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Review

Natural Antioxidants: Advancing Stability and Performance in Sustainable Biobased and Biodegradable Plastics

Norma Mallegni [1], Francesca Cicogna [1], Elisa Passaglia [1], Vito Gigante [2], Maria-Beatrice Coltelli [2] and Serena Coiai [1,*]

[1] National Research Council-Institute for the Chemistry of OrganoMetallic Compounds (CNR-ICCOM), SS Pisa, Via Moruzzi 1, 56124 Pisa, Italy; norma.mallegni@pi.iccom.cnr.it (N.M.); francesca.cicogna@pi.iccom.cnr.it (F.C.); elisa.passaglia@pi.iccom.cnr.it (E.P.)

[2] Department of Civil and Industrial Engineering, University of Pisa, Largo L. Lazzarino 1, 56122 Pisa, Italy; vito.gigante@unipi.it (V.G.); maria.beatrice.coltelli@unipi.it (M.-B.C.)

* Correspondence: serena.coiai@pi.iccom.cnr.it; Tel.: +39-050-3152556

Abstract: The depletion of fossil fuels and environmental concerns have driven the development of sustainable materials, including bio-based and biodegradable plastics, as alternatives to conventional plastics. Although these plastics aid in waste management and climate change mitigation, their vulnerability to oxidative degradation impacts their longevity, durability, and performance. Natural antioxidants such as tocopherols, flavonoids, and tannins, extracted from plants or agri-food waste, present a sustainable alternative to synthetic stabilizers by enhancing the oxidative thermal stability of polymers like poly(lactic acid) (PLA), poly(butylene succinate) (PBS), poly(butylene succinate-adipate) (PBSA), poly(butylene adipate-co-terephthalate) (PBAT), poly(hydroxyalkanoate) (PHA), and starch-based materials. This review highlights recent advances in bio-based plastics stabilized with natural antioxidants, their mechanisms of action, and their role in improving material properties for applications like packaging. Additionally, it explores their impact on recycling processes, advancements in composite production techniques, and future research directions. Bioplastics can achieve enhanced performance, reduce waste, and support a circular economy by incorporating natural antioxidants.

Keywords: bioplastics; phenol compounds; antioxidants; circular economy

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Academic Editor: José Pedro Cerón-Carrasco

Received: 18 December 2024
Revised: 25 January 2025
Accepted: 30 January 2025
Published: 3 February 2025

Citation: Mallegni, N.; Cicogna, F.; Passaglia, E.; Gigante, V.; Coltelli, M.-B.; Coiai, S. Natural Antioxidants: Advancing Stability and Performance in Sustainable Biobased and Biodegradable Plastics. *Compounds* **2025**, *5*, 4. https://doi.org/10.3390/compounds5010004

1. Introduction

Thanks to its low cost, remarkable versatility, and extended durability, plastic is widely used, with global production reaching 400 million tons in 2022, 58 million tons of which were produced in Europe alone [1]. However, the widespread consumption of plastic presents severe environmental challenges. Only 14% of plastic is recycled globally, another 14% is incinerated, and the remainder is either sent to landfills (40%) or leaks into the environment (32%) [2]. In Europe, 39% of total plastic production in 2022 was used for packaging. The primary polymers utilized in this application were traditional petroleum-based plastics such as polyethylene, polypropylene, and poly(ethylene terephthalate). While these polymers are highly efficient for packaging applications due to their excellent properties, they are also extremely resistant to biodegradation, taking hundreds of years to decompose, and even when they fragment into microplastics, these particles continue to pollute water, soil, and air, posing a threat to wildlife and human health [3].

Bioplastics, such as poly(lactic acid) (PLA), poly(hydroxyalkanoate) (PHA), poly (butylene succinate) (PBS), poly(butylene succinate-adipate) (PBSA), poly(butylene adipate-co-terephthalate) (PBAT), and starch-based materials, are emerging as sustainable alternatives for various applications, particularly in the packaging sector [4–10]. The growing interest in these materials reflects their alignment with the sustainability goals of the United Nations' 2030 Agenda, which promotes strategies to reduce plastic waste—a significant issue in the packaging industry. Consequently, the production of biodegradable plastics and the variety of products incorporating them are steadily increasing [11]. Globally, however, bioplastic production reached only 2.22 million tons in 2022, representing less than 1% of the total plastics market [1]. The primary obstacles to their widespread adoption are higher production costs and generally inferior mechanical properties compared to conventional plastics. Nonetheless, the increasing demand for sustainable alternatives to petroleum-based plastics is expected to drive significant growth in the bioplastics market in the coming years. Government policies, such as bans on single-use plastics, are already accelerating the adoption of bioplastics, particularly for short-term applications. For example, the European Commission has assessed the utility of biodegradable plastics across various applications, categorizing them as beneficial (e.g., biowaste bags and teabags) or harmful (e.g., single-use cups and bottles); in contrast, the potential of bio-based polymers remains untapped mainly for applications requiring high durability [12].

Moreover, the great challenge is to produce technologically advanced bioplastics on a large scale using sustainable raw materials, optimizing process parameters to tailor morphology and macroscopic properties [13].

Among the various types of bioplastics, those named "biopolymers"—both bio-based and biodegradable [14]—stand out for their high sustainability potential. These materials align with a circular economy model aimed at reducing the use of fossil-based resources and minimizing waste accumulation. In contrast, bio-based but non-biodegradable bioplastics and biodegradable but non-bio-based ones tend to follow a linear model, limiting their positive environmental impact [15].

Although the benefits of recycling non-biodegradable plastics—whether of biological or synthetic origin—are well recognized, biodegradable plastics are often seen primarily as materials meant for disposal through biodegradation. However, many commercially available biodegradable bioplastics degrade slowly in natural environments, even in the presence of microorganisms, as they are designed to break down under specific conditions, such as those found in composting facilities [16]. For example, PLA has the advantage of significantly shorter degradation times in industrial composting conditions compared to traditional polymers, but PLA products can contaminate soil as they remain stable against degradation at ambient temperatures and obviously cannot be disposed of in the environment. In this context, for example, Van de Perre et al. [17] demonstrated that blending PLA with PBSA or polycaprolactone (PCL)—bioplastics well known for their ability to degrade in soil—proved effective in enhancing the home and soil compostability of PLA. The study showed that achieving a nearly co-continuous phase distribution, influenced by the composition and melt viscosity of the blend components, significantly improved the degradation of PLA under home composting conditions.

It is evident that, following the previous example, beyond simply producing new bio-based materials intended to replace petrochemical polymers, it is necessary to effectively address the end-of-life management of these materials by exploring efficient strategies in the processing phases. To improve the sustainability of bioplastics, it is essential to adopt integrated strategies that combine increased production, primary processing, and shaping with efficient recycling and disposal systems [18]. Mechanical recycling, which can also be used for bioplastics [19,20], plays a central role in this context as it helps reduce emissions, minimize the carbon footprint, and limit the consumption of primary resources, as highlighted by numerous life cycle assessment (LCA) studies [21,22].

Combining biodegradability and recyclability is fundamental for reducing waste and promoting environmental sustainability. However, recycling bioplastics presents several technical challenges. Repeated processing cycles can lead to material degradation primarily due to heat, oxygen, and catalyst residue exposure. This degradation compromises the physical and mechanical properties of the material, reducing its quality and limiting opportunities for efficient reuse. Overcoming these challenges is crucial to developing advanced mechanical recycling technologies that preserve material characteristics, minimize degradation, and extend the lifecycle of bioplastics [23].

Taking these factors into account, it becomes clear that stability and resistance to thermal and oxidative degradation are essential requirements, even for biodegradable bioplastics. A promising solution could be the incorporation of natural antioxidant compounds, such as phenolic compounds. These include simple phenols, like hydroxycinnamic and hydroxybenzoic acids, and polyphenols, such as tannins and stilbenes. Thanks to their powerful antioxidant properties, these compounds can help preserve the integrity of biodegradable polymers during recycling processes, limiting oxidative damage. By reducing the deterioration of material properties during multiple recycling cycles, natural phenolic compounds could enhance bioplastics' environmental and economic benefits. This would make bioplastics more cost-effective and sustainable in the long term, providing a tangible contribution to reducing plastic waste and protecting the environment [24].

Plant-based antioxidants are well established in sectors such as food, cosmetics, and pharmaceuticals [25,26] where they play a crucial role in extending product shelf life and combating free radicals. In recent years, natural antioxidants have also been extensively studied as functional additives for polymers, incorporated either in the bulk material or on its surface to impart specific properties [27,28]. These materials find applications in the active packaging sector, where the polymer film not only serves as a protective barrier for food but also assumes a functional role, particularly in preservation, thanks to the controlled release of the antioxidant additive.

These natural antioxidants have recently been proposed for stabilizing polymers and biopolymers. In the following sections, examples of bio-based polymers selected among those most suitable for packaging applications will be presented. As the data collected demonstrates, the use of natural additives represents an ecological alternative to synthetic stabilizers. Their application not only effectively protects polymers from thermo-oxidative degradation but also ensures that the additives maintain the material's fully bio-based character [28–30].

This review delves into the role of natural antioxidants in bio-based polymeric materials, with particular attention to their capacity to stabilize biopolymers and contribute to greater environmental sustainability. Moreover, it highlights the importance of these plant-derived substances in biopolymer recycling and processing, underscoring their potential to promote sustainable practices.

2. Degradation of Bioplastics

Polymers undergo different forms of degradation throughout their lifecycle, including during synthesis, production, processing, usage, recycling, and final disposal. Thermal and mechanical degradation often occurs during processing, production, and recycling, while additional mechanisms, such as UV and hydrolytic degradation, can occur during usage [31].

The nature of products derived from degradation and the extent of polymer degradation during service life depend on several factors, including the environmental exposition and condition of use, the chemical composition, structure, molecular weight, and crystallinity degrees, as well as on the presence of some impurities or catalysts [32].

Generally, degradation causes bond breakage and chemical alterations, leading to changes in materials' mechanical, optical, or electrical properties. These changes can manifest as cracking, erosion, discoloration, and phase separation [33].

Processes activated by thermal energy, mechanical stress, and UV radiation lead to the formation of free radicals, which react rapidly with oxygen, fueling degradation through an autocatalytic mechanism [34]. Each polymer exhibits a unique degradation pathway influenced by both intrinsic variables and external factors, making complex the description of degradation mechanisms. However, all radical processes have common pathways. Typically, degradation processes occur in three main phases: initiation (formation of free radicals), propagation (reactions between radicals, rearrangement of radicals, and, if oxygen is present, reactions of radicals with oxygen), and termination (combination of radicals) [35].

This review focuses on bio-based and biodegradable polymers, particularly examining the main radical degradation pathways of bio-polyesters such as PLA, PBS, PBSA, PBAT, and PHA.

Numerous studies have investigated the thermal stability of PLA at various temperatures, both above and below its melting point, and under both oxygen-rich and oxygen-limited conditions [35–37]. Degradation pathways can differ at high and low temperatures, and the presence or absence of oxygen can influence the degradation processes. However, since oxygen is invariably present during processing, service life, and eventual recycling, our primary focus is on the thermal-oxidative degradation of PLA. Thermal energy increases the mobility of polymer chains, and all authors agree that random chain breaking is the main initiation step. Rasselet et al. [36], in their studies conducted at lower temperatures (70 and 150 °C) than the melting point of PLA, hypothesized the degradation mechanism shown in Figure 1.

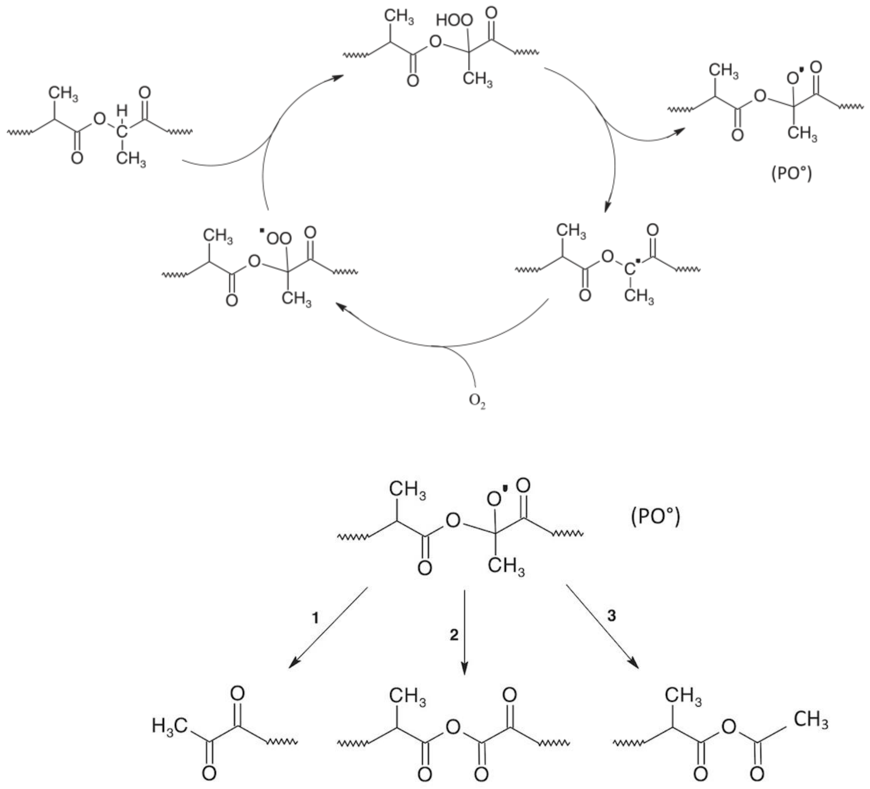


Figure 1. Radical oxidation mechanism of PLA at temperatures below its melting temperature (upper figure) and three possible β-scission pathways (**1**, **2**, and **3**) of the alkoxy radical (PO°) leading to the final products (lower figure). Reprinted (adapted) with permission from Ref. [36]. Copyright 2018 Elsevier.

