL blends. Incorporation of 10 wt% copolymer increased the compatibility between the two phases, as suggested by the observation of well-defined spherulites in the PLLA-PCL-containing PLLA/PCL film (Fig. 11**B**), also resulting in an increase of the elongation at break of 71.4%.

In order to modulate the degradation rate and to reduce the overall cost, biodegradable polyesters are often blended with starch, a readily available, economic and easily compostable natural polymer [301]. Recently, Noivoil et al. synthesized a starch-grafted OLA, which was added to a blend of PLA with TPS to act as a compatibilizer for manufacturing blown films [302]. The addition of OLA-*g*-starch resulted in improved ductility, surface hydrophobicity and gas barrier properties compared to the PLA/TPS blend film (Fig. 11**C**).

Table 3
Bio-based plasticizers, their source, chemical structure, and use in polymer formulations.

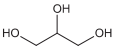
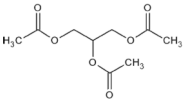
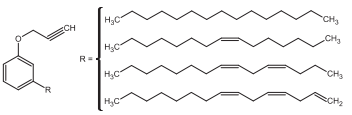
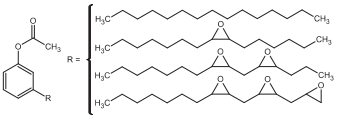
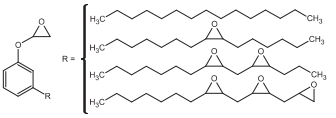
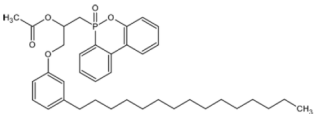
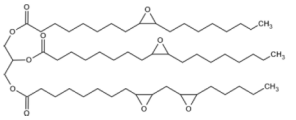
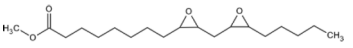
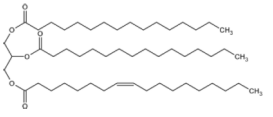
Vegetable oil-based plasticizers		
	Glycerol and derivatives	
Glycerol		10 to 50 wt% in Konjac glucomannan [180] 30, 50 wt% in Wheat starch [182] 15 to 45 phr in Sugar palm starch [187,252] 30 to 47 wt% in Corn starch [243,256] 17 to 67 phr in Chitosan [186] 4 wt%; 50 phr in Whey protein [185,215] 30 phr in Zein [215] 1 to 10 vol% in PLA [256] Up to 36 wt% in TPS in PLA/TPS blends [255]
Triacetine		15 wt% in PLA [267]
	Cashew nutshell oil derivatives	
Propargyl ether cardanol		61 wt% in azide functional PVC [259]
Epoxidized cardanol acetate		70 phr in PVC [260]
Epoxidized cardanol glycidyl ether		4 to 12 phr in PVC [263]
Hydrogenated cardanol glycidyl ether acetic ester containing phosphaphenanthrene group		10 to 40 phr in PVC [262]
	Soybean oil derivatives	
Epoxidized soybean oil		30 to 70 phr in PVC [200,233,260] 30 to 70 phr in PVC [200,233,260]
Epoxidized soybean oil methyl ester		5 to 40 wt% in PLA [204]
	Palm oil and derivatives	
Crude palm oil		1 to 5 wt% in PP [222]

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Table 3 (*continued*)

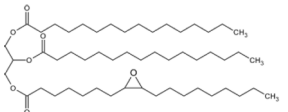
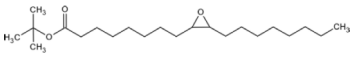
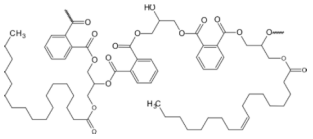
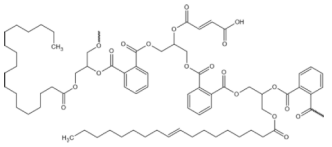
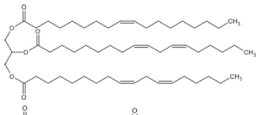
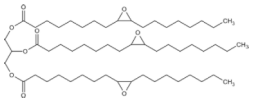
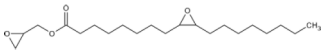
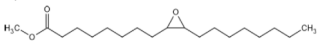
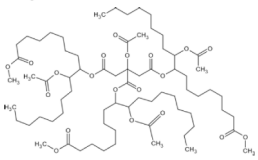
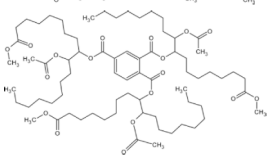
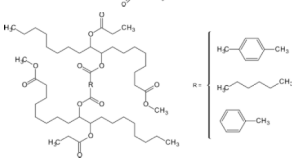
Vegetable oil-based plasticizers		
Epoxidized palm oil		5 to 50 wt% in PLA [226]
Epoxidized and esterified palm kernel oil		15 to 65 phr in PVC [223]
Palm stearin derivatives		83 wt% in PVC [224]
		10, 20 phr in PVC [225]
 **Sunflower oil and derivatives**		
Sunflower oil		2 % in PP [216]
Epoxidized sunflower oil		60 phr in PVC [211] 10 to 40 wt% in PLA [212]
 **Cooking oil derivatives**		
Epoxidized cooking oil		40 phr in PVC [234]
Epoxidized glycidyl ester of cooking oil		40 phr in PVC [234]
Epoxidized methyl ester of cooking oil		60 phr in PVC [234]
Citric acid ester of cooking oil		20 to 50 phr in PVC [233]
Trimellitic acid ester of cooking oil		50 to 70 phr in PVC [235]
Terephthalic, adipic or benzoic acid esters of cooking oil		40 phr in PVC [236]

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Table 3 (*continued*)

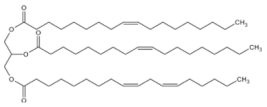
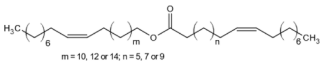
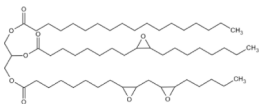
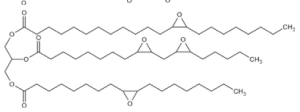
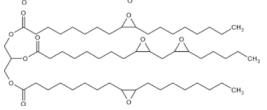
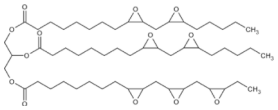
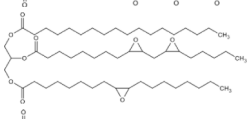
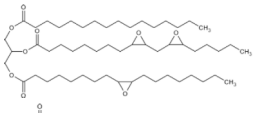
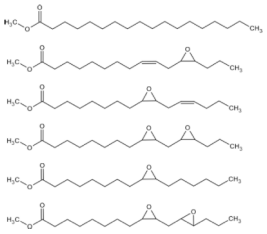
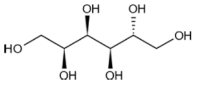
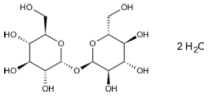
Vegetable oil-based plasticizers		
Other vegetable oils and derivatives		
		
Olive oil		70 phr in Zein [215] 2, 5 % in PP [216]
Jojoba oil		3, 7 wt% in PLA [208]
Epoxidized jatropha oil		1 to 5 wt% in PLA [207]
Epoxidized broccoli oil		3 to 15 % in PHA [209]
Epoxidized cotton seed oil		70 phr in PVC [210]
Epoxidized linseed oil		10 to 50 phr in PVC [213]
Epoxidized karanja oil		1 to 10 wt% in PLA [214]
Epoxidized cardoon oil		3 wt% in PLA in PLA/TPS blend [221]
Grape seed oil fatty acid methyl ester epoxides		1 to 20 wt% in PLA [203]
Sugar-based plasticizers		
Sorbitol		
Sorbitol		10 to 50 wt% in Konjac glucomannan [180] 15 to 45 phr in Sugar palm starch [187,252] 12 to 36 wt% in TPS in PLA/TPS blends [255]
Sugars and derivatives		
Trehalose dihydrate		4, 8 wt% in Whey protein [185]

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Table 3 (*continued*)

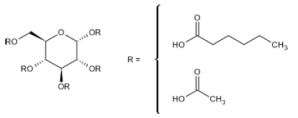
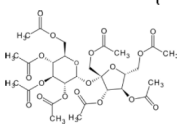
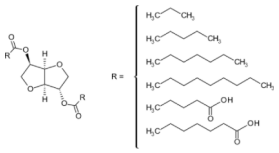
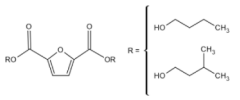
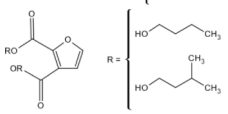
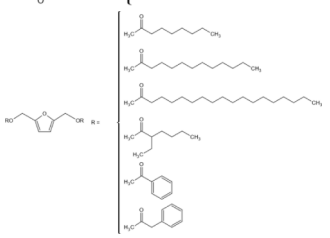
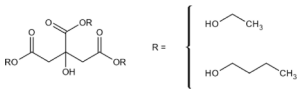
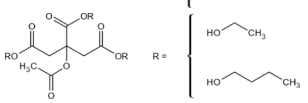
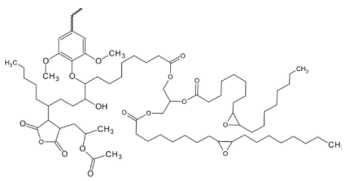
Vegetable oil-based plasticizers		
Glucose derivatives (Glucose -hexanoate ester, -pentaacetate)		20, 40 wt% in PVC [246] 10, 20 wt% in PLA [257]
D-(+)-sucrose octaacetate		20, 40 wt% in PVC [246]
Deep eutectic solvents **Various sugars**		35 phr in TPS [238,241]
Isosorbide and derivatives **Isosorbide**		40 wt% in Corn starch [243]
Isosorbide -dibutyrate, -dihexanoate, -dioctanoate, -didecanoate, -adipate, suberate		20, 40 wt% in PVC [242,244] 5 to 20 wt% in PLA [311]
Furanic derivatives **Di(-butyl, -isoamyl)furan-2,5- dicarboxylate**		Up to 100 phr in PVC [248,249]
Di(-butyl, -isoamyl)furan-2,3- dicarboxylate		Up to 100 phr in PVC [249]
Bis-2,5–2-ethylhexyl, —2-ethylhexanoylmethyl, -octanoylmethyl, —2-phenylacetoxymethyl, -benzoylmethyl, -stearoylmethyl furan		20 to 30 phr in PVC [250]
Others **Citric acid derivatives** **Tri -butyl, -ethyl citrate**		15 wt% in PLA [267]
Acetyltri -butyl, -ethyl citrate		15 wt% in PLA [267]
Lignin and derivatives **ESBO- maleic anhydride- tributyl citrate - vinyl acetate- modified lignin**		Up to 200 wt% in PLA [273]

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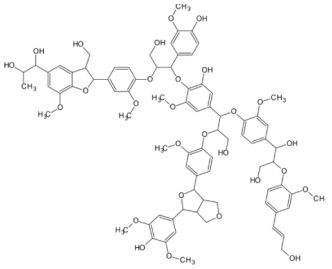
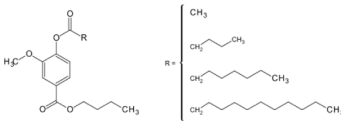
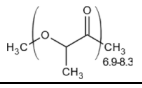
Table 3 (*continued*)

Vegetable oil-based plasticizers		
Organosolv lignin		20 ÷ 23 wt% in PLA [271] Up to 5 wt% in PMMA [272]
Kraft lignin		20 wt% in wheat starch [270]
Vanillic acid derivatives		30, 60 phr in PVC [274]
Others		
Polysaccharides		10 wt% in sodium alginate [253]
Oligomeric lactic acid		15, 20 wt% in PLA/PBH [277]

4.1.2. Bio-based reactive compatibilizers

More effective blend compatibilization can be usually achieved by employing reactive compatibilizers, which bear chemical groups able to form graft and/or block copolymers at the blend interface. Representative functional groups are anhydride, epoxy, isocyanates, etc., grafted to one polymer and able to couple with the other polymer of the blend, through reactive groups including hydroxyl, carboxyl, etc (Fig. 12) [298].

Some relevant examples of this approach have been tackled in the compatibilization of PLA with other biopolymers, such as other biodegradable polyesters or starch. The most used chemical employed to prepare PLA-based compatibilizing copolymers is maleic anhydride (MA), which can be derived from bioresources such as levulinic acid, 5-hydroxymethylfurfural (HMF), and furfural [303,304]. This approach has been reported in the preparation of PLA blends with PBAT [305], PCL [306], soy protein (SP) (Fig. 13**A, B**) [307], and starch [291].

