Phenolic Compounds in Food Packaging

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The use of phenolic-compound-based active-packaging and edible films/coatings with antimicrobial and antioxidant activities is an innovative approach that has gained widespread attention worldwide. As phenolic compounds are natural bioactive molecules that are present in a wide range of foods, such as fruits, vegetables, herbs, oils, spices, tea, chocolate, and wine, as well as agricultural waste and industrial byproducts, their utilization in the development of packaging materials can lead to improvements in the oxidative status and antimicrobial properties of food products.

polyphenols active packaging edible film/coatings bioactive compounds

1. Phenolic Compounds

Phenolic compounds, also referred to as polyphenols, are a large class of phytochemicals that are produced by plants as secondary metabolites. These compounds hold a distinct place among natural products because of their occurrence in a wide variety of foods, including fruits, vegetables, herbs, tea, coffee, chocolate, and wine. Chemically, phenolic compounds are a group of aromatic organic compounds that have at least one hydroxyl group directly connected to a benzene ring [1]. Polyphenols are typically categorized by their origin, structural diversity, and biological function into bioactive components such as flavonoids, tannins, phenolic acids, lignans, stilbenes, lignins, and coumarins. Over 10,000 phenolic compounds with a wide range of functionalities and structural diversity have been identified to date, with flavonoids being the largest group [2]. **Table 1** summarizes the basic skeleton, main sources, and characteristics of the phenolic compounds.

Table 1. Classification, basic skeleton, sources, and characteristics of phenolic compounds.

Phenolic Compounds	Basic Skeleton	Main Sources	Characteristics	References
Flavonoids (flavanones, flavonols, flavanone, isoflavones, flavanols, quercetin, anthocyanin)	C6–C3–C6	Wide range of sources (berries, herbs, cacao, grapes, green and black tea, citrus fruits, spinach, soybeans, olives, cherries, and red wine)	Antioxidant, antimicrobial, anti-infective, and antifungal activities	[3][4]
Tannins (hydrolysable tannins, condensable tannins)	$(C6–C1)_n$	Tea, coffee, chocolate, berries, apples, and wine	Antimicrobial, antifungal, and antioxidant capabilities in	[5]

Phenolic Compounds	Basic Skeleton	Main Sources	Characteristics	References
			addition to UV absorption	
Phenolic acids (hydroxybenzoic acid (gallic acid, sinapic acid, ellagic acid) and hydroxycinnamic acid (caffeic acid, p-coumaric acid, ferulic acid)	C6–C1 and C6–C3	Berries, persimmon, apple juice, grapes, mustard, oranges, rye, coffee, mushrooms, propolis, tea, and wine	Antioxidant, antimicrobial, and anti-infection activities	[6]
Lignans (matairesinol, pinoresinol, secoisolariciresinol)	C6–C3	Oilseeds such as flaxseed, sesame, legumes, whole grains, and berries	Antioxidants and antimicrobial properties	[7]
Stillbenes (resveratrol, pinosylvin, piceid)	C6–C2–C6	Grapes, pine, almond, peanuts, sorghum, berries, and wine	Antioxidant, and anti-infective, activities	[4][6]
Lignins	$(C3–C6)_n$	Spruce, jute, cotton, hemp, pine, and birch	Antioxidants and antimicrobial properties	[8][9]
Coumarins	C6–C3	Cinnamon, cloves, tonka bean, celery, and apricots	Antioxidants and antimicrobial properties	[6]

y derived … aging. To … oxygen, biochemical changes, and microbial deterioration. Among these destructive factors, oxidation in the packaging and microbial growth significantly deteriorate the shelf life of food products. To address the environmental concerns of conventional packaging waste used for preserving food products, techniques such as the use of naturally derived additives with antioxidant and antimicrobial properties emerged for developing active packaging and edible films/coatings. The functional properties of phenolic compounds in terms of their antioxidant activity and antibacterial function have been well established [10][11]. Phenolic compounds, which often exhibit antioxidant and antimicrobial characteristics, show promise as ingredients in active packaging and edible films/coatings due to their unique molecular structure. They maintain the physicochemical properties of food products, improve their sensory attributes, and protect them from oxidation. Furthermore, they can prolong the shelf life of food by preventing microbial development due to their antibacterial characteristics. The two primary characteristics of phenolic compounds—antioxidant and antimicrobial activities—are further discussed in the following subsections to help comprehend the significance of phenolic compounds in active packaging and edible films/coatings.

