Effect of microfibrillated cellulose (MFC) on the properties of gelatin based composite films

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ABSTRACT

Properties of gelatin composite films（with 4% glycerol as plasticizer）with different mass concentrations of microfibrillated cellulose (MFC) (0.2-1.0%) were investigated. The prepared composite films with 1.0 % MFC showed the highest tensile strength (12.32 MPa) with the lowest water absorption rate (391.1 %). The composite films can be dissolved in hot water of 95℃ in less than 5 minutes. However, the addition of MFC had insignificant effect on the heat shrinkage and light transmittance of the resultant composite films.

Keywords: Gelatin films; Microfibrillated cellulose; Physicochemical properties

1. INTRODUCTION

Gelatin is a biodegradable polymer, which can be obtained by thermal denaturation or physical and chemical degradation of collagen.[1] Gelatin has excellent film-forming, biocompatible and biodegradable properties,[2, 3] which make it have a potential application in food packing. However, Gelatin dissolves easily in the 40°C solution, and its mechanical properties are also poor. Therefore, it is a research direction to seek a modification method to improve their dissolving and mechanical properties at present.

The interest in gelatin has recently increased exponentially because of its biodegradable properties. Gelatin contains a large amount of hydroxyl, amino and carboxyl, which makes its modification method more diversified, such as physical,[4, 5] chemical[6, 7] and combining modification etc.[8, 9] For example, the gelatin composite films were modified with starch at different temperature, the results indicated that the crystallinity of the gelatin composite films could be increaseed.[10] The effect of stearic acid and reaction time on the properties of gelatin films were also investigated, and the results showed that the tensile strength and water absorption of the gelatin films decreased with the increase of stearic acid content.[11] The gelatin was modified by crossing-link with transglutaminase, and a bigger molecular weight could be obtained.[12] The modification of gelatin and gelatin-chitosan composite films with enzyme was also investigated, and the results showed that the viscosity modulus of gelatin-chitosan increased rapidly, and the effect on gelatin was not obvious.[13]

Over the past decades, the study of cellulose composites was the most active one in the science and technology field. Cellulose is the main component of plant's cell wall,[14-18] which is the most abundant natural organic matter all over the world and inexhaustible resources.[19,20] It is a micromolecular polysaccharide, which is composed of D-glucose with β-1, 4-glycosidic bond. The chemical formula is $(C_6H_{10}O_5)_n$ and the molecular-weight is about 5.0×10^4-2.5×10^6. Due to the existence of a large number of hydroxyl groups, which makes intermolecular and intramolecular of cellulose produce some strong hydrogen bond, and thus has an active effect on physical and chemical properties. In this paper, microfibrillated cellulose (MFC) was used to modify the dissolving and mechanical properties of gelation composite films, and the effect of MFC on the tensile strength (TS), Elongation at break, thermal and water adsorption properties was studied in detail.

2. EXPERIMENTAL

2.1. Material

The gelatin was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). MFC was procured from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The glycerol was obtained from Tianjin Damao Reagent Factory (Tianjin, China). The gelatin was food grade and other agents were analytical grade, which were used without further purification.

2.2. Preparation of gelatin/MFC composite films

The gelatin/MFC composite films were prepared by solution casting method as described.[21] For the preparation of composite films, 5 g gelatin was added into pure water (50 mL) with stirring until it dissolved completely. Then, 4% glycerol and 0.2-1.0% MFC were added and continued to mix at 60°C for 60 min in digital temperature control agitator (XH-50E, Xianghu Science and development Co. Ltd, Beijing, China). The film-forming solution was cast onto a rimmed silicone plate and dried at room temperature about 72 h. The films were kept in a constant temperature and humidity chamber (HE-WS-408D8, Haoen Testing Instrument Co., Ltd, Dongguan, China) at 25°C and 50% RH for 48 h before further tests.

2.3. Characterization of gelatin/MFC composite films

2.3.1. *Morphological observation*

The microstructure of gelatin/MFC composite films was characterized by scanning electron microscopy (SEM) (JCM-6000 BENCHTOP SEM, JEOL, Japan) with an accelerating voltage of 15.0 kV.

2.3.2. *Mechanical properties*

The tensile strength and elongation at break were determined by intelligent electronic tensile testing instrument (XLW, Blue Light Electrical and Mechanical Technology Co., Ltd, Jinan, China) according to ASTM D882-02 (ASTM, 1995a), and the thickness was measured by thickness indicator (MX-3, DAKOTA ULTRASONICS, Scott, USA). The composite film samples were cut into 2.30 ×10.0 cm, and kept at 50% relative humidity (RH) for 48 h before analysis. Then, the tensile strength (TS) and elongation at break (E) were calculated with the Eq. (1) and Eq. (2), respectively. Where σ and ε were tensile strength (TS) and elongation at break (EAB), respectively. *F*, *b*, and *d* were tensile force and width and thickness of composite film, respectively. l_0 and l_1 were tensi*le elongation and original length, respectively.*

$$\sigma = \frac{F}{b \times d} \times 100\% \quad (1)$$

$$\varepsilon = \frac{l_1}{l_0} \times 100\% \quad (2)$$

2.3.3. *Thermogravimetric and heat shrinkage analysis*

The thermal analysis of the composite films was characterized by Thermogravimetric analyzer (IRPrestige21, shimadzu corporation, Kyoto, Japan). The composite film samples were about 8-10 mg, and kept at 50% relative humidity (RH) for several days before analysis. The samples were tested with a rate of heating of 10 °C/min, between 25 °C and 800 °C in an inert atmosphere (100 ml/min N_2).