Grafting of epoxy groups onto polymer chains is another well-known route to prepare macromolecular compatibilizers. Glycidyl methacrylate (GMA) has been often used to this purpose, as reported by Liu et al. [308], who synthesized GMA-grafted PLA for blending starch with PLA, obtaining compression-molded films with enhanced mechanical properties. Epoxy oligomer and polymers have been used to modify PLA topology to non-linear branched architectures. This resulted in dramatic changes of the blend rheology and significant toughening of the materials. This approach has been successfully applied to compatibilize PLA/PBAT blown films (Fig. 13**C,D**) [309], as well as to prepare toughened compression molded films based on PLA/poly[(butylene succinate)–co-adipate] (PBSA) blends [310].

Very interestingly, MA and epoxy groups have been also grafted to vegetable oils to prepare oligomeric wholly biobased compatibilizers. In this respect, Xiong et al. melt-blended starch with PLA, using tung oil anhydride (TOA) as a plasticizer [311]. The reaction of the anhydride groups with the starch hydroxyls resulted in a well-compatibilized ternary blend with improved toughness

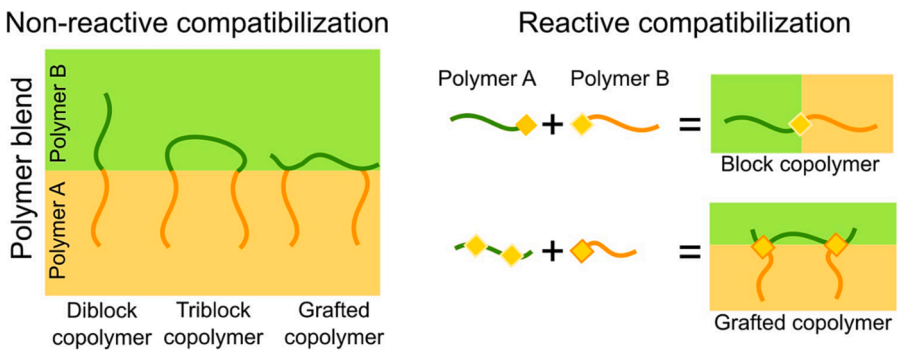


Fig. 10. Schematization of (A) non-reactive and (B) reactive compatibilizers.

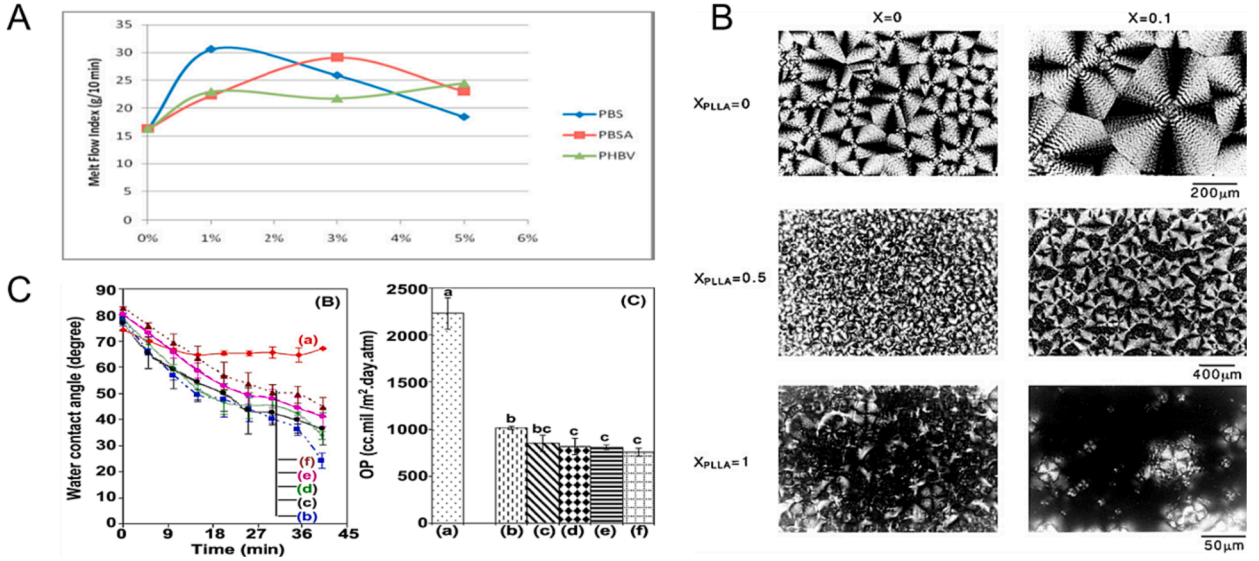


Fig. 11. Different approaches to polymer compatibilization using non-reactive bio-based polymer compatibilizers. (A) Melt Flow Index of a 70:30 w/w PLA/PBAT blend using 1, 3 or 5 phr of PBS, PBSA and PHBV, reproduced with permission from Pivsa-Art et al. [299]; (B) Polarized light micrographs of PCL (XPLLA = 0), PLLA/PCL blend (XPLLA = 0.5) and PLLA (XPLLA = 1) films, neat (X = 0), and containing 10 wt% PLLA-CL copolymer (X = 0.1), reproduced with permission from Tsuji et al. [300]); (C) Water contact angle (B), and oxygen permeability (OP) (C) of: (a) PLA, (b) PLA/TPS blend, and (c-f) PLA/TPS/OLA-g-starch blends containing different concentrations of OLA-g-starch: (c) 1 wt%, (d) 2 wt%, (e) 3 wt %, and (f) 5 wt%. Film samples were characterized at 0% RH and 25 °C, reproduced with permission from Noivoil et al. [302]).

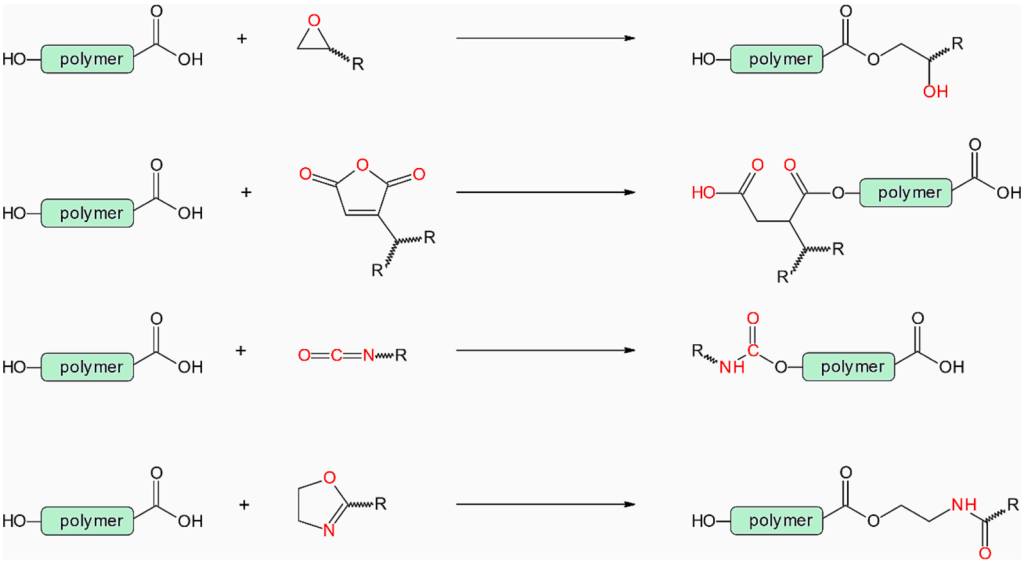


Fig. 12. Formation of a compatibilizing interface through reaction between reactive compatibilizers, bearing epoxy, MA, isocyanate, and oxazoline groups, and terminal groups of polymers in a blend, readapted from Mohanty et al. [298].

and impact strength (Fig. 13**E**). A similar strategy has been reported by Ghiou et al. [312] who demonstrated a positive effect of the epoxidized sunflower oil (ESO) on the miscibility of PVC and nitrile rubbers (NBRs), to form thermoplastic elastomers.

One of the most studied vegetable oils in the preparation of compatibilizers is cardanol, which is vastly employed in petrol-based and bio-polymer matrices. Rigoussen et al. added raw cardanol in the reactive extrusion of ABS with PLA [313,314]. Interestingly, cardanol reacted with ABS chains via free-radical pathway without the need of any prior chemical modification. Similarly, Lin and coworkers showed that 5 to 7 wt% of cardanol grafted to PP by reactive extrusion enhanced the compatibility of PP/poly(styrene) (PS) [315], and PP/ABS blends [316]. Recently, an epoxidized cardanol oligomer (ECP) has been successfully employed as a compatibilizing agent for biodegradable PLA/PBAT blends (Fig. 13**F**) [317]. The incorporation of 3 wt% of ECP significantly increased yield

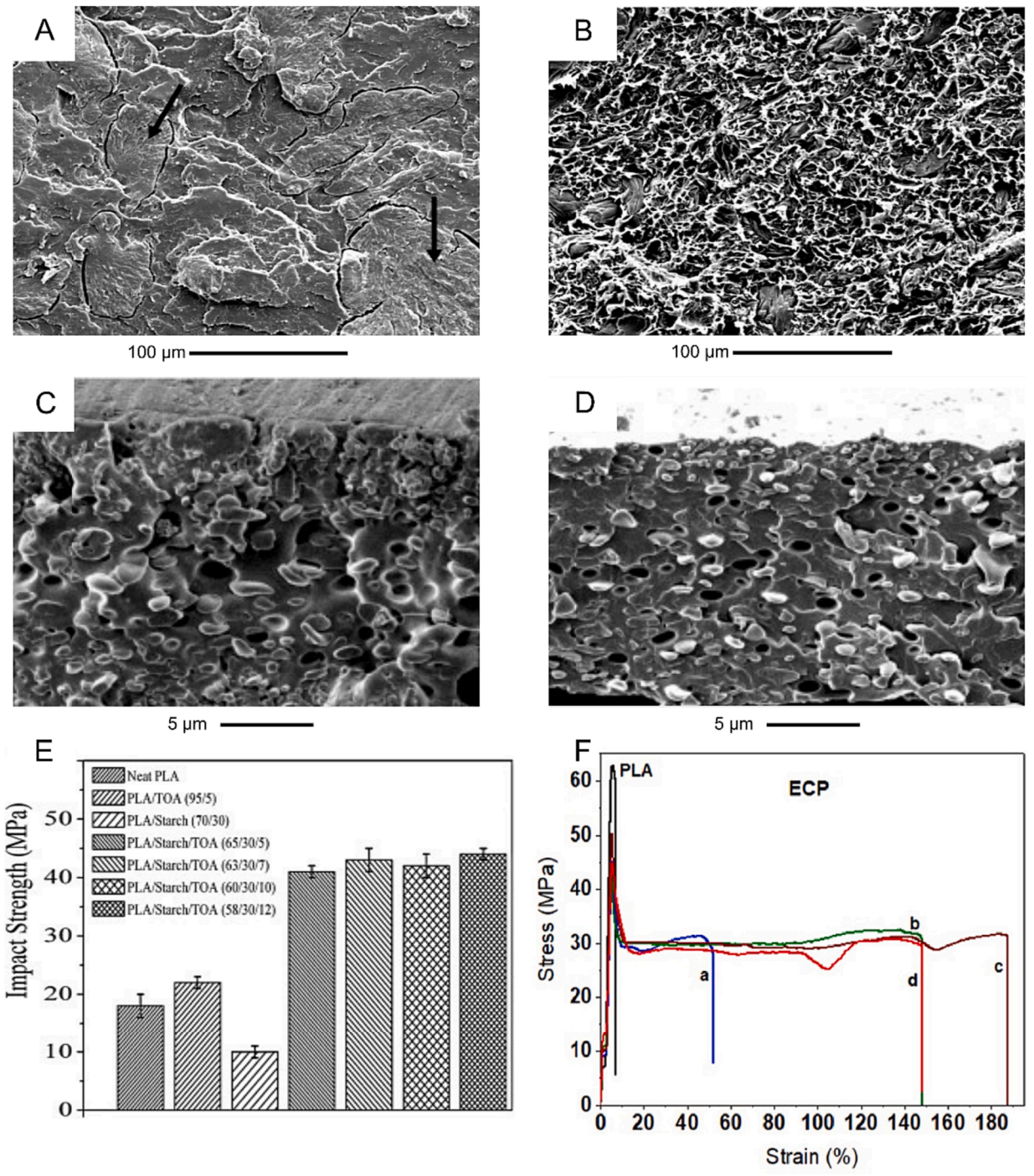


Fig. 13. Different approaches to polymer compatibilization using reactive bio-based polymer compatibilizers. SEM images of tensile fracture surfaces of a 70:30 w/w PLA/SP blend: (A) neat, and (B) containing 4 phr PLA-g-0.90% MA, adapted from Zhu et al. [307]; Micrographs of the fracture surface of a 40:60 w/w PLA/PBAT blend: (C) neat, and (D) containing 0.6 wt% of the Joncryl ADR®4368 epoxy chain extender, reproduced with permission from Cardoso Arruda et al. [309]; (E) Impact strength of PLA, PLA/TOA blend, and PLA/starch blends with or without TOA, reproduced with permission from Xiong et al. [311]; (F) Stress–strain curves of PLA and their 80:20 wt% blends containing varying amounts of ECP: (a) 0%; (b) 1%; (c) 3% and (d) 5%, reproduced with permission from Farias da Silva et al. [317].

stress, elongation at break, Young modulus and toughness of the compatibilized blends. Finally, Xiong et al. functionalized starch with an epoxy derivative of cardanol to improve interfacial adhesion between starch and PLA. The so obtained ternary blends exhibited enhanced impact and tensile properties [318].

