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Impact of functional properties and release kinetics on antioxidant activity of biopolymer active films and coatings

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ABSTRACT

This work deals with the study of the release kinetics of some natural antioxidants (ferulic acid, caffeic acid and tyrosol) from chitosan-fish gelatin edible films immersed ethanol at 96%, as well as the kinetics of their antioxidant activity using the DPPH assay. The aim was to determine how film functional properties influence the release kinetic and antioxidant activity. The addition of antioxidants to chitosan-fish gelatin matrix decreased the water vapour permeability by more than 30%. The tensile strength (TS) increased up to 50% after the incorporation of antioxidants. Some molecular interactions between polymer chains and antioxidants were confirmed by FTIR where spectra displayed a shift of the amide-III peak. Films containing caffeic acid or a caffeic-ferulic acid mixture exhibited the highest radical scavenging activity, leading to a 90% antioxidant activity at equilibrium but the release rate controlled the efficacy of the system.

1. Introduction

Nowadays, the uses of packaging to extend the shelf life of food and bioproducts has become a most important challenge for the modern food industry. Currently, a great number of research works are focused on the use of bio-based and/or edible films and coatings with good water and oxygen barrier properties to protect food, pharmaceutical or cosmetic bioproducts (Fabra, Hambleton, Talens, Debeaufort, & Chiralt, 2011). Meanwhile, the consumer demand has shifted to safe materials, especially from renewable agricultural and food industry waste and by products (Benbettaïeb et al., 2016; Jridi et al., 2017). Natural polymers (proteins, polysaccharides) are processed as biopackaging materials, some of them being edible films and coatings.

Chitosan is nontoxic, biodegradable, biofunctional, biocompatible polysaccharide having intrinsic antimicrobial properties and can be used for encapsulation of active compounds (Moradi et al., 2012). In view of these properties, chitosan films have been used as a packaging material for the quality preservation of a variety of foods (Park & Zhao, 2004). Gelatin is one of the multipurpose biomaterials obtained by the controlled hydrolysis of the insoluble fibrous collagen present in the bones and skin, generated as waste during animal slaughtering and fish processing. Gelatin and chitosan have excellent film forming ability (Hoque, Benjakul, & Prodpran, 2011; Jridi et al., 2017). Gelatin-based films as well as chitosan-based films used for packaging or coating could preserve the quality of foods and tablets during storage period, due to their good barrier properties against oxygen, prevention of lipid oxidation and dehydration, but these properties can be modified by active compound addition (Jongjareonrak, Benjakul, Visessanguan, Prodpran, & Tanaka, 2006). The compatibility of chitosan and gelatin is due to the establishment of electrostatic and dipole-dipole interactions when the two biopolymers are oppositely charged at appropriate pH conditions. Structural modification is a one approach to improve and thus extend the uses of these polymers on a wide range of foods. Incorporation of antioxidants in films have become also popular to prepare active films since oxidation is one of the major problems affecting food quality. Therefore, in order to convert industrial by-products into a performing active packaging for food preservation or active coating for pharmaceutical applications, antioxidants were encapsulated into the biopolymer network. These active compounds could protect packed bioproducts against oxidation and thus extend their shelf life as they limit the oxygen transfer and the reactivity of free radicals (Fabra et al., 2011; Mathew, Abraham, & Zakaria, 2015). Beside their antioxidant properties, antioxidants can also improve the functional properties of films and coatings as side effects.

Extensive research has been conducted to use some natural antioxidants such as phenolic compounds (flavonoids, tannin and phenolic

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acid) as alternatives to synthetic antioxidants (Mathew et al., 2015; Villaño, Fernández-Pachón, Moyá, Troncoso, & García-Parrilla, 2007). Phenolic acids, can quench free radical and therefore inhibit the oxidation of food, because of their higher ability to exchange hydrogen and single electron, and because of resonance stabilization of the resulting phenolic radicals (Mathew et al., 2015). They can also react with amino and sulfhydryl side groups of polypeptides and therefore improve or tailor the properties of protein films (Ou, Wang, Tang, Huang, & Jackson, 2005). Among phenolic substances, ferulic acid is an antioxidant, antimicrobial, anticancer, and anti-cholesterol factor which can react with some amino acids present in proteins such as tyrosine, lysine, and cysteine to form cross-link bounds (Cao, Fu, & He, 2007), possibly by radical polymerization. Caffeic acid is produced from secondary metabolism of plant polyphenols and contains biochemical, antibacterial, antioxidant and antiviral properties (Hagiwara et al., 1991). The possible antioxidant effects of caffeic acid and ferulic acid have been evaluated in different in vitro assays. DPPH, ABTS or superoxide anion are the most often used methods for radical scavenging tests. Tyrosol, a phenyl-ethanoid derived from phenethyl alcohol, is a natural phenolic antioxidant present in a variety of natural sources, and having efficient antioxidant effects on cell ageing and health preservation, particularly in the Mediterranean diet (Covas et al., 2003). The antioxidant activity of tyrosol was also tested in vitro and in vivo assays (Cicerale, Lucas, & Keast, 2012; Vlachogianni, Fragopoulou, Kostakis, & Antonopoulou, 2015). Some interesting works on the antioxidant power of these phenolic compounds, on their release from films into food simulants have been also investigated. However, no study regarding their impact on the film structure and functional properties and on the release kinetics and on the antioxidant activity has been published. The originality of his work is to display how these active compounds could interact in the film structure, and how it affects the release kinetics and the antiradical activity kinetics.