The authors pointed out that the tertiary CH bond has the lowest dissociation energy, which promotes the formation of hydroperoxides (POOH) at this position. These peroxides mainly contribute to the oxidation initiation step. To complete this mechanism, the authors suggest that the alkoxy radical (PO° in Figure 1), formed by the elimination of hydroxyl radical, can decompose through three possible β-scission pathways (Figure 1).

Using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) measures, Badía et al. [38] studied both the thermo-mechanical and thermo-oxidation degradation of PLA. Thermo-mechanical degradation, caused by processes such as grinding, cavitation, and extrusion, can significantly alter the macromolecular structure. This phenomenon is particularly relevant during recycling, granulation, or material molding. Moreover, with repeated (re)processing cycles, deterioration tends to increase, making operational control critical, especially in the presence of oxygen. However, oxidation during the service life of PLA products can alter their properties, leading to issues such as discoloration and cracking. Therefore, understanding the degradation mechanism under both conditions is essential. To simulate PLA recycling, Badía et al. [38] reprocessed the sample through injection molding at 160–200 °C, while to simulate thermal oxidation, they treated the sample in a forced-ventilation oven under an air atmosphere at 60 °C. The authors observed that intramolecular and intermolecular transesterifications, hydrolytic, and homolytic reactions occurred in both conditions. However, they stated that thermo-mechanical degradation after multiple reprocessing processes is more aggressive in inducing changes in molecular weight distribution as polymer chains are exposed to temperatures above PLA's melting point, enhancing reactions among end-groups. Moreover, recycled PLA is more prone to O-acyl and O-alkyl homolysis via β-scission, which is more likely to occur at higher temperatures due to the structural weakness.

Oliveira et al. [39] confirmed that at elevated temperatures and during thermo-mechanical processes, degradation begins with the formation of radicals, which propagate in the presence of oxygen. However, the processing temperature of PLA (about 170–180 °C) is very close to its degradation temperature of approximately 215 °C. Under these conditions, the thermal degradation and decomposition of PLA occur in a complex manner, leading to the formation of various low molecular weight compounds and cyclic oligomers with different molecular weights, including lactides. Additionally, some authors [40,41] have indicated that at temperatures significantly above the PLA's melting point, degradation occurs through a non-radical process, producing lactide molecules, oligomeric rings with more than two repeat units, or acetaldehyde and carbon monoxide. These authors also state that radical reactions only occur at temperatures higher than 270 °C. However, their studies focused on the thermal degradation of PLA under extreme conditions (very high temperatures) and in the absence of oxygen, which certainly plays a crucial role in the degradation of PLA.

PLA photodegradation is caused by UV light and involves the breaking of chemical bonds within the polymer chains, reducing the molecular weight and compromising the material's mechanical and optical properties. Oxygen significantly accelerates this process due to the rapid formation of new chemical species containing oxygen.

Photodegradation is primarily driven by the absorption of photons by some functional groups within the polymer matrix. Different wavelengths also have different energy levels, which can affect and degrade specific chemical bonds in the macromolecules. Therefore, the irradiation wavelength is an important parameter to consider in photodegradation studies. Overall, photodegradation phenomena are described by Norrish reactions, which describe the photochemical cleavage of aldehydes and ketones into reactive species (Norrish I) and the photochemical intramolecular abstraction of a hydrogen atom by carbonyl groups (Norrish II) [35]. However, although the involvement of Norrish reactions in describing the photodegradation of polyesters has generally been reported for poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT), which can directly absorb light in the range of 300–330 nm, in the case of PLA, this hypothesis should be reconsidered. Indeed, aliphatic polyesters, like PLA, adsorb in the UV range, not in the visible part of the electromagnetic spectrum [42]. Therefore, depending on the wavelength of radiation, Norrish reactions may not be suitable to describe the photodegradation mechanism of PLA. Some studies in which PLA was irradiated with sources emitting in the UV range have proposed a Norrish II mechanism to explain the formation of degradation products [43,44]. Other authors [45,46], who studied PLA degradation products under a 300 nm UV source in air at 60 °C to simulate natural outdoor exposure, suggested a different mechanism. Since photooxidation cannot involve the carboxyl groups, which require a lower wavelength to be activated, the degradation is thought to begin with radiation absorbed by impurities or chromophores in PLA. Regardless of the first radical produced, PLA degradation starts with the abstraction of a tertiary hydrogen from the PLA chain, generating a tertiary radical $P^\bullet$ (1) (Figure 2). This radical can react with oxygen to form a peroxide radical (2), which may abstract another hydrogen from a tertiary carbon, producing a hydroperoxide and regenerating the initial radical $P^\bullet$ (3). The hydroperoxide then undergoes photolysis (4), resulting in the formation of a $HO^\bullet$ and a $PO^\bullet$ radical, which can further evolve through β-scission (5a, 5b, 5c). Since the authors observed the presence of anhydrides, they hypothesized that, among the β-scission mechanisms shown in Figure 2, the one producing the anhydride groups (5b) is the most likely.

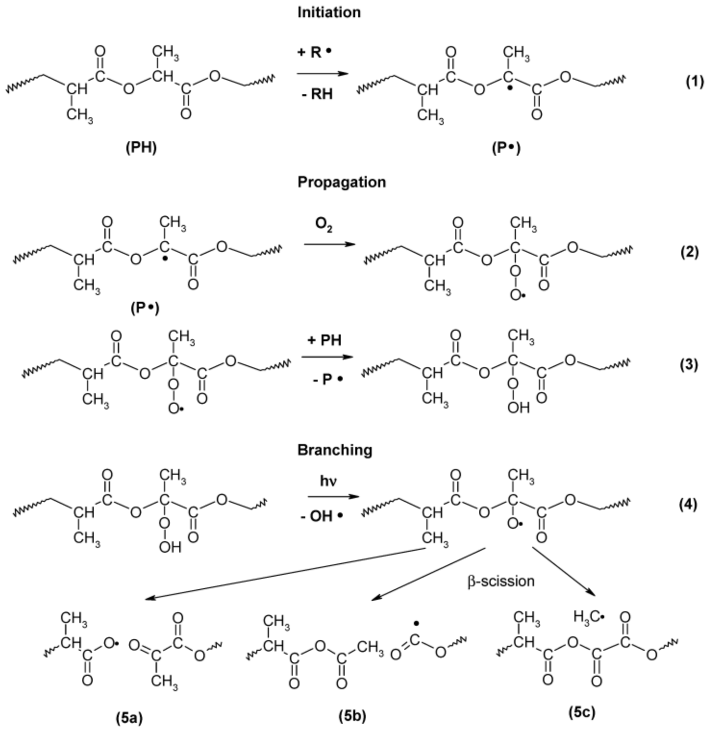


Figure 2. Radical oxidation process of PLA irradiated at 300 nm under air at 60 °C. Reprinted with permission from Ref. [45]. Copyright 2010 American Chemical Society.

Several authors [47–50] have studied the thermal degradation mechanism of PBS and similar polyesters resulting from the polycondensation of succinic acid, 1,3-propane diol, and 1,4-butane diol [48] at different temperatures and under an inert atmosphere. Some researchers employed FT-IR [47] or MS [48] to detect the gas evolved during TGA analysis, while others examined the chloroform-soluble fraction extracted from samples aged at different temperatures using MALDI-TOF analysis [49]. All studies reported a common degradation mechanism that occurs in multiple steps, starting with β-hydrogen bond scission through a cyclic intramolecular process (Figure 3). In this process, the β-hydrogen, near the oxygen bond of the ester, migrates to the adjacent carbonyl group, leading to the cleavage of the -O-CH_2- bonds and producing two chains with alkenyl or carboxylic acid end-groups. After this initial step, several degradation pathways are possible. One principal pathway is the cleavage of the β-hydrogen bond closest to the end of the chain with the carboxylic acid group, which generates succinic acid and a chain terminated with an alkenyl group (pathway 1). Succinic acid is then converted into succinic anhydride through a dehydration reaction. Additionally, the cleavage of the β-hydrogen bond closest to the polymer chain terminated with an alkenyl group produces 1,4-butadiene and chains with carboxylic acid end groups (pathway 2). Subsequently, the carboxylic acid end of the chains can decompose to produce succinic anhydride (pathways 3 and 1) or eliminate CO_2 to form acetate, generating an acid molecule (pathway 4). Finally, intramolecular transesterification reactions have been reported, forming cyclic molecules (pathway 5). Thermal degradation also led to the production of low molecular weight compounds, such as water and carbon dioxide.

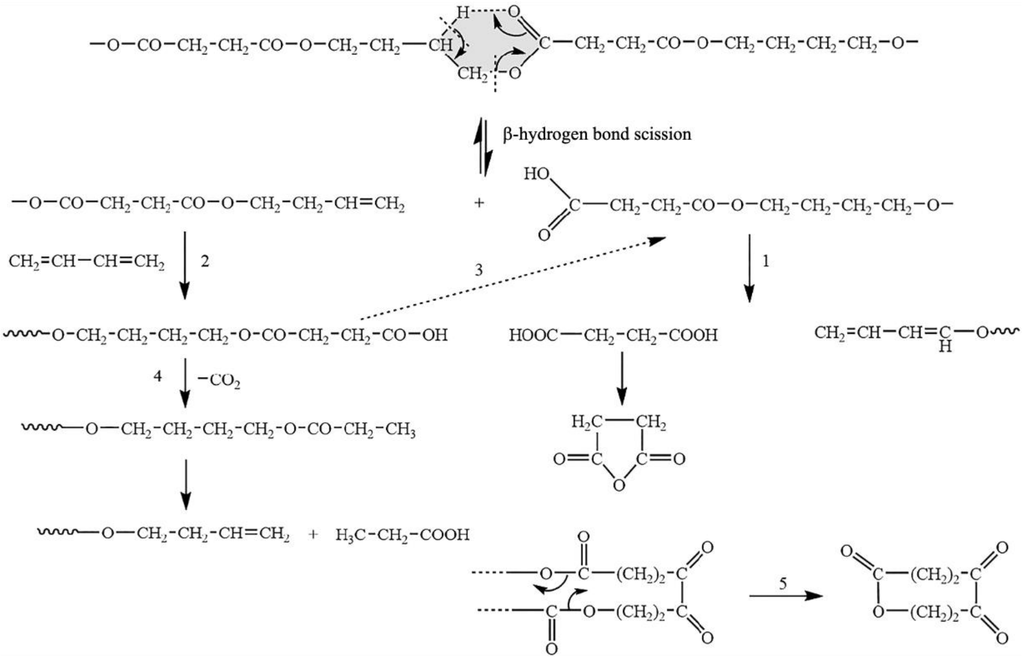


Figure 3. Thermal degradation of PBS under an inert atmosphere. Reprinted (adapted) with permission from Ref. [50]. Copyright 2022 Elsevier.

Georgousopoulou et al. [51] investigated the thermo-mechanical degradation and possible recyclability of PBS through consecutive extrusion cycles at different processing temperatures in air. They found that when reprocessed at temperatures above 190 °C, PBS exhibited branching and recombination reactions, leading to products with higher solution viscosity and a bimodal distribution of molar masses. Since the addition of typical radical antioxidant stabilizers to PBS significantly suppressed the degradation of PBS, the authors supposed that the degradation reactions had a radical character.

Bavasso et al. [52] examined a commercial biodegradable polymer blend composed of PLA and PBS, subjected to ten extrusion cycles, to evaluate the effects of mechanical recycling. The blend retained most of its mechanical properties, with a 53% decrease in ductility. Thermal stability showed a slight decline, with a 2.3% reduction in $T_{5\%}$ onset temperature, attributed to molecular chain scission (resulting in an 8.4% decrease in molecular weight) and crosslinking (evidenced by an increase in complex viscosity).

A similar study on a PLA-PBSA blend by Coltelli et al. [53] demonstrated that these materials could be recycled multiple times through extrusion or injection molding without compromising their thermal and mechanical properties. This recycling process extends the material's lifecycle, maximizing carbon storage before eventual composting.

Rizzarelli et al. [49] provide strong evidence for the radical nature of the thermo-oxidative degradation of PBS. The initial step is a hydrogen abstraction from the methylene group adjacent to the ester linkage, giving a hydroperoxide intermediate (I) that is unstable and undergoes further reaction with the elimination of the hydroxyl radical, producing the radical (II). Radical (II) can follow three possible degradation pathways, with the most energetically favorable leading to the formation of hydroxyl ester (III). The rearrangement reactions of this radical produce oligomers bearing succinic acid, 4-hydroxy butanoic aldehyde, or/and acid end groups. Other degradation pathways of radical (II) are schematically reported in Figure 4. Analogously with PLA, PBS can also degrade when exposed to daylight under air or UV radiation.