4.1.3. Bio-based nanoparticles as compatibilizers

Recently, the possibility of using NPs as compatibilizing agents has been established in the preparation of polymer blends with enhanced properties [319]. The selective localization of the NP within the blend phases plays a key role in the enhancement of miscibility, as NPs can be confined inside one of the two polymer phases or at their interface. Generally, NPs confined at the interface can form a physical barrier against coalescence, refining and stabilizing the blend structure [236]. Historically, the literature has dealt with the effective use of inorganic NP as compatibilizing agents for immiscible polymers [320,321]. For example, Lendvai et al. introduced microgranulated natural bentonite (BT) to produce binary TPS/PBAT blends, finding that the development of continuous PBAT phase in the blends was due to a "compatibilizing" effect of the BT particles [322].

More recently, some papers documented the application of bio-sourced organic NPs to this aim. For example, poly(propylene carbonate) (PPC) and PLA have been compatibilized through the use of core–shell starch (CSS) NPs. Due to the highly improved compatibility between the two polymer phases, ternary PPC/PLA/CSS (60/40/20) blends exhibited a value of 272% in the elongation at break, in comparison with 15% calculated for PPC/PLA (60/40) [323].

Cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) have been demonstrated as good compatibilizers for PVA and poly (ethylene oxide) (PEO) blends (Fig. 14) [324,325]. The effect of the two cellulose-based fillers on physical and mechanical properties of polymer blends was evaluated, demonstrating that CNCs provided higher light transparency and mechanical performance than CNFs. These findings were explained in terms of stronger hydrogen bonding of CNCs with PVA and PEO, ascribed to better dispersion and smaller aspect ratio.

Very recently, bioinspired poly(dopamine) (PDA) NPs have been explored as compatibilizing agents for multifunctional PVA/starch films [326]. The authors demonstrated that PDA NPs were homogeneously dispersed in the polymer matrix, yielding a well compatibilized blend, with enhanced mechanical, thermal and barrier properties with respect to the pristine blend.

4.2. Bio-based coupling agents

Coupling agents usually react with the filler surface and possess at least one side group able to establish a chemical or physical interaction with the polymer matrix.

Among bio-based coupling agents, cardanol is one of the most tested in bio-composite formulations to enhance filler dispersion [327]. For example, Mohapatra et al. have used natural rubber grafted with cardanol (CGNR) to enhance compatibility between the nonpolar rubbers and the polar silica fillers (Fig. 15**A**), leading to systems with potentially reduced rolling resistance and enhanced wet

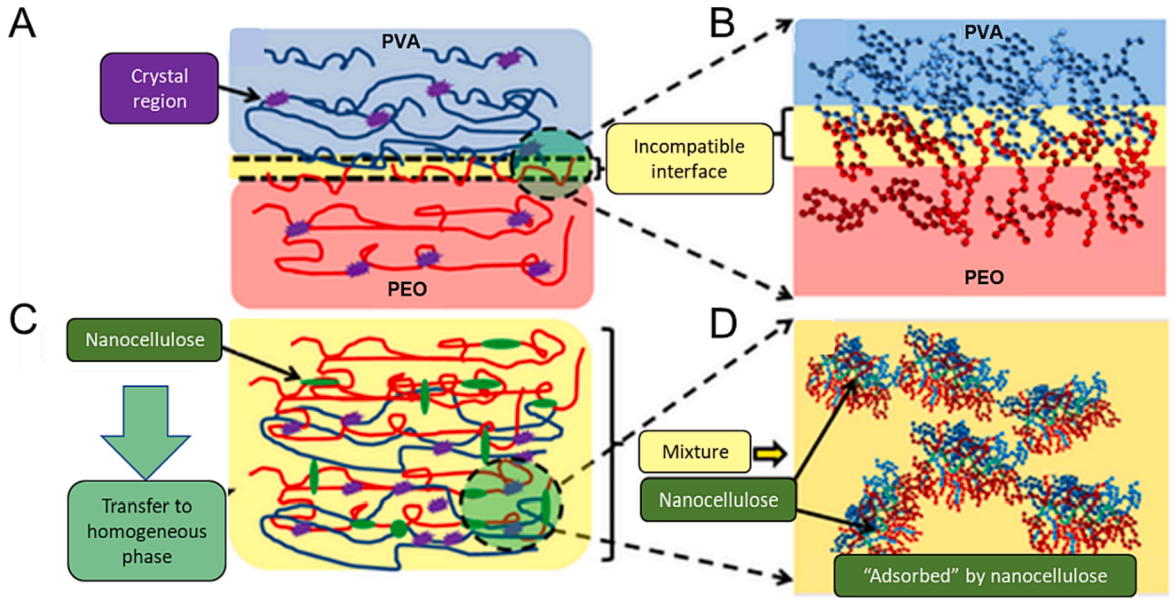


Fig. 14. BSNP: Scheme of the effect of CNCs on the improved interfacial miscibility of PVA and PEO: (a) PVA/PEO blend with an immiscible interface, and (b) higher magnification of the interface, (c) polymer blend compatibilized phase in the presence of CNCs, and (d) higher magnification image of the interaction of PVA and PEO chains with CNCs, reproduced with permission from Yong et al. [324].

grip characteristics [328].

Cardanol was also incorporated in ZnO, TiO_2, and SiO_2 reinforced PLA/PBAT blend composites, to produce cast films for packaging applications. The authors highlighted the key role played by cardanol in improving optical properties and surface hydrophobicity of the materials, which also exhibited high flexibility and improved barrier and mechanical properties [329].

The industrially driven interest towards the production of greener tire tread compounds have generated interesting scientific results in the design of new sustainable coupling agents, such as epoxidized natural rubber (ENR) [330,331], maleated natural rubber [332] and epoxidized polybutadiene rubber [333]. The epoxidation of rubber chain is in fact an excellent synthetic tool to increase the polar character by introducing oxirane rings onto the rubber chain.

Other interesting results are generated from the drive towards totally or partially bio-based composites [334]. Cork, a renewable product that can be harvested from tree barks, has been vastly investigated as a filler in different petrol based and bio-based polymers [335,336]. The development of cork–polymer composites has tackled the increase of the interfacial adhesion using MA [337] and bio-based coupling agents as suberin and lignin [338]. Similarly, polymer/bamboo fiber (BF) biocomposites have been produced, and promising mechanical and thermal properties were achieved by the addition of bio-based coupling agents such as lysin-based diisocyanates (LDI) for PLA/PBS/BF [339] and ramie/PLA composites [340]. In the field of bio-based microcomposites, Dai et al. addressed the compatibilization of hydrophilic microcrystalline cellulose (MCC) with PLA [341]. This route involves the addition of 1–5 wt% epoxidized citric acid (ECA) to the mixture. Due to the presence of numerous epoxy groups, ECA is able to react with the hydroxyl groups of MCC, improving their interfacial adhesion with PLA, and resulting in better impact properties (Fig. 15**B**).

Ortega-Toro et al. [342] used epoxidized sesame oil (EseO) from two Colombian Caribbean crops in thermoplastic yam starch/PLA composites to enhance their interfacial adhesion (Fig. 15**C**). It was demonstrated that EseO acted as an effective coupling agent, leading to increased thermal stability and mechanical performance.

5. Other bio-based additives

5.1. Flame retardants

As all carbon-based materials, plastics have a very low resistance against fire because their composition makes them prone to combustion processes. As a matter of fact, several experimental and Life Cycle Assessment (LCA) studies have been carried out to

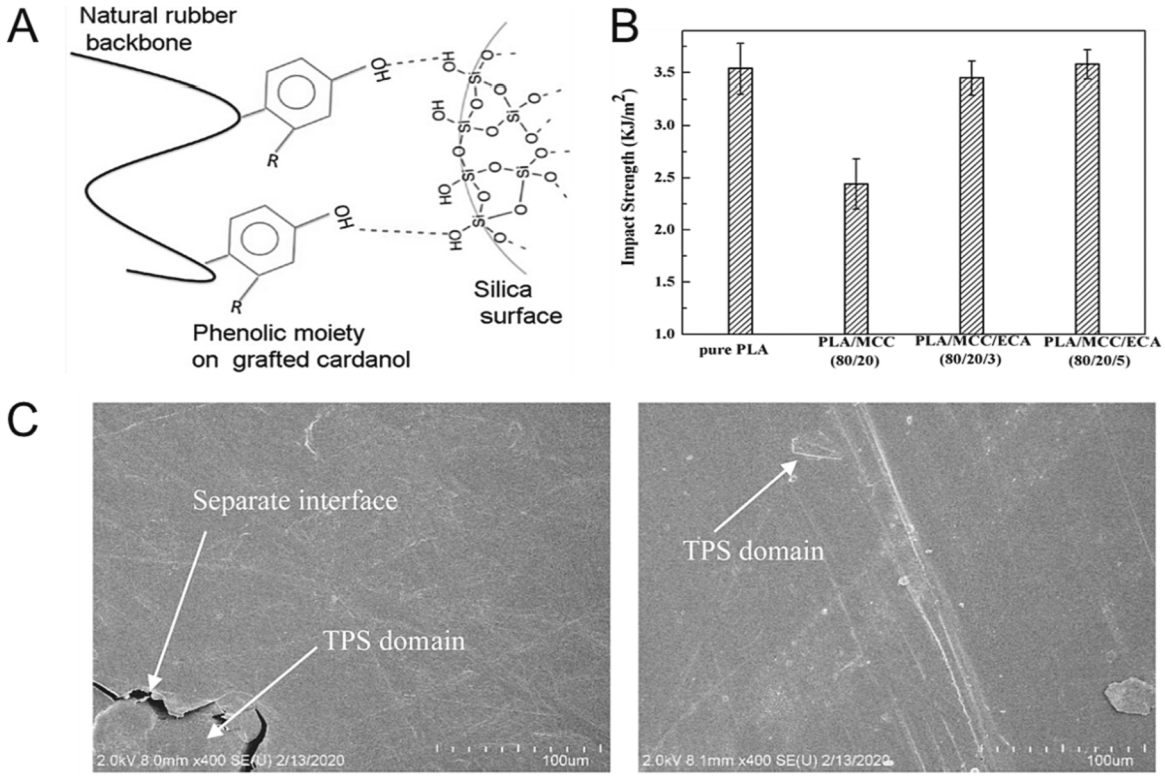


Fig. 15. (A) Sketched representation of the interactions between silica particles surface and cardanol moieties grafted onto natural rubber, reproduced with permission from Mohapatra et al. [328]; (B) Notched impact strength of PLA, PLA/MCC (80/20), PLA/MCC/ECA (80/20/3), and PLA/MCC/ECA (80/20/5), reproduced with permission from Dai et al. [341]; (C) Cross-section SEM micrographs of 75:25 w/w PLA/TPS blend films without (left) and with 3 wt% ESeO, reproduced with permission from Ortega-Toro et al. [342].

explore the possibility to transform end-of-life plastic waste into liquid fuels via cracking processes [343,344]. To minimize fire risk and produce safer materials, synthetic FR additives are usually introduced in the plastic formulations whenever their final products could possibly be exposed to fire hazard [345]. Although the use of FRs substantially increases life-saving chances and damage control during fire, the risks related to their use have been well highlighted. Among the four main classes of commercially available FRs – inorganic, nitrogen-based, organophosphorus and char-forming, halogenated organic – these latter, in particular the brominated flame retardants (BFRs), represent the main cause for concern [346–348]. Indeed, although they are cost-effective, some of them have been reported to possibly induce cancer, reproductive problems, and impaired fetal brain development. Moreover, upon combustion, they are released to the environment, acting as persistent organic pollutants (POPs) [349,350]. Therefore, the use of several BFRs has been severely restricted or even completely banned in the production and use of commercial plastic items, by the Stockholm Convention within the United Nations Environment Programme [24]. Recent research studies even investigate the social perception towards FRs identifying a consumer preferences of "short-term" fire risk safety over a "long term" chemical risk associated to environmental and health hazards of FR littering [351]. A suitable solution to this controversial issue is represented by bio-based and natural FRs [352–354]. As usual, nature offers many examples of FR compounds, such as char-forming compounds, including lignin [355,356], chitin [357] and starch [358].