The heat shrinkage of composite films was characterized by heat shrinkage instrument (RSY-R2, Blue Light Electrical and Mechanical Technology Co., Ltd, Jinan, China). Film samples of 10 × 50 mm dimension were heat treated at 120 °C for twenty seconds.

2.3.4. *Optical properties*

The optical properties of the composite films were determined using ultraviolet spectrophotometer (752N, INESA, shanghai, China). The films were cut into 10 × 50 mm size and tested between 400 nm and 800 nm.

2.3.5. *Water absorption properties*

Dyr composite films were cut into 20 ×20 mm pieces, and soaked in distilled water until the maximum absorption was reached (the films' weight changed within 1%). The Water absorption was calculated with the Eq. (3). Where Q was Water absorption. m_0 and m_1 were the weighs of dry and wet film, respectively.

$$Q = \frac{m_1 - m_0}{m_0} \times 100\% \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Morphology

The surface morphology and cross section of pure gelatin film and gelatin/MFC composite film using scanning electron microscopy are shown Fig.1. In the gelatin/MFC composite film, the surface was much smoother than the pure gelatin film was rough, and the cross section of gelatin/MFC composite film was denser, which might due to cross-linked reaction between gelatin and MFC.

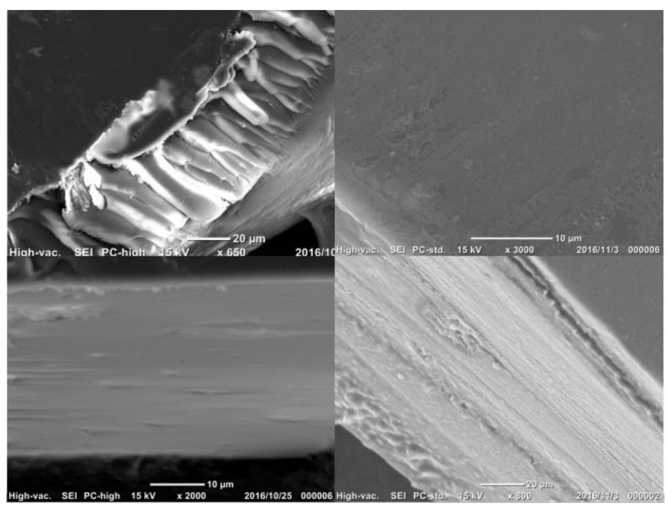

Fig. 1. SEM images of neat gelatin films and gelatin/MFC composite films (top: surface; bottom: cross section; left: neat gelatin films; right: gelatin/MFC composite films)

3.2. Mechanical properties

Fig.2 shows the mechanical properties of gelatin/MFC composite films. The tensile strength changed as the MFC mass concentration varied. Among them, the gelatin/MFC composite film of 1.0% MFC had the highest tensile strength (12.32 MPa). However, the gelatin/MFC composite films showed a decreasing elongation at break, which can be attributed to the decrease of film-forming solution matrix mobility as the MFC content increased.[22] In general, the composite films had more improved mechanical properties than neat gelatin films.

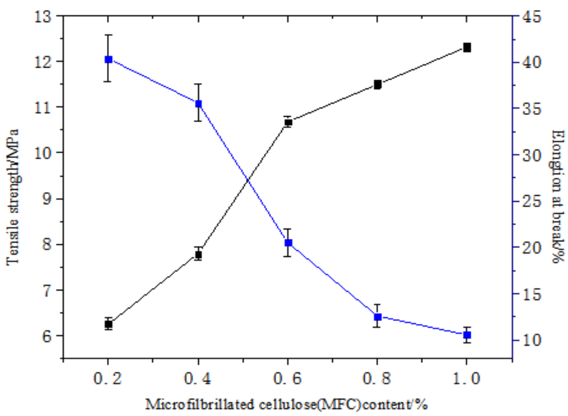

Fig. 2. Tensile strength (TS) and elongation at break (EAB) curves of gelatin/MFC composite films with various MFC mass concentrations: 0.2%,0.4%, 0.6%, 0.8%, 1.0%.

3.3. Thermogravimetric and heat shrinkage analysis

Generally, the thermogravimetric curve of the biopolymer-based film has three stages: the loss of physically absorbed water, structured water and decomposition of biomolecules.[23] From Fig. 3a we can observe that the first stage of weight loss was about 150 °C, which mainly contained free water and volatile substance. However, gelatin/MFC composite film was more stable than pure gelatin film at about 270 °C (weight loss of less than 10%). Moreover, the Maximum weight loss of pure gelatin film and gelatin/MFC was about 500 °C and 600 °C, respectively. From heat shrinkage curves of gelatin/MFC composite films (Fig. 3b), the heat shrinkage of composite film decreased by adding MFC of various mass concentration, which was about 0.67%. All in all, MFC promoted the stability of gelatin film.

