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Preparation and properties of dialdehyde carboxymethyl cellulose crosslinked gelatin edible films

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ABSTRACT

Glycerol-plasticized gelatin edible films with a new kind of dialdehyde polysaccharide, dialdehyde carboxymethyl cellulose (DCMC) as crosslinking agent are successful prepared using casting techniques. The mechanical properties, thermal stability, light barrier properties, swelling behavior as well as water vapor permeability (WVP) of the gelatin–DCMC films are investigated. The results indicate that the addition of DCMC causes tensile strength (TS) and thermal stability to increase and elongation at break (EB) to decrease, suggesting the occurrence of crosslinking between gelatin and DCMC. The light barrier measurements present high values of transparency at 280 nm and low values of transparency at 600 nm of the gelatin–DCMC films, indicating that gelatin–DCMC films are very transparent (lower in transparency value) while they have excellent barrier properties against UV light. Moreover, the values of transparency at 280 nm increase with the increased DCMC and glycerol content, suggesting the potential preventive effect of gelatin–DCMC films on the retardation of product oxidation induced by UV light. Furthermore, the addition of DCMC can greatly decrease the water vapor permeability (WVP) and equilibrium swelling ratio (ESR) down to values about 1.5×10^{-10} g m/m^2 s Pa and 150%, revealing the potential of DCMC in reducing the water sensitivity of gelatin-based films. In common for hygroscopic plasticizer in edible films, the addition of glycerol gives increase of EB and WVP and decrease of thermal stabilities and ESR of the gelatin–DCMC films.

1. Introduction

Biodegradable packaging materials have recently received increasing attention, since plastic packaging materials have led to serious environmental concerns, as a result of their nondegradable and nonrenewable nature. In addition, the increasingly high oil price is another driving force for the development of substitutes for synthetic plastic (Sothornvit, Hong, An, & Rhim, 2010). Biopolymers, such as polysaccharides (Fajardo et al., 2010; Hambleton, Voilley, & Debeaufort, 2011; Sayanjali, Ghanbarzadeh, & Ghiassifar, 2011; Shih, Daigle, & Champagne, 2011), proteins (Cho, Lee, & Rhee, 2010; Leerahawong, Arii, Tanaka, & Osako, 2011; Ozdemir & Floros, 2008; Saremnezhad, Azizi, Barzegar, Abbasi, & Ahmadi, 2011), lipids (Debeaufort, Quezada-Gallo, Delporte, & Voilley, 2000; Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002) and their blends (Abugoch, Tapia, Villamán, Yazdani-Pedram, & Díaz-Dosque, 2011; Jia, Fang, & Yao, 2009) are considered the most promising candidates for this purpose and have potential for use as biodegradable packaging materials because of their biodegradability, abundance and sustainability.

Gelatin is an animal protein obtained by a controlled hydrolysis of the fibrous insoluble collagen present in the bones and skin generated as waste during animal slaughtering and processing (Patil, Mark, Apostolov, Vassileva, & Fakirov, 2000). With the appropriate film forming properties and good barriers against oxygen and aromas at low and intermediate relative humidity, gelatin is suitable for use as raw materials of biodegradable packaging materials (Carvalho et al., 2008; Jongjareonrak, Benjakul, Visessanguan, Prodpran, & Tanaka, 2006; Limpisophon, Tanaka, Weng, Abe, & Osako, 2009; Sobral, Menegalli, Hubinger, & Roques, 2001). However, gelatin has poor barrier against water vapor due to the hydrophilic nature, which is the main drawbacks of gelatin films for the application as a packaging material (Kester & Fennema, 1989). The poor mechanical properties and thermal stability of gelatin itself also limit its application as packaging materials (Bigi, Cojazzi, Panzavolta, Roveri, & Rubini, 2002; Martucci, Vázquez, &

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Ruseckaite, 2007). Therefore, many researchers are working at the realm of reinforcement of gelatin.