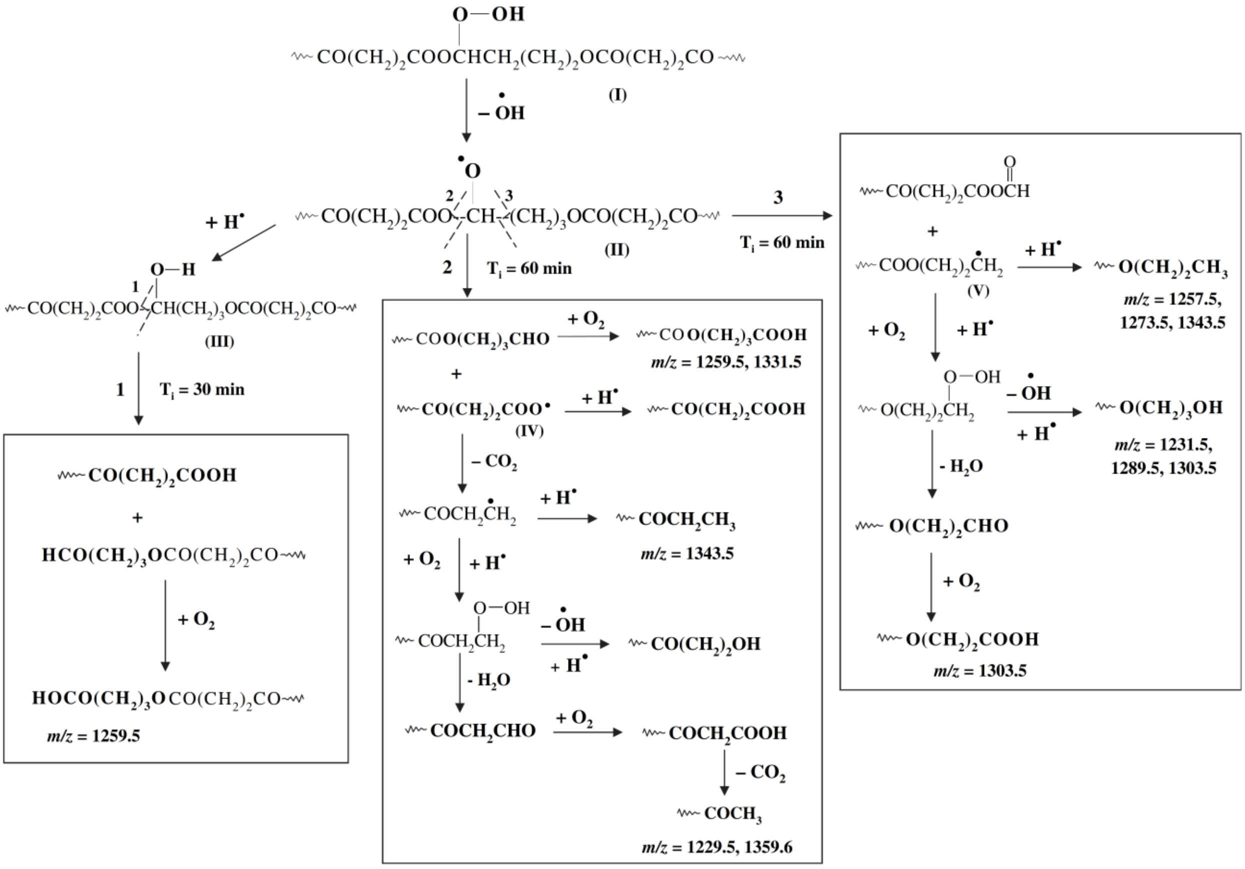


Figure 4. Thermal-oxidation mechanism of PBS. Reprinted with permission from Ref. [49]. Copyright 2018 Elsevier.

Fritz et al. [54] studied the effect of exposing PBS to daylight or UV radiation using atomic force microscopy, contact angle goniometry, FT-IR, synchrotron-assisted X-ray photoelectron spectroscopy, and near-edge X-ray absorption. They observed that aging of PBS affects surface morphology, roughness, and wetting behavior; however, no chemical changes were detected on the surface of the exposed PBS samples. The effects were more pronounced under UV radiation. Zhang et al. [55] exposed both virgin and anti-UV modified PBS to daylight aging and found that the UV additive effectively protected PBS from degradation. However, only Carroccio et al. [56] hypothesized a degradation mechanism for PBS exposed to accelerated photooxidation under daylight radiation. They used the

MALDI-TOF technique to detect the molecules produced during the photooxidation of PBS, and based on these results, they hypothesized that the formation of photooxidation products of PBS comes from several reactions and different possible first attack positions. Indeed, besides the hydrogen abstraction and subsequent hydroperoxide formation, two other cleavage processes operate in PBS, i.e., the chain cleavage reaction Norrish I and the hydroxyl end groups oxidation (Figure 5).

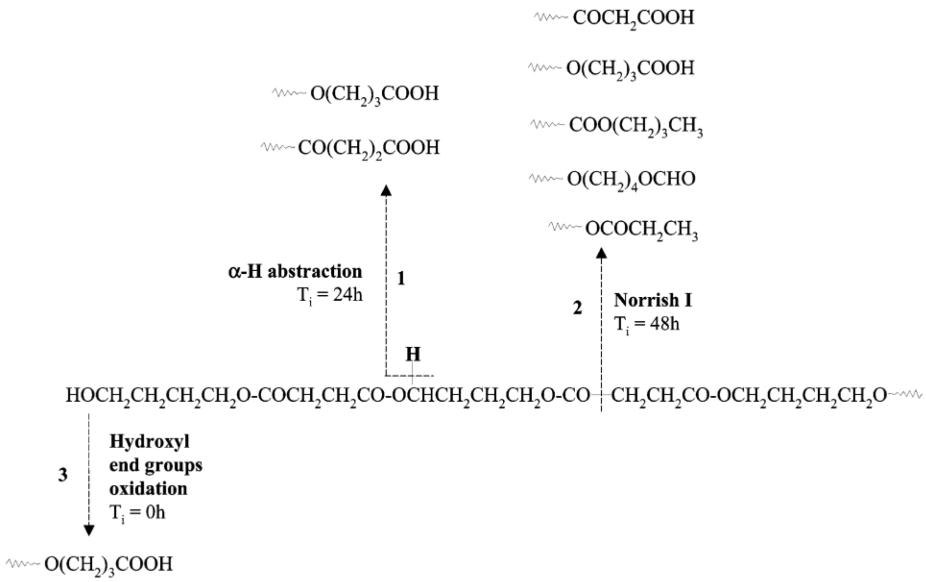


Figure 5. Photooxidation mechanism of PBS. Reprinted with permission from Ref. [56]. Copyright 2004 American Chemical Society.

Nomadolo et al. [57] investigated the recyclability of PBAT through multiple reprocessing cycles, evaluating its mechanical, thermal, physical, chemical, and morphological properties in comparison to low-density polyethylene (LDPE) and other polyesters. Interestingly, PBAT retained its tensile, impact strength, and melt flow index (MFI) throughout seven reprocessing cycles, with values comparable to those of LDPE. In contrast, the properties of PBS and PLA began to decline after the second melt extrusion cycle. Instead, PBAT exhibited better thermal and mechanical stability than PBS and PLA, as also confirmed by FT-IR analysis. These results suggest a limited hydrolytic and radical-controlled degradation mechanism for PBAT compared to PLA and PBS during recycling processes. Nevertheless, the main degradation mechanism of PBAT is hydrolytic or follows a radical process, as reported by Al-Itry et al. [58]. PBAT can also degrade by photooxidation, which is particularly relevant when PBAT is used in biodegradable mulch films. For example, Kijchavengkl et al. [59] studied the photooxidation of PBAT at 300 nm under air to simulate natural outdoor aging. The authors observed that photodegradation causes random main chain scission via the Norrish I or Norrish II mechanisms. The chromophoric carbonyl groups in PBAT make these films especially susceptible to photodegradation. Photodegradation can cause crosslinking within the matrix due to the recombination of free radicals generated by the Norrish I mechanism, resulting in brittle films with altered mechanical properties. Additionally, the Norrish II chain scission mechanism produces degradation products that further reduce mechanical properties, particularly tensile strength.

Referring just to mechanical recycling, La Mantia et al. [60] investigated the impact of reprocessing through five successive extrusion cycles on the rheological, mechanical, and thermal properties of a PBAT-based blend under both dry and wet conditions. The study revealed that material degradation was less pronounced when the samples were processed after drying with wet conditions. Nonetheless, the experimental findings indicated that the decline in rheological and mechanical properties was not severe, suggesting that the material could be reused effectively in both scenarios.

Considering the various degradation mechanisms discussed earlier, it is evident that many involve radical reactions. Therefore, it is crucial to incorporate stabilizing systems capable of trapping and neutralizing free radicals to limit the progression of degradation. The stabilization of polymers and biopolymers to prevent or slow down degradation during production and use can be achieved by adding chemical or natural additives to polymer formulations. Antioxidants, in particular, play a key role in protecting polymers from oxidation.

3. Plant Phenolic Compounds as Natural Antioxidants

3.1. Classification and Sources

Phenolic compounds are complex groups of secondary plant metabolites comprising over 8000 compounds [61] with well-known antioxidant properties, making them valuable in the food and nutraceutical industries and as potential substitutes for synthetic antioxidants in plastics [28]. These compounds are ubiquitous in plants, playing a vital role in protection and defense. Plants face oxidative damage from environmental factors like temperature variations, water availability, soil composition, pest attacks, pollution, and light [62–65]. To counteract these stresses, plants maintain oxidative balance through a complex antioxidant system, with secondary metabolites playing a crucial role. The production of these compounds is influenced by intrinsic factors like the plant's developmental stage and environmental conditions. Phenolics are found in all plant parts, including fruits, vegetables, seeds, nuts, and cereals, as well as in food waste and agricultural byproducts.

Phenolic compounds contain at least a phenol moiety and can be simple phenols with one aromatic ring or polyphenols with multiple rings and hydroxyl groups. They are classified into phenolic acids (e.g., hydroxybenzoic and hydroxycinnamic acids), lignans, stilbenes, tannins, and flavonoids [66–69] (Figure 6).

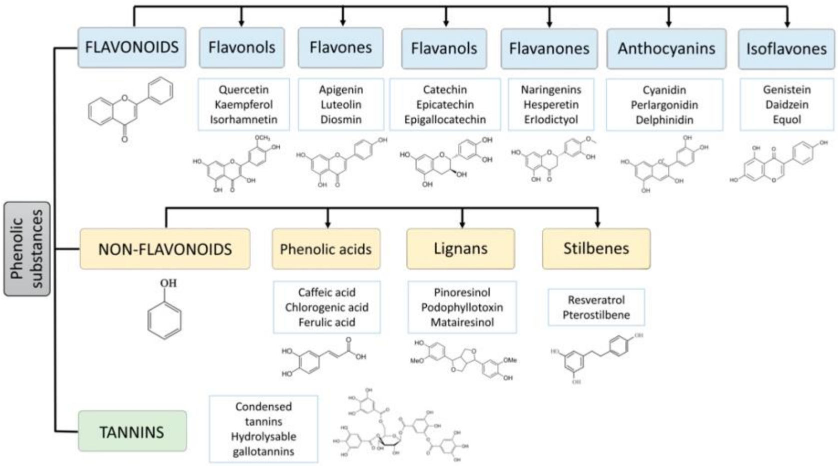


Figure 6. Classification of plant phenolic compounds [69].

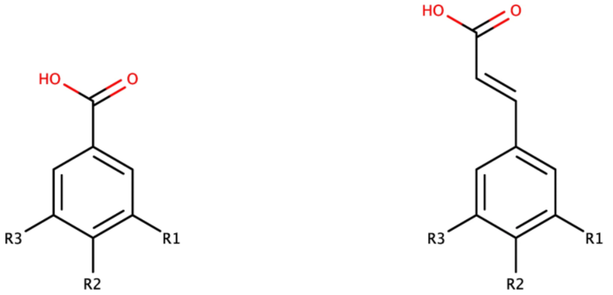
Flavonoids, the most abundant group with over 4000 compounds, have a structure with two benzene rings linked by an oxygenated heterocycle. Subclasses include anthocyanins, flavones, isoflavones, flavanones, flavonols, and flavanols, found in foods like onions, soybeans, berries, and tea. These compounds serve various biological functions, including flower and fruit coloration to attract pollinators [66]. When consumed through the diet, flavonoids offer protection against diseases, with effects such as antioxidant activity (e.g., quercetin), cardiovascular support (e.g., catechins), and anti-inflammatory and anticancer properties (e.g., anthocyanidins) [67].

Stilbenes are phenolic compounds characterized by two aromatic rings connected by a methylene bridge. They are synthesized by plants in response to stress, such as infections, and act as antifungal agents. Resveratrol, found in grapes and peanuts, is particularly notable for its anticancer, anti-inflammatory, and cardioprotective effects [68].

Lignans, derived from cinnamic acid residues, have a structure based on dimerized 2-phenylpropane units. Found in flaxseeds, whole grains, and berries, they exhibit estrogenic and antiestrogenic activities, contributing to hormone-related health [69].

Tannins, or tannic acid, are water-soluble polyphenols found in many plant foods. They are associated with reduced feed intake, growth rate, feed efficiency, and protein digestibility in livestock [69].

Phenolic acids, the most important bioactive compounds, are abundant in foods and classified into hydroxybenzoic acids (e.g., gallic, protocatechuic, salicylic, ellagic acids) with carboxyl groups directly attached to the aromatic ring, and hydroxycinnamic acids (e.g., ferulic, caffeic, p-coumaric acids) with a 2-propenoic acid group (Figure 7) [70]. The number and position of hydroxyl groups and substituents on the aromatic rings contribute to their structural diversity.



1, R1 = R2 = R3 = H, Benzoic acid
2, R1 = R2 = R3 = OH, Gallic acid
3, R1 = R2 = OH, R2 = H, Protocatechuic acid
4, R1 = R3 = H, R2 = OH, *p*–Hydroxybenzoic acid
5, R1 = OCH_3, R2 = OH, R3 = H, Vanillic acid

6, R1 = R2 = R3 = H, Cinnamic acid
7, R1 = R2 = OH, R3 = H, Caffeic acid
8, R1 = R3 = H, R2 = OH, *p*–Coumaric acid
9, R1 = OCH_3, R2 = OH, R3 = H, Ferulic acid
10, R1 = R3 = OCH_3, R2 = OH, Sinapic acid

Figure 7. Structures of benzoic acid (**1**), common hydroxybenzoic acids (**2**–**5**), and common hydroxycinnamic acids (**6**–**10**). Reprinted with permission from Ref. [70]. Copyright 2020 Springer.

