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Release of coumarin incorporated into chitosan-gelatin irradiated films

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ABSTRACT

Chitosan and fish gelatin were used to formulate active biobased films containing an antioxidant (coumarin). After drying, the films were irradiated at 40 and 60 kGy using an electron beam accelerator. The effect of irradiation on the film properties as well as the coumarin release mechanism were investigated and compared with the control. Electron Spin Resonance (ESR) revealed free radical formation during irradiation in films containing coumarin. Antioxidant addition and/or irradiation treatment at a dose of 60 kGy resulted in a shift of amide A and amide B peaks. Furthermore a shift of amide II band was only observed for the control film at the same dose.

Irradiation allowed improving the thermal stability of the control films. Both irradiation process and addition of coumarin increased the surface wettability (increase of the polar component of the surface tension). From the water barrier analysis, neither irradiation nor coumarin addition influenced the permeability at the lower RH gradient used (0–30% RH). Using the higher RH gradient (30–84%) induced a rise of the WVP of all films (containing or not coumarin) after irradiation treatment. At 60 kGy, the tensile strength of only the control films increased significantly. Considering coumarin release from the film in aqueous medium, the apparent diffusion coefficient of coumarin is two times reduced after irradiation. Irradiation also allowed to better protect the incorporated antioxidant. Indeed, the amount of coumarin in the non-irradiated film was significantly lowered compared to the initial quantity, which is probably due to chemical reactivity.

1. Introduction

Maintaining food quality, improving safety, reducing storage losses and limiting wastes are key objectives of a sustainable food system. Nowadays, the modern food industry is facing new challenges, one of which being related to food packaging to extend shelf life. Currently, a great number of research works are focused on the use of bio-based films with good water and oxygen barrier properties to protect food (Fabra, Hambleton, Talens, Debeaufort, & Chiralt, 2011). Since the consumer demand has shifted to safe materials, especially from renewable agriculture by-products and food processing industry wastes (Tharanathan, 2003), natural polymers (proteins, polysaccharides) are processed as packaging materials, which can also be edible films (Gontard, Duchez, Cuq, & Guilbert, 1994). They are considered as active packaging when they contain bioactive compounds, such as antimicrobials, preservatives or antioxidants, which allows to improve food quality and safety (Han, 2002). Chitosan is a natural polymer from fish industry waste obtained by the deacetylation of chitin. It is a nontoxic material, biocompatible, and biodegradable that manifests antibacterial properties. In acidic environment the amino groups are protonated and their positive charges can interact with polyanions such as alginate, carrageenan, gelatin, etc. forming polyelectrolyte complexes (PEC) (Bellini, Oliva-Neto, & Moraes, 2015). Due to these characteristics, chitosan has been widely used for the production of edible films as well as bio-compatible polymeric materials (Aider, 2010; Rivero, García, & Pinotti, 2010). Gelatin is another widely used bio-based material 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.

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Its excellent film forming ability is well-known (Hoque, Benjakul, & Prodpran, 2011). Gelatin-based films also exhibit good barrier properties against oxygen, light and and prevent dehydration and lipid oxidation (Jongjareonrak, Benjakul, Visessanguan, Prodpran, & Tanaka, 2006). Most research on gelatin film has focused on gelatin derived from mammalian sources such as bovine and porcine. Recently, there has been more interest in using fish as an alternative source of gelatin, due to religious considerations or fear of bovine spongiform encephalopathy (Pérez-Mateos, Montero, & Gómez-Guillén, 2009).

Chitosan and gelatin have been shown to be compatible due to the ability to associate through electrostatic and hydrogen bonding. Specifically, it occurs when chitosan is positively charged and gelatin is negatively charged under appropriate conditions of pH. This is particularly important to improve the final network properties as compared to those obtained from the pure polymers (Benbettaieb, Karbowiak, Bornaz, & Debeaufort, 2015a). The incorporation of antioxidants in such biodegradable and edible polymers is an interesting alternative to improve food preservation, since oxidation is one of the major problems affecting food quality as well as film biopolymer stability during ageing (Martins, Martins, Cerqueira, & Vicente, 2012). The use of natural, non-toxic antioxidants such as ferulic acid or α-tocopherol to extend the food shelf life has been investigated (Fabra et al., 2011; Oussalah, Caillet, Salmiéri, Saucier, & Lacroix, 2004). However, little information exists about the influence of these compounds on films structure and physicochemical properties.