1.1. Antioxidant Activity

Food can undergo oxidative changes that lead to lipid rancidity, off-flavors, and a loss of color and flavor. Consequently, the nutritional quality and safety of food are compromised by the development of secondary, potentially toxic compounds [12]. Therefore, antioxidants must be added to maintain flavor and color while preventing metabolic alterations. In general, antioxidants inhibit or delay the oxidation in food by limiting the initiation or propagation of oxidative chain reactions. EC Regulation No. 1333/2008, which governs the use of food additives, defines antioxidants as “substances which extend the shelf-life of foods by preserving them against deterioration induced by oxidation, such as lipid rancidity and color changes” [13]. Among synthetic food additives, butylated hydroxy anisole, butylated hydroxytoluene, propyl gallate, and tert-butyl hydroquinone are commonly used as antioxidants to preserve food products. However, the use of natural antioxidants, including tocopherol, plant extracts, and essential oils from herbs and spices is an alternate strategy that is currently the subject of extensive research [5]. In particular, tocopherol, generally known as vitamin E, is an excellent radical-chain breaker in unsaturated fatty foods and is a lipid-soluble antioxidant that may be derived from food sources such as palm oil, sunflower, and soybeans. Commercially, tocopherols are the most extensively used antioxidants for preventing lipid oxidation in food products and exhibit a tremendous degree of complexity in terms of the various chemical and physicochemical factors involved. Furthermore, tocopherols are employed as antioxidants in food products in four different forms (α, β, γ, and δ), and their effectiveness decreases as follows: $\delta > \gamma > \beta > \alpha$ [14][15].

Among the major naturally derived, functional compounds identified for use in active packaging and edible films/coatings, phenolic compounds (flavonoids, tannins, stilbenes, and phenolic acids), in particular, exhibit excellent antioxidant properties [16]. These compounds have become increasingly popular in recent years due to their antioxidant activities, especially because of their sources and their interactions with biopolymers. Polyphenols have been found to function via mechanisms such as free radical scavenging, single-electron transfer, hydrogen atom transfer, and metal chelation [3][16]. To extend the shelf life and improve the quality of food, active compounds are introduced to films/coatings or created as individual contraptions (sachets, pads, or labels) that can either release or absorb reactive radicals [17]. Numerous phenolic compounds found in fruits, vegetables, herbs, tea, coffee, chocolate, and wine have been reported as strong antioxidants. For example, fruits such as kiwi, prunes, olives, berries, cherries, and citrus fruits have been proven to have antioxidants with significant activity [18][19][20][21][22][23][24][25][26][27][28][29].

1.2. Antimicrobial Activity

Consumers appear to be significantly concerned about foodborne illnesses, particularly in the current era with considerably higher packaged food consumption. Therefore, antimicrobial compounds are individually or collectively applied to food or packaging materials [30]. According to Regulation No. 1333/2008, antimicrobial compounds are described as “compounds which extend the shelf-life of foods by protecting food products against deterioration caused by microorganisms and/or which protect the food products from the growth of pathogenic microorganisms” [16]. The use of antimicrobial packaging systems is an excellent approach to inhibit the activity of specific microorganisms and prevent the growth of foodborne pathogens through the formation of a comprehensive and effective barrier. Several methods exist for incorporating antimicrobial compounds into antimicrobial packaging systems, including fabricating films with antimicrobial substances, directly integrating antimicrobial compounds into packaging films, or coating packaged films [31][32][33]. The application of an antimicrobial compound (migrating or non-migrating) and the potency of its interactions with the packaging and food matrix determine the efficacy of an antimicrobial packaging system. Two theories explain the effectiveness of these systems: (1) the antimicrobial compound reaches the surface of the food (migrating film) and (2) the compound significantly inhibits microbial surface growth without migrating (non-migrating film). Furthermore, the direct addition of synthetic antimicrobial compounds to foods can effectively limit the spread and viability of several microorganisms. Nevertheless, consumers prefer naturally processed and preservative-free food products with an extended shelf life.

The development of packaging materials with natural antimicrobial agents has become increasingly popular. Natural ingredients, such as bacteriocins, enzymes, and plant-derived compounds, are biologically derived components that have been employed in antimicrobial packaging. Plant-derived compounds are mainly secondary metabolites that exhibit several advantages such as antimicrobial properties against harmful and spoilage microbes. Polyphenols, phenolic acids, flavonoids, tannins, quinones, coumarins, terpenoids, and alkaloids are the major classes of compounds responsible for the antimicrobial action. Numerous naturally occurring phenolic compounds that are present in various plant sources such as fruits (apple, grape, pomegranate, and orange); vegetables (cabbage and onion); herbs (garlic, oregano, thyme, and rosemary); and spices (pepper, cardamom, and clove) have been documented to have antimicrobial properties [34][35][36][37][38][39]. Although the efficacy of natural antimicrobials has been demonstrated in laboratory settings, challenges remain in ensuring their effectiveness in practical applications for foods under different environmental conditions [40].