Phenolic acids, found in fruits, vegetables, legumes, cereals, and oils, provide organoleptic characteristics and health benefits (Figure 8) [71]. Their biological activities include antioxidant, anticancer, antidiabetic, anti-inflammatory, antimicrobial, anticholesterolemic, and antihypertensive effects.

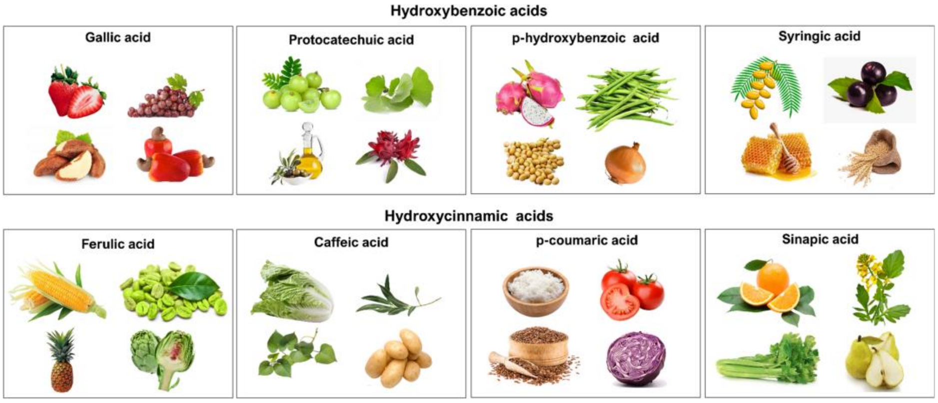


Figure 8. The different categories of food sourced simple phenolic acids. Reprinted with permission from Ref. [71]. Copyright 2023 Springer.

Hydroxybenzoic acids, such as p-hydroxybenzoic acid, occur in most edible plants, with higher concentrations in red fruits, black radish, and onions [72]. Gallic acid, a triphenolic compound found in fruits, nuts, and plants like tea leaves and oak bark, exhibits strong antioxidant and antibacterial properties. It is applied in food packaging, cosmetics, biofertilizers, and biomedical fields [73].

Compared to hydroxybenzoic acids, hydroxycinnamic acids are more common in nature [74]. Cinnamic acid, an aromatic carboxylic acid, is found in Chinese cinnamon, Panax ginseng, fruits, grains, vegetables, and honey [75]. It supports plant growth, reproduction, and disease resistance [76]. Its most common form is trans, though the cis form also exists [77]. Cinnamic acid exhibits antioxidant, antimicrobial, antitumor, neuroprotective, anti-inflammatory, and antidiabetic properties [78], with its para-hydroxyl group enhancing antioxidant power [79]. The delocalization of electrons on its aromatic rings, bonds, and oxygen atoms enables free radical stabilization.

Ferulic acid, derived from cinnamic acid, is abundant in wheat, corn, lettuce, citrus fruits, grapes, and medicinal herbs like reed roots and angelica [80]. Caffeic acid, another hydroxycinnamic acid, is found in olives, coffee beans, fruits, carrots, and propolis. It exists as simple monomers (esters, amides, and glycosides) or complex forms (dimers, trimers, and flavonoid derivatives) [81]. Caffeic acid plays a key role in plant defense, protecting against predators, fungi, bacteria, and UV-B radiation [82].

Rosmarinic acid, a derivative of caffeic acid, is found in Boraginaceae and Lamiaceae plants like sage, rosemary, lemon balm, thyme, oregano, and mint. It contains four phenolic hydroxyl groups and a carboxylic group (Figure 9), which give it potent antioxidant properties. Its sodium salt has superior antioxidant activity compared to other forms [83].

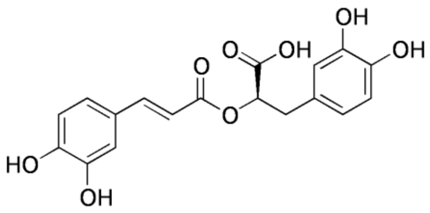


Figure 9. Rosmarinic acid.

Additionally, rosmarinic acid shows antimicrobial, anti-inflammatory, cytotoxic, neuroprotective, and immunomodulatory effects, with potential benefits in preventing Alzheimer's disease and protecting neurons from degeneration [84].

3.2. Antioxidant Mechanism

The antioxidant ability of phenolic compounds depends on their chemical structure and the number and position of the hydroxyl (-OH) groups on the aromatic ring. The benzene ring stabilizes the antioxidant molecule after reacting with free radicals, making phenolic compounds essential in mitigating oxidative damage in biological systems, food chemistry, and polymers [85,86].

The antioxidant activity of phenolic compounds is explained through several mechanisms: (i) scavenging of free radicals, (ii) inhibition of lipid peroxidation, (iii) metal ion chelation, (iv) inhibition of oxidative stress-related enzymes, and (v) stimulation of natural protective mechanisms [87–90]. Among these, radical scavenging is particularly important for enhancing the thermal and oxidative stability of polymers [28].

This process occurs via two key mechanisms: hydrogen atom transfer (HAT) (Equation (1)) and electron transfer (ET) (Equation (2)):

$$\mathrm{ArOH} + \mathrm{R}^{\bullet} \rightarrow \mathrm{ArO}^{\bullet} + \mathrm{RH} \quad (1)$$

$$ArOH + R^{\bullet} \rightarrow ArOH^{\bullet +} + R^{-} \rightarrow ArOH^{\bullet} + RH \quad (2)$$

In the HAT mechanism, the phenolic compound (ArOH) donates a hydrogen atom to the radical species ($R^{\bullet}$), forming a resonance-stabilized phenoxy radical ($ArO^{\bullet}$). This process is influenced by the bond dissociation enthalpy (BDE) of the phenolic O–H bond, where lower BDE values mean higher antioxidant activity. In the ET mechanism, the phenolic compound donates an electron to form a radical cation ($ArOH^{+\bullet}$), releasing a proton to form the phenoxy radical ($ArO^{\bullet}$). Although both mechanisms yield similar thermodynamic products, HAT is typically more favorable for phenolic compounds [28]. A third mechanism, sequential proton-loss electron transfer (SPLET), involves proton loss followed by electron transfer and is pH-dependent but results in the same antioxidant products as the HAT and ET.

The structure of phenolic compounds is critical to their antioxidant effectiveness. Molecules with more hydroxyl groups generally exhibit stronger activity. For example, flavonoids derive their activity from the number and arrangement of hydroxyl groups on the aromatic rings. Quercetin, a flavonol with five hydroxyl groups, demonstrates exceptional antioxidant activity compared to other phenolic compounds. Studies have shown increased activity with a higher number of hydroxyl groups, as in the series myricetin > quercetin > kaempferol > galangin (Figure 10) [85,87]. Additionally, a 3,4-dihydroxy structure on the B-ring further enhances antioxidant activity. Flavonoids also reduce the oxidative activity of transition metals by donating hydrogen atoms or binding to metals at specific sites, such as the 5-hydroxyl and 4-oxo groups.

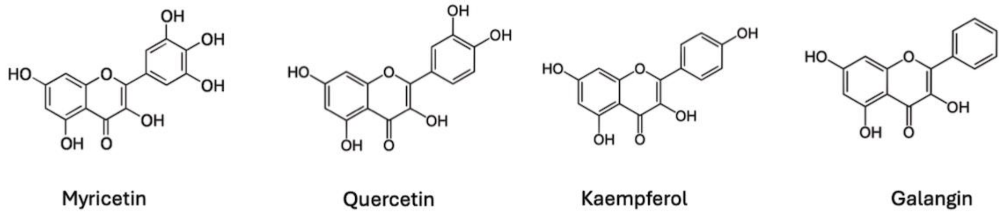


Figure 10. Chemical structure of a series of flavonols: myricetin, quercetin, kaempferol, and galangin. Their free radical scavenging ability follows this order: myricetin > quercetin > kaempferol > galangin.

Phenolic acids also exhibit structural variations that influence their activity. Hydroxycinnamic acids are more effective than hydroxybenzoic acids [86,88]. Structural modifications also play a role: rosmarinic acid, derived from two phenolic acids, is more active than caffeic acid, while esterification (e.g., in chlorogenic acid) reduces caffeic acid's antioxidant potential.

Thermodynamic and structural parameters affect effectiveness. A lower BDE indicates easier hydrogen donation from the phenolic OH group, enhancing activity. Hydroxyl groups in ortho positions lower BDE by 9–10 kcal/mol due to the formation of stabilizing intramolecular hydrogen bonds [89–91].

Substituents on the aromatic ring also play a role. Electron-donating groups (e.g., hydroxyl, methoxy) enhance activity by increasing hydrogen donation, while bulky or branched substituents reduce it due to steric hindrance. Synthetic antioxidants like butylated hydroxytoluene (BHT) stabilize free radicals via bulky groups shielding the aromatic ring [90]. Ionization potential (IP) is another key factor: molecules with lower IP react more readily with free radicals. For example, resveratrol (161.3 kcal/mol IP) is more reactive than cyanidin (246.2 kcal/mol IP). These thermodynamic and structural insights are crucial for designing effective natural antioxidants.

3.3. Advances in Extraction Methods and Stabilization

Natural phenolic compounds present two main challenges: their extraction from plants, including agro-industrial waste, and their stabilization to maintain effectiveness. Extraction is crucial for obtaining biologically active phenolic compounds, with methods chosen based on compound stability, solubility, and process scalability. Furthermore, most phenolic compounds are susceptible to oxygen, light, temperature fluctuations, and pH changes, complicating their handling, especially in high-temperature processes like plastic production. These challenges have led to the development of protective methods, with encapsulation being a standard solution [92–94].

While not exhaustive, this discussion aims to provide insights into phenolic compounds' extraction techniques and encapsulation methods.

Traditional solid–liquid methods—including Soxhlet extraction, steam distillation, maceration, and agitated solvent extraction—remain widely used due to their simplicity and adaptability despite drawbacks like long processing times, high solvent use, and thermal degradation [67,95]. Organic solvents such as acetone, ethanol, and glycerol, which are non-toxic, are commonly employed. However, these solvents alone are often inefficient for highly polar compounds like phenolic acids. Adding 10–70% water can enhance extraction efficiency by increasing the diffusion of phenols through tissue swelling [96].

Recent advancements in extraction and encapsulation techniques have created new opportunities for using phenolic compounds in various sectors. The rising demand for plant-based sources and the potential to repurpose agro-industrial waste have driven the development of innovative, sustainable methods to enhance yield [94]. Phenolic compound content varies widely depending on extraction methods, chemical nature, particle size, and storage conditions [97].

Modern techniques, such as ultrasound-assisted extraction (UAE), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), and subcritical water extraction (SWE), improve efficiency, reduce solvent use, and minimize environmental impact [67,94,98–100]. UAE employs ultrasonic waves to break down plant-based cell walls, shortening extraction time and supporting eco-friendly solvents. SFE utilizes supercritical CO_2 for selective extraction, obtaining high purity extracts with minimal solvent use [101]. Similarly, PLE and SWE use high pressure and temperature to optimize yield while preserving bioactive compounds. Other methods, such as pulsed electric field (PEF) and high hydrostatic pressure extraction (HHPE), enhance cell membrane permeability and mass transfer, enabling faster processing and higher yields. Enzyme-assisted extraction (EAE) uses specific enzymes to release trapped compounds, reducing solvent use and improving selectivity. These innovations promote sustainable and efficient practices, though scalability and cost remain challenges.

Phenolic compounds, valued for antioxidant and bioactive properties, are highly vulnerable to environmental factors, limiting their use in food, cosmetic, and pharmaceutical industries. Encapsulation techniques improve phenolic extracts' stability, bioavailability, and bioactivity, enabling broader industrial use and the controlled, targeted release of active ingredients [96,102,103]. Encapsulation strategies include spray drying, where phenolic solutions are atomized into fine droplets and dried with hot gas, and freeze drying, ideal for heat-sensitive substances as it removes water by sublimation while preserving structure. Although freeze drying is slower and costlier [104,105], supercritical CO_2-based methods also stabilize phenolics and are mainly used in the pharmaceutical and food industries [105,106].

Micro- and nano-encapsulation techniques using polymeric carriers, like coacervation or liposomes, enhance the bioavailability and targeted release of phenolic compounds [107,108]. Lipid nanotechnologies, for instance, improve skin penetration and preserve the antioxidant and anti-inflammatory properties of rosmarinic acid [109,110]. Cyclodextrins, with hydrophobic cavities, protect phenolic compounds from oxidative degradation, improve solubility, and modulate release while enhancing antioxidant activity [111,112]. Similarly, chitosan, a natural polysaccharide, forms nanoparticles or microparticles that effectively protect and release bioactive molecules [113–116]. Chitosan powders complexed with rosmarinic acid offer remarkable chemical stability and controlled release [117–119]. Alginate beads are another effective system for encapsulating phenolic acids, such as rosmarinic and caffeic acids, preserving their properties and enabling gradual release to enhance pharmacological effects. Synthetic polymers like PLGA, PLA, and PCL protect active molecules (e.g., β-carotene and tocopherol) from degradation, improving bioavailability [120,121].