Lignin was investigated as a sustainable FR agent both for traditional oil-based and bio-based/degradable polymers [359,360]. The use of lignin as FR for isotactic PP was reported in the early 2000s by De Chirico et al. [361], who observed that lignin, in combination with phosphate compounds and $Al(OH)_3$, increased the thermal degradation temperature, combustion time and the char yield of PP, while decreasing heat release and weight loss rate during combustion. Kraft and sulfonated lignin have been also found to modify thermal stability and fire retardancy of bio-based polyamide 11 microcomposites. Vertical flame spread tests demonstrated that 15 wt % of either kraft or sulfonated lignin improved flame retardancy, enabling the composites to achieve a V1 rating. Moreover, while sulfonated lignin significantly reduced the Heat Release Rate (HRR) and the Total Heat Release (THR), kraft lignin caused HRR and THR to increase [362]. Costes et al. studied fire properties and thermal behavior of PLA composites containing 20 wt% of both pristine and phosphorus/nitrogen chemically modified lignins [363].

Results (Fig. 16**A**) showed that both kraft and organosolv lignin after chemical modification imparted interesting properties to PLA fire response: time to ignition (TTI) increased from around 35 s in the case of untreated lignin to around 85 s when modified lignin was used. Moreover, a significant reduction of the peak of Heat Release Rate (PHRR) testified an increased resistance to ignition, especially when kraft lignin was used. This was attributed to the presence of ammonium groups, which are able to dilute the gas phase, and phosphorous groups, that allow char layer formation before ignition. The improved behavior of phosphorous-nitrogen modified lignin, due to the formation of a compact, continuous, and thick char layer is reported also elsewhere [364–366]. Phosphorus-nitrogen modified lignin was proved also to impart flame retardancy and thermal stability to PP [367–369], ABS [370], natural rubber [371], PBS [372], epoxy resins [373–375], and poly(urethane) (PU) [376–379].

Some organic renewable oils have been employed as raw material for the synthesis of bio-based FRs, such as castor oil phosphate polyol [380], polycardanol [381], and phosphorylated linseed oil (PLO) and corn oil (PCO) [382].

In particular, Cabo et al. [383] reported on one-pot synthesis of a FR thermoset resin derived from epoxidized corn oil (ECO) using liquid inorganic catalyst and hydrogen peroxide. Microscale combustion calorimetry was used to measure HRR and PHRR, indicating the maximum PHRR of the epoxidized corn oil was significantly lower than that of vinyl ester and epoxy. The evaluation of the HRR curve also indicated that combustion of ECO was a two-step process (two distinct peaks are shown in Fig. 16**B**): the first step involves the melting and degradation of the epoxides into tar, and the second step indicates the combustion of the tar previously produced.

Organic salts, such as metallic phytates, are another well-studied class of bio-based FRs. Costes et al. [384] studied the effect on PLA of sodium, aluminum, iron and lanthanum phytate. Similarly, Cheng et al. [385] reported the performances of PVC additivated with copper, zinc, aluminum and tin phytate. In these two studies aluminum and zinc phytates were identified as the most performing FR alternatives showing also good smoke suppression ability.

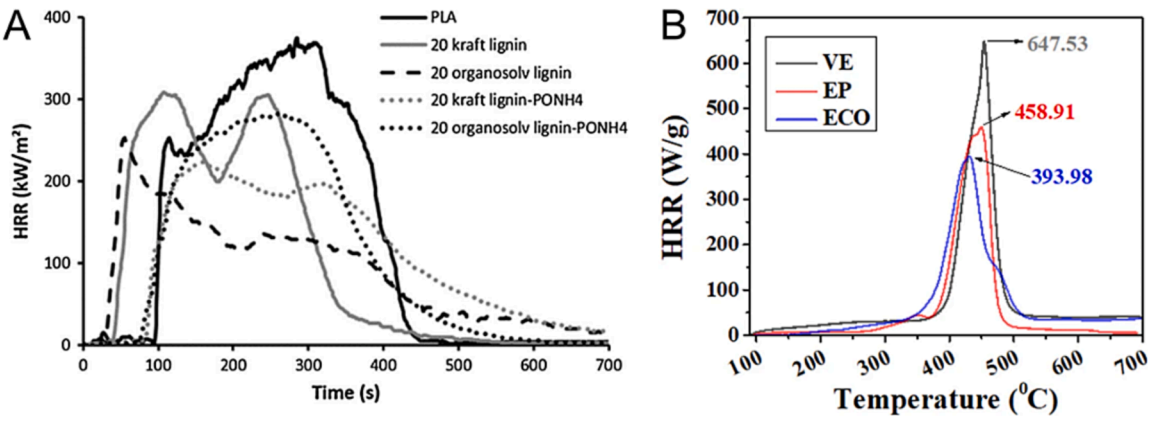


Fig. 16. (A) HRR curve of neat PLA and PLA/20 lignin composites, reproduced with permission from Costes et al. [363]; (B) HRR curves of ECO, vinyl ester, and epoxy thermosets resins, reproduced with permission from Cabo et al. [383].

Nanostructured minerals, such as montmorillonite and zeolite clays, alone or combined with intumescent FRs, have been also tested for a variety of polymer matrices [386], including PE and PP [387–391], PVC [392], PVA [393], PU [394], and polyamide [395]. More recently, these approaches have been also reported for PLA [396]. For example, natural sepiolite (SEP) was grafted with 9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide (DOPO) and incorporated into PLA to enhance its fire resistance. The synergetic effect between DOPO and SEP in composites containing 10 wt% DOPO/SEP resulted in a 40.7% decrease of the PHRR [397].

In the frame of nanostructured materials, aerogels are being actively studied as highly performing FR bio-based materials. Aerogels are solids made up of a porous network fully percolated by air pockets. Since they are about 99.8% air, aerogels have the advantage of being extremely lightweight. They are manufactured from inorganic, organic, or hybrid precursors [398]. The most relevant bio-based aerogels are made of cellulose, starch, or other polysaccharides, as well as natural proteins, possibly doped with functional or structural additives [399]. Their low density, alongside high porosity and surface area, make them ideal FR materials to replace conventional oil-based foams. In this respect, hybrid organic–inorganic systems based on polysaccharides including silica, clay, possibly combined with low-flammability materials, have been recently reported for the engineering of flame retarded aerogels. MCC composite aerogels containing 50 wt% hydroxyapatite (HAP) nanorods achieved a 94% decrease in PHRR, compared to pure MCC aerogel. Two main mecanisms are involved in the improvement in FR properties, that is the increased thermal dynamic transfer, which reduces TTI and PHRR, and the formation of a nonflammable HAP-backbone char able to slow heat and mass diffusion [400]. Similarly, CNF aerogels with good fire-retardant properties have been prepared by *in situ* supramolecular assembly of melamine (MEL) and phytic acid (PAc), which is an intrinsically low-flammable bio-based additive. The modified aerogels displayed high thermal stability and fire retardancy, self-extinguished after flame removal, and showed a weight loss of less than 15% in burning tests, compared to the almost complete degradation of an unmodified CNF aerogel [401].

Fire-retarded aerogels have been maufactured also using combinations of natural polysaccharides and proteins. Konjac glucomannan (GM)-based aerogels with varying content of plant polysaccharides, proteins, and wheat straw have been recently described, and the effect of the components on structure, heat insulation and FR behavior have been assessed [402]. PHRR and THR of konjac GM-based aerogels were significanly lower than those of insulation materials based on PU and expanded PS, further confirming the potential of bio-based aerogels in the preparation of sustainable FR building materials.

5.2. Lubricating agents

Polymer extrusion and other forming procedures require attentive design to ensure product quality and rates of production. Industrial demand for process optimization relies on the use of lubricating agents as processing aids to ensure flow enhancement and instability elimination [403,404]. Before 1940s vegetable oils made from castor beans and rape seed were used [405,406], while synthetic lubricants were developed during WWII for military purposes and their use was quickly spread to other industrial fields. In the field of lubrication the concern has been focused on the large amount of lubricants lost in environment, which constitutes a potential long-term threat to water and soil [407]. A similar trend is pursued in the field of polymers, where synthetic oils usually used as processing aids mainly for natural and synthetic rubbers, are being gradually substituted by bio-based counterparts from vegetable or animal resources [36,406]. The work of Dasgupta et al. [408], dating back to 2007, analyzed 10 types of naturally occurring oils as an alternative to polyaromatic hydrocarbon-rich oils later banned in 2009. The use of vegetable oils has several advantages, including their easy availability, human and environmental safety, low cost, potential biodegradability, as well as for reducing our dependence on petroleum [409]. Most importantly, chemical modification of vegetable oils can significantly improve the processability of polymer based compounds [410]. Recent literature reports the use of vegetable oils as additives to improve the melt flow of polymers during processing [411,412]. In this context, epoxidized palm oil (EPO) was investigated as a suitable lubricant to replace aromatic oils in styrene-butadiene rubber processing [406]. More recently, ESO with varying oxirane content have been compounded with silica-filled styrene-butadiene rubber formulation to improve its processability. It turned out that the incorporation of ~0.8 vol% of a fully epoxidized ESO was responsible for a 7% decrease in mixing energy (see Fig. 17**A**).

This outcome was explained in terms of enhanced hydrogen bonding between epoxy and silica silanol groups, that made the silica surface hydrophobic, thus enhancing processability [413]. Among vegetable oil derivatives, fatty amides are among the most widely used lubricating agent in polymer processing. In particular, erucamide (EA), oleamide (OA), and stearamide (SA) are very cost effective commercial amides, widely employed for years [414]. Alongside EA, OA, and SA, several monounsaturated amides (MMAs) of fatty acids have been investigated as processing aids. Swanson et al. demonstrated that MMAs from meadowfoam (*Limnanthes alba*) possessed lubricant properties comparable to those of commercial amides [415]. More recently, few papers dealing with the effect of bio-based amides on the processability of polymer and composite formulations appeared in literature, although in some case they did not provide significant improvement compared to EA [416–418].

The introduction in polymer formulation of naturally occurring additives intended for other purposes can sometimes contribute to processing improvement. For example, a study presented by Auriemma et al. showed that tannic acid, a naturally occurring polyphenol, significantly increased processing properties of PHB as well as its thermal stability [132,184]. In a very recent study, the effect of polysaccharide gums such as gum acacia (GA) and guar gum (GG) as additives for lubricant formulations based on soybean oil and organoclay (25 wt%) has been demonstrated [419]. Data gathered from four-ball tests (schematized in Fig. 17**B**) highlighted a 60% increase in tribological performance compared to a commercial grease (see Fig. 17**C**). The observed outstanding lubricating performance was explained in terms of formation of a polymer-layered silicate nanocomposite at the interface of the contacting surfaces. A similar approach has been reported by Chukwunonso Opia et al., who investigated the effect of *Eichhornia crassipes* carboxylmethyl cellulose (EC-CMC) as additive in rapeseed oil, demonstrating that EC-CMC provided good wear reduction, also showing excellent shear stability [420].

