

POLIMERY

Antioxidants in biodegradable food packaging polymer materials – a review

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Abstract: This review summarizes the recent advances in the incorporation of antioxidants into biodegradable polymer-based food packaging materials. Natural antioxidants such as polyphenols, carotenoids, and vitamins, as well as selected synthetic compounds, are discussed in the context of their origin, mechanism of action, and application methods including blending, encapsulation, and surface coating. The review also compares antioxidant efficiency across various biopolymer matrices including PLA, chitosan, PHA, PBAT, PVA, TPS, and PBS. Special attention is given to the functional performance, regulatory considerations, and future prospects of active packaging systems aimed at prolonging food shelf life and enhancing sustainability.

Keywords: biodegradable packaging, antioxidants, food preservation, polyphenols, active packaging.

Antyoksydanty w biodegradowalnych materiałach polimerowych do pakowania żywności – przegląd literatury

Streszczenie: Podsumowano aktualny stan wiedzy na temat stosowania przeciwutleniaczy w biodegradowalnych materiałach opakowaniowych do żywności. Omówiono naturalne przeciwutleniacze, takie jak polifenole, karotenoidy i witaminy, a także wybrane związki syntetyczne, uwzględniając ich pochodzenie, mechanizm działania i metody integracji (mieszanie, enkapsulacja, powlekanie). Przeanalizowano efektywność dodatków w różnych osnowach polimerowych, m.in. PLA, chitozanie, PBAT, TPS, PBS i PHA. Szczególną uwagę poświęcono właściwościom funkcjonalnym, aspektom regulacyjnym oraz przyszłości aktywnych opakowań wspierających trwałość i zrównoważony rozwój.

Słowa kluczowe: opakowania biodegradowalne, przeciwutleniacze, trwałość żywności, polifenole, opakowania aktywne.

In recent years, there has been a growing interest in biodegradable packaging materials. This trend is driven by increasing awareness of environmental pollution [1]. Half-life of common polymer materials depends on their storage conditions and can range from 4.6 years (buried

LDPE bags) to even 5000 years (buried HDPE pipes) [2], which contributes to numerous problems related to waste storage and management [3, 4]. Improper disposal of packaging leads to the release of microplastics into the environment, causing negative effects such as pollution

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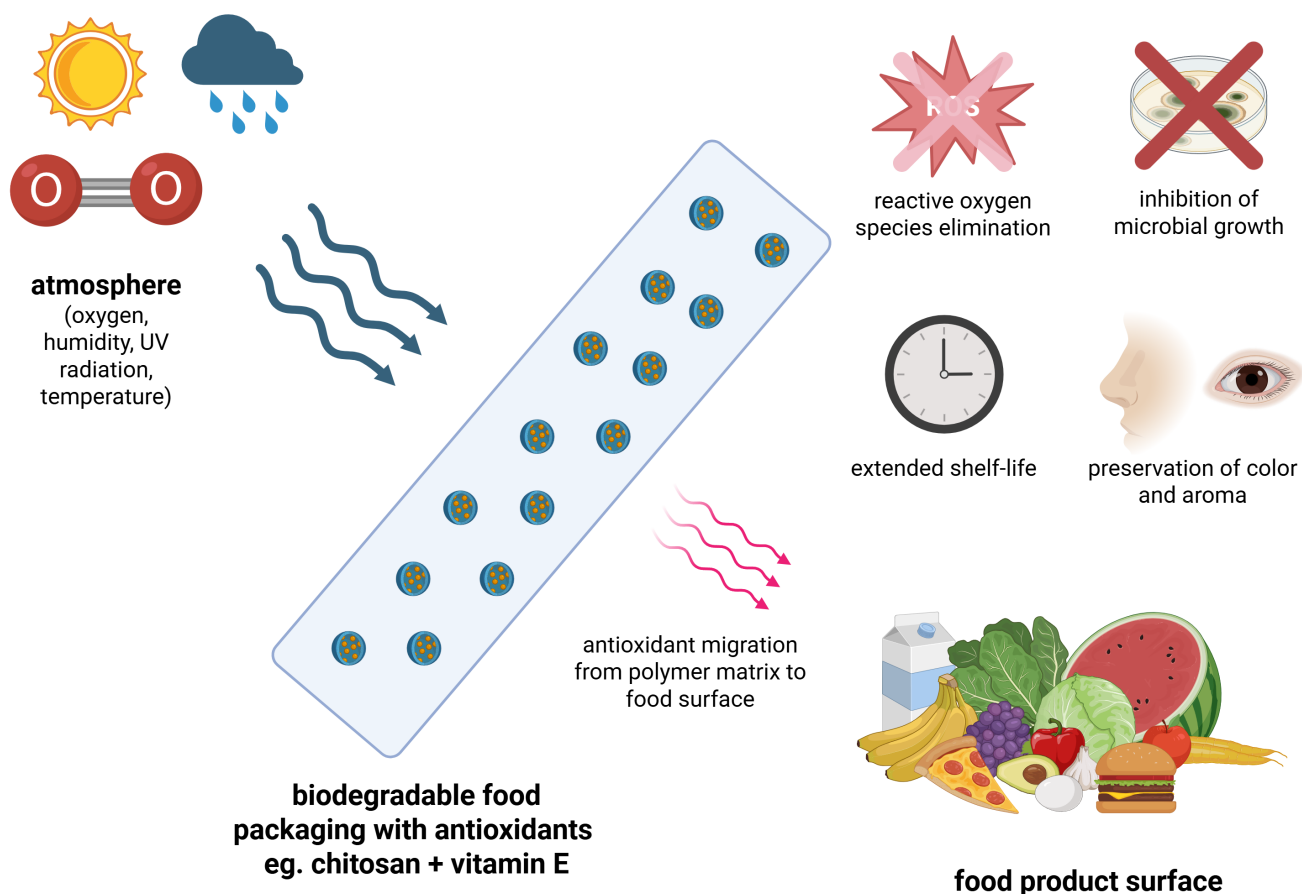


