



Structural properties of films and rheology of film-forming solutions of chitosan gallate for food packaging



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ABSTRACT

The chitosan gallates (CG) were obtained by free-radical-initiated grafting of gallic acid (GA) onto chitosan (CS) in this work. The chemical structures of the CG were corroborated by UV–vis, GPC and ¹H NMR analysis. The grafting reaction was accompanied with a degradation of the CS molecule. The shear-thinning flow behavior of CG film-forming solutions (CG FFS) decreased with the grafting amount of GA into CS chain, while the CG FFS grafted at a lower GA value behaved like a networks containing entangled or cross-linked polymer chains with a more elastic behavior. The increasing of GA grafting onto the CS chain led to a reduction of tensile strength, elongation at break and water resistance in the corresponding films, but increases in the antioxidant and antimicrobial activities were observed. The microstructure of the film was investigated using scanning electron and atomic force microscope, and the results were closely related to the observed film properties.

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1. Introduction

Active packaging, which represents a new generation of food packaging, has gained great interests from researchers and industry over the past few years due to enhancements of food quality and safety by innovative packaging systems with special functions, in addition to acting as moisture and gas barriers (Yu, Tsai, Lin, Lin, & Mi, 2015). Chitosan (CS), a cationic polysaccharide (poly-β-1-4-amino-2-deoxy-D-glucan) derived from chitin by chemical deacetylation, is the second most abundant polysaccharide found in nature after cellulose. It is a promising material for potential applications in a variety of fields, including in the food, cosmetic, biomedical, agricultural and chemical industries (Rubenthaler, Ward, Chee, & Tang, 2015; Schreiber, Bozell, Hayes, & Zivanovic, 2013). Due to their nontoxic, biodegradable, biocompatible, antioxidative and antimicrobial properties, CS films and coatings have been successfully developed and widely used in the packaging of foods, such as fruits, vegetables, and meats (Hu, Sun, & Wu, 2013; Qiu et al., 2014). However, for protein-rich and unsaturated fatty acid-rich foods, the limited antioxidative and antimicrobial activ-

ities of pure CS films do not satisfy the needs of the consumers (Wan, Xu, Sun, & Li, 2013). To overcome these disadvantages, a great number of antimicrobial or antioxidative agents have been directly incorporated in CS-based packaging materials, which may enhance their functional activities and expand the scope of their applications (Regiel-Futryra et al., 2015). However, these incorporated materials usually lead to low stability, low efficiency and rapid leakage of the embedded active substance. More recently, chemical modification by conjugating antimicrobial or antioxidative agents to CS has attracted increasing attention due to improvements in those properties.

Gallic (GA) is a well-known natural phenolic acid with strong antioxidant and antimicrobial activities (Hager, Vallons, & Arendt, 2012). Grafting of GA to CS has already been accomplished via enzymatic grafting reactions (tyrosinase, laccase or peroxidase) (Božič, Gorgieva, & Kokol, 2012; Božič, Štrancar, & Kokol, 2013) and carbodiimide (EDC)-mediated and activated ester reactions (Pasanphan & Chirachanchai, 2008; Schreiber et al., 2013; Xie, Hu, Wang, & Zeng, 2014). However, these methods are either time consuming or contain toxic compounds that are not suitable for edible packaging. Compared with other conventional modifications, H₂O₂/Vc grafting reactions (Cho, Kim, Ahn, & Je, 2011; Curcio et al., 2009; Lee & Je, 2013; Liu, Lu, Kan, & Jin, 2013) are novel eco-friendly grafting procedures because toxic reaction products are

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not generated, and it is possible to perform these reactions at room temperature to avoid degradation of antioxidants. Moreover, the preparation procedure is very simple and has a higher efficiency than the other two methods. Although grafting of GA to CS showed better antioxidant and antimicrobial properties, the rheological and packaging properties of chitosan gallates (CG) have never discussed before, which is very important for making good edible films.

To make a good film or a level coating on a solid surface, the viscosities of film-forming solutions (FFS) must be suitable to prevent sagging by gravity effects and to allow capillary leveling (Bai, Sun, Xu, Dong, & Liu, 2015). A high viscosity or a gel type structure of FFS would make it difficult to eliminate air bubbles, thus hindering the casting of thin layers. It is noted that rheological properties, which are sensitive to variations in the molecular structure, are useful in developing structure-function relationships for systems of polysaccharide solutions (Maloy, Martin, Atanassov, & Cooney, 2012; Xiao, Tong, & Lim, 2012). Therefore, understanding the rheological properties of FFS is important for the casting process of pre-formed films, or for applying coatings in the liquid phase directly onto the surfaces of food products by dipping, brushing or spraying. Moreover, the desired mechanical properties of coating or packaging films depend on the viscoelastic properties of FFS (Silva-Weiss, Bifani, Ihl, Sobral, & Gómez-Guillén, 2013, 2014). Several studies have been carried out on the rheological behavior (including the viscoelasticity) of CS-based FFS, which were directly incorporated with plant polyphenol-rich extracts, natural essential oils and nanoparticles or blended with other polysaccharide solutions (Fakhreddin Hosseini, Rezaei, Zandi, & Ghavi, 2013; Han, Yan, Chen, & Li, 2011; Silva-Weiss et al., 2014). However, to the best of our knowledge, few studies have investigated the rheological properties of water-soluble active compounds incorporated into CS FFS (Cho, Grant, Piquette-Miller, & Allen, 2006; Pang, Chen, Park, Cha, & Kennedy, 2007). Furthermore, the influence of the grafting degree on rheological properties and the packaging material characteristics of CG have not been studied. Therefore, the aim of the current study was to evaluate the effect of the GA grafting degree on the flow and viscoelastic properties of CG FFS. The mechanical, water vapor barrier (WVP) and functional properties (antioxidant and antioxidant activities) and the microstructures, as well as the relationship among these properties of the resulting films, were also tested. These results are very important for developing CG films as food packaging materials.