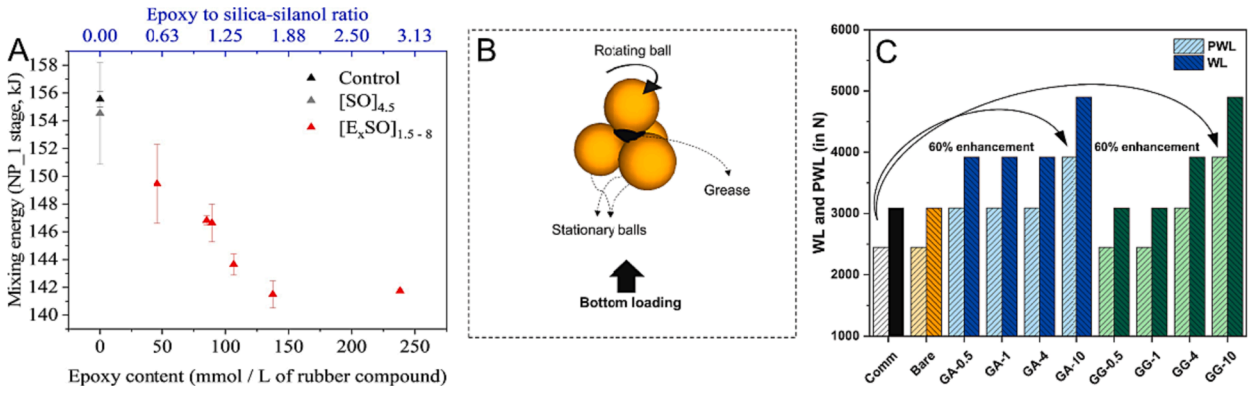


Fig. 17. (A) Mixing energy during formation of silica-filled rubber compounds, as a function of both epoxy content (bottom x-axis) and epoxy to silica-silanol ratio (top x-axis), where SO and ESO refer to soybean oil and epoxidized soybean oil respectively, reproduced with permission from Sarma et al. [413]; (B) Schematic representation of the contact condition in four-ball tester during extreme-pressure (EP) test, and (C) EP performance characteristics: weld loads (WLs) and pre-weld loads (PWLs) of soybean oil-based greases containing varying amounts of gum acacia (GA) and guar gum (GG), determined at speed = 1770 ± 60 RPM, temperature = 27 ± 8 °C, and duration = 10 s, reproduced with permission from Saxena et al. [419].

5.3. Antimicrobials

Antimicrobials can provide effective defense against bacteria, fungi, algae, molds and other microorganisms, inhibiting or altering their cell membrane functions or the synthesis of cell wall, protein or nucleic acids [421]. The addition of antimicrobial additives to polymer formulations enables their active protection and avoids their surface contamination, possibly ensuring that the surroundings is sterile [422].

By using antimicrobial polymers, the functional lifetime of a variety of different plastic goods can be extended, since the growth of microorganisms and consequent formation of surface bioburden, which leads to degradation of mechanical and aesthetic features, is prevented. When employed, polymers with antimicrobial properties are able to reduce health risks and improve hygiene standards. Moreover, the shelf life of packed products is prolonged, enabling their use in a variety of applications, ranging from medical devices, food packaging to textiles [423]. As schematized in Fig. 18, active antimicrobial polymers can be obtained either by incorporation of antimicrobial compounds into the polymer formulation during its manufacturing process, or by chemical functionalization of polymer chains or surface with the bioactive molecules [424,425]. Moreover, intrinsically antimicrobial polymers can be also developed [426,427].

The choice of antimicrobial agent depends on many factors, such as the application field, the duration and effect of antimicrobial activity needed, as well as the microorganisms that may be present and develop during the commodity lifecycle. Conventionally used antimicrobial actives are metallic ions and oxide NPs, including silver [428,429], ZnO [430], TiO_2 [431] and quaternary ammonium salts [432,433], as well as other synthetic molecules [434–436]. However, nature offers manifold solutions to replace these active ingredients with environmentally friendly compounds of various chemical structure.

Among bio-sourced antimicrobial agents, essential oils (EOs) (i.e. volatile oils that give to the plants their characteristic smell and taste) and their components (e.g. carvacrol, thymol, geraniol, etc.) are the most widely employed, due to their low costs and availability. In addition, their low toxicity makes them an interesting option in cosmetic industries and food packaging, as EOs are labelled as Generally-Regarded-As-Safe (GRAS) [437,438], even if their strong odor can sometimes alter the food taste. A large variety of EOs

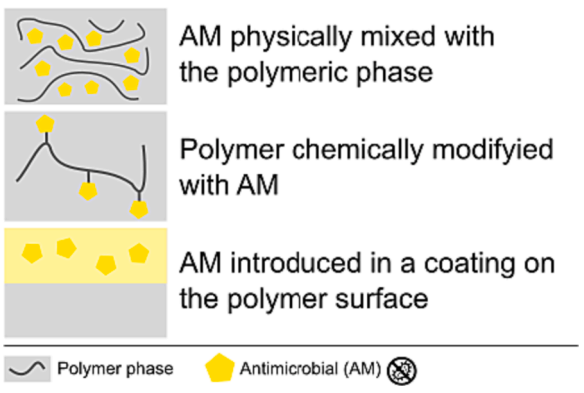


Fig. 18. Different mechanisms of functionalization of a polymer with an antimicrobial additive.

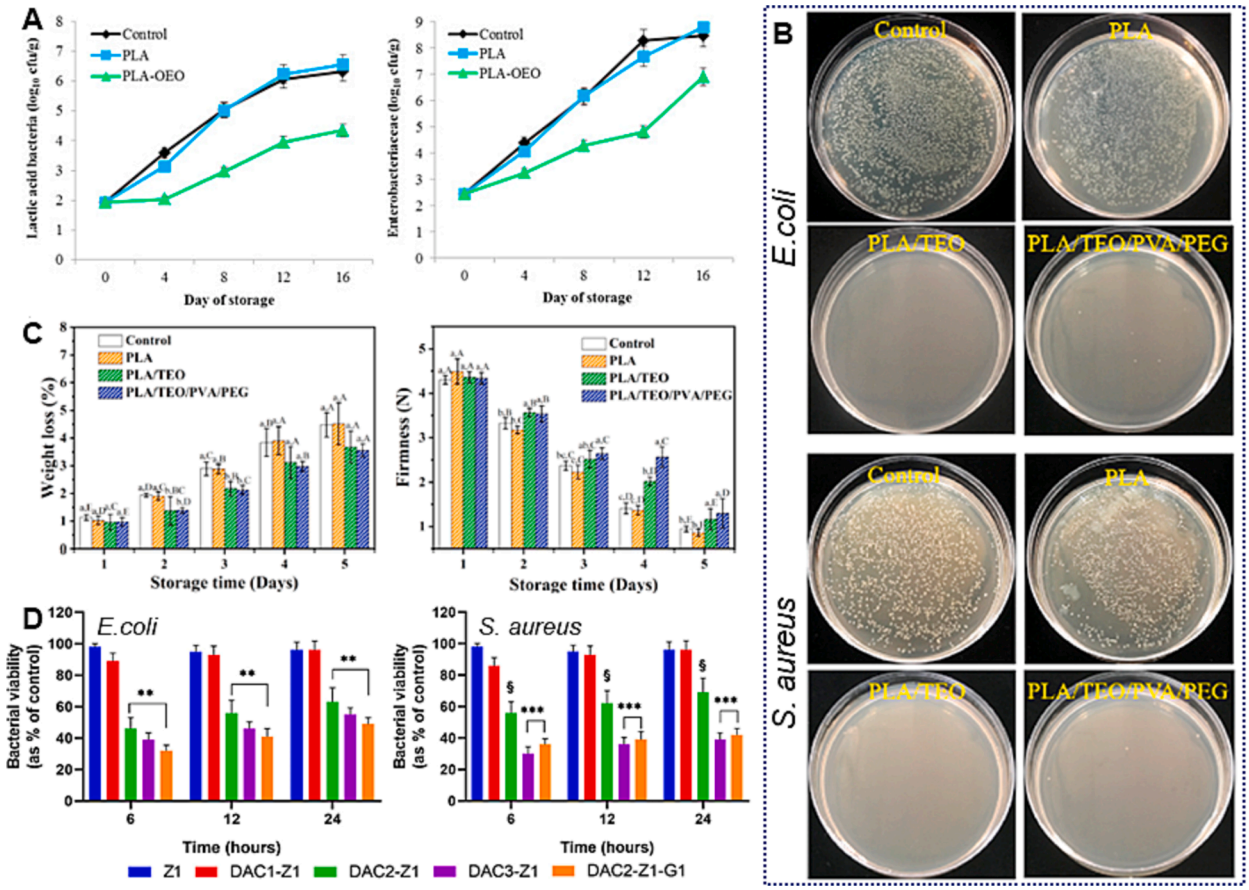


Fig. 19. (A) Lactic acid bacteria and Enterobacteriaceae counts for unwrapped trout samples (Control), PLA film wrapped samples (PLA) and samples wrapped with PLA film containing oregano essential oil (PLA-OEO), reproduced with permission from Javidi et al. [441]; (B).Antibacterial activities against E.Coli and S.Aureus colonies of unloaded PLA nanofibers films (PLA), thyme essential oil loaded PLA nanofibers (PLA/TEO) and loaded fibers coated with PVA/PEG (PLA/TEO/PVA/PEG); (C) Weight loss and firmness of strawberries packed into PLA, PLA/TEO and PLA/TEO/PVA/PEG, after up to 5 days at 25 °C, reproduced with permission from Min et al. [446]; (D) Bacterial inhibition rate of E.Coli and S.Aureus in liquid medium containing 50 mg of zein (Z1), dialdehyde cellulose-zein films at various raw material ratios (DAC1-Z1, DAC2-Z1, DAC3-Z1) and dialdehyde cellulose-zein-gelatin (DAC2-Z1-G1) films, reproduced with permission from Mayer et al. [491].

obtained from plants of different nature has been applied to polymers as antimicrobials, in particular for food packaging applications [439]. Oregano (*Origanum vulgare L.*), basil (*Ocimum basilicum L.*), garlic (*Allium Sativum L.*), cinnamon (*Cinnamomum Verum*) and clove (*Syzygium Aromaticum*), vanillin (*Vanilla Plantifolia*) are some examples of used vegetable sources [440]. *Origanum vulgare L.* EO has been employed as antimicrobial additive into a variety of polymers formulations, including PLA (Fig. 19**A**) [441], and nanocomposite films for food packaging based on gelatin and chitosan NPs [442,443], and was able to reduce the spread of *Staphylococcus Aureus*, *Listeria monocytegenes*, and to a lesser extent *Salmonella enteritidis* and *Escherichia coli*.

The antimicrobial properties of cinnamon, garlic, and clove EOs, incorporated into PLA, were tested against *Staphylococcus aureus* and *Campylobacter jejuni*, demonstrating that the latter is highly sensitive and susceptible to cinnamon and clove oil [444]. In a paper by Talebi et al., the organoleptic impact of EOs, generally recognized as a drawback, resulted in a positive effect on *in vivo* tested meat. In facts, *Mentha piperita* and *Bunium percicum* EOs were added at different percentages to PLA for minced beef packaging, increasing the product shelf life from 4 to 7 days, while enhancing the flavor of meat [445]. Complex systems engineered to release EOs in a controlled way have been also reported. As an example, PLA/thyme EO blends can be electrospun into nanofibers and coated with PVA/PEG to obtain films able to release the active substance in a humidity-controlled way (Fig. 19**B,C**) [446]. A general statement can be drawn from all of these studies: whatever the EO, they modify the polymer physical properties, in particular they can act as plasticizer by lowering the glass transition temperature and increasing elongation at break, and may increase the water barrier properties as well.

To make the most of EOs, their main constituents are often extracted and directly used as antimicrobial agents. Carvacrol and thymol have shown their ability as active additives in PP films for food packaging applications, with the dual function of controlled release antimicrobial to foodstuff against *Staphylococcus Aureus* and *Escherichia coli,* and the ability to replace commonly used synthetic antioxidants in PE and PP formulations [447–449]. Vanillin, instead, loaded into a PHB matrix, was more efficient against fungi than

bacteria present in preserved foods, and contextually reduced the PHB mechanical strength and melting point [450]. Interesting is the study conducted by Gressier et al. which infused thymol, geraniol, cinnamaldehyde, *ortho*-vanillin and *para*-vanillin into poly(ethylene terephthalate) (PET) fabrics, and evaluated their toxicity and ecotoxicity in addition to their antimicrobial efficiency against *Staphyloccocus aureus* and *Klebsiella pneumoniae* [451]. Chitosan/PVA/ fish skin gelatin ternary blend, with a formulation previously optimized by the same research group, have been recently modified with *trans*-cinnamaldehyde, leading to a biofunctional quadripartite films with increased tensile strength and proved antimicrobial activity against *Salmonella enteritidis*, *Listeria monocytogenes*, *Staphylococcus aureus*, and *Escherichia coli* [452].