Fig. 1. Diagram of antioxidant action in biodegradable food packaging

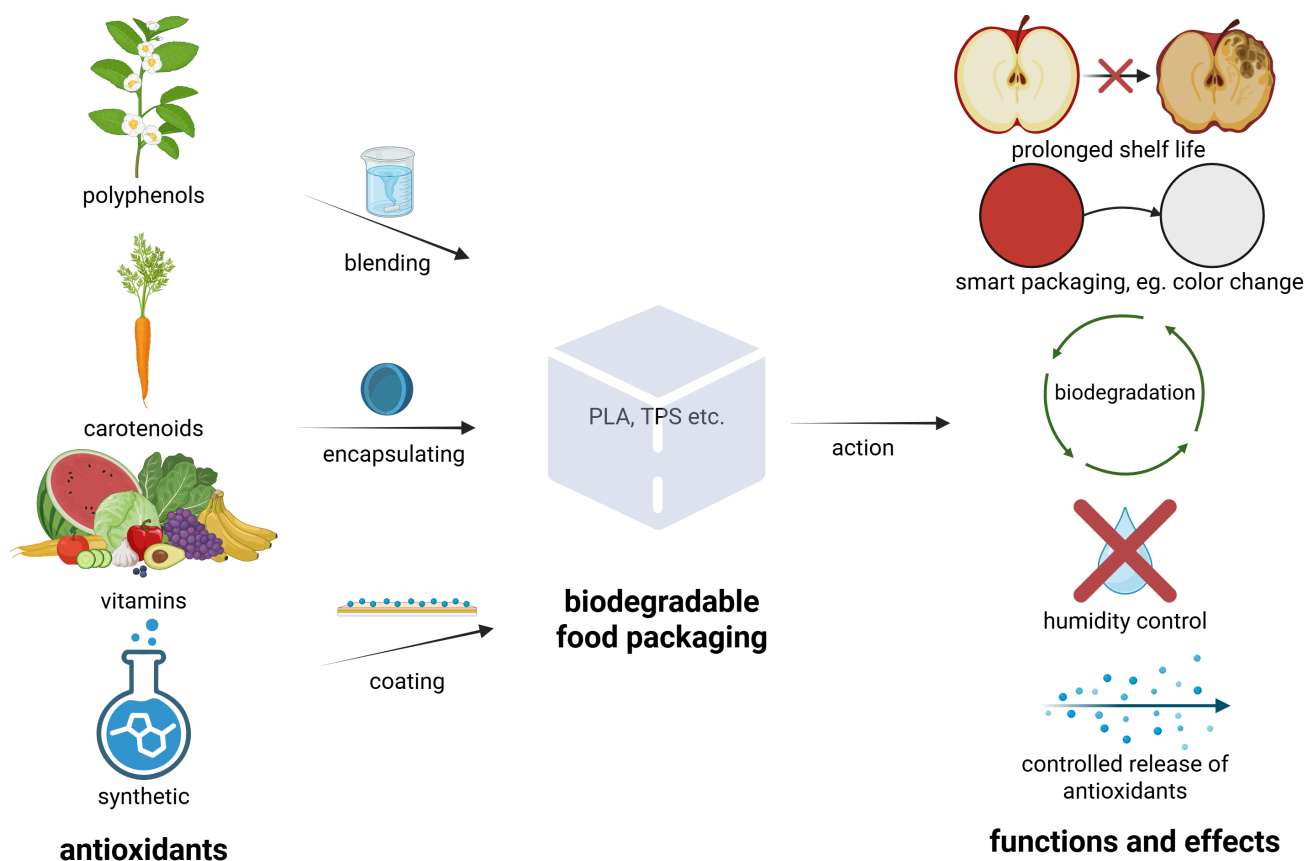


Fig. 2. Functions and mechanisms of antioxidant-enriched biodegradable food packaging

of seas, oceans, soils, and groundwater, and also harming plants, animals and humans [5–10]. Market research has shown that many people are willing to pay more for food products packaged in environmentally friendly materials [11–14]. This trend forces manufacturers to make changes in their packaging strategies [15, 16] and lawmakers to amend regulations [17], leading to the search for or improvement of biodegradable packaging materials. As a result, technological advancements in the production of biodegradable materials have increased their availability and competitive pricing [18–20]. Innovative solutions in raw materials and manufacturing processes allow for the creation of materials with improved functional properties, promoting their broader use in the packaging industry. Additionally, public awareness of the environmental impact of polymer materials is growing [21–23], and campaigns promoting biodegradable solutions are emerging [24]. Educating society about the benefits of choosing biodegradable packaging influences consumer attitudes and purchasing decisions. All these factors result from a complex interplay of elements, including environmental protection, regulatory changes, consumer preferences, technological innovations, sustainable development strategies, and public education. As these factors continue to evolve, a further increase in interest and the use of biodegradable materials in the packaging industry is expected.

Food products are packaged to protect them from contamination, microbial activity, and mechanical damage (e.g., during transport). Packaging also helps extend shelf life and assures consumers that the product's composition remains unchanged from production to purchase. Besides protection, packaging also serves as a branding and design medium, helping to differentiate products from competitors. It contains essential information such as ingredients, expiration dates, nutritional values, storage instructions, and allergen warnings. Packaging is often designed for easy opening, dispensing, and storage, enhancing functionality and consumer convenience [25–27]. A particularly important function of packaging is ensuring appropriate conditions to prevent the harmful effects of oxygen or microorganisms, which can lead to the oxidation of product ingredients. Oxidation is one of the major chemical processes that degrade food quality [28, 29]. Fats [30, 31], proteins [32, 33] and vitamins are particularly vulnerable to oxygen exposure, which significantly reduce the nutritional value and alter the sensory properties of food. Vitamins A (retinol), C (ascorbic acid), and E (tocopherols) are especially sensitive to oxygen, leading to a loss of their beneficial properties [34–37], which is particularly crucial for foods intended as vitamin sources for consumers. Oxygen exposure also contributes to the development of unpleasant odors and flavors, especially in fat-containing products, due to rancidity. Additionally, oxidation affects the structure and appearance of products, creating the impression that they have expired even if they are still within their shelf life.

One strategy to mitigate oxygen's impact on food products is the use of antioxidants.

Antioxidants are atoms, molecules, or compounds that, even in low concentrations relative to oxidants (such as reactive oxygen species or free radicals), can slow down or inhibit oxidation reactions [38, 39]. Despite their various applications [40, 41], antioxidants always serve the same purpose – to stop or slow down radical reactions. For this reason, they have been incorporated into food packaging. They help prevent food degradation caused by oxygen, changes in taste and odor, and loss of nutritional value. Studies suggest that antioxidants can migrate into food, thereby providing additional protection and prolonging shelf life (Fig. 1). Consequently, only antioxidants as safe for food contact should be used.

This review provides a systematic comparison of natural and synthetic antioxidants used in biodegradable food packaging, emphasizing their compatibility with different polymer matrices (polylactic acid, thermoplastic starch, chitosan, polycaprolactone, polyvinyl alcohol, polybutylene succinate, polybutylene adipate terephthalate, polyhydroxyalkanoates), integration methods (blending, coating, encapsulation), and food-related performance. An overview of these relationship is illustrated in Fig. 2. By presenting this information in a comparative format, supported by structured tables and safety considerations, this article serves as a practical reference for researchers and packaging developers.