2. Phenolic Compounds in Food Packaging

2.1. Flavonoids and Tannins

The majority of phenolic compounds are flavonoids, which include over 8000 different compounds grouped into subclasses of flavanones, flavonols, flavanones, isoflavones, flavanols, quercetin, and anthocyanins [5][41]. The basic structural component of flavonoids typically includes three hydroxyl groups and hydroxylated phenolic compounds with a C6–C3–C6 link in the aromatic ring [6]. Flavonoids with antimicrobial, antioxidant, anti-infective, and antifungal activities are abundant in nature and are derived from a wide range of sources such as berries, herbs, cacao, grapes, green and black tea, citrus fruits, spinach, soybeans, olives, cherries, and red wine. Incorporating flavonoids into packaging materials is an effective strategy to enhance the safety of packaged foods and preserve their quality. These compounds can inhibit microbial growth by releasing antioxidizing agents [42]. Flavonoids are increasingly preferred for use in active packaging and edible films/coatings; however, their stability (due to the extraction process and storage conditions) makes their use as active ingredients challenging.

Tannins are water-soluble, astringent, and complex phenolics that are available from diverse sources such as tea, coffee, chocolate, berries, apples, and wine. They can be classified into hydrolyzable and condensed tannins based on their resistance to hydrolysis [7]. Because tannins are regarded as generally recognized as safe (GRAS) additives by the US Food and Drug Administration (FDA), the characteristic features of tannins, including antimicrobial, antifungal, antioxidant, and UV absorption properties, can be readily exploited for active-packaging applications [3]. In a study on the development of active-packaging films, the incorporation of tannin was found to be effective in improving the UV-blocking and antioxidant properties of tannin-cellulose films [43]. Similarly, tannin-containing films composed of chitosan and cellulose demonstrated significant antioxidant and antibacterial activities [44].

2.2. Phenolic Acids—Hydroxybenzoic and Hydroxycinnamic Acids

Phenolic acids are non-flavonoid polyphenolic substances that are present in various food sources and are characterized by a carboxyl group connected to a benzene ring [4]. Natural phenolic acids are categorized into two main groups based on the number of carboxylic acids, hydroxybenzoic (C6–C1) and hydroxycinnamic acids (C6–C3), which are derived from benzoic and cinnamic acids, respectively [7]. They are the simplest class of phenolics and serve as building blocks for several other compounds. Gallic, sinapic, and ellagic acids are some of the main hydroxybenzoic acids, whereas caffeic, p-coumaric, and ferulic acids are the main hydroxycinnamic acids. Numerous studies have found that phenolic acids exhibit biological activities, such as antioxidant, anti-inflammatory, antibacterial, and other functional characteristics. Moreover, phenolic acids are considered desirable food preservatives because they significantly inhibit the development of numerous harmful bacteria and fungi, including *E. coli*, *Bacillus cereus*, *Staphylococcus aureus*, *Aspergillus flavus*, and *Aspergillus parasiticus* [7][45][46]. For instance, gallic acid, which exists in high amounts in red wine, tea leaves, berries, mango, citrus fruits, and soy, is recognized primarily for its antioxidant properties as well as antibacterial and anti-inflammatory properties [47]. Similarly, ellagic acid, which exhibits an array of biological activities, is a significant polyphenol antioxidant found in several fruits, nuts, and seeds. It contains potential biomolecules with interesting biological properties such as antioxidant, antimicrobial, and UV-barrier characteristics [48]. Notably, numerous phenolic acids have been employed as valuable components in active packaging and edible films/coatings to achieve sustained antimicrobial, antioxidant, and other functional characteristics.

