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Effect and mechanism of cellulose nanofibrils on the active functions of biopolymer-based nanocomposite films

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ABSTRACT

Cellulose nanofibrils (CNFs) are superfine cellulose fibrils with a nanoscale diameter and have gained increasing attention due to their great potential in the food industry. However, the applications of CNFs in active food packaging are still limited. The objectives of this study were to develop biopolymer-based edible nanocomposite films using CNFs, corn starch, and chitosan, and to investigate the effect and mechanisms of CNFs on the active functions and properties of the nanocomposite films. Important functional properties of the films were measured and the films were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Zetasizer. The results demonstrate that CNFs increased the rigidity of the films due to more hydrogen bonds being induced by CNFs (≥ 60%). Incorporating a high content of CNFs (≥ 60%) in the film resulted in enhanced filling effect on the structure of the biopolymer films, which significantly improved the light barrier, oxygen barrier and water vapor barrier capacities. As CNF content increased to 100%, the film opacity increased by 59%, while the peroxide value of corn oil protected with edible films was reduced by 23%. Furthermore, the antimicrobial properties of the edible films with 80% and 100% CNFs were increased by up to 2 log CFU/g on day 8 in a beef model, due to more positive charges in the films and improved blocking effects on oxygen. These results demonstrate that CNFs can effectively enhance the antimicrobial effect and barrier properties of biopolymer-based nanocomposite films and have great potential in applications of active packaging for food products.

1. Introduction

Nanocellulose is a biomaterial composed of nanosized cellulose fibrils with a high length-to-width ratio. Nanocellulose is lightweight, biodegradable, and renewable and it has high strength and high stiffness. In particular, cellulose nanofibrils (CNFs) have gained growing attention recently in the food industry because of their great potential to improve the functional properties of food packaging materials (Nechyporchuk, Belgacem, & Bras, 2016). CNFs have been incorporated in various types of food packaging to improve the water resistance, mechanical performance, and oxygen barrier effect of the materials (Chaabouni & Boufi, 2017; Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009; Ghaderi, Mousavi, Yousefi, & Labbafi, 2014).

CNFs can be used to develop an edible film that is a thin layer of edible material wrapped or coated on the outside of food products (Galus & Kadzińska, 2015; Skurtys et al., 2010). Biopolymer-based edible films have many advantages over traditional food packaging such as plastics that have low degradability and are even toxic to humans (Tavassoli-Kafrani, Shekarchizadeh, & Masoudpour-Behabadi, 2016). Edible films are mainly made of edible components such as polysaccharides and proteins, thus they decompose easily in the environment and are quite safe (Jiménez, Fabra, Talens, & Chiralt, 2012). In addition, biopolymers such as CNFs can be obtained from agricultural byproducts or wastes that are abundant and cost-effective (Galus & Kadzińska, 2016; Mohajer, Rezaei, & Hosseini, 2017).

In recent years, the concept of active packaging has received much attention in the food industry because it can extend the shelf life of food products and improve food quality (Lin & Zhao, 2007; Mei et al., 2013; Mellinas et al., 2016; Tomé et al., 2012). Active packaging possesses active functions such as antimicrobial properties beyond the inert passive protection of the food product. However, the applications of nanocellulose in the development of active packaging are still limited.

The objective of this study was to use corn starch, chitosan, and CNFs to develop edible biopolymer-based nanocomposite films. The physical properties, barrier capacities and antimicrobial effect of the

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films were determined using texture analyzer, ultraviolet-visible spectroscopy, water vapor permeability measurement, oxygen barrier test in a corn oil model, and antimicrobial assay in fresh beef products. To investigate the possible mechanisms for the enhanced properties, the films were further characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). In addition, the zeta potential of the film-making solutions was evaluated using a Zetasizer.

2. Materials and methods

2.1. Materials

Corn starch (~73% amylopectin and 27% amylose), chitosan with medium molecular weight (190–310 kDa; 75–85% deacetylated), glycerol, glacial acetic acid, and anhydrous calcium chloride were purchased from Sigma-Aldrich (St. Louis, MO, USA). CNF slurries prepared from bleached wood pulp (~2.8% dry weight; width, 20–50 nm; length, up to several hundred microns) were obtained from the University of Maine. Pure corn oil was obtained from ACH Food Companies, Inc. (Memphis, USA). Fresh top sirloin beef was purchased from the Meat Market of the University of Missouri, Columbia, MO, USA. All other chemicals were purchased from commercial sources.

2.2. Preparation of edible films

Starch dispersion (4%, *w/v*) was incubated with constant stirring at 80 °C for 20 min and then cooled to room temperature. Meanwhile, chitosan solution (1%, *w/v*) was prepared by dissolving chitosan powder in 1% (*v/v*) acetic acid solution. After incubation at 50 °C for 1 h, the chitosan solution was filtered through three layers of cheesecloth and mixed with the starch solution in a ratio of 1:1 (*v/v*). Then, 20% (*w/w*) of glycerol based on the dry weight of starch and chitosan was added. The CNF slurries at different concentrations (20, 40, 60, 80, and 100%, *w/w*) based on dry weight of starch and chitosan were added to the mixture, respectively. The film-making solutions were casted into to square petri dishes (12 cm × 12 cm) and then dried at 37 °C and 20% relative humidity for 36 h. Films without CNFs were used as the control. All the dried films were stored at room temperature and 55% relative humidity for 3 d before further measurements were taken.