Inorganic materials like nanoclay and layered double hydroxides (LDHs) facilitate controlled releases and protect bioactive compounds from oxidation and thermal degradation [122,123]. For example, ferulic, caffeic, and rosmarinic acids intercalated into these nanostructures create nanoantioxidants, addressing bioavailability and scalability challenges [96,124–126]. Incorporating these systems into polymeric matrices enhances thermo-oxidative stability and prolongs active ingredient release, making them ideal for applications like active packaging, which requires an extended release to preserve product quality and shelf life.

4. Bioplastics with Natural Antioxidants

As previously discussed, owing to their sustainable origin and ability to prevent oxidative degradation, natural antioxidants have gained increasing interest as polymer additives, particularly in petroleum-derived polymers such as polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) [27,28,35,127]. The main biobased antioxidants that have shown significant stabilizing potential for these polymers are polyphenols, carotenoids, and vitamins.

Among flavonoids, quercetin, rutin, dihydromyricetin, and curcumin have proven to be particularly effective. For example, quercetin increases PP's oxidation induction time (OIT) by ten times at 210 °C, outperforming synthetic stabilizers such as Irganox 1010 [128]. Additionally, polymeric flavonoids such as condensed tannins obtained from Pinus radiata and Acacia mearnsii have demonstrated the ability to improve thermal stability and UV resistance in polymers like linear low-density polyethylene (LLDPE) and biodegradable polyesters [27,129,130].

Innovative methods are being developed to leverage agro-industrial byproducts as sources of antioxidants, an approach that will be further explored in the subsequent sections on bioplastics. A successful example is hydroxytyrosol, derived from olive oil production residues, which has proven effective in stabilizing PP against thermal degradation [131]. In addition to research on plant extracts or agro-industrial wastes for the extraction and use of antioxidant molecules, there has been a growing interest in the direct use of these byproducts as functional biofillers [132]. A well-known and practical example is lignin, a paper industry byproduct, which has been shown to improve PP stabilization, especially when combined with Irganox 1010 [133]. Other biofillers with antioxidant properties, such as cork extracts (rich in suberin and lignin) and residues like grape pomace, turmeric waste, and spent coffee grounds, have been successfully used as additives for LDPE and PP [134–136]. The resulting composite materials maintain their properties even during aging and recycling cycles.

The results obtained for these commodities, combined with the growing development and use of biopolymers—often applied in similar contexts—have driven the incorporation of polyphenols or their derivatives as natural antioxidants in bio-based and biodegradable plastics. The following sections will present specific examples of biopolymers selected for packaging applications, addressing both extracts rich in phenolic compounds and biofillers.

4.1. Poly(lactic acid)

The literature reports numerous works and reviews [27,137–142] on the incorporation of natural compounds into PLA to develop active packaging with enhanced antioxidant, antibacterial, and antifungal properties. Natural additives are also used as colorants, indicators of food freshness, and markers for exposure to weathering or thermal oxidation. For example, Stoll et al. [143,144] incorporated bixin, a carotenoid extracted from annatto seeds with both coloring and antioxidant properties, into PLA films to increase the light barrier of the packaging and to provide antioxidant properties. Similarly, rice straw extract, the second most widely produced agro-industrial byproduct rich in phenolic compounds, was shown to reduce or slow oxidative processes when incorporated into biodegradable food packaging materials [145]. Siddiqui et al. [146] developed PLA-based films via solvent-casting, creating single, triple, and quadruple blends containing natural additives such as thymol, carvacrol, limonene, and cinnamaldehyde derived from natural resources (e.g., thyme, oregano, citrus, and cinnamon). These formulations effectively extended food shelf life and improved consumer safety. Ramos et al. [147] further demonstrated that thymol had a plasticizing effect on PLA without compromising its thermal stability.

Several authors have investigated the incorporation of thymol and carvacrol into PLA films, examining their effects on the physicochemical, thermal, and morphological properties of the polymer [148]. These PLA-based films containing thymol or carvacrol successfully extended the shelf life of various foods, including salmon slices [149], lettuce [150], ground meat [151], blackberries, and raspberries [152].

Ortenzi et al. [153] used phenolic antioxidants as initiators in the ring-opening polymerization of L-lactide. Among the resulting PLA materials, PLA synthesized with vanillic alcohol as an initiator showed the greatest potential for active food packaging applications as it effectively reduced color and fat oxidation in salami during its shelf life. Similarly, Gallego et al. [154] dispersed dry or lyophilized thyme and rosemary plants in PLA films to protect O/W emulsions from oxidation. Apicella et al. [155] investigated the use of cardanol as a stabilizing agent combined with microfibrillated cellulose (MFC) to produce PLA/PBSA/cardanol/MFC films. Their work achieved a favorable balance of ductility, barrier properties, and sealability, making these films suitable for packaging applications.

Since this review focuses on natural additives added to preserve the properties of PLA and other bio-based matrices during reprocessing, thermal and photo-oxidation, and weathering, we limit our discussion to the relevant literature on this topic.

Moraczewski et al. [156] studied the effectiveness of natural extracts from coffee, cocoa, and cinnamon added to a PLA-based material to reduce the adverse effects that occur during repeated mechanical recycling of the biopolymer. To benchmark their performance, the authors also tested a synthetic additive. The recycling process was simulated by granulating recycled PLA materials and producing paddles and bars through injection molding, repeating this process for three cycles per sample. The increase in melt flow rate (MFR) is typical when reprocessing PLA; the synthetic anti-aging compound had the most favorable effect on MFR stability during multiple processing cycles. However, cocoa extract limited the increase in MFR better than the other extracts. Moreover, the extracts did not adversely affect the mechanical properties of the materials even after reprocessing, and products containing extracts had almost identical or even better mechanical properties than those made of pure PLA. Importantly, the properties of these products were not different from those of PLA containing a synthetic anti-aging compound. Furthermore, extracts increased the resistance of PLA to the oxidation process, as observed by the authors carrying out oxidation onset temperature (OOT) measures, and, as stated by DSC analysis, PLA samples containing the extracts were characterized by parameters that allowed their correct processing.

Valero et al. [157] used the extracts of green tea residues, pomegranate peels, pomace, blackberry leaves, and yellow onion peels to thermally stabilize PLA. The efficiency of the natural additives as thermal stabilizers was also compared with that of a synthetic antioxidant. The authors simulated the thermal aging of the materials under accelerated conditions in an incubator oven with natural convection, heating the samples for 5 weeks at 100 ± 2 °C. UV stability was studied by photo rheology combining viscoelastic analysis with UV exposition. The authors first observed that since polymers undergo a primary degradation during processing at high temperatures, the presence of thermal and processing stabilizers as antioxidants can be used to reduce the impact of processing. For this reason, they carried out melt rheology measurements before and after extrusion because this technique makes it possible to follow the evolution of the macromolecular structure, providing information on the degradation mechanisms, including the competition between chain scission and recombination. The authors observed that grape marc and pomegranate peel extracts exhibited stabilizing effects and protected PLA from thermo-mechanical degradation during extrusion. The first had antioxidant action comparable to that of the commercial antioxidant. On the contrary, green tea residues demonstrated a pro-degradant effect that accelerated the chain scission mechanism. During the thermal aging of the samples at 100 °C, the authors observed that pomegranate peel and grape marc extracts exhibited significantly high stabilizing effects at this low temperature. However, the authors noted an increase in the PLA viscosity in the early stages of thermal aging when pomegranate peel and grape marc extracts are added to PLA. Moreover, the authors observed that the presence of 2 wt.% of polyphenol extracts notably inhibited the drop in PLA molecular weight due to chain scission during photodegradation. They stated that the high stabilization of the natural extracts against UV radiation could result from synergistic effects between UV absorbance and antioxidant properties. Indeed, phenolic compounds have both UV-filtering abilities correlated to absorption in the UV region and antioxidant properties to scavenge UV-generated reactive oxygen species.

Latos-Brozio et al. [158] evaluated the addition of (+)-catechin and polydatin in PLA, studying how the mechanical and thermal properties, as well as the color, of both PLA, and PLA with additives varied after controlled UV exposure, thermal oxidation, and weathering. Catechins, identified in fruit (apples, blueberries, kiwi, and strawberries), green and black tea, red wine, and cocoa, are polyphenols with high antioxidant properties and significant positive effects on human health. Polydatin is present in grape skins, nuts, pomegranates, and other plants. It has anticancer, anti-inflammatory, anti-allergy, and high antioxidant properties. In this study, the authors exposed samples for 100 h, 200 h, and 300 h to two alternately repeating day and night cycles with radiation on or off at 60 °C and 50 °C, respectively, to simulate the UV exposure. Thermo-oxidation was carried out by exposing the samples to air at 70 °C for 100 h, 200 h, and 300 h; weathering aging was carried out by exposing the samples to two variable cycles simulating daytime (300–400 nm at 60 °C, 240 min, humidity at 80%, rainwater on), and night cycle (no radiation, temperature at 50 °C, humidity of 60%, for 120 min). The authors noted that after 200 h of weathering, the samples underwent significant degradation, making it impossible to perform some tests; after 300 h of aging, the samples crumbled, which made most tests impossible. The authors determined the mechanical properties of PLA and PLA with additives after 100 h of UV and thermo-oxidation. They observed that the presence of both polyphenols increased the resistance of the matrix to thermo-oxidative and UV-aging. They also evaluated the Vicat softening temperature of the samples after 100 h of thermo-oxidation and UV-aging, observing that UV aging did not affect changes in softening temperature. However, thermal oxidation caused a significant increase in the Vicat temperature that increased by about 15% for reference PLA and 30% for PLA with polydatin and (+)-catechin. The authors associated this increase with a higher crystalline phase content in the samples, which can increase due to the chemical crystallization process accompanying the aging processes of polyesters. The authors also observed an increase in the oxidation OOT determined by DSC analysis under air flux when both additives were added to PLA, concluding that both additives act as natural stabilizers of PLA. Moreover, TGA analysis showed that the presence of additives did not modify the thermal stability of PLA. Moreover, all aging conditions, but especially UV and weathering, changed the color of all samples due to the oxidation of the natural compounds under the influence of aging factors. However, since polyphenols absorb UV radiation, they can protect PLA against UVA and UVB radiation, and the change in the color of polyphenols can be used to indicate the lifetime of the materials.

The same authors also tested the addition of gallates to PLA to protect the matrix from degradation during thermo-oxidation UV-aging and weathering [159]. Gallates are antioxidants used as preservatives in the food, cosmetic, and pharmaceutical industries. For example, in industry, synthetic derivatives of gallic acid, i.e., propyl gallate (E310), octyl gallate (E311), and dodecyl (lauryl) gallate (E312), are commonly used. The authors tested ethyl gallate, propyl gallate, octyl gallate, and lauryl gallate in PLA. OOT measures showed a significant increase in the oxidation temperature for PLA containing ethyl, propyl, and octyl gallate, corresponding, respectively, to about 50, 61, and 45 °C and a lower increase in oxidation temperature was observed for lauryl gallate (about 13 °C). Thermo-oxidation and UV-aging caused an increase in tensile strength and a decrease in the elongation at break after 100 h of aging.

Masek et al. [160] evaluated the stability of PLA and PLA with rutin and hesperidin, two flavonoids, under thermo-oxidation, UV-aging, and weathering conditions. The authors carried out the thermo-oxidation by exposing the samples to air at 110 °C for 10 days in a dryer with thermo-circulation. UV aging was performed for 288 h, exposing the samples to two alternately repeating segments: the first, the daily segment, contained irradiation at 60 °C for 8 h, and the second, the night segment, where there was no UV radiation, was performed at 50 °C for 4 h. Weathering was carried out by using two variable segments simulating day and night conditions, and the samples were subjected to two different cycles: a daily cycle, with irradiation at 60 °C for 240 min, humidity = 80%, and rainwater, followed by a night cycle with no radiation, at 50 °C, humidity = 60%, for 120 min. The authors observed a noticeable increase in the oxidation temperature with the addition of the antioxidants, and, after thermal-oxidation aging, all tested antioxidants acted as stabilizers as opposed to weathering aging agents; only Chimassorb 944, not a natural product, seemed to protect PLA from degradation.

OOT measures were also used by Latos-Brozio et al. [161] to show that the impregnation of PLA with extracts from Cistus Linnaeus and green walnut husk effectively increases the oxidation temperature of PLA. Analogously, Arrieta et al. [162] showed that catechin added to PLA or PLA-polyhydroxy butyrate (PHB) significantly increased the OOT of pure PLA. Catechin, one of the major active constituents of green tea, is a natural food-grade additive that inhibits lipid oxidation, increasing the shelf life of foods. It is a nonvolatile compound suitable for melt processing to avoid or reduce its loss during polymer processing.

Moraczewski et al. [163] also tested adding coffee, cocoa, or cinnamon extracts as anti-aging compounds of PLA. In this work, the authors exposed the compounds to an accelerated aging process (720, 1440, or 2160 h) at 45 °C and 70% relative humidity under continuous UV radiation. The authors compared the effectiveness of the tested extracts to a commercially available anti-aging compound. The MFR analysis was carried out before and after UV-aging, considering samples with different content and extracts' sources. Results showed that MFR increased for PLA and all samples containing extracts or commercial anti-aging, but the increase was lower, even than pure PLA when 1 wt.% of cinnamon or 0.5 wt.% of cocoa extracts were added to PLA. TGA analysis and mechanical tests (tensile strength and impact tensile strength) showed that the addition of small amounts of extracts positively influenced the stability of samples subjected to accelerated aging. The presence of extracts inhibited the loss of mechanical strength observed in the case of PLA, and their effectiveness was better than that of the reference anti-aging compound.

