



Effects of chitin nano-whiskers on the antibacterial and physicochemical properties of maize starch films

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ABSTRACT

We investigated the effects of chitin nano-whiskers (CNWs) on the antibacterial and physicochemical properties of maize starch-based films. The microstructures, crystalline structures, and thermal, mechanical and barrier properties of the nanocomposite films were characterized by using transmission electron microscopy, X-ray diffraction analysis, thermogravimetric, differential scanning calorimeter, and texture profile analysis. The tensile strength of the maize starch films increased from 1.64 MPa to 3.69 MPa ($P < 0.05$) after CNW reinforcement with up to 1%. The water vapor permeability of the nanocomposite films decreased from 5.32×10^{-12} to $2.22 \times 10^{-12} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ with the CNW content increasing from 0% to 2%. The onset temperature, peak temperature and the gelatinization enthalpy of the films containing CNWs were higher than those of the pure starch films. Furthermore, the nanocomposite films exhibited strong antimicrobial activity against Gram-positive *Listeria monocytogenes* but not against Gram-negative *Escherichia coli*.

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1. Introduction

resources caused by petroleum-based plastics has focused attention to the development of environmentally benign polymer nanocomposites for applications in the food, cosmetics, and pharmaceutical industries. Renewable and abundantly available biopolymers are the most viable alternative for producing green materials in the near future. Nature has provided various natural biopolymers, such as polysaccharides (starch, cellulose, and chitosan) and proteins (soy protein, wheat protein, casein, and gelatin). Utilization of natural biopolymers for making biodegradable packaging films, edible film, and coating materials has increased considerably in the literature (Rhim, Park, & Ha, 2013). Among such natural biopolymers, starch is one of the most commonly used raw materials to prepare biodegradable films or edible packaging films, because it is an inexpensive renewable source that is widely available and relatively easy to handle. Unfortunately, poor performances such as lower water vapor barrier, relatively lower mechanical properties, and processing difficulty are the main limitations of these biopolymer-based films. Thus, to overcome above problems, a number of studies have been performed by rein-

forcing nanofiller materials (Martins et al., 2013; Rhim et al., 2013). Inorganic (metallic nanoparticles and nano-clays) and organic synthetic material (carbon nanotubes, nanographite) nanofillers have been used as reinforcing materials (Chandrasekaran, Seidel, & Schulte, 2013; Du, Ye, Fu, Lv, & Zheng, 2014).

Polysaccharides such as starch, cellulose, and chitin are potential renewable sources of nano-size reinforcement because of their completely biodegradable nature. Promising fillers are biopolymer nanocrystals, in which the nano-size fillers can impart enhanced mechanical and barrier properties, such as tensile strength, flexibility, and the modulus of elasticity. Following this strategy, nanocomposite materials have been prepared from plasticized starch reinforced with starch nanoparticles (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Dai, Qiu, Xiong, & Sun, 2015; Shi, Wang, Li, & Adhikari, 2013), cellulose nanocrystals (Chang, Jian, Yu, & Ma, 2010a; Reddy & Rhim, 2014; Savadekar & Mhaske, 2012), and protein reinforced with chitosan nanoparticles (Hosseini, Rezaei, Zandi, & Farahmandghavi, 2015). Moreover, adding chitosan or chitin nanoparticles as nanofillers not only improves the physicochemical properties but also endows the composite films with antimicrobial functions and thus broadens the application fields of biopolymer composite materials (Hosseini et al., 2015; Salaberria, Diaz, Labidi, & Fernandes, 2015). Chitin nano-whiskers (CNWs), because of their unique chemical and physical properties and pronounced antibacterial activity, provide one of the most cost-effective alternatives for the development of new antibacterial

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agents in applications in food packaging, cosmetics, and pharmaceutical products (Zeng, He, Li, & Wang, 2012). Starch has received considerable attention as a natural thermoplastic film matrix; however, few studies have been reported on the preparation of maize starch-based films reinforced with CNWs.

Chitin nano-whiskers of slender parallelepiped rods have been successfully prepared from chitin, which has been recently explored in nanotechnology applications (Mincea, Negulescu, & Ostafe, 2012; Muzzarelli, 2011). CNWs have many excellent properties, including biodegradability, biocompatibility renewability, and antibacterial properties (Ifuku & Saimoto, 2012). Among food-borne bacteria, *Escherichia coli* and *Listeria monocytogenes* are observed in a wide range of food products. In addition, these bacteria are human pathogens that cause the most economically important food-borne diseases throughout the world (Elizaquível & Aznar, 2008). These bacteria are present in foods and can multiply quickly at room temperature. Consequently, the presence of these bacteria should be controlled in the food industry. Shankar, Reddy, Rhim, and Kim (2015) reported that carrageenan/CNW nanocomposite films showed strong antibacterial activity against a Gram-positive food-borne pathogen, *L. monocytogenes*, after CNWs were added. To the best of our knowledge, reports on the reinforcement of maize starch-based biopolymer films with CNWs are not available in the literature. The objective of this study was to develop antibacterial composite films based on maize starch/CNWs and to determine the microstructures, crystalline structures, and thermal, mechanical, and barrier properties by using transmission electron micrograph (TEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). In addition, the in vitro antibacterial activities of nanocomposite films were evaluated against *L. monocytogenes* and Gram-negative *E. coli* bacteria. The results of this research on antibacterial, renewable, and biodegradable CNWS starch nanocomposite films can contribute to their application in the food industry or medical fields.