Recently, Tammineni, Rasco, Powers, Nindo, and Ünlü (2014) reported that mechanical and barrier properties of bovine gelatin films were improved after tannic acid incorporation. Furthermore, crosslinking bovine gelatin films with tannic acid resulted in the reduction of film solubility by about 80% (Zhang, Xu, & Wang, 2010). Kavoosi, Rahmatollahi, Mahdi Dadfar, and Purfard (2014) studied antioxidant and antibacterial activity of gelatin films containing *Zataria multiflora* essential oil (2–8% w/w of gelatin). They reported that beside their excellent antibacterial properties against both Gram-positive and Gram-negative bacteria, bioactive films have new functional properties. Peng and Li (2014) demonstrated that the water vapour permeability of chitosan films decreases while tensile strength inversely increases when essentials oils are incorporated. We were interested in the present work in incorporating such natural compounds into chitosan-gelatin blend edible films. Moreover, physical methods including dehydrothermal treatment, ultraviolet, heat and gamma irradiation (Bigi, Bracci, Cojazzi, Panzavolta, & Roveri, 1998) help modify the polymeric network through the cross-linking of the polymer chains and also help improve the functional properties of polysaccharide (Sabato et al., 2000) or protein (Vachon, Yu, Yefsah, St-Gelais, & Lacroix, 2000) based films. The structural modifications induced by irradiation could increase the capacity of cross-linked edible films to control the release of embedded antimicrobial or antioxidant compounds. However, very few studies have been published on the impact of irradiation on the release of bioactive compounds from natural biopolymers. Tin, Lai, Shyan, and Paul (2002) showed that the release-retarding property of alginate and alginate–chitosan beads is significantly enhanced after the beads irradiated by microwave. In the same way, Lacroix et al. (2002) displayed that gamma-irradiation induces cross-links in calcium caseinate edible films and thus allows a better control of enzyme and bioactive compounds release. Previous works displayed that ferulic acid, quercetin or tyrosol addition affected differently the functional properties of gelatin-chitosan films according to the irradiation dose (Benbettaieb, Karbowiak, Brachais, & Debeaufort, 2015b). Irradiation accentuated the wettability and the hydrophilicity of the film containing antioxidants whereas oxygen barrier and thermal stability were enhanced.

The aim of this study is to further investigate the effect of coumarin addition and electron beam irradiation on the mechanical, thermal, barrier and structural properties of chitosan-fish gelatin edible films. The effect of irradiation on the coumarin release in liquid medium was also studied.

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 200 FG, commercial grade, having a 180 Bloom degree, a 4 mPa s viscosity (at 45 °C and at a concentration of 6.67% in water and at pH = 5.4)) were used as 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 helped to improve their solubility. Silica gel and potassium chloride saturated salt solution (KCl, Sigma–Aldrich, France) were used to fix the relative humidity at <2% and 84% for water vapour permeability measurements. Coumarin (minimum purity 99%, Sigma Aldrich, was used as a model of natural antioxidant molecule (molecular weight = 146 g mol^{-1}, molar volume = 117 cm^3 mol^{-1}, melting point = 70 °C, LogP = 1.39, solubility in water = 1.9 g L^{-1} (at 25 °C)), *data from Chemspider.com*).

2.2. Film formation

Chitosan powder (20 g) was dispersed in 1 L of a 1% (v/v) aqueous acetic acid to obtain a 2% (w/v) film forming solution. The solution was homogenized at 1200 rpm with a high shear homogeniser (Ultra Turrax (RW16 basic- IKA-WERKE) at 25 °C. As a clear film-forming solution was obtained, no more treatment was applied to the chitosan solution for improving the solubilisation. 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 solubilized in 1 L of distilled water under continuous stirring and heating at 70 °C for 30 min to obtain a 6% w/v solution (pH ≈ 6.5). 6.6 g of glycerol (10% w/dry matter) were added to this film forming solution after the complete solubilisation of gelatin.

Subsequently, equal weights of the respective solution were mixed at 1:1 ratio and stirred for 30 min pH was adjusted to 5.6 with acetic acid. This condition was specifically designed to obtain a polyelectrolyte complex between chitosan and gelatin since the iso-electric point (IP) of gelatin is 4.5–5.5, while the pKa of chitosan amino group is 6.2–6.5. At this pH, gelatin is negatively charged while chitosan is positively charged thus favouring ionic bindings and avoiding any phase separation upon mixing. Coumarin was added to the final film forming solution at a concentration of about 50 mg/g polymer (corresponding to a 47 mg/g total dry weight of film). The aqueous dispersions were homogenized at 1200 rpm using the Ultra Turrax homogenizer until complete dissolution.

A volume of 30 mL of the film forming solution (FFS) in the presence and absence of coumarin was then poured into plastic Petri dishes (13.5 cm diameter). A minimum of 30 film samples (ie 30 Petri dishes) were prepared for each formulation. The aqueous solvent was removed by drying in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) at 25 °C and 45% RH for 18–24 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 each