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Molecular interactions in gelatin/chitosan composite films

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ABSTRACT

Gelatin and chitosan were mixed at different mass ratios in solution forms, and the rheological properties of these film-forming solutions, upon cooling, were studied. The results indicate that the significant interactions between gelatin and chitosan promote the formation of multiple complexes, reflected by an increase in the storage modulus of gelatin solution. Furthermore, these molecular interactions hinder the formation of gelatin networks, consequently decreasing the storage modulus of polymer gels. Both hydrogen bonds and electrostatic interactions are formed between gelatin and chitosan, as evidenced by the shift of the amide-II bands of polymers. X-ray patterns of composite films indicate that the contents of triple helices decrease with increasing chitosan content. Only one glass transition temperature (T_g) was observed in composite films with different composition ratios, and it decreases gradually with an increase in chitosan proportion, indicating that gelatin and chitosan have good miscibility and form a wide range of blends.

1. Introduction

Gelatin, a product of partial hydrolysis of collagen, is a traditional water-soluble biopolymer with distinctive advantages of biodegradability, non-toxicity, biocompatibility and low cost. The applications of gelatin in food, pharmaceutical and photographic industries are generally attributed to its good film-forming ability. However, these applications may be hindered due to its high hygroscopicity and relatively poor mechanical properties (Gómez-Guillén et al., 2009). Thus, modification of gelatin films has attracted great attention. For example, chemical modification (Zhang et al., 2010) and enzymatic treatments (Spanneberg et al., 2010) have been applied to improve the physical properties of gelatin films. However, the toxicity and high cost of some chemical and enzymatic agents may limit their application in films (Cao, Fu, & He, 2007). The blending of gelatin with other biopolymers is one effective strategy to improve the physical performance of gelatin films (Rivero, García, & Pinotti, 2009).

Chitosan is another biopolymer obtained from deacetylation of chitin. It is a natural cationic polysaccharide, and is frequently used as a biomedical material due to its antimicrobial activity, biocompatibility, biodegradability and nontoxicity (Dutta, Tripathi, Mehrotra, & Dutta, 2009). In addition, it is a potential packaging material with the advantages of excellent film-forming abilities and good mechanical properties (Martins, Cerqueira, & Vicente, 2012).

It is known that polymer blending can result in an improvement of the physical properties of pure components (Chen, Mo, He, & Wang, 2008). Moreover, the properties of the polymer blends may be enhanced by the formation of new bonds (Denavi et al., 2009). Thus, mixing of gelatin with chitosan seems to be a promising way to obtain biocomposites with novel properties (Huang, Onyeri, Siewe, Moshfeghian, & Madihally, 2005; Mao, Zhao, Yin, & Yao, 2003; Sionkowska, Wisniewski, Skopinska, Kennedy, & Wess, 2004). The composite films prepared from gelatin and chitosan have been found to possess improved mechanical and physical properties compared with those of pure gelatin films (Hosseini, Rezaei, Zandi, & Ghavi, 2013; Jridi et al., 2014; Nagahama et al., 2009). In addition, the influences of chitosan molecular weight and degree of deacetylation (Liu et al., 2012), and gelatin origin (Gómez-Estaca, Gómez-Guillén, Fernández-Martín, & Montero, 2011) on the physico-chemical properties of gelatin-chitosan composite films have been investigated.

An important issue in the study of the formation of composite film is the miscibility in polymer blends, which can be assigned to specific interactions between different components. The molecular interactions in gelatin and chitosan blends have been probed by viscometry and wide angle X-ray scattering (Sionkowska et al., 2004), and Fourier transform infrared spectroscopy (Staroszczyk, Sztuka, Wolska, Wojtasz-Pajak, & Kołodziejska, 2014). It has been shown that both electrostatic interactions and

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hydrogen bonds occur between gelatin and chitosan (Taravel and Domard, 1995). Furthermore, these strong interactions lead to the formation of multiple complexes of the two biopolymer molecules (Voron'ko, Derkach, Kuchina, & Sokolan, 2016; Yin, Li, Sun, & Yao, 2005).

Generally, the molecular interactions between gelatin and chitosan affect their miscibility, as a result they affect the structure of composite films and accordingly determine the physical properties of composite films. Thus the knowledge of the molecular interactions in gelatin and chitosan blends is crucial for understanding the relationship between the structure and the properties of the composite films. Although many studies of gelatin and chitosan complex films have been performed, the information on the molecular interactions in gelatin and chitosan blends is still limited. In this work the molecular interactions between gelatin and chitosan in both solution and film were investigated in detail by Rheology, FTIR, XRD and DSC techniques, as well as their effect on the structure and physical properties of the composite films. The information of the molecular interactions in biopolymer blends at the molecular level will be a benefit for the application of these composite films.

2. Materials and methods

2.1. Materials

Gelatin (type B, limed-hide hydrolysis) used was purchased from Sinopharm Chemical Reagent Co., Ltd. The average molecular weight is about 100,000, and its isoelectric point (pI) was approximately at pH = 5.0. Chitosan (90% DD, degree of deacetylation) was also purchased from Sinopharm Chemical Reagent Co., Ltd. The average molecular weight of chitosan is about 260,000. All aqueous solutions were prepared using ultrapure water (18 MΩ·cm) from a Milli-Q system (Millipore). All chemicals were of analytical grade.