To date, many attempts have been made to modify the poor properties of protein films including crosslinking, blending, compounding with natural fibers or with nanosized clay dispersed in the biopolymer matrix in order to produce bio-nanocomposites (Martucci & Ruseckaite, 2010). Genipin (Bigi et al., 2002), glyoxal (de Carvalho & Grosso, 2004), formaldehyde (de Carvalho & Grosso, 2004), polyphenols (Gómez-Guillén, Ihl, Bifani, Silva, & Montero, 2007), transglutaminase (Chambi & Crosso, 2006) and surfactants (Andreuccetti, Carvalho, Galicia-García, Martínez-Bustos, & Grosso, 2011) are the effective crosslinked means of different methods. In addition, milk proteins (Barreto, Pires, & Soldi, 2003), konjac glucomannan (Li, Kennedy, Jiang, & Xie, 2006), soy protein (Guerrero, Stefani, Ruseckaite, & de la Caba, 2011), chitosan (Pereda, Ponce, Marcovich, Ruseckaite, & Martucci, 2011), cinnamon, clove and star anise extracts (Hoque, Benjakul, & Prodpran, 2011a) are successfully blended with gelatin to prepare composite films. Montmorillonite (Kumar, Sandeep, Alavi, Truong, & Gorga, 2010a, 2010b; Mascheroni, Chalier, Gontard, & Gastaldi, 2010; Sothornvit et al., 2010; Tunç & Duman, 2010) is introduced into protein edible films to improve the mechanical properties and thermal stability too. Dialdehyde polysaccharides have received a great deal of attention as an ideal crosslinking agent of protein. The oxidation of polysaccharides by periodate is characterized by the specific cleavage of the C2–C3 bond of glucose residues. This cleavage results in the formation of the two aldehyde groups per glucose unit, forming 2, 3-dialdehyde polysaccharides (Li, Wu, Mu, & Lin, 2011). The aldehyde groups in dialdehyde polysaccharides can crosslink with ε-amino groups of lysine or hydroxylysine side groups of gelatin by C$=$N linkages (Schiff's base) to improve the properties of gelatin, as show in Fig. 1 (Dawlee, Sugandhi, Balakrishnan, Labarre, & Jayakrishnan, 2005). Dawlee et al. (2005) had reported a new class of gelatin hydrogel using aldehyde chondroitin sulfate as a crosslinking agent. This new class of hydrogel without employing any extraneous crosslinking agents was expected to have potential as wound dressing materials. Dialdehyde starch (DAS) has been used as a crosslinker to prepare a 3D spongy collagen cryogel. The results indicate that the cryogels have improved thermal stability in comparison with pure collagen. Moreover, the water uptake of the cryogel decreases with DAS content (Mu et al., 2010). DAS has been introduced into gelatin films as environmentally friendly crosslinking agent too (Martucci & Ruseckaite, 2009). However, some degree of phase separation in gelatin-DAS films has been observed, which causes the lower transparent at visible light. And the polymeric nature of DAS does not introduce severe restrictions within gelatin matrix as usually occurs with short chain dialdehyde such as formaldehyde or glutaraldehyde, resulting in the poor TS of gelatin-DAS films (Martucci & Ruseckaite, 2009). Furthermore, DAS does not easily dissolve in water, which limits its application as a crosslinking agent in water environment. On this basis, a new kind of dialdehyde polysaccharide, dialdehyde carboxymethyl cellulose (DCMC), has been successfully prepared in our previous work, which shows some properties as short chain dialdehyde and good solubility in water (Li et al., 2011).

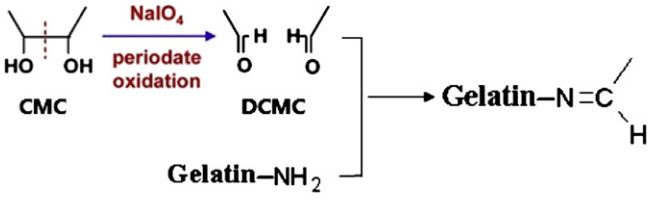

Fig. 1. Periodate oxidization of CMC and the Schiff's reaction between gelatin and DCMC.

In the present work, glycerol-plasticized gelatin edible films with DCMC as a crosslinking agent are successful prepared using casting techniques. The article is focused on the evaluation of the thermal stability, mechanical properties, light barrier properties and moisture resistance of the DCMC crosslinked gelatin films.

2. Materials and methods

2.1. Materials

Bovine hide gelatin type B was purchased from Aladdin Reagent Database Inc. (Shanghai, China). Carboxymethyl cellulose sodium (CMC), sodium periodate and glycerol were purchased from Kelong Chemical Reagent Company (Chengdu, China). The viscosity of the 2% (w/v) CMC in water was reported by the company to be ≥1200 mPa s and confirmed in our laboratory. The degree of substitution (DS) was ∼0.90 according to Fourier transform infrared (FTIR) analysis (Li et al., 2011). Periodate and glycerol were of analytical grade.

2.2. Preparation of dialdehyde carboxymethyl cellulose

Dialdehyde carboxymethyl cellulose (DCMC) was prepared using a method similar to the conventional procedure (Li et al., 2011). About 1.0 g CMC was dissolved in 20 mL distilled water in the flask which was immersed in a DF-101S temperature controlled water bath with a magnetic stirrer (Shanxi Taikang Biotech., China). Then, 10 mL periodate solution (0.11 g/mL) was added to the CMC solution under stirring. The pH was adjusted to 3.0 with 1 M sulfuric acid solution. After the mixture was stirred in the dark at 35 °C for 4 h, the oxidized product, referred to DCMC was precipitated by pouring the solution into a large amount of ethanol. It was then recovered and cross-washed with distilled water and ethanol until all iodic compounds were removed. The product was dried at 37 °C to constant weight for the subsequent use.

2.3. Preparation of gelatin–DCMC edible films

Gelatin solution (10%, w/v) was prepared by dissolving gelatin powder in distilled water for 30 min and then heated at 60 °C for 30 min under continuous stirring. Glycerol was added as plasticizer at a certain concentration (based on dry gelatin weight). DCMC powder was dissolved in distilled water under stirring for 12 h at room temperature to produce a 1% (w/v) solution. Then certain volume gelatin and DCMC solution was mixed and stirred at 60 °C for 1 h. The resulting mixture was poured on teflonated Petri dishes (9 cm diameters) and conditioned at 40 °C for 24 h to obtain gelatin–DCMC edible films. The contents of gelatin, glycerol and DCMC in each gelatin–DCMC edible film are shown in Table 1. The obtained films were named G*x*D*y* where *x* and *y* correspond to the ratio of glycerol and DCMC to gelatin, respectively. Films were stored in a desiccator at 25 °C and 50 ± 3% relative humidity before measurements.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the samples were obtained from discs containing ∼2.0 mg sample in approximately ∼20 mg potassium bromide (KBr). The measurements were carried on a Perkin–Elmer Spectrum One FTIR spectrophotometer at the resolution of 4 cm^{-1} in the wave number region 400–4000 cm^{-1}.