Olejnik et al. [164] incorporated green tea extract (polyphenone 60) and caffeic acid into PLA and PLA-containing starch (sPLA) to obtain smart and ecological packaging materials. The authors tested the samples' resistance to UV-aging and weathering by determining the dynamic mechanical properties (DMA), color change, Vicat softening temperature, and chemical structure. The addition of natural antioxidants to the PLA matrix caused a significant increase in the OOT, as determined by DSC analysis. The OOT value of PLA-containing additives increased by 46 °C and 52 °C if compared to the OOT of PLA. The authors observed that adding green tea extract did not change the rheological behavior of PLA but enhanced PLA resistance to UV irradiation. The rheological curves of PLA in the presence of green tea extract are almost the same after different types of aging in comparison to the unaged material. The authors also stated that caffeic acid was a less effective PLA stabilizer than green tea extract. UV-aging and weathering caused a variation in the samples' color, and UV-aging had a higher impact on the final color of the samples than weathering. This color variation can be used as an indicator of UV aging. Finally, the Vicat softening temperature values of samples with natural antioxidants were raised after the UV exposure and weathering except for PLA enriched with caffeic acid, where this parameter after weathering was equal to the value before aging.

Agustin-Salazar [165] evaluated the effect of the addition of resveratrol on the photo-oxidative degradation of PLA. Resveratrol is a naturally occurring polyphenol with antioxidant properties associated with anti-inflammatory activity and possible prevention of cardiovascular diseases. The authors carried out the photo-oxidative aging by irradiating the samples in dry conditions at 40 °C with a mercury UV lamp ($\lambda > 250$ nm) and collecting the aged samples at different times to follow changes in crystallinity, molecular weight, functional group formation, and mechanical properties. Molecular weight determination carried out by SEC analysis before and after different UV-oxidation times evidenced that resveratrol can partially control the molecular decrease observed for pure PLA and that higher concentrations of resveratrol better control molecular weight. From FT-IR analysis, the authors observed that different functional groups formed during photo-oxidation and resveratrol can slow oxidative chain reactions by acting as a hydrogen donor antioxidant. Nevertheless, the photo-oxidation reaction can directly involve resveratrol, leading to the formation of phenanthrene derivatives via electrocyclic ring closure or to a dioxetane derivative that can spontaneously decompose, yielding two carbonyl species identified as hydroxy benzaldehydes. Finally, the authors observed that the addition of resveratrol had a positive effect on PLA rupture and yield strength.

Dintcheva et al. [166] studied the UV-aging of PLA films containing different amounts of ferulic acid, vanillic acid, vitamin E, and quercetin. Photo-oxidation of the samples was carried out using a UVB lamp (313 nm). The weathering conditions were 8 h of light at 55 °C and 4 h of dark at 35 °C for 800 h. Interestingly, the authors observed that a low ferulic acid, vitamin E, and vanillic acid content had a protective action against the photooxidation of PLA, as determined by FT-IR analysis. In contrast, high contents of the same additives lead to an unexpected pro-degradant action, especially at high exposure time. The quercetin, irrespective of the amount, had a significant protective action against the photo-oxidative degradation of PLA. Dintcheva et al. [148] further confirmed the pro-oxidant activity of ferulic acid, vanillic acid, and thymol during UV and thermal aging of PLA containing a high amount (2–3 wt.%) of these additives.

López-Rubio et al. [167] added b-carotene to PLA and studied the UV stability of the sample by exposing it to a 300 W lamp. The lamp produced a mix of radiation very similar to natural sunlight and was equipped with special glass that allowed only part of the natural sunlight to pass through. The authors observed a fast degradation of b-carotene under radiation; however, the PLA containing b-carotene had greater modulus and similar ultimate tensile strength than before UV treatment while keeping a greater elongation at break than the pure PLA.

Grigsby et al. [168] added esterified tannins to PLA. The authors esterified tannin using anhydrides to synthesize tannin esters with different chain lengths and degrees of substitution. Artificial weathering of modified PLA samples was carried out by exposing the samples to UVA-340 lamps and water regimes according to ASTM D4329-99. Samples were randomly rotated every 169 h and were exposed for 504 h. The results of the mechanical tests on aged PLA containing tannins esterified with acetate, propionate, and butyrate evidenced that flexural modulus values were like the original values, suggesting that the presence of tannin esters may confer a protective role on PLA during extended exposure.

The literature also reported using natural molecules and plant extracts immobilized on different substrates to protect bio-polyester matrices from degradation during reprocessing or as an active additive to impart functional properties to the matrix [126,169]. Immobilization of active additives has the important role of protecting the natural compounds from premature thermal- or photo-degradation and controlling the kinetic release of the active molecules to extend the activity of the additive for a longer time.

For example, Li et al. [170] prepared a PLA composite containing cardanol-loaded halloysite nanotubes (HNT-CA) and studied the thermal-oxidation aging of the composite, comparing the result with pure PLA, PLA containing free cardanol (CA), and PLA containing only halloysite nanotubes. The authors carried out thermal oxidation aging in an aging oven at 120 °C, 100% fan and damper for 1 to 12 days. The authors evaluated the OOT values of all the samples before and during different aging times and observed that, for short aging time, the PLA/cardanol system had longer OOT than PLA/HNT-CA. For a longer aging time, the PLA/HNT-CA worked better than PLA/CA to stabilize PLA. Similar results were obtained by analyzing the evolution of molecular weights of the samples.

Alternatively, the literature also reported the preparation of nanocomposites based on PLA and containing bio nano-filler for various applications [171–175]. For example, Spiridon et al. [176] prepared composites based on PLA and lignin extracted from softwood (LB) and hardwood (LO) and evaluated the stability of these composites under accelerated weathering conditions. The authors observed that lignin in PLA determined an increase in the thermal stability of PLA. Furthermore, the composites containing 7% softwood or hardwood lignin retained much of the initial mechanical properties compared with neat PLA after weathering, and organosolv lignin derived from hardwood displayed the best mechanical properties, both before and after 600 h of accelerated weathering.

4.2. Poly(butylene succinate), Poly(butylene succinate-co-adipate), and Poly(butylene adipate-co-terephthalate)

PBS and PBSA are biodegradable polymers derived from biological sources, increasingly adopted in various industrial sectors due to their significant advantages in sustainability and performance. PBS is a semi-crystalline polymer known for its thermal stability, high ductility, and ease of processing [50]. It is bio-based up to 80% and fully biodegradable, making it an environmentally friendly alternative to polyolefins, particularly in the flexible packaging sector. Additionally, its relatively low melting temperature prevents the degradation of heat-sensitive compounds, such as polyphenols, during processing.

PBSA, on the other hand, is a thermoplastic aliphatic copolyester obtained through the direct esterification of succinic and adipic acids with 1,4-butanediol. It is a highly versatile material used in various applications, including the production of agricultural mulch films, bag linings, disposable products, rigid and flexible packaging, and automotive interior components [10,177,178].

Thanks to advances in synthesizing 1,4-butanediol from renewable resources, the production of PBS and PBSA is gradually moving toward a completely biomass-based approach. This shift further enhances their ecological value and contributes to reducing environmental impact. Despite their many advantages, both polymers are susceptible to thermal and oxidative degradation during processing and their service life. However, research has demonstrated that this instability can be significantly mitigated using antioxidants, both natural and synthetic, which improve their resistance and help preserve the material's properties [51,179].

Grigsby et al. [129], for example, tested tannins extracted from the bark of Pinus radiata, both in their native and esterified forms, as antioxidants for PBS. The results of this study demonstrated the adequate UV protection of these compounds, comparable to the results obtained with synthetic UV stabilizers at equivalent concentrations. Nanni et al. [180] explored the antioxidant effectiveness of two natural extracts, a lab-produced grape pomace extract (GPext) and a commercial grape seed extract (T), used as stabilizers for PBS under various degradative conditions: thermo-mechanical, thermo-oxidative, and biodegradation. GPext contains 15.9% total polyphenols, predominantly in the form of oligomeric polyphenols, while T has a significantly higher total polyphenol content (55%), with a dominant polymeric fraction composed of proanthocyanidins. The different polyphenolic compositions of the two extracts resulted in differentiated antioxidant capacities. The data showed that T was highly effective in preserving PBS stability, maintaining the polymer's molecular weight even after six recycling cycles (Figure 11a) and nearly 300 h of thermal aging at 110 °C (Figure 11b) while also ensuring consistent MFR values up to 180 h of thermal aging (Figure 11c).

The performances of this natural extract were comparable to those of the synthetic antioxidant Irganox 1010. Furthermore, T increased the degradation temperature of PBS by over 20 °C, thanks to long-chain polyphenols forming stable hydrogen bonds, thus protecting the material.

In contrast, the grape pomace extract showed lower effectiveness as a stabilizer due to the oligomeric polyphenols, which undergo auto-oxidation in the presence of oxygen, generating peroxides and free radicals (Figure 12). These reactive intermediates accelerate PBS degradation as the catecholic polyphenols of GPext quickly oxidize, forming unstable radical quinones that produce additional radicals and trigger a degradation cycle. Nevertheless, GPext accelerated the biodegradation of PBS, suggesting a possible use as a natural agent to promote polymer biodegradation.

Bianchi et al. studied the effectiveness of natural extracts derived from coffee residues, which are rich in phenolic compounds, as antioxidants for PBS [181]. The extracts were incorporated into the polymer matrix at various concentrations (1% to 5% by weight) through melt blending. The antioxidant power of these extracts was evaluated using a kinetic approach based on the Kissinger–Akahira–Sunose (KAS) method, the Flynn–Wall–Ozawa (FWO) method, and the Friedman models by calculating the apparent activation energy (Ea) of thermo-oxidative degradation carried out through TGA experiments at different heating rates in air atmosphere. The results showed that PBS without additives had an average Ea value of about 150 kJ/mol. The addition of 5% coffee extract (exCGB) increased

Ea to about 170 kJ/mol, indicating greater resistance to thermo-oxidative degradation. Furthermore, a comparison between PBS containing 1 wt.% exCGB and 1 wt.% Irganox 1010 revealed comparable Ea values. This result highlights that exCGB, despite containing only 0.1 wt.% of active phenolic compounds, is as effective as a synthetic antioxidant. In addition, it was observed that increasing the concentration of exCGB gradually improved the thermo-oxidative stability of PBS.

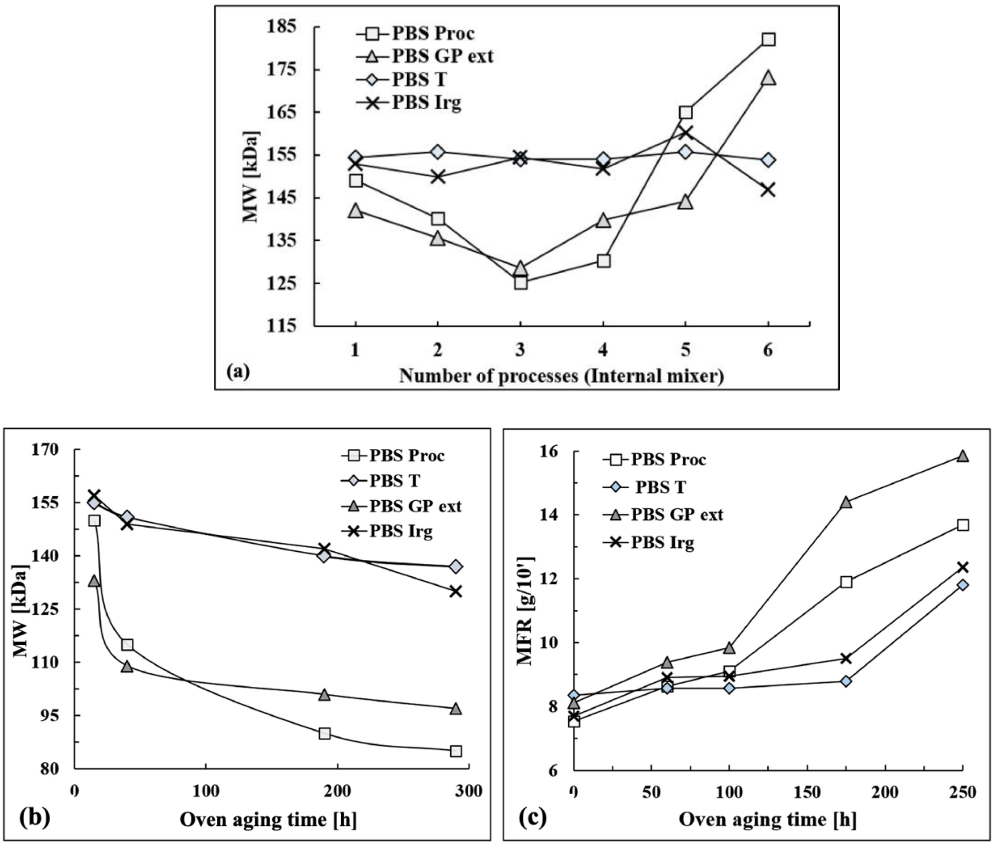


Figure 11. (**a**) Weight average molecular weight (MW) of PBS (PBS Proc) and PBS samples containing GPext, T, and Irganox 1010 (PBS GPext, PBS T, and PBS Irg) as a function of the number of processes in a mechanical mixer. (**b**) MW and (**c**) MFR of PBS Proc, PBS GPext, PBS T, and PBS Irg samples as a function of oven aging time. Reprinted (adapted) with permission from Ref. [180]. Copyright 2020 Elsevier.

