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Effect of cross-linking in surface properties and antioxidant activity of gelatin films incorporated with a curcumin derivative

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ABSTRACT

Gelatin was chemically cross-linked with lactose in order to analyze the effect of this reaction in the antioxidant capacity of gelatin films. Since phenolic compounds are formed during cross-linking, the antioxidant activity of gelatin films was assessed. Although these cross-linking films showed certain antioxidant capacity, the incorporation of tetrahydrocurcumin (THC) into the films forming solutions greatly increased the antioxidant capacity of gelatin films. Total phenolic content, expressed as mg gallic acid equivalent (GAE), increased from 14 to 43 mg GAE/L. Furthermore, free radical scavenging capacity showed a three-fold increase, as shown by inhibition values. The changes observed were related to the differences found in the film surface, such as lower gloss and higher roughness.

1. Introduction

Gelatin is a protein, obtained by hydrolysis of collagen, present in bones, skins and connective tissues of land and marine animals. Among gelatins, fish gelatin is attracting much attention as an alternative of mammalian (porcine and bovine) gelatins, due to socio-cultural reasons (Arfat, Ahmed, Hiremath, Auras, & Joseph, 2017; Benjakul, Kittiphattanabawon, & Regenstein, 2012). The abundance, availability and low cost of gelatin promote its use in a wide variety of applications (Hu, Meng, Ren, Yan, & Peng, 2016; Li et al., 2016; Ogino et al., 2016; Su & Wang, 2016). Furthermore, gelatins are materials with excellent biocompatibility, biodegradability, and film forming ability (De Clercq et al., 2016; Karim & Bhat, 2008; Stroganov et al., 2014). However, as gelatins are water-soluble, gelatin modification is required for specific applications in packaging, pharmaceutical and biomedical fields (Aggarwal, Deb, & Prasad, 2015; Amalraj, Pius, Gopi, & Gopi, 2016; Bergo, Moraes, & Sobral, 2013). Physical and chemical methods have been reported for tailoring the structure and properties of gelatin by means of cross-linking, which is gaining attention in pharmaceutical and food packaging fields with the aim to prepare films with controlled release of bioactives (Benbettaïeb, Chambin, Karbowiak, & Debeaufort, 2016; Farris, Song, & Huang, 2010; Revathi & Raju, 2012). With this regard, sugars have been used to crosslink proteins by means of a non-enzymatic glycation, known as Maillard reaction, which produces ultra-violet absorbing intermediates, compounds with strong antioxidant activity (Hong, Gottardi, Ndagijimana, & Betti, 2014; Karnjanapratum, O'Callaghan, Benjakul, & O'Brien, 2016; Kim & Lee, 2009; Samira, Thuan-Chew, & Azhar, 2014; Yu, Zhao, Hu, Zeng, & Bai, 2012). Additionally, gelatin films can be used as vehicles for the release of antioxidant compounds (Etxabide, Uranga, Guerrero, & de la Caba, 2016; Haddar et al., 2012; Kowalcyzk & Biendl, 2016; Tongnuanchan, Benjakul, & Prodpran, 2013). Currently, naturally occurring bioactive compounds are preferred by both consumers

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and companies due to concerns over the potential risks of synthetic compounds. In this context, plants are a valuable source of antioxidants, such as polyphenols, used for pharmaceutical, medical and food applications (Bandyopadhyay, Ghosh, & Ghosh, 2012; Freile-Pelegrín & Robledo, 2014; Gómez-Guillén et al., 2009; Ozdal, Capanoglu, & Altay, 2013; Rao & Ravishankar, 2002). Among plant-derived antioxidant compounds, tetrahydrocurcumin (THC), a hydrogenated metabolite of curcumin (*Curcuma longa* L.), is attracting more and more interest within food, pharmaceutical and cosmetic industries due to a greater antioxidant capacity than curcumin, vitamin E and α-tocopherol (Mehanny, Hathout, Geneidi, & Mansour, 2016; Priyadarsini, 2014; Venkatesen, Unnikrishnan, Kumar, & Rao, 2003). Furthermore, in contrast to curcumin, THC is colorless and tasteless (Portes, Gardrat, & Castellan, 2007). Besides the antioxidant capacity of THC (Somporn, Phisalaphong, Nakornchai, Unchern, & Morales, 2007), this compound has showed antidiabetic (Murugan & Pari, 2006), anticancer (Plyduang, Lomlim, Yuenyongsawad, & Wiwattanapatapee, 2014), and antiinflamatory activities (Murakami et al., 2008). Therefore, the incorporation of THC into film forming solutions could lead to the development of active films for food packaging applications, contributing to food shelf-life extension, but also providing health benefits for consumers.