2.3. Characterization of the edible films

2.3.1. Color measurement

The color variations of the edible films were measured using a Chroma Meter CR-410 (Konica Minolta Sensing, Inc., Japan) equipped with a pulsed xenon lamp through 0° viewing angle. After the colorimeter was calibrated with the standard white plate (L_0*, 97.8; a_0*, 0.03; and b_0*, 1.91), each film sample was placed on the calibration plate and measured using the color space of L*, a*, and b*. The total color difference ($\triangle E$) was calculated according to a previous method (Zhang, Zhao, & Shi, 2016) by the following equation: $\triangle E = [(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2]^{1/2}$, where L_0*, a_0*, and b_0* are the color parameters of the white plate and L*, a*, and b* are the color parameters of film samples.

2.3.2. Moisture content

Three identical film samples (2.5 cm × 2.5 cm) were placed in a weighing glass bottle. Then, they were dried at 105 °C until a constant weight was determined. The moisture content was calculated according to the following equation: Moisture content (%) = $(m_1 - m_2) / m_1 \times 100$, where m_1 and m_2 are the initial weight (g) and final dry weight (g) of edible films, respectively.

2.4. Solubility

The edible films were incubated at 105 °C for 24 h to gain the initial dry weight. The samples (100 mg) were then placed in a beaker containing distilled water (50 mL) and gently stirred at room temperature for 24 h. After that, the films were kept at 105 °C until a constant weight (final dry weight) was obtained. The water solubility of the films was calculated according to the following equation: Water solubility (%) = $(m_1 - m_2) / m_1 \times 100$, where m_1 and m_2 are the initial dry weight (g) and final dry weight (g) of film samples, respectively.

2.5. Mechanical properties

A TA-XT2i texture analyzer (Texture Technologies Corp., UK) was used to determine the mechanical properties of the edible films. The samples were cut into rectangular pieces (2 cm × 7 cm) and clamped with grips with an initial distance of 50 mm. The upper grip stretched the film with a speed of 1 mm/s before its rupture. Young's modulus was determined as the slope of the linear portion of a stress-strain curve. The force-distance curves for each measurement were collected to calculate tensile strength and elongation at break according to Eq. (1) and Eq. (2).

$$\text{Tensile strength (MPa)} = F_{max}/A \quad (1)$$

$$\text{Elongation at break (\%)} = \triangle H/H_0 \times 100 \quad (2)$$

where F_{max} is the maximum force (N), A is the cross-sectional area (thickness × width) of the film sample (m^2), $\triangle H$ is the increased height of the edible film (mm), and H_0 is the initial distance between grips (mm).

2.6. The transmittance and opacity of the films

A Cary 50 Bio UV–Visible spectrophotometer (Varian, Inc., USA) was used to acquire the transmittance of the edible films in the wavelength range from 200 to 800 nm. An empty quartz cuvette was used as the blank. Each film sample was attached to the wall of the cuvette before measurements. In addition, the absorbance at 600 nm was used to determine O value, a parameter positively related to film opacity (Siripatrawan & Harte, 2010). The O value was calculated with the following equation: $O = A_{600nm}/N$, where A_{600nm} is the absorbance of film at 600 nm, and N is the film thickness (mm) measured by a digital electronic micrometer (Model 35-025; iGaging, USA).

2.7. Water vapor permeability (WVP)

The WVP of the edible film was measured by a gravimetric method (Fitch-Vargas et al., 2016). In brief, glass jars were filled at the bottom with 15 g of anhydrous calcium chloride (0% relative humidity) and sealed with the edible films. Then, the jars covered with film samples were placed in a desiccator that contained saturated sodium chloride solution to generate an environment with 75% relative humidity at 25 °C. The weight change of the jar was determined at 1, 2, 4, 6, 8, 10, 12 h. WVP was calculated with the following equation: WVP ($g\ m^{-1}\ s^{-1}\ Pa^{-1}$) = $(M \times K)/(T \times A \times \triangle p)$, where M is the weight change (g), K is the average thickness of edible film (m), T is the time (s), A is the covered area by edible film (m^2), and $\triangle p$ is the partial pressure difference between two sides of the film (Pa).

2.8. Oxygen barrier capacity

The oxygen barrier ability of the edible films was indirectly determined through a corn oil model (Du et al., 2016). Briefly, glass jars (50 mL) containing 25 mL of fresh corn oil were covered with the edible films and incubated at 70 °C for 7 days. Then, the peroxide value (POV) of the corn oil was measured by sodium thiosulfate titration