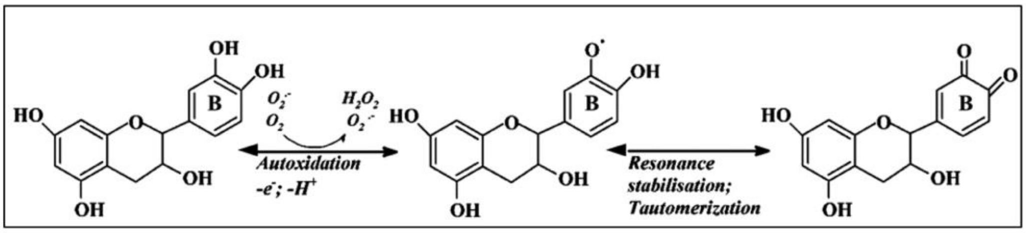


Figure 12. Schematic representation of a generic flavonoid subjected to auto-oxidation under aging conditions. Reprinted with permission from Ref. [180]. Copyright 2020 Elsevier.

Rossi et al. [182] used lauryl gallate (LG) as a natural antioxidant to improve the thermal stability and recyclability of PBSA. This antioxidant is thermally more stable than other gallates, which is advantageous as it can withstand the high temperatures required for processing. PBSA and PBSA/LG mixtures (0.5% by weight of LG) were analyzed by subjecting them to consecutive extrusion cycles at 170 °C to study the thermo-oxidative radical degradation of the polymer and evaluate its recyclability. Incorporating

LG enhanced the processability and thermal stability of PBSA, allowing the polymer to withstand up to twelve extrusion cycles, compared to six cycles for pure PBSA, before signs of degradation emerged (Figure 13). Mechanical tests and GPC analysis also showed less molecular fragmentation of PBSA chains when LG was added, with less pronounced changes in TGA values and a slower reduction in crystallinity. LG also stabilized the MFR and rheological properties (complex viscosity, zero-shear viscosity) of reprocessed PBSA.

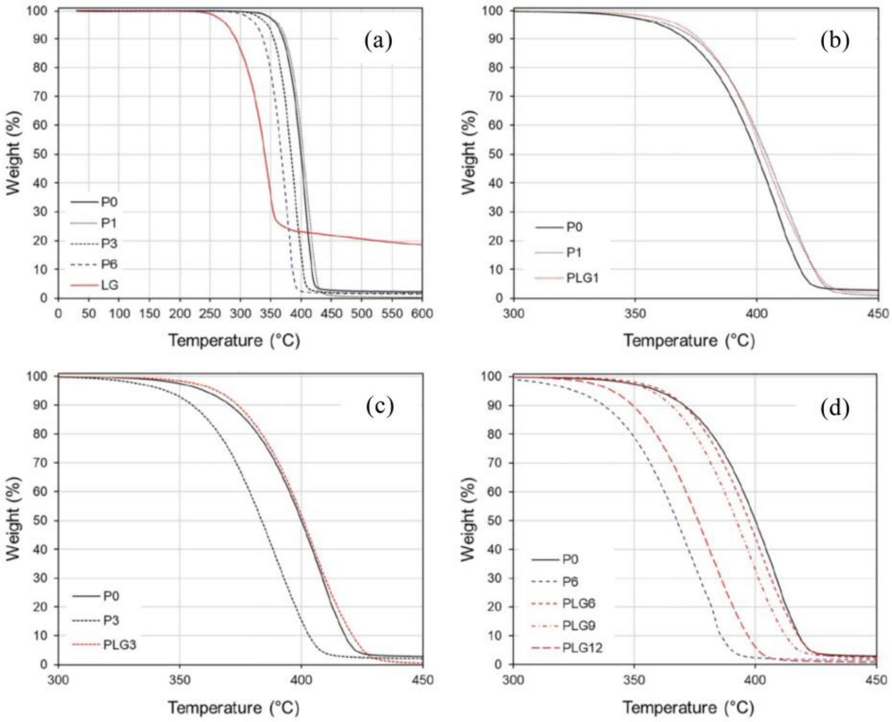


Figure 13. TGA curves of neat PBSA samples subjected to increasing extrusion cycles up to 6 cycles (PX: from P0 to P6) and PBSA blended with 0.5 wt.% LG treated up to 12 cycles (PLGX: from PLG1 to PLG12). The analyses were performed under a nitrogen atmosphere with a heating rate of 1 °C/min. Figure (**a**) compares neat PBSA (P0) with PBSA treated up to 6 cycles; (**b**) shows the comparison between P0, P1, and PLG1; (**c**) shows the comparison after 3 extrusion cycles with and without LG, always compared to neat PBSA; (**d**) compares the extreme treatments with and without LG, relative to neat PBSA. Reprinted (adapted) with permission from Ref. [182]. Copyright 2024 Springer.

In another study, a series of more thermally stable bis/tris phenols based on ferulic acid was synthesized and tested as antioxidants for PBS [183]. These compounds were found to be more suitable for high-temperature processing compared to their precursor. The thermo-oxidative degradation of PBS samples containing bis/tris phenols at elevated temperatures were assessed using OIT analysis. Additionally, the oxidative degradation of macromolecules under the polymer's service conditions was evaluated through aging tests at room temperature. Data showed that tris-o-dihydroferuloylglycerol (GTF) was more effective than the commercial Irganox 1010 in stabilizing the thermo-oxidative degradation of PBS. While accelerated aging tests of PBS over six months showed that all antioxidants positively impacted the stability of the average molecular weights, there were no significant differences regardless of their structure. The authors rationalized the results considering that the reaction mechanism of these antioxidants includes radical scavenging and intermolecular dimerization, favored by more flexible molecular structures.

Other natural derivatives rich in polyphenols, such as olive mill wastewater (OMW), have also been successfully tested to stabilize PBS against oxidation [184]. OMW contains a significant organic fraction of phenolic compounds, including tyrosol, hydroxytyrosol, p-coumaric acid, ferulic acid, sinapic acid, protocatechuic acid, and tannins. Sisti et al. exploited the ability of layered double hydroxides (LDHs) to intercalate carboxylic acids, creating host–guest systems tested both as functional additives for PBS to develop antioxidant and antimicrobial materials [185] and as durability-enhancing agents. The capacity of LDHs to intercalate organic anions is well known, enabling the improved thermal stability of materials and controlled release effects in specific environments [122,125,186]. Based on these properties, OMW was used as an intercalating agent for ZnAl-LDH. For comparative purposes, model systems were also prepared by intercalating individual phenolic acids selected from those found in OMW. The organo-modified LDHs were used to prepare PBS composites through melt blending. The composites were then exposed to UV radiation in a photo-accelerated aging device, and structural modifications were analyzed using IR spectroscopy. The results revealed a significant protective effect of the hybrid LDH-OMW system, contributing to improved PBS resistance to oxidative and photo-degradation conditions. Moreover, this approach stands out for its sustainability and cost-effectiveness as the biowaste requires no pretreatment, reducing costs and environmental impact.

Studies have also been conducted in which plant precursors containing natural antioxidants were used without undergoing extraction processes, thereby retaining all the associated benefits. For example, wine grape pomace (WP), which contains a significant percentage of polyphenols, including phenolic acids, tannins, flavan-3-ols, and anthocyanins (the latter if derived from red grapes), has been tested as a biofiller in PBS and as a thermo-oxidative stabilizer, without the need for additional extraction steps [187–189]. These studies have demonstrated that adding pomace to PBS can improve various mechanical properties, like fracture toughness and thermo-oxidative stability, giving results comparable to that of conventional antioxidants, such as Irganox [190]. Hiller et al. indeed mixed varying amounts of WP ranging from 5 to 20% by weight into PBS, demonstrating that all the composite materials obtained showed an increase in OIT compared to pure PBS. In particular, the lowest WP content resulted in the highest thermo-oxidative stability [190]. In a more recent study, Hiller et al. investigated how annual variations in this by-product of the wine industry, which affect its biochemical composition, could influence its stabilizing properties [191]. The results concerning thermo-oxidative stability, measured through dynamic OIT tests, showed that these bio-fillers, regardless of grape variety and growing climatic conditions, stabilize PBS by 24% with a bio-filler content of 3 wt.%.

Lignin has well-known antioxidant properties, which were utilized in a study by Domínguez-Robles et al. [192], where this natural polymer was combined with PBS to obtain biocomposites containing up to 15% lignin by weight. DPPH tests showed that all materials can reduce DPPH concentrations by up to 80% in less than 5 h. Additionally, significant antibiofilm activity was demonstrated against the nosocomial pathogen *Staphylococcus aureus*, with a 90% reduction in bacterial adhesion compared to pure PBS.

Besides PBS and PBSA, even PBAT is a highly promising biodegradable polymer for food packaging. Its high elasticity, ease of processing, and biodegradability make it a valid alternative to LDPE. Although PBAT is synthesized from fossil-based butanediol (BDO), terephthalic acid, and adipic acid, there is a progressive shift towards fully bio-based sources, mainly by replacing fossil-derived BDO with BDO obtained through industrial fermentation [20]. However, despite its advantages, PBAT applications are limited by certain factors: high production costs, low tensile strength, poor barrier properties, and polymer degradation during processing and use. Specifically, during processing and utilization stages, and in the presence of heat, oxygen, and mechanical stress, PBAT can undergo unwanted chain-breaking reactions caused by the production of oxidative free radicals.

As with other polyesters, studies in the literature have shown that this drawback can be overcome by improving thermo-oxidative stability through the addition of phenolic compounds. For example, in a recent study, Kong et al. [193] achieved effective thermo-oxidative stabilization of PBAT while simultaneously improving processing performance and maintaining good mechanical properties. This result was obtained by melt blending with a natural extract of Chrysanthemum morifolium (CME), which contains a mixture of phenolic compounds such as chlorogenic acid, luteolin, gallocatechin, rosmarinic acid, galuteolin, and apigenin-7-O-glucoside. The results showed that the addition of CME significantly increased the OOT (onset oxidation temperature) values by 42 °C and 52 °C for samples with 1.5 wt.% and 2.5 wt.% CME, respectively, demonstrating a clear improvement in thermo-oxidative stability.

In the case of PBAT, biofillers have also been tested as antioxidants. In particular, Tavares et al. [194] used kraft lignin, preparing samples through extrusion and thermo-compression processes. Lignin improved PBAT's thermal stability by increasing the oxidation induction time and oxidative and thermal degradation temperatures, with an optimal effect at a 1% weight concentration.

Examples of thermo-oxidative stabilization using phenolic compounds have also been reported for the blends of the polyesters analyzed so far. Mucilli et al. [195], for example, improved the antioxidant properties of a PLA/PBAT blend for mulching by adding a walnut shell extract rich in phenolic compounds in low concentrations (0.5–1.5 w/w). The results showed a significant increase in the bioplastic's antioxidant capacity and UV resistance, making it more suitable for packaging applications after 7 days of UV-accelerated aging. In a recent study, Scarfato et al. [196] showed that hazelnut perisperm can impart antioxidant qualities to PLA/PBAT bioplastic films, allowing them to be sealed at different temperatures. A separate study showed that PLA/PBAT-based films with grapefruit seed extract have good antibacterial properties against Listeria monocytogenes and excellent UV-blocking capabilities [197].

Although it is not the primary focus of this review, it is worth noting that various studies have explored the addition of natural phenolic compounds to PBS, PBSA, PBAT, and their blends to enhance the antimicrobial or antioxidant functionality of the final product. Compounds such as carvacrol, curcumin, quercetin, gallic acid, and others have been incorporated into PBS and PBSA to create functional materials, imparting properties like antimicrobial, antibiofilm, and antioxidant activities, which significantly enhance their overall performance [198–200]. Similarly, studies on PBAT and its blends have also shown the addition of natural phenolic compounds for similar functional improvements [201,202].

4.3. Poly(hydroxy alcanoate)

Polyhydroxyalkanoates (PHAs) are a promising class of biodegradable polyesters valued for their sustainability, biocompatibility, and non-toxicity. Produced by microorganisms, these materials find applications in fields such as medicine, agriculture, and active food packaging [203]. However, their industrial use could be improved by certain limitations, including brittleness, low elongation at break, and thermal instability during melt processing. This instability leads to material degradation primarily through a cis-elimination mechanism, which reduces the polymer's molecular weight, forming low-molecular-weight fragments with carboxylic acid and unsaturated propene terminal groups, thereby compromising mechanical performance [204]. Although this mechanism is predominant in PHA degradation, the literature reports indicate that minor thermo-oxidative reactions may also occur in the presence of oxygen, which the addition of phenolic antioxidants could potentially mitigate [205].

Natural polyphenols have been incorporated into PHAs to enhance their thermal stability and circularity while maintaining their biodegradability [206]. Studies have shown that compounds such as gallotannins, catechin, proanthocyanidins, and kraft lignin can prevent molecular degradation and improve the mechanical properties of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-HV) [207–209]. Derivatives of ferulic acid esterified with butanediol (BDF), pentanediol (PDF), and glycerol (GTF) have also been tested as antioxidants for PHB, resulting in improvements in both the mechanical properties of the polymer and its thermal stability and flame resistance limits [210]. Furthermore, Latos-Brozio et al. [159] recently demonstrated that gallates, alkyl esters of gallic acid (3,4,5-trihydroxybenzoic acid), offer an eco-friendly alternative to petrochemical additives, effectively controlling the aging process of poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3/4HB).

The stabilizing effect of phenolic compounds on PHB is also confirmed by a study by Masek and Latos-Brozio [160], where the impact of two natural antioxidants, hesperidin and rutin, was evaluated and compared with a synthetic antioxidant. The two flavonoids were added to PHB at a concentration of 1 phr, and the samples were subjected to thermal aging and UV exposure. The results show that the oxidation temperature of the polymer, determined by DSC analysis, increases by 44 °C with hesperidin and by 30 °C with the commercial antioxidant, suggesting a stabilizing effect of the flavonoids on PHB. Furthermore, the data show that the two phenolic compounds primarily enhance the resistance of PHB to solar aging, while their effect on long-term thermo-oxidative reactions is less significant. This outcome is attributed to the thermal instability of the flavonoids, which may affect their ability to stabilize the material over time, particularly under high-temperature conditions.