The effective incorporation of gallic acid has been achieved by electrospinning it into hydroxypropyl methylcellulose nanofibers, which were found to be an effective active-packaging material for delaying oxidation during the storage of walnut [45]. Similarly, the antioxidant capacity of gallic acid to scavenge free radicals has been shown to delay lipid oxidation in numerous edible coating materials [49][50][51]. Phenolic acid, ellagic acid, and chitosan have been used to fabricate active food-packaging films with high antioxidant, antimicrobial, and UV-light-resistance characteristics [52]. Furthermore, numerous studies have shown that the addition of phenolic acids, such as caffeic acid and p-coumaric acid, to fatty food products, such as processed fish and fish products, delays or prevents oxidative degradation [53][54][55]. Hydrocolloid films prepared from chitosan and fish gelatin and filled with the naturally occurring antioxidants of caffeic and p-coumaric acids demonstrated excellent results in terms of preventing the oxidation of fatty food products [56]. Additionally, films containing caffeic acid had higher levels of chelating iron, reducing power, and antioxidant activity than those of films containing p-coumaric acid.

2.3. Lignans

Lignans are secondary plant metabolites with complex phytoestrogen-related chemical compositions. Their basic structure includes a combination of phenylpropanoid dimers (C6–C3) connected by the central carbons of the side chains [5][6]. Lignans are primarily derived from oilseeds of flaxseed and sesame, legumes, whole grains, and several types of berries. Similarly to several other phenolic compounds, lignans exhibit a wide range of bioactivities and have been used by humans for a long time. Due to their significant bioactivity as antioxidants and antimicrobials, lignans have been used in food science and nutrition since ancient times. Lignans have antioxidant capacities because they function as hydrogen donors and complex divalent transition metal cations [57].

2.4. Stillbenes

Stilbenes are a class of plant polyphenols that received significant interest because of their complex chemical structures and wide range of biological functions. The basic structure of stilbenes is C6–C2–C6, which has two benzene rings joined by a double bond [5][58]. Food sources that contain stilbenes include grapes, pine, almonds, peanuts, sorghum, berries, and wine. The use of stilbenes is attracting attention because of their potential bioactive components. For instance, the stilbene resveratrol has been shown to possess a range of bioactive properties, such as antioxidant, anti-inflammatory, and antibacterial activities [59][60].

Cellulose bilayer films incorporated with resveratrol have been prepared. These films showed antimicrobial activity against Campylobacter and exhibited potential bioactive packaging properties for improving food safety [60]. Similarly, a study on assessing the antioxidant and antibacterial properties of carboxymethyl cellulose films containing resveratrol and eugenol suggested that the addition of resveratrol and eugenol to the films increased their total phenolic content, free-radical-scavenging activity, reducing power, and antibacterial activities [61].

2.5. Lignins

The phenolic chemicals present in lignins, which are naturally occurring antioxidants, are derived from numerous renewable sources such as spruce, jute, cotton, hemp, pine, birch, and agricultural crops [62]. Due to their functional groups, lignins have an aromatic, highly cross-linked structure and are particularly reactive. Consequently, they can combine with various polymers to modify their morphological, hydrophilic, and strength-related properties. The considerable antioxidant activity is caused by the properties of lignins induced by their phenolic hydroxyl groups, aliphatic hydroxyl groups, low molecular weight, and narrow polydispersity [63][64]. Because lignins are typically immiscible, their incorporation into polymer matrices requires considerable time and has limited practical applications and industrial-scale use [64]. However, the influence of lignins on the physicochemical and functional characteristics of natural polymers in the preparation of various films has been thoroughly investigated in the recent past.

Lignin nanoparticles have been used as a filler to investigate the antioxidant and antibacterial characteristics of films developed using polyvinyl alcohol/chitosan for active-packaging applications [65]. The antioxidant capacity and antimicrobial performance of the films enhanced over time, inhibiting the growth of Gram-negative bacteria, including *Xanthomonas arboricola* pv. *pruni* and *Erwinia carotovora* subsp. *carotovora*. Moreover, lignins have been found to be applicable as a competitive material for active food packaging. A poly(lactic acid) composite films with lignin showed excellent UV resistance and enhanced antioxidant capacities [66].

2.6. Coumarins

Coumarin is a naturally occurring phenolic compound found in several plants, such as cinnamon, cloves, tonka beans, celery, and apricots. It consists of an aromatic ring fused to a condensed lactone ring and has a spicy, fresh-hay, or vanilla fragrance [67]. Coumarin exhibits bioactive characteristics such as anticoagulant, antimicrobial, antifungal, and antioxidant effects. For instance, chitosan and fish gelatin have been used to create coumarin-containing bioactive films, which have demonstrated antioxidant properties. Films containing coumarin were found to release more free radicals than a control film [68]. Contrary to other phenolic compounds, the use of coumarin in active packaging and edible films/coatings has not been investigated, providing a good opportunity to investigate and demonstrate its active qualities.

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