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Preparation and physical properties of tara gum film reinforced with cellulose nanocrystals

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ABSTRACT

Cellulose nanocrystals (CNC) prepared from microcrystalline cellulose were blended in tara gum solution to prepare nanocomposite films. The morphology, crystallinity, and thermal properties of the CNC and films were evaluated by using transmission electron microscopy, X-ray diffractometry, and thermogravimetric analysis, respectively. The resultant CNC was rod-shaped with diameters of around 8.6 nm. The effect of CNC content on physical and thermal properties of films was studied. The composite film tensile strength increased from 27.86 to 65.73 MPa, elastic modulus increased from 160.98 MPa to 882.49 MPa and the contact angle increased from 55.8° to 98.7° with increasing CNC content from 0 to 6 wt%. However, CNC addition increased the thermal stability slightly and CNC content above 6 wt% decreased the tensile strength by CNC aggregation in the matrix. The nanocomposite film containing 6 wt% CNC possessed the highest light transmittance, mechanical properties, and lowest oxygen permeability. CNC addition is a suitable method to modify tara gum matrix polymer properties.

1. Introduction

Recently, biopolymer packing has been given increased attention over synthetic polymers because of the non-degradable nature of synthetic polymers, i.e., polyethylene, polypropylene, polyethylene terephthalate and polystyrene, which causes serious 'white pollution' [1] . Furthermore, plastic materials originate from crude oil, which exerts pressure on the environment. Therefore, the development of biopolymer packing could be extremely beneficial.

Of these biopolymer materials, polysaccharides are feasible film-forming materials, and their resultant films have good oxygen- and carbon dioxide-barrier properties [2]. However, the films usually have poor mechanical properties but high affinity to water. Similar limitations exist for other polysaccharides, including alginate, chitosan, and starch. Therefore, natural polymers are usually blended with other reinforcing fillers to create composite films with higher tensile strength and hydrophobic properties.

Nano/microscale cellulose has gained much interest as a reinforcing filler in polymeric matrices because of its good mechanical properties with high bending strength and stiffness (e.g., Young's modulus of ~150 GPa [3]). Nanocellulose is prepared from cellulose (a carbohydrate polymer chain that consists of D-glucopyranose units joined by β-1,4- glycosidic linkages) and consists of highly ordered crystalline domains and disordered amorphous domains. Cellulose nanocrystals (CNC) are obtained once amorphous domains have been removed from cellulose by acid hydrolysis. So, CNCs are highly crystalline nanometer particles, which provide superior mechanical and barrier properties. Nanoscale dimensions have a proportionally larger surface area and more surface atoms than their microscale counterparts [4]. Therefore, interactions between nano-elements and the hydrophilic matrix are much stronger because of a percolated network that is connected via hydrogen bonds in the interphase region [5,6]. The presence of nanocellulose reinforces the polymer matrix properties. In this perspective, several studies have evaluated the incorporation of CNC into polymers. For example, CNC has been incorporated into polyvinylalcohol (PVA) [7], chitosan [8], and soybean protein isolates [9]. 6 wt% addition of CNC improved the tensile strength and Young's modulus of PVA-composited films by ~2.8 and 2.4 times that of neat PVA, respectively. A study on chitosan/CNC-composited films proved that the films with 0.18% ($w/w_{chitosan}$) CNC had superior mechanical properties with ~47% elongation-at-break, ~245 MPa tensile strength, and ~4430 MPa Young's modulus. Soybean protein isolate nanocomposited film with 20 wt% whisker content at 43% relative humidity increased in tensile strength and Young's modulus to 8.4 MPa and 158 MPa, respectively.

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Tara gum (TG) is a natural polysaccharide that is extracted from seeds of Tara trees, one of commercial products. It is a typical galactomannan consisting of a linear main chain of (1-4)-β-D-mannopyranose units linked with branched chains of (1-6)-α-D-galactopyranosea and the mannose/galactose ratio (M/G) is 3. Compared to the guar gum and fenugreek, tara gum has lower galactose substitution so that it can produce a stronger film [10]. In addition, it has a synergistic effect to produce improved gel and colloid stabilities and properties when used in combination with other gums (such as guar and locust bean gums) [11]. It also presents a low relative cost and has been used in food and industrial applications as a thickener and stabilizer [12]. So far, TG has not been extensively used for food packaging. But, it has been tested to prepare environmentally friendly films in recent years [13]. Besides, a good filler–matrix interaction is essential in polymer nanocomposites and no report has been conducted in compatibility between TG and CNC. TG and CNC blend films with active packaging functions could be further studied in the future because of environmental concerns and expectations for high food quality.

Therefore, the main objective of this study was to prepare TG-based nano-composites films reinforced by CNC. Whether the TG-based nano- composited films could be used in food packaging, depends on the mechanical, water barrier, optical and thermal properties. So, the mechanical, optical, and barrier properties of TG/CNC films were also evaluated in this study.