2. Materials and methods

2.1. Materials

Chitosan from shrimp (M_w/M_n and degree of deacetylation of approximately 98.72/54.40 kDa and 92%, respectively) was purchased from Qingdao Yunzhou Biochemistry Co., Ltd. (Qingdao, China). Gallic acid (GA) and Folin-Ciocalteu reagent were purchased from Sigma Chemical Co. (St. Louis, MO, USA). All other reagents were of analytical grade and commercially available.

2.2. Preparation of CG derivative

The preparation of CG was performed according to the method of Curcio et al. (2009) with slight modifications. Briefly, CS (1 g) was dissolved in 100 mL of 1% acetic acid (v/v) in a 200 mL three-necked round bottom flask. Then, 3 mL of 1.0 M H_2O_2 containing 0.27 g of Vc was added into the reactor, and a slow stream of oxygen-free nitrogen gas was passed for 30 min with stirring. Afterwards, GA was added to the mixture at different amounts with the following molar ratios of the repeating unit of CS to GA: 1:0.1, 1:0.5 and 1:1 (labeled as CG-1, CG-2 and CG-3, respectively). The reaction was carried out under a continuous flow of oxygen-free nitrogen

gas. After 24 h, the reaction was stopped by letting air into the reactor and then dialyzed with distilled water with an 8–14 kDa molecular weight cutoff membrane for 72 h to remove unreacted GA. A CS blank sample, which acted as a control, was prepared under the same conditions but in the absence of GA (labeled as CS-0). Structural characterization of the blank CS and CG were performed by UV-vis, GPC and 1H NMR analysis. The UV-vis spectra were determined using a UV-2600 spectrophotometer (Shimadzu, Kyoto, Japan) by scanning from 200 to 600 nm. The molecular weights of the CS derivatives were analyzed by GPC with a multi-angle laser light scattering detector (MALLS, Dawn DSP, Wyatt Technology Corp., CA). All chitosan samples were dissolved in MQ water (5 mg/mL), filtered through a 0.22 μ m syringe filter (Millipore Corp., MA) and injected onto a TSK 3000 PWXL column. The samples were then eluted using 0.2 M ammonium acetate (pH 4.5) at a flow rate of 0.5 mL/min. 1H NMR spectra were recorded at 25 °C with samples dissolved in CD_3COOD/D_2O (v/v, 1%) using a 600 MHz NMR Spectrometer (Bruker, Switzerland). The degree of substitution (expressed as DS which is defined as the GA content in CG derivatives) was measured by the Folin-Ciocalteu method according to Liu et al. (2013). GA was used to calculate the standard curve, and the DS was expressed as milligrams of GAE per gram of the dry weight copolymer (mg GAE/g).

2.3. Preparation of film-forming solutions (FFS) and casting of the films

CS-0 and CG FFS (2% w/v) were prepared by dissolving 2 g of copolymer in 100 mL of acetic acid (1% v/v) with magnetic stirring for 24 h 20 ± 1 mL portions from each FFS were cast onto glass culture dishes with diameters of 16 cm for the film-forming area, and dried at ambient condition. The obtained films (chitosan gallate concentration, 2.0 mg/cm²) were conditioned in an environmental chamber at 25 °C and 50% relative humidity (RH) for 48 h before testing.

2.4. Rheological measurement of FFS

The rheological properties of FFS were performed on a Haake Rheostress 6000 rheometer (Thermo Scientific Instruments, Inc. Germany) fitted with a cone-plate geometry (diameter = 25 mm, cone angle = 2) with a gap of 0.104 mm. Dynamic oscillatory measurements were carried out in the linear viscoelasticity range (LVR). Storage modulus (G') and the loss modulus (G'') were recorded in the 0.1–100 rad/s angular frequency sweep at a strain amplitude of 0.2% (in the LVR). The apparent viscosity as a function of the shear rate was determined in the range from 0.1 to 300 s⁻¹. Samples were individually loaded on the measuring geometry and allowed to stand for 2 min prior to testing. All measurements were performed at 25 ± 0.1 °C and performed in triplicate.

2.5. Film analysis

Film thickness was measured using a digital micrometer (Mitutoyo, Tokyo, Japan). Five measurements were taken at different positions on each sample. All films were cut in strips with 90 mm length and 10 mm wide for the determination of mechanical properties. The tensile strength (TS, MPa) and elongation to break (EB, %) of the films were determined by a PARAM XLW (M) Auto Tensile Tester (Jinan Labthink Technology Company, China) according to ASTM standard methods (2002). The WVP of the films was determined gravimetrically at 25 ± 1 °C according to ASTM E96 standards (2003).

The antioxidant activities of the film samples were evaluated using (2,2-diphenyl-1-picrylhydrazyl) (DPPH) and 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS⁺) radical scavenging

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