Therefore, this work deals with the study of the antioxidant activity (DPPH assay) and the release kinetics of a phenyl ethanoid compound (tyrosol) and of phenolic acids (ferulic acid, caffeic acid, mixture of ferulic and caffeic acid), from chitosan-fish gelatin films in an alcoholic medium. This work focuses on the relationship between the migration kinetic of antioxidants from the films and their radical scavenging activity.

2. Materials and methods

2.1. Materials and reagents

Commercial grade chitosan (CS) (France Chitine, MW = 165 kDa, low viscosity, 85%, deacetylation degree, France) and a fish gelatin (G) (Rousselot 200FG, commercial grade, having a 180 Bloom degree, a 4 mPa·s viscosity at 45 °C and for a concentration of 6.67% in water and at pH = 5.4) were used as a film-forming matrix. Anhydrous glycerol (GLY) (Fluka Chemical, 98% purity, Germany) was used as a plasticizer in order to improve the mechanical properties of the films. Glacial acetic acid (Sigma, 99.85% purity) was used to prepare the solvent for chitosan and to improve its dispersion. Silica gel and a sodium bromide saturated salt solution (NaBr, Sigma-Aldrich, France) were used to control the relative humidity at < 2% and 58% for the water vapour permeability measurements. A magnesium nitrate saturated solution ($Mg(NO_3)_2$, Sigma Aldrich, France) was used to fix the relative humidity at 53% for mechanical property measurements. Ferulic acid (minimum purity 99%), caffeic acid (minimum purity 98%), and tyrosol (minimum purity 98%) were purchased from Sigma Aldrich and used as model of natural antioxidant molecules. The chemical structure and the physicochemical parameters of these compounds are given in Table 1. Ethanol (Sigma Aldrich, 96% (v/v) purity, Germany) was used as the food simulant medium for the antioxidant release.

2.2. Film formation

Chitosan powder (20 g) was dispersed in 1 L of a 1% (v/v) aqueous acetic acid to obtain the film forming solution. The solution was homogenized at 1200 rpm with a high shear homogeniser (Ultra Turrax, RW16 basic- IKA-WERKE) at 25 °C. Then, 2.2 g of glycerol (10% w/w dry matter) were added to this solution, under stirring. The pH of the chitosan solution was about 4.9 ± 0.2. Fish gelatin powder (60*g*) was separately dispersed in 1 L distilled water at 70 °C under continuous stirring for 30 min to obtain a 6% w/v solution (pH ≈ 6.5). 6.6 g of glycerol (10% w/w dry matter) were added to this film forming solution after complete dispersion of gelatin.

Subsequently, gelatin and chitosan solutions were mixed at 1:1 (w/w) ratio at 50 °C (temperature of mixing) and stirred for 30 min. pH was adjusted to 5.5 with acetic acid. This condition was specifically chosen to obtain a polyelectrolyte complex between chitosan and gelatin. At this pH, the gelatin is negatively charged while the chitosan is positively charged, thus favoring ionic interactions and avoiding any phase separation upon mixing. Indeed, the isoelectric point of gelatin is 4.85 (Hitchcock, 1931), while the pKa of chitosan amino group is ~6.5 (Pillai, Paul, & Sharma, 2009). Each antioxidant was added to the final film forming solution at a concentration of 5% (50 mg/g total biopolymer content corresponding to a 47 mg/g total dry matter of film). The concentration of 5% was chosen according to the literature survey that display that most of active films contain from 1% to 15% antioxidants or antimicrobials. In order to study the synergistic effect of ferulic acid and caffeic acid, 25 mg/g of biopolymer of each of these compounds were added to another film-forming solution. The aqueous dispersions were homogenized at 1200 rpm using the Ultra Turrax until complete dissolution of the active compound.

An aliquot of 30 mL of each film forming solution (FFS) was then poured into plastic Petri dishes (13.5 cm diameter). The aqueous solvent was removed by drying in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) at 25 °C and 45% RH for 18 to 24 h. After drying, films were peeled off from the surface and stored up to weight equilibrium in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) at 50% RH and 25 °C before analysis.

2.3. Film characterizations

2.3.1. Thickness measurement

The film thickness was measured with an electronic gauge (PosiTector 6000, DeFelsko Corporation, USA). Five measurements were taken for each film sample, one from the center and four close to the perimeter. A mean value was used in further calculations.

2.3.2. Water vapour permeability

The water vapour permeability (WVP) was determined according to the standard gravimetric method ISO-2528 and adapted to edible and bio-based films by Debeaufort, Martin-Polo, and Voilley (1993). Two relative humidity gradients were used: 0–30% and 30–58%. Prior to WVP measurements, all film samples were equilibrated at 25 °C and 30% relative humidity for 72 h. Film samples (6.44 cm^2 discs) were placed between two Teflon rings on the top of the glass cell containing silica gel (~0% RH) for the first RH gradient (0–30%) or a salt solution of NaBr (58% RH) for the second RH gradient (30–58%). The permeation cells were then introduced into a climatic chamber (KBF 240 Binder, ODIL, France) maintained at 30 ± 1% RH and 25 ± 0.5 °C and periodically weighed.

The WVP ($g{\cdot}m^{-1}{\cdot}s^{-1}{\cdot}Pa^{-1}$) calculation was based on the absolute weight change of the permeation cell versus time once the steady state was reached (Benbettaïeb et al., 2016). Five replicates for each film formulation were performed.

2.3.3. Mechanical properties

A universal traction testing machine (TA.HD plus model, Stable