The antimicrobial capacity of this family of compounds can be implemented by the addition of natural carriers as clays, micro- and nano-capsules [277,453,454] and/or fibers [455–457] that can improve mechanical properties of the matrices and enable the control of the release kinetics of active agents. As an example, the *in vivo* antimicrobial efficiency of a fully bio-based strawberry packaging, obtained by melt extrusion of a blend of TPS/montmorillonite loaded with thymol and carvacrol, was described in [458]. In this case, the presence of the clay allowed a slow and sustained release of EOs without affecting the strawberries organoleptic properties. Several of these compounds, including thymol and curcumin, can also be incorporated into biocompatible materials as gelatin films or hydrogels for wound dressing, promoting fibroblast cells growth and eliciting specific antimicrobial activity [459–463]. Also resinous compounds, as gum rosin, used as additive for PLA and PBAT, after being pre-loaded into organoclay, are able to inhibit the growth of bacteria (*Pseudononas aeruginosa* and *Staphylococcus aureus*) and fungi (*Candida albicans*) [464].

Just like other additives, in the perspective of the circular economy also compounds obtained from waste products have been tested for their potential as antimicrobial additives. Among them is the grapefruit seed extract, added to several polymeric matrices for food packaging, as PVA [465], LDPE, PLA and TPS [466], which yields materials with antimicrobial resistance against *Listeria monocytogenes* and *Escherichia coli*, as well as with improved UV-barrier properties. The addition of ground tea leaves waste to PEG-plasticized PLA makes it effective against gram-positive bacteria, like *Staphylococcus aureus* and *Bacillus subtilis*, and fungi as *Candida albicans*. This kind of material can therefore be used to produce fibers with dye removal and anti-bacterial properties, valuable for wastewater treatment [467]. Edible films for food packaging can instead be attained by adding pomegranate peel to starch [468]. In this way, it is possible to produce films with good mechanical properties, and antimicrobial activity against *Staphylococcus aureus* and *Salmonella*.

Among natural antimicrobials, peptides are widely used as bacteriocides for food applications, thanks to their established non-toxicity, heat stability and lack of off-flavors that make them good candidates also in biomedical sector [469–471]. Nisin, produced by strains of *Lactococcus Lactis,* exhibits a wide-spectrum antimicrobial action against Gram-positive bacteria and is recognized as a GRAS bioactive. This antimicrobial additive, with different activity grades, can be incorporated into EVA, to impart antimicrobial properties against *Micrococcus luteus* to film blown packaging [472], or loaded into a PHB/PCL/organoclay nanocomposite film to exert antimicrobial activity against *Lactobacillus plantarum* [473]. Its inhibition against *Listeria monocytogenes, Staphylococcus aureus,* and *Clostridium perfringens* was confirmed also when nisin is loaded into PP/cloisite composite films, even though it negatively affects the films mechanical and oxygen barrier properties [474]. For this reason, nisin is generally deposed as coating layer on different substrates, as chitosan/PLA [475], corn zein [476] films, confirming its bactericidal activity against *Staphylococcus aureus*, *Micrococcus luteus* or *Listeria monocytogenes* and *Salmonella Enteritidis*, respectively.

The approach based on chemical functionalization of polymer substrate or surface coating with antimicrobial actives has been also actively pursued [477]. As an example, antimicrobial polymers such as epoxy, lactones and PUs, including carvacrol and thymol [478], eugenol [479], curcumin [480–482], p-anisaldehyde [483], molecules onto the polymer chain have been produced. Besides plant derivatives, also microorganisms have been used as source for bioactive agents. In their work, Huang et al. incorporated yeast-based microcarriers on activated PVA-co-PE films. This approach inhibited significantly the growth of Gram-negative (*Escherichia coli*) and Gram-positive (*Listeria innocua*) bacteria [425].

The use of intrinsically antimicrobial polysaccharides [484,485] is also a valuable approach for the development of active materials. Among them, chitosan deserves a particular mention. Chitosan is a cationic polysaccharide mainly obtained from crustaceans and extensively used as polymeric bulk material, with intrinsic antioxidant and antimicrobial features [486]. The addition of further antimicrobic substances, as tannic acid and pullulan (another polysaccharide produced from starch by the fungus *Aureobasidium pullulans*) allowed Xu et al. to develop biocompatible nanofibers with the ability to cell attachment and growth (focal point for wound dressings), besides their activity against *Escherichia coli* spread [487]. Pullulan has also been added, together with silver NPs, to PVA for the preparation of relevant antibacterial nanofibers in wound dressing application [488]. Special antimicrobial activity of micromotors obtained embedding Prussian blue into chitosan/alginate beads, was demostrated by Zhang and coauthors. These systems are capable to adhere to biofilms, degrade it, kill bacteria, and, thanks to the motor motion, physically remove the debris and clean the contaminated surface [489].

Cellulose modification has been also tackled to produce antibacterial polysaccharides [490]. Mayer et al. prepared 2,3-dialdehyde cellulose (DAC) films blended with zein and gelatin, and tested their antimicrobial activities against Gram-positive and Gram-negative bacteria, demonstrating a remarkable performance for wound dressing applications (Fig. 19**D**) [491].

6. Commercially available bio-based additives

As part of the shift to a more sustainable and circular economy, bio-based polymer additives derived from biomasses are gaining increasing importance from the commercial standpoint. One of the main reasons relies on the growing awareness towards the potential migration of toxic substances from food contact materials (FCM) [492,493]. In addition, the restricted legislation about the use of oil-based and toxic products coupled to the expanding variety of biomasses used as feedstocks for the production of new building blocks

made costs more affordable. As a consequence, the commercially available range of bio-based additives allows to cover a wide range of specific functionalities. Currently, more than 1600 bio-based additives for polymers are found on the market [494]. Several authors reported how commercial bio-based additives are able not only to compete with traditional additives, but also to impart new and improved properties to the material. These findings are schematized in Table 4, where the column "Observed property enhancement" highlights the extent of improvement provided by some commercial bio-based additives to specific functional properties of the polymer formulation.

In Table 5, a list of several commercial bio-sourced additives is provided, including their trade name and manufacturers.

Fatty acids, including stearic and sebacic acids, and epoxidized oil derivatives (EOD) are mostly employed as a source to manufacture bio-based additives for different applications. EOD are primarily derived from C18 acids such as oleic, linoleic, and linolenic acid, and primary alcohols (diols or triols) extracted from soybean, linseed, and castor oils. Already in 1970's, some EOD were recognized as safe for the environment and health by Food and Drug Administration (FDA) [495], according to their similarities with metabolic products of fats in microbial, aquatic and mammalian organisms [36,178,496–498].

Among protective additives, heat stabilizers are used to hinder thermal degradation occurring upon polymer processing, especially in PVC compounds. Valtris Specialty Chemicals and Eastman Company UK Limited offer a series of thermal stabilizers consisting in mixed metal ESBO blends suited for calendering, extrusion, and closed mold processes (Table 5). Some producers, like Peter Greven and Acme-Hardesty, manufacture additives based on stearic acid, which can be also used as activators, accelerators, or thickeners. As regards stabilization against light- and oxygen-induced degradation, HALS are well known as the most active oil-based protecting agents for polymer formulations. Their activity relies on the formation of nitroxide radicals (Denisov cycle) through different reaction pathways [499]. Recently, a bio-based HALS from sebacic acid (CAPLIG 770TM) has also been commercialized (Table 5).

Regarding bio-lubricants, in 2020, a 20% increase in their production was already forecast for the next five years. The main natural sources of these bio-based additives are vegetable oils or animal fats, which are suited to a wide range of applications, including hydraulic and gear oils, mold release agents, and greases [500]. Specific vegetable-based lubricants are EOD from cocoa butter, soybean, palm, coconut, olive, and corn oils. They are used to improve processability, enhance rheology, reduce friction during extrusion process, and optimize the surface quality of the final product. Esters can be also used as lubricants, either as stand-alone base stock or in combination with other fluids. TotalEnergies, ExxonMobil, Shell plc, Chevron Co., BP plc, BioBlend Renewable Resources, among others, are the key players in the bio-lubricants market [501]. In particular, most ExxonMobil Esterex products are claimed as biodegradable and appropriate for contact with the environment.

The market of bio-plasticizers is constantly growing, mainly pushed by the food packaging industry, and its awareness to the health concerns raised by the use of oil-based plasticizers [501]. Bio-plasticizers are mainly based on epoxidized oils, sebacates, succinic acid, glycerol esters, and particularly used for the production of flexible PVC and PLA items. Arkema, Vandeputte Oleochemicals, Varteco, Novance are important bio-plasticizer manufacturers. In particular, Bioamber Inc., DuPont, Danisco, Akros, Chitec, SI group, Baerlocher, and Jayant Agro-Organics can be mentioned for the production of biodegradable food grade plasticizers [178].

The FRs market can be divided in two different categories depending on the chemical nature (halogenated or halogen free), and end-user industry (electrical, construction, transportation, and textiles-furniture). Since construction industry is the main consumer of these products, COVID-19 pandemic strongly impacted the FRs market. However, as well as for other bio-based additives, a growth of this market (5% CAGR) is expected for the next five years [502]. As reported in Table 5, bio-based FRs are mainly derived from cashew nutshell or lignin. The main producers and distributors are Perstorp, Great Lakes, Composite Technical Services.

Since food products utilize raw materials of different nature, and can be found in a number of presentations, packaging requires numerous types of additives to provide a variety of functionalities, including flexibility, printability, as well as the ability to preserve

Table 4
List of commercial bio-based additives selected from literature highlighting the observed enhancement on polymer properties.

Commercial name/ supplier	Additive composition	Source	Polymer matrix and additive content	Observed property enhancement	Ref
Cardolite®NC-514/ Cardolite	Epoxidized cardanol-based oligomer	Cashew nutshell liquid	PLA (78.5%) /PBAT (18.5%) + 3 wt% additive	265% increase in tensile strain compared to Joncryl® ADR 4300	[317]
C4767/Merck	β-cyclodextrin ester	Starch	PVC + 4 wt%	3% increase in tensile strain compared to DEHP	[550]
412333 AESO/Merck	Soybean oil, Acrylated Epoxidized	Soybean	PLA + 10 wt% additive	100% elongation at break and 80% Charpy impact increase with respect to pristine polymer	[551]
G7384/Merck	Gallic acid	Grapes, plant leaves	PA1010/bio-HDPE	18% thermal stability and 85% tensile strain with respect to pristine polymer	[552]
VEOMER LIN/ Vandeputte	Maleinized linseed oil	Linseed	PA1010/bio-HDPE + 0.8 phr	15.6% thermal stability, 92% tensile strain with respect to pristine polymer	[552]
BC-C-100/ Biochempia Co. ESBO/Sajo Haepyo Corp.	Cardanol/ ESBO	Cashew nutshell liquid and soybean	PVC + 50 phr	3% mechanical strain + 82% thermal stability with respect to DOP	[553]
Horphag Research LTD, London (UK)	Pycnogenol®	French maritime pine bark	PP + 1 wt% additive	Similar thermal stabilization than Irganox® (petrol-based commercial additive)	[108]

*STAB: Hypermer LP1 "Batch 4B", **ICI-1: R7698/13 from Imperial Chemical Industries.

Table 5
Commercially available bio-based polymer additives, their trade name and manufacturers.

