



Biomimetic polyphenol coatings for antioxidant active packaging applications



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ARTICLE INFO

Article history:

Received 8 February 2016

Received in revised form 1 June 2016

Accepted 6 June 2016

Available online xxxx

Keywords:

Catechol
Catechin
Antioxidant active packaging
Metal chelator
Radical scavenger
Biomaterial

ABSTRACT

Oxidative instability of food, pharmaceutical, and consumer products can be promoted by trace metals, especially iron and copper, with subsequent propagation of free radicals. Plant-derived phenolic compounds that contain catechols are reported to have free radical scavenging, metal chelating and surface adhesion properties upon polymerization. The objective of this study was to synthesize biomimetic polyphenol coatings for development of antioxidant active packaging materials. Two synthetic routes were explored to apply polyphenol coatings to the surface of polypropylene by *in situ* polymerization of a mixture of catechol and catechin and oxidative polymerization with laccase and in alkaline saline. Both polyphenol coatings demonstrated potent metal chelating and radical scavenging capacity, which suggest potential antioxidant capacity. Dual functionality of polyphenol coatings as potent antioxidants and anchors makes them a promising candidate for active packaging coatings that can inhibit metal-promoted oxidative degradation.

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A major challenge to food, consumer products, and pharmaceutical industries is retaining stability of oxidation-sensitive bioactive compounds, such as unsaturated fatty acids, carotenoids, flavonoids, vitamins, and drugs. Oxidative stability of such compounds is determined by the propagation of free radicals. In dispersions containing bioactive compounds, trace amounts of metals, especially iron and copper, are key prooxidants that contribute to product instability as they promote hydroperoxide decomposition that catalyzes free radical chain reactions [1]. Since it is difficult to fully remove trace metals from raw materials and the processing environment, metal chelators, such as ethylenediaminetetraacetic acid (EDTA), and free radical scavengers, such as butylated hydroxytoluene (BHT), are often added to formulations as antioxidants to stabilize these products. In an effort to reduce use of synthetic additives due to consumer perception of toxicity risk, there has been increasing interest in alternative methods of product preservation using antioxidants obtained from natural sources. Directly substituting natural antioxidants into product formulations is challenging because they tend to be less potent than synthetic additives and therefore must be added in larger amounts that may change a product's organoleptic properties (*i.e.* color, flavor, viscosity). In order to overcome this challenge, researchers have explored incorporation of natural antioxidants into active packaging coatings. Antioxidant active packaging coatings may be applied to the product contact surface of common packaging materials by non-covalent or covalent attachment of

antioxidants that are applied with or without a carrier polymeric resin [2]. These coatings are designed to either scavenge prooxidants from the product or slowly release antioxidants from the packaging material.

The majority of research on antioxidant active packaging coatings has been focused on application of free radical scavengers on the surface of packaging materials. Contini et al. [3] spray deposited citrus extract on plasma pretreated polyethylene terephthalate trays that inhibited oxidative degradation of cooked meats. Garces et al. [4] patented an antioxidant active varnish for use on packaging materials composed of polymeric resin blended with plant extracts that is designed to scavenge free radicals in packaging headspace [5]. Arrua et al. [6] covalently attached a polymer containing caffeic acid to the surface of polypropylene and demonstrated its ability to scavenge free radicals and inhibit degradation of vitamin C in orange juice. Recently, antioxidant active packaging coatings by graft polymerization of metal chelating polymers, such as poly(acrylic acid) and poly(hydroxamic acid), have been developed that exhibit functionality across a broad range of pH values and viscosity conditions and in the presence of competing ions [7–11]. Metal chelating active packaging coatings extended the lag phase of lipid oxidation in soybean oil-in-water emulsions and demonstrated improved performance for metal chelating polymers with high iron affinity [12,13].

Among free radical scavenging antioxidants derived from natural sources, plant-derived phenolic compounds that contain catechols are reported to have high affinity for iron (*e.g.* catechol $\log \beta^{\text{Fe(III)}} = 43.76$, catechin $\log \beta^{\text{Fe(III)}} = 47.4$) [14,15]. In addition to their antioxidant capacity, phenolic compounds that contain catechols have been researched as biomimetics of mussel adhesive proteins making them

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ideal candidates for coating technologies [16–18]. With this in mind, the reported work seeks to design biomimetic catechol-based polyphenol surface coatings for the development of antioxidant active packaging materials that provide dual antioxidant functionality, both by scavenging free radicals directly and by removing trace transition metals from the system.

A facile method of coating plant phenols onto material surfaces is through oxidative polymerization. Polymerized plant phenols have been noted to have adhesive properties on many materials relevant to packaging due to their structural similarities to the widely researched mussel adhesive proteins. Jeon et al. [19] demonstrated that plant phenols can be polymerized onto a variety of material surfaces, including aluminum, glass, polyethylene terephthalate, and polypropylene, with the assistance of the oxidase enzyme, laccase. Barrett et al. [20] prepared polyphenol coatings from plant phenols by polymerization in an alkaline aqueous buffer, similar to reported methods for the preparation of polydopamine coatings [17]. However, there has yet to be an investigation of the ability of such polyphenol coatings to function as both free radical scavengers and metal chelators for antioxidant applications. The objective of this study was to synthesize a biomimetic polyphenol coating for development of antioxidant packaging materials with both metal chelating and free radical scavenging character. Polyphenol coatings were applied to the surface of polypropylene by *in situ* polymerization of a mixture of catechol and catechin (2.5 mg/ml catechol; 2.5 mg/ml catechin) via enzymatic polymerization with laccase (1 mg/ml in 100 mM sodium acetate buffer, pH 5 and methanol (9:1)) or oxidative polymerization in alkaline saline (100 mM bicine, 600 mM sodium chloride, pH 8). Ability of the polyphenol coatings to chelate copper and iron ions and scavenge free radicals was demonstrated.