TYPES OF BIODEGRADABLE POLYMER PACKAGING MATERIALS

Polylactic acid

Polylactic acid (PLA) is classified as an aliphatic polyesters. Because lactic acid contains an asymmetric carbon atom, it exists in two stereoisometric forms: L- and D-lactic acid, which differ in optical activity but have similar chemical properties [42]. The monomer is obtained from fermented plant starch, such as corn, potato, sugarcane, sugar beet pulp, cassava and lignocellulosic feedstocks [43]. PLA was first synthesized by DuPont in 1932 by heating lactic acid under vacuum. A method of its purification was patented in 1954 [44]. Currently, three main processes are used for synthesizing PLA: ring opening polymerization (ROP) of lactide (a cyclic dimer of lactic acid), direct polycondensation and azeotropic condensation polymerization [45–49].

PLA's mechanical and thermal properties depend on its molecular structure, particularly the L-/D-lactide ratio, molecular weight, and degree of crystallinity [50–52]. High L-lactide content increases stiffness and melting point, while D-lactide improves flexibility. Additives like plasticizers, fillers, and stabilizers further tailor its properties [53–56]. Processing parameters such as temperature and cooling rate also affect its final characteristics [57–61].

PLA's biodegradability is one of its most appealing features, but it also influences its durability under certain environmental conditions. From chemical point of view, polymer degradation can occur through scission of the ester bonds in main, side or intersectional chains [62], followed by microbial biodegradation, where bacteria and fungi convert lactic acid into CO₂ and water in aerobic conditions. In nature, degradation of PLA can be induced by hydrolysis, thermolysis, enzymolysis, biodegradation and photodegradation. In industrial composting facilities, PLA degrades significantly faster compared to natural environments. For instance, research indicates that PLA bioplastics fully biodegrade within four to six weeks in industrial composting settings, where temperatures reach approximately 58°C [63]. High temperatures and humidity levels accelerate the hydrolytic degradation of PLA [64, 65], making it suitable for applications where biodegradability is desired, such as in compostable packaging. The degradation of PLA depends on several factors, such as molecular weight, purity, crystallinity, pH, water permeability, the presence of thermal hydroxyl or carboxyl groups, and various additives that can act as catalysts (e.g., enzymes, bacteria, or inorganic fillers) [66–68].

Thermoplastic starch

Thermoplastic starch (TPS) is a biodegradable material obtained from natural starch, typically derived from renewable resources such as potatoes, corn, cassava, or wheat [69]. Native starch is a polymeric carbohydrate (C₆H₁₀O₅)_n, composed of glucose units linked by glycosidic bonds. It consists of linear, helical amylose (with α-1,4-glycosidic bonds) and branched amylopectin (with α-1,6-glycosidic bonds) [69, 70]. Thermal and chemical modifications transform starch into plastic-like material, suitable for shaping like petroleum-based polymers [71].

TPS has several important properties: it is biodegradable, hydrophilic and thermoplastic. When plasticizers such as glycerol or sorbitol are added, TPS becomes flexible and can be processed using conventional methods such as extrusion or injection molding [72]. The plasticization process involves heating starch with plasticizers to break hydrogen bonds, creating an amorphous material suitable for shaping.

The mechanical properties of TPS depend on the crystalline and amorphous regions of starch. Plasticizers act as lubricants, improving the mobility of polymer chains and preventing retrogradation [73]. TPS is widely used for packaging, disposable items, biodegradable plant protection covers, and shopping bags [74, 75].

TPS biodegrades rapidly in natural environments due to microbial activity, breaking down into water, CO₂ (in aerobic conditions), and biomass. The degradation rate depends on environmental factors like humidity and temperature but is generally faster than that of conventional plastics. Despite being renewable, cost-effective, and environmentally friendly, TPS is sensitive to mois-

ture, which can compromise its mechanical properties. To improve its stability, it is often blended with other biodegradable polymers [76–78].

Chitosan

Chitosan is a biodegradable polysaccharide derived from chitin, extracted from crustacean shells or fungi through deacetylation [79, 80]. Its notable properties—mechanical strength, barrier properties, and antimicrobial activity—make it suitable for food packaging [81–83]. It is often used as edible coatings for fresh produce and meat [84].

One of the most important features of chitosan is its biodegradability. When introduced into the environment, chitosan undergoes biodegradation through the action of naturally occurring microorganisms, such as bacteria and fungi, that break down its polymer chains into smaller molecules. This process is facilitated by the enzymes chitinase and lysozyme, found in soil and aquatic environments. Chitosan degradation does not generate toxic residues, making it an environmentally friendly alternative to conventional plastic packaging. Its decomposition is accelerated in moist, biologically active environments such as compost, where full breakdown can occur within weeks to a few months [85].

Polycaprolactone

Polycaprolactone (PCL) is a biodegradable polyester valued for its flexibility, mechanical strength, and compatibility with other polymers [86]. It is typically synthesized via ring-opening polymerization of ε-caprolactone, often using tin(II) octanoate as a catalyst. While traditionally sourced from petrochemicals, recent efforts focused on developing renewable pathways to enhance its sustainability [87].

PCL readily blends well with other biodegradable polymers, such as polylactic acid (PLA), starch, and cellulose, improving mechanical properties and expands its use in biodegradable packaging [88]. Though primarily used in biomedical fields, PCL is increasingly explored for packaging due to its biodegradability and safe interaction with food products [89].

PCL undergoes natural degradation through enzymatic and microbial activity, with hydrolysis of its ester bonds facilitated by moisture and enzymes like lipase. In composting conditions, it biodegrades within months, depending on environmental parameters. Unlike conventional plastics, PCL decomposes into non-toxic byproducts, making it a promising eco-friendly alternative [90, 91].

Polyvinyl alcohol

Polyvinyl alcohol (PVA) is a biodegradable, water-soluble synthetic polymer increasingly used in eco-friendly

packaging [92]. It is produced by polymerization of vinyl acetate followed by hydrolysis, which replaces acetate groups with hydroxyl groups. The degree of hydrolysis affects its solubility, flexibility, and mechanical properties.

Despite being mostly petrochemically derived, PVA's biodegradability and water solubility make it a more sustainable alternative to conventional packaging materials. It forms strong, transparent films with good barrier properties and can be blended with biopolymers like starch, cellulose, and chitosan to enhance functionality [93].

PVA biodegrades through microbial activity, with enzymes cleaving its polymer chains into water and carbon dioxide. The rate of degradation depends on environmental conditions, with controlled composting allowing decomposition within weeks to months, whereas degradation in natural settings may take longer [94, 95].

As industries pursue sustainable alternatives to traditional plastics, PVA has emerged as a promising candidate, especially for food and single-use packaging. Despite challenges in optimizing biodegradability, its unique properties make it a valuable material for reducing plastic waste [96].