Type of additive	Chemical composition/ Source	Commercial name	Manufacturer	Application
Stabilizers	Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate	CAPLIG 770TM	Nanjing Capatue Chemical	UV heat controller
	Barium-cadmium-zinc/ epoxidized soybean oil blend	Akcrostab™ Series	Valtris Specialty Chemicals	Facilitates processing
	Barium/cadmium/ dodecanoic acid	Ligastab series Barium-cadmium laurate	Peter Greven THE BioTek, BenchChem, MuseChem	Heat stabilizer used in manufacture of PVC with high metal content
	12-Hydroxystearic acid	Ligastar CA 12 OXY® Calcium salt of castor oil derivative.	Peter Greven Acme Harvesty	Heat stabilizer for PVC, thickener for silicon grease, rubber activator /accelerator
	Docosanoic acid, calcium salt	Liga Calcium behenate	Peter Greven	Facilitates processing, especially in manufacture of PVC
	Epoxidised soybean oil	Baerostab series	Baerlocher	Processing of PVC plastisol and calendaring
	Hydroxylamine from palm oil*	Revonox® 420 V*	Chitec Technology	Polyolefin stabiliser
	Blend of amines from rape oil*	GENOX® EP*	SI Group	Polyolefin stabiliser
	ESBO*	Baerostab NT 170 PS*	Baerlocher	PVC stabilizer
Lubricants	Calcium/magnesium stearate	Ceasit AV Veg® SAK series	Baerlocher Sun Ace	Lubricant for polyolefins, processing aid, acid scavenger, and water repellent agent
	Adipate/neopolyol/ phthalate/ trimellitate esters	Esterex®	ExxonMobil	Improves processability in automotive, textile, industrial, aviation, turbine, and compressor industries
	Pentaerythritol esters of stearic acid	LOXIOL®	Emery Oleochemicals	Improves processability (rheology during melting, reducing friction, and sliding resistance) and mechanical performance
	EOD*	Incroslip™ SL*	Croda	Biopolymers processing, film production, injection moulding
Plasticizers	Polyadipate ester	Syncroflex Series	Croda	It is used in coatings, food packaging and fabrication of oil resistant materials
	Trimellitic anhydride/ aliphatic alcohols	EDENOL series	Emery Oleochemicals	Imparts low migration, low volatility, high permanence and weatherability
	Sucrose benzoate	Uniplex series	Lanxess	Improves UV stability and processing
	Benzoic acid derivatives	VELSIFLEX series	Velsicol	Vinyl plasticizer and hardening agent
	Tributyl 2-acetylcitrate	Proviplast® 2624	Proviron	Self-curing fluorescence bisacrylic resin
	Tributyl citrate	HALLGREEN® R-C Discontinued	Hallstar	General-purpose film and packaging, compatible with cellulosic polymers, PHA, PLA, polyester resin and PVC
	Acetyl tributyl citrates	OXBLUE® ATBC Citroflex® 4	Oxea Vertellus Specialties	Biodegradable plasticizer in PVC and cellulose derivatives
	EODs	ADK CIZER® O-130P Epoxol® 7–4 Paraplex® G-60 Plasthall® ELO Lankroflex™	Adeka American Chemical Service Hallstar Hallstar Akcros	Manufacturing of PVC, PS, ABS, TPU, PS, Chlorinated rubber
	Acetylated monoglyceride	Radiamuls® 2130	Oleon (Avril Group)	
	Polyadipate ester	Syncroflex™ 3114	Croda	
	Butyl stearate	Radia® 7051	Oleon (Avril Group)	
	Dibutyl sebacate	Proviplast® 1944	Proviron	
	Dimethyl sebacate	Oleris® Dimethyl Sebacate	Arkema	Manufacturing of cellulosic polymers
	Kqetalized levulinic acid esters	Levulinic ketals	GFBiochemicals	PVC flexible or Rigid, PUR
	PLA-based	HD-*L*01	Polyvel	PLA masterbatch
	Glycerol ester	Atmer™ 1013	Croda (UK)	Applied in expanded PE
	Erucamide	Crodamide™ ER	Croda (UK)	Applied in polyolefin films
	Ethylene-bis-oleamide	Crodamide™ EBO	Croda (UK)	Applied for wood plastic composites
	Epoxy-type random copolymer	BioMaster® SG-20	BioMaster	Chain extender for PLA, PBAT, PBS
	Renewable raw material, not food competing	Ceridust® 8090 VITA	Clariant	Bio-based additive for wood coatings
	Isosorbide diester plant fatty acid	POLYSORB ID®	Roquette	Enhance processability of PVC resins for end-users (hospital floorings, decorative indoor surfaces, school furniture, etc)
	Plant-based	DOW ECOLIBRIUM series	Phifer Inc.	Improves heat stability, flame retardant optimization, and odour

(*continued on next page*)

Table 5 (*continued*)

Type of additive	Chemical composition/ Source	Commercial name	Manufacturer	Application
	Diethyl hexylisosorbate	IsDEH	Evonik Operations GmbH	Production of plasticized PVC
	Glycerineacetate mixture	UNIMOLL AGF	LANXESS	Manufacturing of polymers (PVC)
	Castor oil/based	LAPOL®	LAPOL	Melt viscosity enhancer in standard processes (injection molding, extrusion coating, thermoforming and cast films)
	Saturated polyesters*	POLIMIX 100*	Polynt	Plasticizer
	acetylated monoglyceride derived from hydrogenated castor oil*	GRINDSTED® SOFT-N-SAFE®*	Danisco	PVC plasticizer
	Triethyl citrate*	CITROFOL® AI*	Jungbunzlauer	PVC plasticizer
Flame retardants	Aromatic diol with a primary and a secondary hydroxyl group.	Polycard XFN™ series	Composite Technical Services	Especially for coatings
	Triaryl phosphate ester	Kronitex® CDP	Great Lakes (Chemtura Group)	Synthetic and natural rubbers
	Pentaerythritol derivative	Charmor™ PM40 Care	Perstorp	Fire resistant char barrier produced upon heating

* Additives permitted for use in food contact applications.

food quality during transportation, distribution, and storage [503,504]. One of the main concerns in food packaging is the potential migration or accumulation of hazardous substances or additives into the food products, which affect the quality of the product and pose a risk for consumers. Such contaminants may include lubricants, plasticizers, photoinitiators among others, the most representative of which are bisphenol A, mineral oil hydrocarbons (MOH), perfluoroalkyl substances (PFAS), and phthalates. Following the worldwide regulatory efforts, which heavily limited the use of several of these high-profile FCM contaminants, the industry has developed new bio-based food contact additives. Some of them, acting as stabilizers, plasticizers, lubricants, and antifogging agents, are reported in Table 5 [505,506]. In particular, stabilizers, lubricant and plasticizers are mainly sourced from vegetable fatty acids, including polyglycerol esters, glycerol mono-stearates, epoxidized oils or amine derivatives.

7. Socioeconomic issues of bio-based polymer additives

7.1. Health and legislative issues related to bio-based polymer additives

In this review, health issues concerning the release of polymer additives into natural environment, and their contact with living organisms, have already been mentioned. In particular, scientists are constantly studying the outcomes of additive leaching [507–509]. One of the most discussed problems of our era is the dispersion of plastic items in the environment. Erosion and weathering of plastic materials lead to their fragmentation, in turn increasing microplastic pollution and additive leaching into the environment. Several studies have shown that microplastic pollution involves not only the ocean environment, but also more secluded and unexpected places, such as freshwater [510], atmosphere [511], polar regions [512]. A study in the USA reported that average American children and adults are exposed to around 74,000 to 113,000 micro-nano-plastics (MNP) every year [513]. Another study suggests that, following the intake of microplastics into the human body, their journey and effects are still mostly unknown. In theory, only microplastics smaller than 20 μm should be able to penetrate organs, and those with a size of about 10 μm should be able to access all organs, cross cell membranes and blood–brain barrier, and enter the placenta [21]. These risks are associated with the presence of potentially harmful additives, which can be conveyed by microplastics and penetrate organs and tissues. Bio-based and biodegradable plastics are not avoiding the problem, since they are still able to carry and release toxic additive compounds [514]. Rodgers and coworkers [515] demonstrated that weathering phenomena promoted by marine water were able to induce leaching of toxic additives from four bio-based plastic polymers (PLA, PCL, polyvalerolactone, polypentadecalactone).

In some studies, the focus was directed towards the toxicity of specific materials. For example, Zimmermann et al. [516] characterized the toxicity and chemical composition of bio-based and biodegradable materials, and their findings indicated that 67% of the tested bioplastics and plant-based products contained toxic chemicals.

Bio-based additives are considered safer for the environment compared to their oil-derived equivalents. However, since they are intended to interact with the environment, their safety evaluation represents a novel concern that is regulated in most countries worldwide [517,518].

In Europe, a specific legislation for bio-based chemicals is still lacking, however all marketable chemicals must be registered under EU's Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation [519]. Persistence in the environment, bioaccumulation, and health toxicity are the main priorities addressed in the REACH risk assessment process.

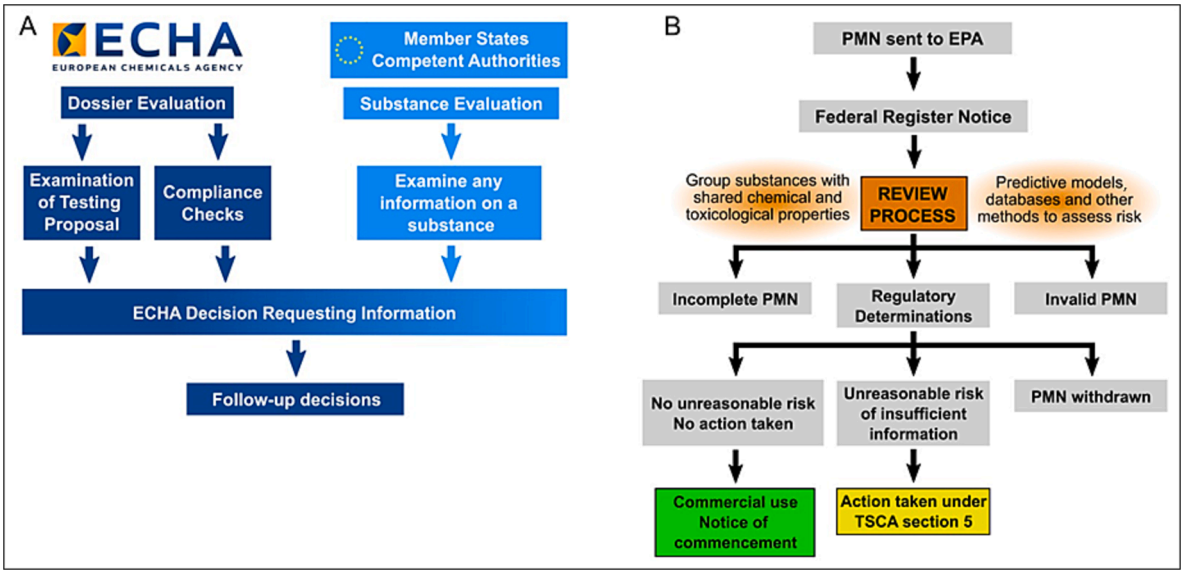


Fig. 20. Evaluation process of chemicals under EU REACH legislation, reproduced with modifications from Glass [517].

According to the REACH regulation, each importer or manufacturer is obliged to identify risks associated to the use of a specific chemical and provide information about the associated mitigation measures to the European Chemical Agency (ECHA). In particular, data related to chemical and physical properties, in vitro, *in vivo* and environmental toxicity, and biodegradability are mandatory. This procedure should be applied also to bio-based substances used as polymer additives that, if recognized as safer than their oil-based counterparts, are supposed to replace them in the REACH inventory. Therefore, any new bio-sourced chemical that is produced in Europe or distributed in a yearly amount higher than 1 ton must be registered. Several bio-based compounds, which are already classed as negligible risk substances, are exempted from registration (Annex IV of the REACH Regulation). This is also applied to naturally occurring, not chemically treated, substances (Annex V of the REACH Regulation) [520]. Nonetheless, even for exempted substances, the authorization under REACH Regulation is required [521].

Each authorization request is examined by the ECHA and the member state competent authorities. The evaluation process is based on the validity of testing proposals and compliance checks, and the risk assessment to human health and the environment. A flow diagram of the process is reported in Fig. 20**A**.

In the United States, manufacturing and commercialization of bio-based chemicals is regulated by the Toxic Substances Control Act (TSCA), which provides notification to the Environmental Protection Agency (EPA) for any potentially hazardous chemical that is not yet regulated by other federal legislation. For any new chemical compound that is not included in the TSCA Inventory, a Premanufacture Notice (PMN) must be notified to EPA The PMN must report data on chemical nature and intended application of the substance, predicted production volumes, potential human and environment exposure and relevant mitigation measures. Unlike the European legislation, toxicology tests are not mandatory, even though applicant are mandated to provide EPA with any relevant information regarding potential health or safety risk [522]. Once submitted, the PMN is reviewed by EPA within 90 days. EPA determines the potential hazard related to the substance by analyzing the relationship between structure and activity [517]. A flow diagram of the EPA review process is reported in Fig. 20**B**. The possible outputs of the process are: i) the substance presents an unreasonable risk or insufficient information; ii) the substance is not likely to present an unreasonable risk. In the former case (case i), EPA may take certain actions under section 5 of the TSCA, while in the second case no action is needed. As a matter of fact, the majority of bio-based compounds are expected to fall into case ii), thereby being exempted from additional restrictions.

7.2. Sustainability of bio-based polymer additives

Bio-based polymer additives are often referred to (even in this review) as *sustainable additives,* as by instinct humans tend to recognize that nature-derived materials or items are more eco-friendly than synthetic ones. This can sometimes be tricky to prove without turning to a technical and economic analysis aimed to determine the feasibility of their use in polymer formulations. However, until now only few studies have addressed such issue. Recently, McGauran et al. examined the use of poultry waste materials, including bone, meal and feathers, as polymer additives, and quantified energy, cost and carbon implications in terms of oil saving compared to conventional polymers. In particular, they concluded that using poultry waste as polymer additive is 5 times more convenient than its use as a bioenergy source in terms of crude oil consumption [523].