Polymerization of the catechol and catechin by laccase (pH 5) and in alkaline saline (pH 8) was immediately observed by a change in the color of the reaction solution to a dark brown color, characteristic of polyphenol formation. Deposition of the polymerized phenolic coating onto the surface of polypropylene was identified by similar generation of a dark brown color on the polypropylene film after 24 h in the reaction solution (Fig. S1). It is important to note, that for the oxidative polymerization reaction conducted at pH 8 without laccase, preliminary experiments revealed that a minimum of 200 mM sodium chloride was necessary for the polyphenol to be deposited on the surface, with optimum surface deposition at 600 mM sodium chloride (data not shown). Salt ions may shield charges on polyphenols formed under alkaline conditions to allow for better interactions with the hydrophobic polypropylene surface. Previous work in agreement with our findings was conducted by Sileika [21] who found that alkaline saline enabled improved surface deposition of polymerized phenolic compounds compared to pure water.

Surface chemistry of the polyphenol coated materials was characterized by ATR-FTIR spectroscopy (Fig. 1). Laccase assisted polyphenol coatings exhibited a strong O—H absorbance band (3000–3680 cm^{-1}), two C=C absorbance bands (1590, 1518 cm^{-1}) attributed

to benzene rings on catechol and catechin, and several C—O absorbance bands that may be attributed to crosslinks of catechol and catechin or catechol ligands (1050–1290 cm^{-1}). These results are in agreement with reported spectra collected from laccase-assisted polymerization of catechol, catechin, and their combination [19]. The polyphenol coating produced by alkaline saline polymerization of catechol and catechin exhibited a similar ATR-FTIR spectrum, with slight differences in the intensity and number of absorbance bands for C=C (1606, 1575, 1537 cm^{-1}) and C—O bonds (1050–1290 cm^{-1}), which suggests that this polyphenol coating may have a different structure than the polyphenol coating formed by laccase assisted polymerization. Oxidation of a phenol by laccase typically involves loss of a single electron that results in the formation of a cationic radical, whereas alkaline oxidation results in the formation of an anionic radical. Different reactive radicals may influence the structure of the polyphenol formed by subsequent polymerization reactions. Further characterization of polyphenol molecular structure is necessary to confirm such differences as well as hypothesize polymerization reaction pathways and will be the subject of future work. The number of available catechol groups on the surface was assessed by Folin Ciocalteu assay (Fig. 1B). Laccase assisted polyphenol coatings contained more than twice the number of available phenolic groups than alkaline saline polyphenol coatings (86.7 ± 12 nmol catechol eq. cm^{-2} and 33.1 ± 7.3 nmol catechol eq. cm^{-2} , respectively), while uncoated PP contained an insignificant amount of phenol groups (0.791 ± 0.14 nmol catechol eq. cm^{-2}).

To determine the effect of coating preparation method on surface morphology, surface scanning electron microscopy (SEM) images of coated and uncoated materials were taken (Fig. 2). Uncoated PP exhibited a smooth, uniform surface (Fig. 2A). SEM micrographs confirmed the deposition of laccase assisted and alkaline saline polyphenol coatings onto the surface of polypropylene films. Laccase assisted polyphenol coatings significantly changed the surface morphology of the polypropylene to a rough surface with aggregates of polyphenols throughout the coating (Fig. 2B). The coated surface also exhibited cracks throughout most likely caused by dehydration of the hydrophilic surface prior to imaging. The alkaline saline polyphenol coating was smoother than the laccase assisted polyphenol coating and did not have any visible cracking (Fig. 2C). Compared to the uncoated PP material, both polyphenol coated surfaces were rougher with presence of polyphenol aggregates. These observations are consistent with previous research on *in situ* polymerization of dopamine on glass and aluminum [22], which suggests that the hydrophobic surface properties of polypropylene did not significantly affect coating morphology. Changes in the surface morphology of coated PP materials were evident across the surface, demonstrating uniform application of the polyphenol coatings. Laccase assisted polyphenol coatings were approximately twice the thickness of alkaline polyphenol coatings (laccase assisted coating: 1087 ± 45.3 nm, alkaline coating: 506.5 ± 32.1 nm). This disparity between coating thickness corresponds with differences in the coatings available phenolic groups (Fig. 1B).

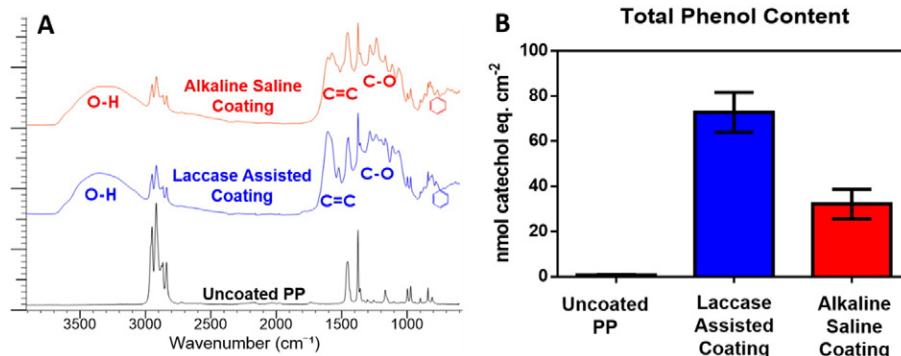


Fig. 1. (A) Representative ATR-FTIR spectra and (B) total phenol content ($n = 4$) of native PP and polyphenol coated PP.

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