Polybutylene succinate

Polybutylene succinate (PBS) is a biodegradable aliphatic polyester synthesized from renewable resources such as succinic acid and 1,4-butanediol. Polycondensation of these monomers yields a material with favorable mechanical properties, good thermal stability, and high biodegradability [97]. PBS can be synthesized via various methods, including direct polymerization and copolymerization with other monomers, resulting in diverse property profiles. Owing to its flexibility, processability, and moldability, PBS is gaining attention in sustainability-oriented industries, particularly packaging [98].

PBS and its blends have attracted significant attention as eco-friendly alternatives for food packaging. Its excellent barrier properties against gases and moisture, along with good mechanical strength and thermal stability, make it an effective material for protecting food and extending shelf life [99]. Additionally, its ability to be processed using standard plastic manufacturing techniques, such as extrusion and injection molding, allows for easy adaptation to current packaging systems [97, 98]. Moreover, PBS can be blended with other biodegradable polymers to improve specific properties like flexibility and water resistance, making it versatile for different food packaging needs [100, 101].

PBS undergoes microbial degradation when exposed to environmental conditions such as humidity, temperature, and microbial activity [102]. Under industrial composting, PBS can degrade within a few months into water, carbon dioxide, and biomass [103]. This biodegradation process makes PBS an environmentally friendly alternative to traditional petroleum-based plastics. However, the rate

of PBS degradation depends on environmental factors and may be significantly slower in colder or microbially inactive conditions [102, 103]. Despite this, PBS remains a promising option for reducing plastic waste, especially when used in food packaging applications where quick disposal and environmental sustainability are essential.

Polybutylene adipate terephthalate

Polybutylene adipate terephthalate (PBAT) is a biodegradable copolymer synthesized from adipic acid, terephthalic acid, and 1,4-butanediol [104]. By combining aliphatic and aromatic units, PBAT exhibits both flexibility and strength, making it highly suitable for packaging applications [104]. PBAT is synthesized via polycondensation and exhibits low crystallinity, which contributes to its flexibility and ease of processing. It is compatible with conventional techniques such as extrusion and injection molding, enabling seamless integration into current packaging systems [105].

PBAT and its composites or blends are widely used in food packaging due to their mechanical performance, moisture resistance, and biodegradability [106]. It is commonly applied in films and bags, offering effective protection for food products through its barrier properties. PBAT is often blended with other biodegradable polymers, like PLA or PBS, to enhance its performance, meeting the needs of sustainable packaging [107].

PBAT is biodegradable and undergoes microbial degradation in the presence of moisture and microorganisms [108]. Under industrial composting conditions, it decomposes into water, carbon dioxide, and biomass within approximately six months [109]. Its ester bonds are cleaved by microbial enzymes, facilitating the biodegradation process in appropriate environments. However, degradation rates can vary depending on temperature and humidity [108].

Polyhydroxyalkanoates (PHA)

Polyhydroxyalkanoates (PHAs) are a family of biodegradable polyesters naturally produced by various microorganisms as intracellular carbon and energy storage materials. This occurs under nutrient-limited conditions in the presence of excess carbon sources [110]. The most common type, poly(3-hydroxybutyrate) (PHB), has high crystallinity and mechanical properties similar to polypropylene, but is brittle [111]. Other variants, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), offer improved flexibility and processability, making them more suitable for packaging [112].

PHA materials are widely studied for food packaging due to their biodegradability, barrier properties, and antimicrobial potential. While pure PHB is stiff and brittle, PHBV and other copolymers provide enhanced flexibility. PHA-based films act as oxygen and moisture barriers, helping extend food shelf life, and can incorporate

natural antimicrobial agents for active packaging applications [113].

A major advantage of PHA is its biodegradability in soil, marine, and composting environments, where microorganisms break it down into water and carbon dioxide or methane without leaving microplastics [114]. The degradation rate depends on polymer composition and environmental conditions, with softer PHA types degrading faster than rigid PHB [115]. Despite its sustainability, high production costs remain a challenge, though advances in biotechnology are making large-scale production more feasible.

TYPES OF ANTIOXIDANTS USED IN POLYMER PACKAGING MATERIALS

Polyphenols

Polyphenols are a diverse group of naturally occurring organic compounds primarily found in plants, renowned for their strong antioxidant and antimicrobial properties. In nature, they act as protective agents, helping plants defend against oxidative stress and various pathogens [116]. In recent years, polyphenols have found increasing application in the field of food packaging, particularly in biopolymer-based materials, where they are used to enhance preservation and prolong shelf life [117]. The growing demand for sustainable and biodegradable packaging has intensified interest in biopolymers combined with natural additives such as polyphenols, which enable the development of innovative, eco-friendly materials that fulfill both functional and environmental criteria.

Polyphenols are characterized by their multiple phenolic structures, which allow them to act as effective free-radical scavengers. This structural feature grants them strong antioxidant capabilities, as they can donate hydrogen atoms to neutralize reactive oxygen species (ROS) and other free radicals. Polyphenols are categorized into several classes, such as flavonoids, phenolic acids, lignans, and stilbenes, each with varying degrees of antioxidant and antimicrobial activity. These compounds are predominantly derived from fruits, vegetables, herbs, and spices, making them a sustainable alternative to synthetic additives in food packaging [118].

The integration of polyphenols into biopolymer-based food packaging provides two main benefits: antioxidant protection and antimicrobial effects [119]. The first benefit helps to mitigate oxidation processes in foods by reducing lipid oxidation and maintaining the nutritional quality of food products. This is particularly valuable for packaging foods that are prone to oxidative spoilage, such as oils, dairy, and meats. By delaying oxidation, polyphenols can help extend the shelf life of products and preserve their sensory qualities (e.g., flavor, color, and texture). The second benefit affects certain polyphenols, that exhibit significant antimicrobial effects, making them effective

in inhibiting the growth of bacteria, yeasts, and molds. This feature is beneficial for packaging perishable items, as it helps to prevent microbial contamination and spoilage. Studies have shown that polyphenols like catechins, resveratrol, and flavonoids can inhibit a wide range of foodborne pathogens, which supports their potential use in active packaging materials [120].

Polyphenols can be integrated into these biopolymers through different methods, including:

- **Blending:** Polyphenols can be blended with biopolymer matrices during the extrusion or injection molding processes, enabling their even distribution throughout the material. This method ensures that antioxidant and antimicrobial properties are present throughout the entire packaging structure [121],

- **Coating:** Polyphenol-based coatings can be applied to the surface of biopolymer packaging, creating an active barrier that interacts directly with the food product. This approach allows controlled release of polyphenols, which can be advantageous for maintaining food quality over time [122].