3.4. Optical properties

The light transmittance of pure gelatin films and gelatin/MFC composite films was illustrated in Fig.4. At the center of the visible light 600 nm, which showed some differences between pure gelatin (86.5%) and five gelatin/MFC composite films with the date of 82.9%, 83.4%, 82.2%, 83.1% and 78.2%, respectively. The decrease in light transmittance was mainly due to the phenomenon of reflection or scattering at the interface between gelatin and MFC,[24] which might be confirmed by scanning electron microscopy (SEM). However, the gelatin/MFC composite film still kept a much higher transmittance in general, which also reflected the good compatibility between gelatin and MFC.

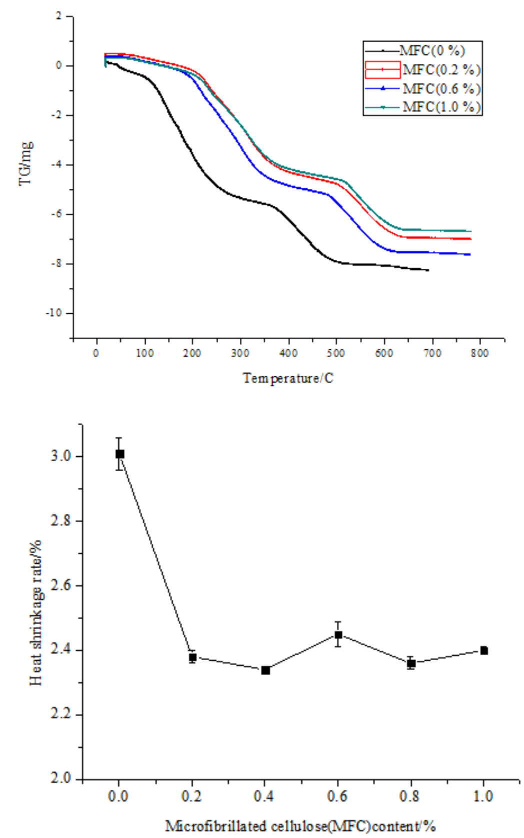

Fig. 3. TG and heat shrinkage curves of pure gelatin film and gelatin/MFC composite films with various MFC mass concentrations: 0.0 %, 0.2 %,0.4 %, 0.6 %, 0.8 %, 1.0 %.

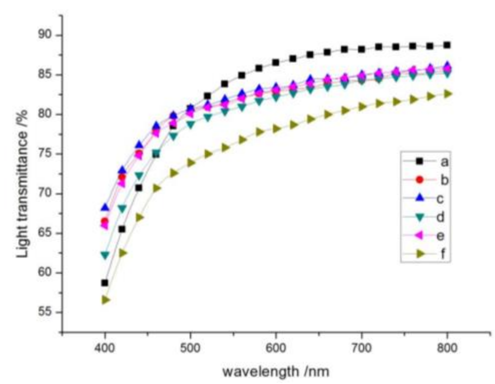

Fig. 4. Light transmittance curves of neat gelatin films and gelatin/MFC composite films with various MFC mass concentrations: 0.0% (a), 0.2% (b), 0.4% (c), 0.6% (d), 0.8% (e), 1.0% (f).

3.5. Water absorption properties

From Fig. 5 we can observe that the water absorption of the films emerged vast change in the first 2 hours. The curve didn't mark the water adsorption of the pure gelatin film for much damage in a few minutes. Moreover, the water adsorption of the composite film is lower than pure gelatin film, and the result showed that the water adsorption was decreasing with the raise of MFC (391.1% contain 1.0% MFC). Generally, the cross-linking of gelatin molecules would promote a reduction in the swelling of composite. The result illustrated MFC benefited the formation of more cross-linkage and net structure between gelatin and MFC.[25]

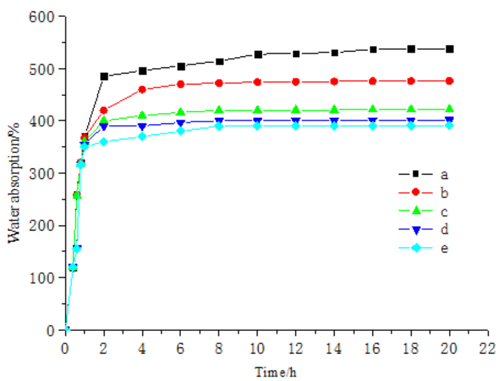

Fig.5. Water absorption curves of gelatin/MFC composite films with various MFC mass concentrations: 0.0% (a), 0.2% (b), 0.4% (c), 0.6% (d), 0.8% (e), 1.0% (f).

4. CONCLUSIONS

Gelatin/MFC composite films with improved mechanical properties were fabricated by solution casting method with various MFC mass concentrations. With the addition of MFC, the tensile strength increased and the elongation at break decreased. MFC addition decreased the water adsorption and the light transmittance of the gelatin films.

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