Another key aspect in the sustainability of polymeric materials is the evaluation of end-of-life options for plastic products. Post-consumer PVC, for example, is usually assigned to municipal solid waste in the landfill. The study of the behavior of plasticized PVC in contact with the soil is of key importance to determine more sustainable end-of-life options [524]. It was verified that, even

when bio-based additives are employed [525,526], their migration in the landfill can have a detrimental effect on mechanical properties of the artifact and leads to the contamination of soil with potentially harmful components present in the plastic material.

LCA is a powerful tool to evaluate the environmental impact of a product throughout its life cycle, from raw materials extraction, to processing, distribution, use and finally end-of-life options [527]. The principles and framework for LCA are described in the ISO 14040:2006 which includes: (1) definition of the goal and scope of the LCA, (2) the Life Cycle Inventory (LCI) analysis phase, (3) the Life Cycle Impact Assessment (LCIA) phase, (4) the life cycle interpretation phase (critical review, limitations, and recommendations).

Considering all aspects of a material's life is certainly not easy, and sometimes different "interpretations" of the LCA parameters can lead to controversies. For example, in 2022 an entire review [528] was dedicated to the comparison between LCA studies to determine which was the most sustainable alternative between plastic bags and their alternatives (paper, cotton). Interestingly, conclusions show that plastic bags, when reused, have the least environmental impact. The authors, however, reported the lack of a parameter related to marine litter as one of the main issues of the LCA methodology.

The attention to this analytical tool in the field of polymer sustainability is somehow recent, and it is proven by few papers, which, although not strictly related to bio-based additives, are relevant for renewable polymeric materials. As an example, a recently published review has readdressed several aspects regarding the sustainability of polymer composites, specifically highlighting the relative contributions of matrix and filler to LCA assessment [529]. As a result, the most relevant studies found the environmental benefit of using natural fiber composites in comparison to synthetic ones. Further, the potential of waste as raw material for composite production has been highlighted, in terms of resources savings and reduced disposal of residues.

In the mist of hundreds of papers reporting on LCA of bio-based plastics [530,531] literature regarding the LCA of bio-based additives for polymer is still scarce, since these materials are undergoing a massive experimentation phase and their LCA inventory results incomplete. For example, Samani et al. [532] recently published a review on LCA studies on FR additives, and concluded that a balance between developing novel harmless FRs for both environment and human health and emerging innovative waste management techniques is mandatory. In this context, bio-based FRs, such as tannic acid, PAc and lignin should be reviewed using LCA in future studies. Indeed, the current lack of data regarding bio-based additives in LCA databases highlights the key importance of enlarging them in view of the spreading of wholly bio-based polymer formulations.

According to Lokesh et al. [533], even the way consumers will welcome bio-based products depends on the sustainability framework and its LCA indicators that the authors identified in hazardous chemical use, waste generated, resource circularity and energy efficiency. Therefore, the choice of the methodologies used to measure sustainability and associated limitations of bio-based products is of paramount importance. In this frame, Dahiya et al. [534] reviewed different LCIA methods (namely, CML, TRACI, ReCiPe, Impact 2002 +) for LCA assessment of bio-based products compliant to the ISO Standard 14040, and described two case studies: the production of MCC from sugarcane using CML method, and the preparation of biopropionic acid by acidogenic fermentation employing Impact 2002 + tool. Since each method refers to different mid-point and end-point impact categories, the LCA analysis can result in different environmental impact scenarios.

Despite the fact that LCA studies on bio-based additives are still fragmentary there are valuable example in literature that provide meaningful results related to their sustainability. For example, in a work regarding LCA of encapsulated olive leaves' extract, Kritsotakis and coworkers [535] were able to determine that, among different extraction techniques and solvents employed, the solid–liquid extraction (SLE) using ethanol as solvent led to the lowest overall environmental footprint per kg of final product. In another work, the use of walnut husk extract (obtained using solar photovoltaic energy) in the production of waste cooking oil-based biodiesel, was evaluated as antioxidant [536]. The results revealed that, at a constant concentration of 200 ppm, the natural antioxidant capacity was comparable to that of the synthetic counterpart. Moreover, LCA showed that the formulation containing the natural antioxidant was more environmentally advantageous in all the investigated damage categories (+0.32% in an ecosystem quality, +12.13% in human health, +8.37% in climate change, and + 614% in the resources). The same authors [537] reported a LCA study on a natural antioxidant derived from olive wastes. Their findings indicated that a transition from linear agri-food system to a bio-economy oriented olive production with integrated agro-biorefinery, offers a wide spectrum of value-added bioproducts but also helps mitigating the environmental impact per ton of olive oil produced. The overall environmental impact of the processes employed in the manufacturing of bioplasticizers through LCA has also been evaluated. For example, Rojas-Bringas et al. [538] prepared starch-Brazil nut fiber biocomposites plasticized with sorbitol or glycerol, which provided similar mechanical properties. However, LCA results demonstrated that glycerol is preferable, as its production process is less complex, resulting in a lower environmental impact. Kopsahelis et al studied the impact of bioplasticizers production on factors such as air emissions, electricity and thermal requirements [539]. They concluded that the environmental impacts due to energy consumption could be mitigated with the use of renewable energy sources able to decrease the carbon footprint.

7.3. Economic assessment of the use of bio-based additives

The economic importance of the plastic additives market, currently evaluated more than 45.6 billion USD, and its growing trend, with an estimated CAGR of 5.6% [540], represents a safe bet for the generation of new materials in this field. In this scenario, bio-based additives play an important role in the transition to a fossil-free economy due to their renewable nature and the potential benefits of their large-scale production [541,542]. However, in several cases bio-based chemicals are not yet cost-competitive compared to fossil-based counterparts, therefore a thorough assessment of processing costs and impact on feedstock and product markets should be undertaken to gain information on their economic performance.

Table 6 lists some relevant examples of recent papers addressing the techno-economic analysis regarding the production of additives and chemicals from biomass.

Table 6
Representative overview of techno-economic data regarding the use of bio-based additives reported in literature.

Raw material	Product (yield)*	Operating cost (million US-$/year)	Revenue (million US-$/year)	Ref
Lignin	Oxygenated aromatic monomers, heavy organics (56%)	104	142	[543]
Pecan nutshell (*Carya illinoinensis*)	UV and thermal stabilizer (14%)	1.9	2.7	[545]
Acai (*Euterpe oleracea*) byproduct	Polyphenols (16%)	6.6	82.1	[554]
Purple yam (*Dioscorea alata*)	Polyphenols (30%)	3.0	3.5	[555]
Moriche palm (*Mauritia flexuosa*)	Oil (45%) Polyphenols (14%)	183.7	417.1	[522]
Grape (*Vitis vinifera*) pomace	Seed oil (5%) Polyphenols (4%) Biochar (16%)	16.3	47.7	[544]
Passion fruit (*Passiflora edulis*) rinds	Polyphenols (9 %)	0.025	–	[556]

* Expressed as weight percent with respect to raw material.

For example, the assessment of the techno-economical feasibility of the conversion of lignin into aromatics was carried out by Vural Gursel et al. [543]. The authors analyzed three lignin conversion routes, namely lignin pyrolysis, direct hydrodeoxygenation, and hydrothermal upgrading, and concluded that lignin upcycling via hydrodeoxygenation was profitable, as it yielded a positive net present value (51 MUSD), high return on investment (12%), and a payback period (PBP) of 5 years.

Polyphenols are the most investigated class of biomolecules as concerns the economic evaluation of their production from bio-resources. In this respect, several vegetable raw materials have been considered as potential feedstocks (Table 6). Moriche palm (*Mauritia flexuosa*) is an Amazonian palm with commercial importance, particularly in south America, due to its high content of phenolic compounds, carotenoids, essential fatty acids, vitamin E, and dietary fiber. In their study, Best et al. obtained oil and phenolic-rich extracts from moriche palm (fruit and pulp) considering three extraction processes, namely conventional solvent extraction (80% ethanol), supercritical fluid extraction, and the combination of both [522]. The third scenario was the most economically viable, as it allowed to recover almost 60% of the initial matter. In this case, the internal rate of return (IRR) was projected as 33.5%, while the PBP was lower than 3 years.

Agrifood byproducts have been also evaluated as a suitable source of functional biomolecules. Among them, grape pomace from winemaking industry is regarded as a major source of polyphenols. This agrifood waste represents around 12% by weight of the grape production worldwide. In a recent study, Jin et al. [544], proposed three downstream routes to utilize grape pomace: (1) seed oil, polyphenols, and biochar production, (2) seed oil and polyphenols production, and (3) only seed oil. Among the three routes, the whole biorefinery process (1) showed the highest economic performance, with an IRR equal to 34%, and 2.5-years PBP, recovering at least 25 % by weight of the initial matter as high value products.

In another case, pecan nut (Carya illinoinensis) waste (shell) was employed to obtain polyphenolic extracts by conventional solvent extraction (60% ethanol) [545]. Considering a solvent recovery of 95%, the process cost was 4.64 USD/kg extract, with an IRR of 14% and a PBP equal to 7 years. It is worthy to say that in this last case, pecan nutshell extract was employed as an additive in PE and PLA films. In both polymers, it acted as a thermal processing stabilizer, antioxidant, and UV stabilizer. At the time, the cost of this bio-based additive resulted similar to Irganox 1076 (5–15 USD/ kg). Moreover, the pecan nut byproduct was also rich in lignocellulosic biomass that was used as filler in PLA biocomposites [546–548].

In the light of the above, the use of agri-food waste as raw materials for based additives represents a significant investment. Nonetheless, in many cases it turns to be profitable after few years from the start-up, proving to be an economically sustainable alternative to the manufacturing of oil-based products.

8. Conclusions and future perspectives

In the last decades, the necessary transition to a circular economy less dependent on fossil fuels has pushed both academic and industrial worlds towards the development of bio-sourced products. In the specific field of polymer materials, two approaches are actively pursued: the growth of the bio-plastics sector, and the replacement of oil-derived additives with natural compounds. This review outlines the most recent advances in research and development on bio-based functional additives for polymer formulations. In particular, a classification in terms of functionality, action mechanism, source and applications is provided.

The literature overview has highlighted that a constantly growing number of substances from natural sources and their wastes represent a valuable alternative to synthetic additives in polymer formulations for specific applications. However, in most cases tailoring of the functionality and efficiency improvement are still required. To this aim, implemented and more sustainable technologies for the recovery and modification of platform molecules should be developed, with a particular focus to the enhancement of solubility, compatibility and long-term stability.

Bio-based polymer additives are expected to have a remarkable impact on the market as long as they will guarantee performances

comparable to their non-renewable counterparts, while being a safer and more sustainable option. In this respect, several gaps should be filled to achieve a "polymer additives bioeconomy". The first one is related to the lack of data for their health and environmental risk assessment. Although the majority of natural compounds are virtually safe, most of the best performing bio-based additives are obtained by chemical reactions. Therefore, systematic studies are needed to consolidate pre-normative analytical practices, which will drive future revision of the relevant test methods and legislation.

The second concern regards the economic and social impacts associated with the development of bio-based additives. In particular, their costs are still higher than those of fossil-derived counterparts, indicating that optimized production processes are needed. However, the quantification of the overall sustainability of bio-based additives should encompass a comprehensive life cycle sustainability assessment (LCSA), and the evaluation of their economic, societal, and environmental impacts.

Finally, as a long-term perspective, an integrated manufacturing model should be developed, in which biotechnology and informational production systems converge into a close interaction, leading to the so called biointelligent manufacturing [549].

This approach encompasses the use of bio-based resources, favoring microorganisms (such as fungi, bacteria, enzymes) to plants, and the creation of more decentralized, autonomous, and scalable production sites. In this frame, the conversion of biomass into functional additives should be performed in biorefineries, where metabolically engineered microorganisms in combination with sustainable, automated and digitally controlled manufacturing technologies are used to transform renewable resources into industrially valuable compounds.

In this way, the transition to resource-efficient and regenerative polymer additives will pave the way for the evolution of the plastics industry towards circularity and greenhouse gas emission neutrality, fostering technological progress, and allowing market access to new players.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors acknowledge the contribution of Dr. Giacomo Cesaro, for his help in the design of tables and figures.

The authors acknowledge the support from the H2020-EU.3.2.1.2 project "Plastic in Agricultural Production: Impacts, Lifecycles and Long-term sustainability - PAPILLONS", grant agreement ID: 101000210.

Dr. S. Agustin-Salazar thanks funding from the EU H2020 CE-BG-06-2019 project "Developing and Implementing Sustainability-Based Solutions for Bio-Based Plastic Production and Use to Preserve Land and Sea Environmental Quality in Europe - BIOPLASTICS EUROPE", grant agreement ID: 860407.

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