- **Encapsulation:** Encapsulation of polyphenols in carriers, such as nano- or micro-capsules, can protect these compounds from degradation during processing and extend their release within the packaging. This technique also enhances the stability of polyphenols, making them more effective over the product's shelf life [123].

Polyphenol-enriched biopolymer packaging offers several advantages over traditional plastic and other biodegradable packaging alternatives. The first is their sustainability. Polyphenols are derived from natural sources, aligning well with the principles of green chemistry and the demand for renewable resources in packaging. Combined with biodegradable biopolymers, polyphenol-based packaging reduces plastic waste and minimizes the environmental footprint [124]. The second is enhancing the food safety by actively protecting food from oxidative damage and microbial contamination, polyphenols improve the safety and quality of packaged goods. This benefit is particularly important for minimally processed and natural food products, which are more vulnerable to spoilage [125]. The third is the reduction in synthetic preservatives usage. Incorporating polyphenols into packaging materials can reduce the need for synthetic preservatives in food products, which is advantageous from both a health and regulatory perspective [126]. Consumers are increasingly seeking preservative-free options, and polyphenol-enriched packaging supports this preference.

Polyphenols offer a promising natural solution for enhancing the functional properties of biopolymer-based food packaging. Their antioxidant and antimicrobial properties make them highly suitable for active packaging applications, helping to extend food shelf life and reduce spoilage. Integrating polyphenols into biopolymers aligns with the growing demand for sustainable, biodegradable packaging solutions that prioritize

T a b l e 1. Polyphenol enriched biodegradable polymer food packaging

Polyphenol source	Polymer matrix	Integration method	Product/ Application	Studied food-related property	Citation
<i>Piper betel</i> leaf ethanolic extract	PLA	Blending	Tuna meat	Total phenol/flavonoid content, antimicrobial/antioxidant properties, packaging-related attributes	[127]
Gallic acid	PLA	Coating	–	Release kinetics, antioxidant properties	[128]
Tomato and lemon by-products extracts	PVA, PLA	Blending	–	Migration, controlled release	[129]
Green tea extract	Starch	Blending	Butter	Packaged product oxidative stability, active film stability	[130]
Strawberry	Chitosan	Encapsulation	–	Polyphenol loading efficiency, in vitro release, release kinetics	[131]
Green/black tea extracts, grape seed extract	Polycaprolactone	Blending	Kimchi	Deodorizing activity, polyphenol/flavonoid content, water barrier properties	[132]
Green tea extract	Polycaprolactone/ PLA	Blending	Sausage	Phenolic/major component content, antioxidant/ antimicrobial/food packaging properties,	[133]
Yerba mate extract	Starch/PVA	Blending	–	Phenolic content, antioxidant properties, degradation in compost	[134]
Quercetin	PBS	Blending	–	Water barrier properties, free radical scavenging/antimicrobial activity, migration into food model	[135]
Tannic acid	PBAT/lignin composite	Encapsulation	Fresh onion/ potato slices	Barrier properties, application as barrier in food packaging, biodegradation of composite film	[136]
Clove essential oil	PHB/bacterial cellulose	Blending	–	Oil permeability, antimicrobial activity	[127]

food safety and environmental impact. As research continues to refine methods for stabilizing and incorporating polyphenols in biopolymers, it is likely that polyphenol-enriched packaging will play a significant role in the future of sustainable food packaging technology. Table 1 presents examples of the use or study of polyphenols in biodegradable food packaging.

Carotenoids

Carotenoids are a class of naturally occurring pigments primarily synthesized by plants, algae, and photosynthetic bacteria. These compounds can be divided into two main categories: carotenes (e.g., β -carotene and lycopene) and xanthophylls (e.g., lutein and zeaxanthin). They possess a long conjugated double-bond system, which gives them strong antioxidant properties by enabling them to scavenge free radicals and prevent oxidative reactions. Carotenoids play a role of pigments, their color range from vibrant yellow, orange, to red. These compounds are also valued for their potential health benefits, including their role as precursors of vitamin A [138]. In recent years, carotenoids have gained

attention as functional additives in food packaging, particularly in biopolymer-based materials, due to their ability to protect food products from oxidative damage and enhance the stability of packaged foods [139]. The trend towards sustainable, biodegradable packaging materials has spurred research into incorporating natural compounds like carotenoids, which can serve as both active and intelligent packaging agents, contributing to both the preservation and monitoring of food quality.

Carotenoids are compatible with a variety of biopolymer materials. Different methods are employed to incorporate carotenoids into biopolymer packaging, including blending, coating and encapsulation. Carotenoids can be blended directly into the biopolymer matrix during the extrusion or molding processes, ensuring a uniform distribution of their antioxidant properties throughout the material. This technique provides stable antioxidant protection for the food product over time [139, 140]. In addition, due to the carotenoids' vibrant colors, they can be added to biopolymers as colorants [141]. Encapsulating carotenoids in carriers like lipid-based or polymeric nanoparticles helps stabilize these compounds and prevents degradation during processing. Encapsulation can

Table 2. Carotenoid enriched biodegradable polymer food packaging

Carotenoid source	Polymer matrix	Integration method	Product/ Application	Studied food-related property	Citation
β -carotene, lycopene and bixin extract	PLA	Blending	Sunflower oil	Oxygen permeability, release study, antioxidant activity,	[147]
β -carotene	Starch	Encapsulation	Sunflower oil	Water barrier properties, oxidative stability, biodegradability	[149]
Carotenoproteins from blue crab <i>Portunus segnis</i>	Chitosan	Blending	–	Water barrier/antioxidant properties, metal chelating, antimicrobial activity	[150]
β -carotene	Methylcellulose/polycaprolactone	Encapsulation	–	Wettability, antioxidant activity, release from film	[151]
Carotenoid extract from <i>B. infantis</i>	Electrospun PVA	Blending	–	Loading efficiency, antioxidant activity, antibacterial activity	[152]
Sea buckthorn (<i>Hippophae rhamnoides</i> L.) extract	PBS film	Blending	–	Moisture content, antimicrobial activity, antioxidant potential	[153]

also enable a controlled release of carotenoids over time, enhancing the longevity of their antioxidant effects in packaging materials, while adding color to the biopolymer [142–144]. Other method of incorporating carotenoids involve supercritical CO₂ impregnation [145].