2. Materials and methods

2.1. Materials

Normal maize starch (with an amylose content of approximately 26.33%) was obtained from Zhucheng Xingmao Corn Development Co., Ltd., (Shandong, China). Chitin was supplied by Zhejiang Aoxing Biotechnology Co., Ltd., (Zhejiang, China) with a degree of *N*-acetylation of 0.96, as determined with elemental analysis. Glycerol was supplied by Tianjin Jiangtian Chemical Co., Ltd., (Tianjin, China). All other chemicals used in the present study were of analytical grade.

2.2. Preparation of CNWs

The CNWs were prepared from the original raw material of chitin from crab shells based on Nair and Dufresne's (2003) method with minor modifications. Chitin (30 g) were dissolved in 900 mL H_2SO_4 solution (3 mol L^{-1}) and then incubated at 95°C for 12 h under vigorous stirring. After acid hydrolysis, the suspension was diluted with deionized water and followed by centrifugation (5000g for 15 min). This process was repeated three times with deionized water until neutral. Subsequently, the nano-whiskers were dried by lyophilization for 48 h to obtain the dried CNWs.

2.3. Preparation of the films

Maize starch and maize starch/CNW composite films were prepared using a solution casting method (Sun, Xi, Li, & Xiong, 2014), with some modifications. Briefly, 7.0 g of maize starch and 3.0 g of plasticizer (glycerol) were added to 100 mL of deionized water

to form starch–plasticizer slurries. Each dispersion was thoroughly stirred for 30 min in a thermostatic water bath at boiling temperature and then cooled to 50°C . Aliquots of CNWs (0, 0.5, 1.0, 2.0, and 5.0 wt%, based on maize starch) were added to 50 mL of deionized water and then treated with an ultrasonic wave (KQ-400KDE, Kunshan Ultrasonic instrument Co., Ltd., Jiangsu, China) at 100 W for 10 min to ensure uniform suspension. After the CNWs were introduced, the suspensions were stirred for an additional 30 min at 300 rpm. Then, the film-forming dispersions were degassed under a vacuum (0.1 MPa) for 15 min, and the samples (about 65 g) were spread evenly over Petri dishes (15 cm diameter) and dried for more than 8 h at 45°C . All dried starch films were preserved in a relative humidity (RH = 53%, 25°C) chamber for further testing.

2.4. Characterization and properties testing of the films

2.4.1. Transmission electron micrograph

Transmission electron micrographs (TEM) were obtained with a Transmission electron microscope (TEM, HT-7700, Hitachi Instruments Ltd., Tokyo, Japan) at an accelerating voltage of 80 kV. A droplet of film-forming dispersion was placed on a carbon-coated copper grid and then freeze dried.

2.4.2. X-ray diffraction of the films

The crystalline structure of the films was analyzed using an X-ray diffractometer (Bruker D8 ADVANCE, Karlsruhe, Germany). The instrument employed nickel-filtered Cu K α radiation ($\lambda = 0.15406 \text{ nm}$) at 36 kV and 20 mA. The diffractograms were recorded over an angular range (2θ) of $3\text{--}40^\circ$, with a step size of 0.02° and a step rate of 2 s per step. The crystallinity of the samples was determined by plotting the peaks' baseline on the diffractogram and calculating the area using the software spectrum viewer (Version 2.6) according to Jivan, Madadlou, and Yarmand's (2013) method. The relative crystallinity degree was determined by the ratio of the crystalline area to the total curve area:

$$\text{Relative crystallinity (\%)} = \frac{\text{Area under the peaks}}{\text{Total curve area}} \times 100 \quad (1)$$

2.4.3. Mechanical properties

A TA.XTplus texture analyzer (Lloyd Instruments, London, England) was used to determine the film's tensile strength (TS) and elongation at break (E%). The film specimens were tested as suggested by Mehyar, Al-Ismael, Han, and Chee (2012), with minor modifications, and the tests were carried out according to the ASTM D828-97 standard test methods (ASTM, 1997). The composite films were cut into strips ($1 \times 10 \text{ cm}$), and then preconditioned at 75% (RH) for 48 h inside a sealed desiccator containing saturated sodium chloride solution at room temperature ($25 \pm 1^\circ\text{C}$). The films were loaded into the testing system, which was set at an initial sample length and a grip speed of 2 cm and 100 mm min^{-1} , respectively.

2.4.4. Thickness measurement

The thickness of the films was determined using a digital micrometer (Vernier, Ningbo, China, 0.001 mm accuracy) taking measurements at different positions on the film.

2.4.5. Water vapor permeability of the films

Before testing, the films were conditioned at 25°C for 48 h in a desiccator with a relative humidity (RH) of 67%. The gravimetric method was used to determine the water vapor permeability (WVP) of the maize starch/CNW composite films, and the tests were

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