In previous works, the characterization of lactose-incorporated gelatin films was carried out (Etxabide, Uranga, Guerrero, & de la Caba, 2015) and the cross-linking reaction between lactose and gelatin was assessed (Etxabide, Urdanpilleta, Guerrero, & de la Caba, 2015). Since the formation of phenolic compounds was found and these compounds are believed to show antioxidant activity, the aim of this work was to analyze the antioxidant capacity of those cross-linked gelatin films. Additionally, the incorporation of a bio-based antioxidant, such as THC, to improve the antioxidant capacity of gelatin films was analyzed, as well as the surface properties of the THC-incorporated films.

2. Materials and methods

2.1. Materials and reagents

Commercial fish gelatin (type A, 200 bloom) was purchased from Weishardt International (Liptovsky Mikulas, Slovakia). Glycerol and lactose were purchased from Panreac Química S.A. (Barcelona, Spain) and were used as plasticizer and crosslinker, respectively. Tetrahydrocurcumin (THC) was gifted by Sabinsa Corporation (East Windsor, New Jersey, USA) and was used as antioxidant. 2,2-diphenyl-1-picryl hydrazyl (DPPH), Folin Ciocalteu reagent and gallic acid were purchased from Sigma-Aldrich (Saint-Louis, USA). Sodium carbonate (Na_2CO_3) was gained from Merck (Fontenary Sous Bois, France) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) was supplied by Sigma-Aldrich (Saint-Louis, USA). Methanol (MeOH) was analytical grade and the water was distilled.

2.2. Film preparation

Gelatin films were prepared by the solution casting method. Firstly, 5 g of gelatin and 20 wt% lactose (on gelatin dry basis) were dissolved in 100 mL of distilled water for 30 min at 80 °C under continuous stirring to obtain a good blend. After that, a mixture of 10 wt% glycerol and 5 wt% THC (on gelatin dry basis) was added to the solution and the pH was adjusted to 10 with NaOH (1.0 N). Then, the solution was placed in an ultrasonic device (Elmasonic S 30 (H), Singen, Germany) at room temperature for 5 min. Finally, the film forming solution was maintained at 80 °C for 30 min under stirring, poured into polypropylene Petri dishes (90 mm diameter), and kept at room temperature during 48 h to evaporate water and form the film. Films were peeled from the Petri dishes and their thickness was measured to the nearest 1 μm using a QuantuMike Mitutoyo hand-held digimatic micrometer (Neurtek, Spain). Afterwards, films were heated at 105 °C for 24 h to obtain G films (gelatin films without lactose), G-THC films (gelatin films with THC but without lactose), GL films (gelatin films with lactose), and GL-THC films (gelatin films with lactose and THC). All films were conditioned in a controlled bio-chamber (Climacell, MMM Medcenter, Planegg, München, Germany) at 25 °C and 50% relative humidity for 48 h before testing.

2.3. Characterization of films

2.3.1. Color measurements

Color was determined with the CR-400 Minolta Croma Meter colorimeter (Konika Minolta, Valencia, Spain). Films specimens were placed on the surface of a white standard plate (calibration plate values $L^* = 97.39$, $a^* = 0.03$ and $b^* = 1.77$) and color parameters L^*, a^*, b^* were measured using the CIELAB color scale: $L^* = 0$ (black) to $L^* = 100$ (white), $-a^*$ (greenness) to $+a^*$ (redness), and $-b^*$ (blueness) to $+b^*$ (yellowness). Color difference (ΔE^*) for GL-THC films was calculated referred to the G-THC films as follows:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

2.3.2. Gloss measurements

Gloss was measured at 60° incidence angle according to ASTM D-523 (ASTM, 1999) using a flat surface Multi Gloss 268 plus gloss meter (Konika Minolta, Valencia, Spain). Measurements were taken ten times for each sample at 25 °C.

2.3.3. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

FTIR analysis of films was carried out on a Nicolet Nexus FTIR spectrometer using ATR Golden Gate (Thermo Scientific, Madrid, Spain). A total of 32 scans were performed at 4 cm^{-1} resolution. Measurements were recorded between 2000 and 800 cm^{-1}.

2.3.4. X-ray photoelectron spectroscopy (XPS)

A K-Alpha spectrometer (ThermoFisher Scientific) was used for the chemical surface analysis. The monochromatized AlKα source ($h\nu = 1486.6$ eV) was activated with a spot size of 200 μm in diameter. The full spectra (0–1350 eV) were obtained with a constant pass energy of 200 eV, whilst high resolution spectra were obtained with a constant pass energy of 40 eV. Depth profiles (about 3–10 nm) were obtained through Ar^+ sputtering. Quantification and fitting of C 1s, N 1s and O 1s spectra were performed using the AVANTAGE software provided by ThermoFisher Scientific.

2.3.5. Optical microscopy

Optical microscopy was used to analyze the film surface and the optical micrographs with a magnification of 40× were captured with a digital microscope (Leica).

2.4. Antioxidant activity

2.4.1. Thermal stability of THC

Thermo-gravimetric analysis (TGA) was performed in a TGA-Q 500 (TA Instruments, USA). Sample (10 mg) was placed in a platinum pan and test was running at 105 °C for 24 h under nitrogen atmosphere (60 mL/min) to avoid thermo-oxidation.

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