The incorporation of carotenoids into biopolymer-based packaging materials offers multiple benefits, including sustainability and biodegradability, enhanced food quality and safety, visual quality indicator and reduction in chemical additives. Derived from natural sources, carotenoids align with environmentally friendly practices and the demand for biodegradable packaging solutions. Combined with biopolymers, they provide a sustainable alternative to synthetic antioxidants, minimizing environmental impact. Carotenoid-enriched packaging actively protects food products from oxidative degradation, which is particularly valuable for packaging fresh produce, processed meats [146], and oils [147]. This helps maintain the nutritional and sensory quality of food, improving product safety and extending shelf life [148]. As carotenoids are sensitive to environmental factors like light, oxygen, and temperature, their natural color change can serve as a visual quality indicator for food freshness [139]. Intelligent packaging with carotenoids can alert consumers to changes in food quality, enhancing transparency and confidence in product safety. Carotenoids are providing natural antioxidant protection, thus can reduce the need for synthetic preservatives and additives in food products. This is advantageous in clean-label products and responds to consumer preferences for more natural, additive-free foods.

Incorporating carotenoids into biopolymers aligns with the shift toward sustainable and biodegradable packaging solutions that prioritize food safety and environmental responsibility. As research advances in stabilizing and enhancing carotenoid functionality in

biopolymers, carotenoid-enriched packaging is likely to become a valuable component of next-generation food packaging technologies. Table 2 presents examples of the use or study of polyphenols in biodegradable food packaging.

Vitamins

Vitamins are essential micronutrients with well-documented health benefits, widely recognized for their antioxidant, antimicrobial, and nutritional properties. They play a crucial role in human health [154], but they are also increasingly being explored for their applications in food packaging, particularly in biopolymer-based materials. The integration of vitamins in packaging aligns with the growing trend towards sustainable, functional packaging solutions that extend shelf life, preserve food quality, and reduce spoilage [155]. By leveraging the natural properties of vitamins, biopolymer-based packaging can serve as an effective medium to protect food products from oxidation and microbial contamination, while also providing potential health benefits.

Vitamins such as vitamin C (ascorbic acid), vitamin E (α -tocopherol), and some B-complex vitamins (class of water-soluble vitamins) are commonly used in packaging due to their antioxidant and preservative capabilities:

- Vitamin C: Known for its potent antioxidant properties, vitamin C helps prevent oxidative degradation in food products, particularly for items susceptible to color and flavor changes. It is also water-soluble, making it effective in protecting aqueous environments within packaging [156].

- Vitamin E: As a fat-soluble antioxidant, vitamin E is particularly useful in preventing lipid oxidation, making it suitable for packaging products high in fats and oils. Its ability to stabilize fatty acids helps in prolonging the

T a b l e 3. Vitamin enriched biodegradable polymer food packaging

Vitamin	Polymer matrix	Integration method	Product/ Application	Studied food-related property	Citation
Vitamin C (ascorbic acid)	Carboxymethyl cellulose (CMC)/PVA	Blending	–	Soil burial degradation, water vapor transmission rate, antibacterial behavior	[164]
Vitamin C and/ or vitamin E (α -Tocopherol)	Chitosan nanoparticles	Encapsulation	–	Antioxidant capacity, association efficiency of vitamins, in-vitro release of vitamins	[166]
Vitamins C, A (retinol) and Bs	PLA/chitosan	Coating	Minced chicken breast	Water vapor permeability, antioxidant capacity, application on fresh minced chicken breast	[162]
Vitamin C	Starch	Encapsulation (nanoliposomes)	Apples and beans	Encapsulation efficiency of vitamin C, measurement of release profile and kinetics modeling	[163]
Vitamin E	PLA	Encapsulation	Raw beef	Vitamin E release, antioxidant capacity, lipid oxidation of beef samples	[168]

freshness of foods prone to rancidity, such as nuts and dairy products [157, 158].

– B-Vitamins: Riboflavin [159], niacin [160] and other B vitamins [161], have demonstrated antimicrobial properties. While they are less commonly used in packaging than vitamins C and E, they offer potential for niche applications, especially where microbial contamination is a concern.

The addition of vitamins to biopolymer-based packaging provides antioxidant protection, antimicrobial effects, and potential nutritional fortification. Vitamins C and E are widely used as antioxidants, scavenging free radicals and preventing oxidative degradation of food, which is particularly beneficial for fresh produce, dairy, and meat products [162]. Additionally, innovative packaging approaches explore vitamin fortification, though controlled release and stability remain challenges [163].

Biopolymers such as PLA, PHA, and starch-based materials are suitable carriers for vitamins due to their biodegradable nature and compatibility with bioactive compounds. Vitamins can be incorporated into biopolymer packaging through blending [164], coating [165], or encapsulation [166]. Blending ensures uniform distribution, while coatings create active barriers that interact with food, particularly for fat-soluble vitamins like vitamin E. Encapsulation in nanoparticles protects vitamins from degradation and enables controlled release over time, enhancing stability and prolonging their antioxidant and antimicrobial effects [166].

Vitamin-enriched biopolymer packaging offers sustainability, improved food quality, and potential health benefits. These natural additives reduce reliance on synthetic preservatives, aligning with consumer demand for cleaner-label products [167]. Challenges such as vitamin stability, cost, and release mechanisms must still be addressed, but ongoing research suggests vitamin-based packaging could become an integral part of future food packaging technologies.

Synthetic antioxidants (BHT and BHA)

Butylated hydroxytoluene (BHT, E321) is one of the most widely used synthetic antioxidants, primarily in plastic materials, including biodegradable packaging made from PLA and PVA. BHT is a phenolic compound that prevents the oxidative degradation of polymers by scavenging free radicals that could otherwise break down polymer chains, especially in polyolefins [169]. BHT works by interfering with the propagation step of oxidation, where it donates a hydrogen atom to free radicals, stabilizing them and preventing further reactions with the polymer matrix [170].

In biodegradable packaging, BHT contributes to preserving the structural integrity of the polymer during processing, as well as during the product's shelf life. Its ability to stabilize the polymer matrix and prevent oxidative scission is particularly important in packaging made from PLA, which can be prone to oxidation when exposed to heat during processing or UV light during storage. However, it is essential to note that BHT can migrate into the packaged food [171]. This migration raises concerns about its safety, as excessive consumption of BHT may lead to adverse health effects, including potential carcinogenicity (in 1991) [172], but this information recently has been proved untrue [173]. Besides this findings, its use is strictly regulated, and the amount used must not exceed certain thresholds to ensure that migration does not exceed safe limits [174].

In food packaging, BHT provides essential protection for lipid-based foods, such as oils, snacks, and meat products, by preventing rancidity. The antioxidant activity of BHT helps preserve the flavor, color, and nutritional value of food by preventing oxidative spoilage [174]. Its ability to extend the shelf life of food is particularly beneficial in reducing food waste and ensuring product quality.