2.2. Preparation of the film-forming solutions and films

The gelatin solutions with concentration of 5.0 wt% were prepared by dissolving 5 g gelatin powder in 100 ml deionized water for 30 min and then heated at 50 °C for 30 min under continuous stirring. Chitosan solution (2.0 wt%) was prepared by dissolving 2 g chitosan powder in 100 ml 1% (v/v) acetic acid, stirred overnight at room temperature. All the polymer solutions were filtered through 0.45 μm pore-size PTFE membrane filters to remove impurities.

The gelatin/chitosan film-forming solutions were prepared by mixing a 5.0 wt% gelatin solution with a 2.0 wt% chitosan solution, in an appropriate proportion, to obtain a film-forming solution with different mass ratios of gelatin (G) to chitosan (Ch), respectively (solutions 80G:20Ch, 50G:50Ch, 20G:80Ch). In this work the chitosan concentration is fixed at 1.0 wt%, and the gelatin concentration is 4.0, 1.0 and 0.25 wt% for 80G:20Ch, 50G:50Ch and 20G:80Ch bends, respectively. The pH values of gelatin and chitosan solutions were 5.2 and 3.1, respectively. The pH values of mixtures were in the range of 3.5–4.1 (below pI of gelatin). It should be noted that no plasticizer was added in the film-forming solutions. All mixtures were warmed and stirred at 50 °C for 20 min to obtain a homogenous solution. Then 20 ml of film-forming solutions were coated on a PTFE mold and dried at room temperature for 24 h. Then they are dried at 60 °C for 48 h in a vacuum oven, yielding five groups of the dry films with different ratios of gelatin to chitosan (100G:0Ch, 80G:20Ch, 50G:50Ch, 20G:80Ch, 0G:100Ch). The films were peeled off and kept in an evacuated desiccator over fresh silica gel for further analysis.

2.3. Rheological properties of the film-forming solutions

The dynamic viscoelastic analysis of the film-forming solutions was carried out by a rotational rheometer (DHR, TA Instruments, USA) with a Peltier temperature control. The parallel plate geometry (d = 40 mm) was used with a gap of 1 mm. Samples were placed onto the rheometer plates at 40 °C and held at this temperature for 10 min to eliminate thermal history effects. The solutions were cooled from 40 to 10 °C at a scan rate of 1 °C/min with a frequency of 10.0 rad/s and controlled strain 1% (within the linear viscoelastic range). The elastic modulus and viscous modulus were determined as functions of temperature.

2.4. Characterization of the films

2.4.1. Fourier-transform-infrared (FTIR) spectroscopy

FTIR spectra of gelatin, chitosan, and composite samples were recorded on a Nicolet iS10 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA), equipped with an attenuated total reflection (ATR) accessory. FTIR spectra were recorded from wave number 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and 128 scans. All samples were conditioned before their analysis for a week in a desiccator containing silica gel.

2.4.2. X-ray diffraction (XRD)

XRD patterns of gelatin, chitosan and composite films were measured by a BDX3300 X-ray diffractometer equipped with a multichannel detector by use of a Cu Kα1 (λ = 0.15406 nm) monochromatic X-ray beam. All the samples were measured within 2θ range of 5–50° with a scan rate of 1°/min.

2.4.3. Thermo-gravimetric analysis (TGA)

TGA was performed on a TGA-1 (Mettler Toledo Instrument) from room temperature to 600 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

2.4.4. Differential scanning calorimetry (DSC)

DSC measurements were carried out by a Q2000 DSC (TA instrument, USA). Due to the potential effect of moisture content in determining the T_g of biopolymers, DSC data of each film were collected during the second heating run from 30 to 230 °C at a rate of 10 °C/min, after the first run of heating up to 190 °C and cooling to 30 °C at the same rate of 10 °C/min. Dry nitrogen was used as the purge gas at a flow rate of 50 ml/min. Thermal data were determined at least by triplicate on each film sample.

3. Results and discussion

3.1. Rheological properties

The changes of storage modulus (G') and loss modulus (G'') with temperature for the film-forming solutions have been plotted in Fig. 1. It was shown that the crossover temperature of G' and G'' of the film-forming solutions decreased with an increase in the proportion of chitosan component. This is indicative of a notable loss of the gelatin's capacity to refold into triple-helix chains with chitosan addition. When the ratio of gelatin to chitosan is decreased to 50:50, G'' is always larger than G' over the whole temperature range. The absence of the crossover in G' and G'' indicates that the physical gelation of gelatin does not occur at the experimental temperatures, which is validated by the photo shown in Fig. 1. This result suggests that the presence of chitosan hinders the formation of a gelatin network as a result of gelatin-chitosan interactions (Gómez-Estaca et al., 2011). Our results were also consistent with the early observation by Arvanitoyannis that an incor-