The same authors also tested (+)-catechin and polydatin as natural antioxidants for PHA [158]. The selected polyphenols demonstrated a stabilizing effect, highlighted by increased oxidation temperatures and a slowdown in degradation processes, as confirmed by surface-free energy analyses and the polymer's aging coefficient. Furthermore, the addition of these compounds to PHA caused color changes, which could serve as visual indicators of the material's lifespan. The authors also evaluated tested tannins and β-carotene as thermal stabilizers for PLA/PHB blends, observing a significant improvement in thermal oxidation resistance [211]. In this case, the samples also exhibited color changes under UV radiation and thermal oxidation, visually indicating the blend's degradation progress.

Considerable research efforts have focused on utilizing polyphenol-rich extracts from by-products of the agro-industrial supply chain, with the goal of valorizing these waste materials and converting them into valuable resources. Nanni et al. [204], for example, investigated the thermostabilizing effect of a grape seed extract (Sext) containing 16% polyphenols (such as catechins and gallic acid) during high-temperature processing of PHB. To assess the effectiveness of Sext, the additive was incorporated into PHB through extrusion, followed by injection molding to produce samples. GPC results showed that, after processing, the average molecular weight of PHB decreases by approximately 50% compared to its initial value. However, the addition of Sext exhibited a stabilizing effect, maintaining a slightly higher molecular weight than unstabilized PHB and reducing the formation of oligomers. This effect was linked to Sext's capacity to stabilize active radical species ($P^{\cdot}$, $POO^{\cdot}$, $PO^{\cdot}$) generated during thermo-oxidation. While the stabilizing effect is moderate, this can be due to the limited occurrence of these reactions in PHB. The efficacy of Sext was further confirmed by TGA analyses, which showed an increase of 5–6 °C in degradation temperatures and by OIT tests. These results suggest that the type of polyphenols, rather than their quantity, is crucial for improving PHB stabilization. The authors hypothesize that long-chain polyphenols may promote crosslinking between polymer chains, enhancing the material's stability (Figure 14). However, such crosslinking could reduce PHB's biodegradability, which is critical in some applications.

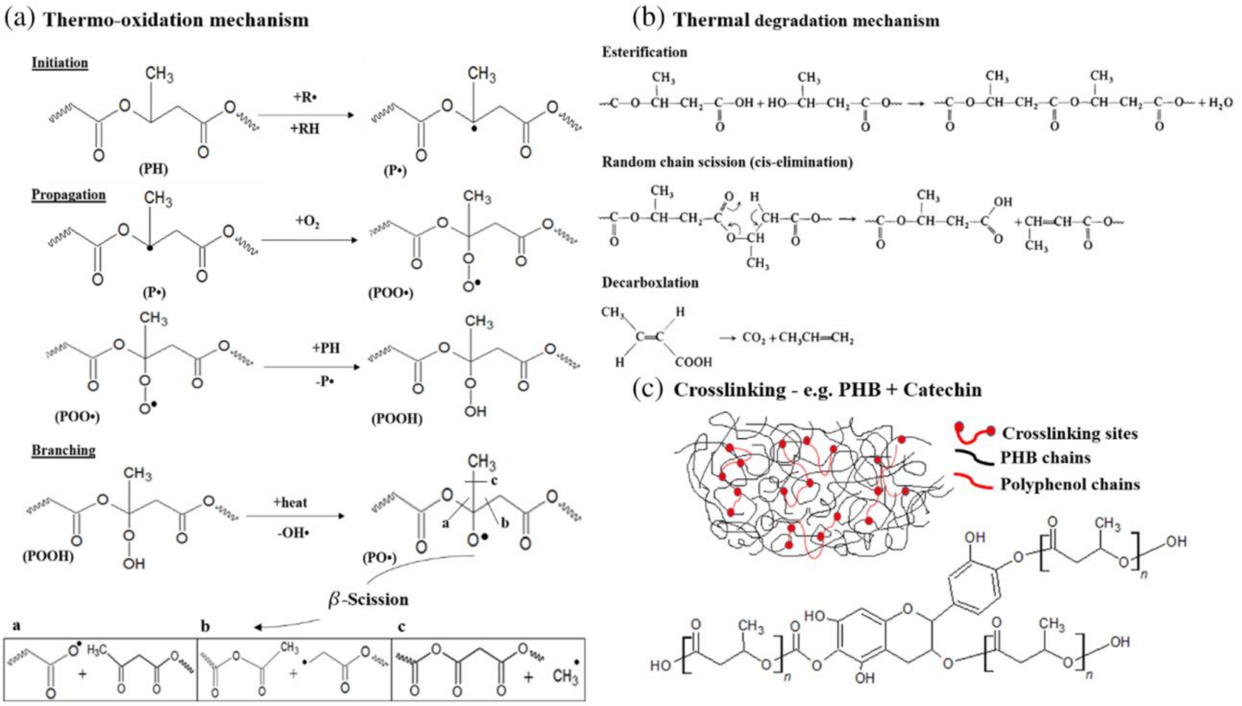


Figure 14. (**a**) Possible radical reactions during thermo-oxidation, (**b**) thermal degradation via random non-radical chain scission (a widely accepted mechanism), and (**c**) polyphenols as crosslinking agents within PHB. Reprinted with permission from Ref. [204]. Copyright 2020 Wiley.

Persico et al. [207] also tested a natural extract derived from winery pomace (EP) as a stabilizer for PHB during high-temperature processes. The results showed that EP significantly improves the thermal stability of PHB, maintaining high molecular weights after processing, as confirmed by GPC analysis. This behavior was further highlighted by the slighter decrease in viscosity over time, observed through rheological tests. Specifically, the rheological properties of pure PHB and mixtures containing EP were compared at 190 °C. While pure PHB undergoes a drastic reduction in viscosity due to thermal degradation, the samples containing EP showed greater stability, maintaining a constant viscosity. The authors hypothesized that EP stabilizes PHB through hydrogen bonds between the extract’s polar groups and the polymer’s carbonyl groups, acting as a chain extender. This behavior improved the melt viscosity and the polymer’s resistance during processing without triggering crosslinking reactions. Therefore, EP proved to be an effective additive in stabilizing PHB against thermal degradation, extending its residence time in processing equipment and expanding its potential applications.

Finally, as highlighted in the previous sections for other bioplastics, numerous examples of phenolic compounds added to PHAs or their blends impart active properties to the material, particularly for active packaging applications. Below are only a few examples. Mirpoor et al. [212] incorporated phloretin, a flavonoid found in apples and kumquats, into PHA, resulting in improved antioxidant and antimicrobial properties and reducing the growth of foodborne pathogens. Ferri et al. [213] developed an innovative food packaging made of PHBV with tannins, using them as a multifunctional additive. This combination allows the material to serve as a food deterioration indicator, chromatically detecting ammonia vapors and fish spoilage. Vostrejs et al. [214] explored the use of lignin extracted from grape seeds (GS-L) for its antioxidant properties, applying it to PHB/PHA films for packaging purposes. Arrieta et al. [215] developed new bio-based and biodegradable dual-layer active packaging with antioxidant properties. The outer layer was based on PHBV, while the inner layer was electrospun fibers based on PLA and PHB, containing catechin, a natural antioxidant. These obtained packings have demonstrated effective catechin release even in contact with fatty food simulants and antioxidant properties, as well as rapid biodegradability.

4.4. Starch-Based Materials

Starch, the most abundant polysaccharide found in plants, has garnered significant interest due to its renewability and low cost [216]. Thermoplastic starch (TPS) is typically developed by combining starch with aliphatic polyesters, glycerol, and water. Starch sourced from plants like potato, corn, wheat, cassava, or tapioca serves as the base material, with linear aliphatic polyesters added to create compostable products such as films, sheets, and plastic bags. However, not all starch-based materials are suitable for food packaging due to potential additive migration, particularly plasticizers [217].

While efforts to create starch-based plastics have been extensive, starch's inherent limitations—such as instability from water absorption, retrogradation with age, poor mechanical properties, and limited processability—necessitate blending starch with additives to produce TPS [218].

Several studies have explored the potential of starch-based materials by also adding antioxidant biomolecules to the recipe. The primary goal of these studies is to obtain functional materials with antimicrobial and antioxidant properties. However, despite the instability during processing being an issue for starch as well, no studies have yet been published exploring the use of thermo-oxidative stabilizers of biological origin to counteract the effects of thermo-degradation during processing or the material's service life. Below are some notable examples of the use of natural-origin phenolic compounds in starch.

For instance, Pankaj [219] incorporated antifungal grapefruit seed extracts into bionanocomposite films made of corn starch and chitosan. These films exhibited low hydrophilicity, excellent water barrier properties, enhanced mechanical strength, and strong antifungal activity. In fact, it resulted effective in preserving bread at 25 °C and 59% RH for 20 days. Similarly, Promhuad et al. [220] incorporated maltol into acetylated cassava starch films, achieving an improvement in antioxidant properties. Another innovative approach was proposed by Rodrigues et al. [221] which produced active films and coatings from fruit starch (SPFS) and phenolic stem bark extract (SBPE) from *Spondias purpurea* L.; indeed, SBPE provided active properties (antioxidant and UV-absorbing) to the films. Interestingly, in the work of Bajer [222], where novel materials were designed from potato starch (NS) reinforced with antioxidants such as dialdehyde starch (DS) and caffeic acid (CA)/quinic acid (QA) for packaging perishable food susceptible to oxidizing agents, it was found that dialdehyde starch improved flexibility, whereas acids (particularly caffeic acid) improved film stiffness. Finally, noteworthy is the research of Talon et al. [223], where starch films containing eugenol, either free or encapsulated with whey protein or lecithin, were produced by casting. The physical and antioxidant properties, eugenol release in food simulants, and their ability to prevent sunflower oil oxidation during storage were assessed. Encapsulation improved eugenol retention, reduced water affinity and oxygen permeability, and enhanced antioxidant activity.

5. Conclusions

This review examines the pivotal role of natural antioxidants in enhancing the stability and sustainability of bio-based polymeric materials. These antioxidants, derived from plant sources and agri-food waste, have proven particularly effective in stabilizing biopolymers such as PLA, PBS, PBSA, PBAT, PHA, and their blends, including various biopolyester-starch blends. By surveying the scientific literature, the review explores the mechanisms of polymer degradation during processing and under oxidative conditions, offering insight into the selection of antioxidants and radical stabilizers tailored to specific degradation pathways.

Phenolic compounds, renowned for their potent antioxidant and bioactive properties, emerge as the primary focus. These compounds, extracted from natural sources, are highly valued for their ability to counteract oxidative stress in polymers. However, their vulnerability to environmental factors limits their direct application in industries such as the food, cosmetic, and pharmaceutical industries, as well as their effectiveness as thermal stabilizers during processing and the product's service life. Encapsulation techniques are highlighted as a transformative solution, significantly improving the stability, bioavailability, and bioactivity of phenolic extracts. These techniques enable the controlled and targeted release of active ingredients, broadening their applicability across diverse industrial sectors.

The review identifies two main methodologies for incorporating antioxidants into biopolymers: (1) pure antioxidant molecules extracted from plants and used to understand the specific chemical mechanisms underlying their stabilizing effects; (2) mixtures from agri-food waste, cost-effective and environmentally integrated blends that leverage agricultural residues and align with biocircular and sustainable strategies.

While the first approach provides valuable insights into the molecular dynamics of stabilization, the second strategy holds greater promise for industrial applications due to its affordability and compatibility with bioeconomic principles.

Biofillers, such as kraft lignin and winery industry waste, also emerge as effective natural antioxidants. While these materials serve as fillers, they also offer antioxidant activity due to the molecules acting as thermo-oxidative stabilizers during processing and in the final use of the bioplastics they have been tested.

Despite the encouraging results from the studies discussed in this review, challenges persist, particularly the need for further research, both at the fundamental and applied levels. At the fundamental level, deeper investigations into the chemical behavior of various antioxidant molecules within biopolymers are required. At the applied level, industrial scalability and integration of these materials into bioeconomy frameworks must be addressed to fully capitalize on their potential.

In summary, this review underscores the transformative potential of plant-derived antioxidants in advancing biopolymer recycling and processing. By improving polymer stability and performance while promoting sustainability, these natural compounds pave the way for innovative practices that align with the goals of a circular economy. Future research and technological advancements will be crucial in bridging knowledge gaps and facilitating the widespread industrial adoption of these sustainable solutions.

Author Contributions: Conceptualization, S.C., F.C. and M.-B.C.; investigation, N.M., F.C. and V.G.; writing—original draft preparation, N.M., F.C., V.G. and S.C.; writing—review and editing, F.C., E.P. and M.-B.C.; supervision, S.C. and M.-B.C.; funding acquisition, E.P. All authors have read and agreed to the published version of the manuscript.

Funding: This study was conducted within the MICS (Made in Italy—Circular and Sustainable) Extended Partnership, supported by the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR)—MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3—D.D. 1551.11-10-2022, PE00000004). Additionally, it was carried out as part of the Innovation Grant projects "Agro-industrial Waste valorization through Machine-learning Accelerated Design (AWAD)" and "Harnessing HPC, Granarolo's Bio-Driven Revolution for Sustainable Packaging (PISA)" within the ICSC, the Italian National Center for Research in High Performance Computing, Big Data, and Quantum Computing, funded by the European Union (Next Generation EU, grant number CN00000013)—PNRR, Mission 4 Component 2 Investment 1.4. This manuscript reflects only the authors' views and opinions, and neither the European Union nor the European Commission can be held responsible for them.

Data Availability Statement: Not available.

Conflicts of Interest: The authors declare no conflicts of interest.

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