Butylated hydroxyanisole (BHA, E320) is another synthetic antioxidant commonly used in biodegradable pack-

T a b l e 4. Synthetic antioxidant enriched biodegradable polymer food packaging

Antioxidant	Polymer matrix	Integration method	Product/ Application	Studied food-related property	Citation
BHT and TBHQ (Tert-butyl hydroxy quinon)	PLA	Blending (heating method)	–	Migration test	[174]
BHT, BHA and TBHQ	PLA	Blending	–	Release test, calculation of diffusion and partition coefficients	[177]
Vitamin C and BHT	Starch	Blending	–	Solubility, water permeability, release test	[178]
BHA	Polycaprolactone/ PLA	Blending	Mango	Water permeability, antioxidant activity, release of BHA, <i>in vitro</i> and <i>in vivo</i> antibacterial activity, application as mango packaging	[179]

aging materials. Like BHT, BHA functions by inhibiting the oxidation process, which can lead to the degradation of both the polymer material and the food products it contains [169]. BHA is used in the same way as BHT, it scavenges free radicals, preventing them from reacting with the polymer chains and causing oxidative breakdown [170]. This is particularly important for ensuring the longevity of biodegradable polymers, which are more susceptible to environmental degradation compared to conventional plastics.

While BHA is effective in stabilizing biodegradable materials during processing and throughout the shelf life of products, it also has the potential to migrate into food. Furthermore, similar to BHT, BHA is under scrutiny due to potential health risks associated with its consumption, but recent study shows, that BHA poses no safety concern to humans at the levels found in diet [176]. Consequently, its use is subject to stringent regulations, and manufacturers must ensure that the amount of BHA used in food packaging remains within safe limits [174].

Despite these concerns, BHA is still widely used in food packaging applications due to its ability to protect food from oxidative spoilage. BHA is particularly effective in protecting lipid-rich products like oils, nuts, and baked goods from becoming rancid. By extending the shelf life of food, BHA contributes to reducing food waste and maintaining the quality of food products for longer periods.

SAFETY AND REGULATORY COMPLIANCE OF ANTIOXIDANTS IN BIODEGRADABLE FOOD PACKAGING

The use of antioxidants in biodegradable food packaging is essential for extending the shelf life of both the packaging materials and the food products they protect. However, the application of antioxidants in food packaging is subject to strict safety standards and regulatory compliance to ensure that these substances do not pose a risk to human health. As biodegradable packaging materials such as PLA (polylactic acid), thermoplastic starch (TPS), chitosan, polycaprolactone (PCL), poly-

vinyl alcohol (PVA), PBS, PBAT and PHB gain increasing popularity, the safety of the antioxidants used in these materials becomes an essential concern for both manufacturers and consumers.

Safety considerations of synthetic antioxidants

Synthetic antioxidants, such as BHT and BHA, are frequently used in biodegradable packaging to improve the oxidative stability of the material. However, the safety of these additives has been a subject of ongoing debate. High levels of BHT and BHA have been linked to potential health risks, including carcinogenicity and hormonal disruption, but only few reports are available [180]. As a result, their use in food packaging is regulated by various health and safety organizations, such as the Food and Drug Administration (FDA) in the United States [181] and the European Food Safety Authority (EFSA) in Europe [182]. While EFSA limited daily dose of BHT and BHA at 0.5 mg/kg of body weight, FDA requires that the migration of these substances into food be monitored and limited to a level that does not pose a health risk, without setting precise quantitative limits.

In both Japan and China, the use of antioxidants in food contact materials is regulated through comprehensive frameworks aimed at ensuring consumer safety. In Japan, the Food Sanitation Act governs food packaging, and a positive list system implemented in 2020 specifies authorized substances, including natural and synthetic antioxidants [183]. Similarly, China regulates food contact materials under the Food Safety Law, with key standards such as GB 9685-2016 outlining permitted additives and their migration limits [184]. Both countries require compliance with positive lists and mandate safety assessments for any substances not previously approved, reflecting a stringent approach to the use of functional additives in food packaging systems.

In addition to concerns about migration, the potential for toxic byproducts resulting from the breakdown of synthetic antioxidants in biodegradable polymers during storage or under heat is another safety consideration. When antioxidants like BHT or BHA degrade,

they may release potentially harmful substances that could leach into the food, raising further health concerns. Manufacturers of biodegradable packaging must therefore ensure that these antioxidants are used in ways that minimize migration into food and that they do not degrade into harmful byproducts during the product's lifecycle [185, 186].

Natural antioxidants and their safety profile

Natural antioxidants, such as vitamins, carotenoids, and polyphenols, are increasingly being favored over synthetic options due to their generally recognized safety for human consumption. These natural compounds are derived from plant sources, which have a long history of use in food applications, making them a safer alternative.

Despite their safety advantages, the use of natural antioxidants also requires careful consideration. While they are generally safe, the concentrations and migration rates must still be closely monitored to ensure that they do not negatively affect the packaged food product. Natural antioxidants may sometimes interact with food components, potentially altering the food's flavor, texture, or nutritional content. Regulatory agencies assess these interactions to ensure that the antioxidants do not cause unintended side effects when migrating into the food product [181, 182].

Regulatory frameworks and compliance

The use of antioxidants in food packaging made from biodegradable polymers is governed by stringent regulations to ensure food safety. In the European Union, for instance, the use of additives, including antioxidants, is regulated under the European Regulation (EC) No 1333/2008 on food additives, which specifies acceptable levels of food additive migration into food packaging [187]. In the United States, the FDA provides guidelines for the safe use of antioxidants in food packaging through the Food, Drug, and Cosmetic Act and its subsequent amendments. These regulations include maximum allowable migration limits, testing procedures for migration, and safety assessments for each antioxidant used in food packaging materials [188].

The safety evaluation process involves assessing the toxicological properties of each antioxidant, including its potential to cause carcinogenic, mutagenic, or reproductive toxicity. If the antioxidant is deemed safe within established limits, it is allowed for use in packaging materials that come into direct contact with food. The compliance with these regulations is crucial not only for consumer health but also for manufacturers, as non-compliance can result in product recalls, penalties, or loss of consumer trust.

Biodegradability and environmental considerations

In addition to human health concerns, the environmental impact of antioxidants used in biodegradable pack-

aging materials must also be considered. Biodegradable polymers, by definition, break down in the environment through natural processes, and the use of antioxidants must not hinder this process or result in harmful residues. Therefore, antioxidants must be chosen with consideration of their environmental impact and their potential to biodegrade alongside the packaging material.

Natural antioxidants, such as tocopherols and polyphenols, are often preferred for their biodegradability and minimal environmental impact. Synthetic antioxidants, such as BHT and BHA, are more challenging to degrade and may persist in the environment, which could be a concern for biodegradable packaging's eco-friendly credentials. Regulatory frameworks are evolving to address these concerns, and manufacturers must ensure that the antioxidants they use are compatible with the biodegradation properties of the polymer matrix.

The safety and regulatory compliance of antioxidants in biodegradable food packaging are critical factors in ensuring that these materials are both effective and safe for consumers. While natural antioxidants are generally regarded as safer and more environmentally friendly, synthetic antioxidants, though effective in preventing oxidative degradation, require careful monitoring to ensure they do not pose health risks through migration into food or degradation into harmful byproducts. As regulations continue to evolve, manufacturers of biodegradable food packaging must balance the need for effective antioxidants with the safety standards and environmental considerations that are paramount in the development of sustainable packaging solutions.

FUTURE PERSPECTIVE AND INNOVATIONS

The development of biodegradable food packaging enriched with antioxidants is a rapidly evolving field that integrates advances in materials science, food technology, and sustainability. While natural antioxidants (polyphenols, carotenoids, and vitamins) are gaining popularity due to their biocompatibility and low toxicity, several challenges still need to be addressed to fully exploit their potential in commercial applications. Possible perspectives are presented in Fig. 3.

One of the key future directions is enhancing the stability and controlled release of bioactive compounds. Current research is focusing on micro- and nanoencapsulation techniques, which allow for the gradual release of antioxidants in response to environmental triggers such as humidity, temperature, or pH. This strategy can significantly prolong the protective effect of packaging materials and optimize the dosage of active agents.

Another emerging trend is the development of smart packaging systems, where antioxidants play a dual role—not only in preserving food quality but also in serving as indicators of freshness or spoilage. Carotenoids, for instance, are being explored for their color-changing pro-

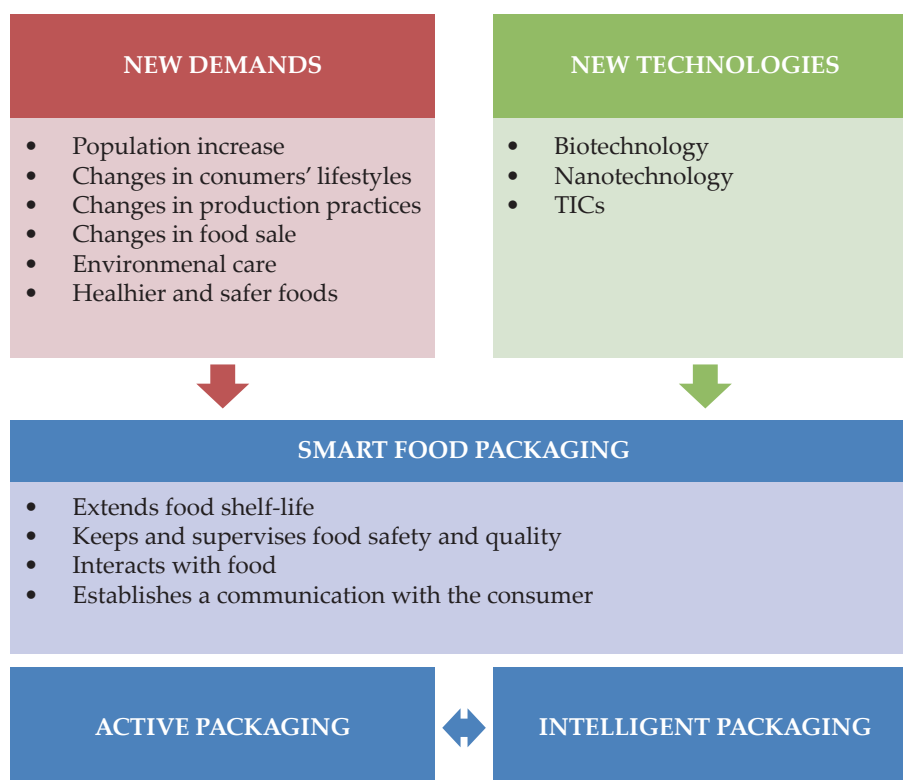


Fig. 3. Possible future perspective and innovations of biodegradable food packaging with antioxidants. Reprinted from [189]

perties in response to oxidative changes, enabling visual monitoring of product quality.

Biorefinery approaches are also gaining traction, where agricultural or food industry by-products rich in antioxidants are valorized as functional ingredients in biopolymers. This circular economy model reduces waste and lowers production costs, while contributing to sustainability.

In terms of materials, future innovations will likely involve hybrid systems - combinations of biodegradable polymers with tailored antioxidant blends - that balance mechanical strength, barrier performance, biodegradability, and bioactivity. This includes optimizing blends of PLA, PHA, PBS, PBAT, and natural polymers like starch or chitosan to improve functionality and reduce environmental impact.

Finally, regulatory harmonization and safety validation of active compounds - especially natural antioxidants - will be crucial for broader market adoption. Robust toxicological data and standardized migration testing protocols are essential to gain approval from food safety authorities and build consumer trust.

CONCLUSIONS

In summary, the future of antioxidant-enriched biodegradable packaging lies in multifunctionality: protecting food, informing users, and aligning with environmental goals. Among the various antioxidant classes reviewed, polyphenols remain the most extensively used due to

their high radical-scavenging efficiency and compatibility with diverse polymer matrices. In contrast, vitamins, though effective, are more sensitive to processing conditions, and their migration behavior is less predictable. These limitations may explain their less frequent application in commercial active packaging.

To meet future expectations, packaging systems must go beyond biodegradability and basic preservation. There is growing demand for smart functionalities, such as real-time freshness indicators, selective gas permeability tailored to food types, and integrated antimicrobial effects. Packaging materials should also be recyclable or compostable under home conditions, not just industrial settings.

Further research should address:

- the development of triggered release systems that respond to specific stimuli (e.g., pH, moisture, temperature),
- the synergistic effects of combining multiple natural antioxidants or antioxidant-antimicrobial systems,
- standardized evaluation methods for migration, degradation, and shelf-life extension in real-world food products,
- and comprehensive life cycle assessments (LCA) to evaluate environmental impact and scalability.

In terms of product innovation, future systems may include hybrid biopolymer matrices enriched with antioxidant cocktails derived from agricultural waste streams, designed specifically for high-fat, high-moisture, or sensitive food categories. Such innovations will

enhance packaging performance while aligning with sustainability principles.

Critically, these novel packaging systems can significantly reduce food waste by extending shelf life, preserving quality, and improving consumer awareness (e.g., via colorimetric indicators). By integrating biofunctionality, sustainability, and safety, they will support the transition toward circular and resilient food supply chains, where packaging plays an active and measurable role in reducing environmental impact and ensuring food security.

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Conflict of interest

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