2. Materials and experiments

2.1. Materials

Microcrystalline cellulose (MCC, Comprecel M101; degree of polymerization (DP) = 200) was purchased from Shanghai Shenmei Pharmaceutical Technology Co., Ltd. (Shanghai, China). Tara gum (TG) produced in Peru was obtained from Dymatic Fine Chemical Co., Ltd. (Guangzhou, China). The molecular weight was around 1000 kDa from gel permeation chromatography (GPC) measurement. Sulfuric acid and glycerol were analytical reagent grade from Yongda chemical Reagent Co., Ltd., China.

2.2. Preparation of cellulose nanocrystals

An aqueous suspension of cellulose nanocrystals was prepared following the literature procedures with a slightly modification [14]. MCC was dispersed in 55 wt% sulfuric acid contained in a three-necked glass flask equipped with mechanical stirrer and a thermometer. The flask was placed into a water bath at 42 °C for 96 min. And then the suspension was diluted with 2 L distilled water, and centrifuged at 10,000 rpm for 10 min. The process was repeated three times to remove sulfuric acid. The resulting suspension was dialyzed for seven days until the pH reached 7. At last, the suspension was sonicated at 1000 W for 20 min and stored in a refrigerator for further use. Besides, a specified amount of the CNC suspension was dried in a weighted glass at freeze drying equipment (Scientz-18N, Ningbo Xinzhi Co., China) to calculate the CNC content in the suspension. The final yield of CNC was 69.10% according to the method discussed above.

2.3. Preparation of TG films reinforced with CNC

TG films were prepared by casting mold shown in Fig. 1. Firstly, TG was milled into particles with a size of 80–120 mesh for the experiment. After that, TG was dissolved in deionized water under constant stirring for 3 h at 45 °C to achieve a solution of 0.75 wt%. Then, the CNC suspension was added at 0%, 2%, 4%, 6%, 8% (w/w, TG basis) and glycerol was then added at 30% (w/w, TG basis). The final solution (600 mL) was cast into the plexiglass plate (26 cm × 26 cm × 4 cm) after removing bubbles and dried at 60 °C for 24 h in a vacuum drying oven. The blend films (thickness of about 0.057 mm) denoted as TG-N0, TG-N2, TG-N4, TG-N6, TG-N8 contained 0, 2, 4, 6 and 8 wt% of CNC, respectively. Dried films were conditioned in desiccators (45% RH) according to the ASTM standard D-882 before other tests.

2.4. Characterization of CNC and blended films

The morphology of samples was examined by Quanta 200 scanning electron microscope (Philips-FEI Co., AMS, Netherlands) after coated with gold. The accelerating voltage was 20 kV. The morphology of CNC was observed using a JEM-2100 transmission electron microscope (TEM). The diameter distribution of CNC was measured by dynamic light scattering using a laser light scattering instrument (Masterizer 2000, Malvern Instruments Ltd., Malvern, UK) under the following conditions: particle index 1.330, viscosity 0.8872 cp, material adsorption 0.100, temperature 25 °C and general calculation model for irregular particles. The average was obtained using software (Zetasizer software, Ver. 2.2 from Malvern). FTIR spectra were conducted using a Thermo Nicolette 6700 spectrophotometer (Thermo Fisher Scientific Co., Ltd., MA, USA) with attenuated total reflection (ATR) mode from 500 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. XRD patterns of the films were obtained by using a D/max-2200 diffract meter (Cu-Kα target, 40 kV, 30 mA) operated at 1200 W (Rigaku, Japan) and the crystallinity index (CI) was calculated using the Segal method [15,16] . CI (%) = $(1 - I_{am}/I_{002}) \times 100$, I_{am} represents an amorphous material obtained from the intensity minimum between the peaks at 2 0 0 and 1 1 0 ($2\theta = 18°$), I_{002} represents both a crystalline and an amorphous material obtained from the height of the 2 0 0 peak ($2\theta = 22.6°$). The light transmittance spectra of the TG films were measured ranging from 200 to 800 nm using an ultraviolet–visible (UV–vis) spectrophotometer (UV- 2600, Shimadzu, Kyoto, Japan). A Perme OX2/230 (Labthink, Jinan, China) was utilized to measure oxygen permeability values of the films for three replicate measurements. Water contact angle measurement (CA) was used by 20 μL water droplets on the film surface using contact angle analyzer (OCA20, Dataphysics Company, Germany). Thermogravimetric analysis (TGA) was conducted from room temperature to 600 °C at a rate of 20 °C/min using a TA Instruments (TGA Q500, Newcastle, DE, USA) and the curves of derivative thermogravimetric analysis (DTG) were obtained from the first-order derivative of curves for weight loss vs. temperature.

Tensile tests of the films including tensile strength, elongation at break and elastic modulus were carried out using an auto tensile tester (XLW-PC, PARAM, Jinan, China) equipment with a 500 N load cell. Measurements were performed with a strain rate of 300 mm/min. The samples were cut into 15 mm × 80 mm. Five specimens of each sample were tested.

2.5. Statistical analysis

The data were presented as the mean ± standard deviation of each treatment. Statistics on a completely randomized design using analysis of variance (ANOVA) in the SPSS program (Version 17.0, SPSS Inc., Chicago, IL). Duncan's multiple range tests ($p < 0.05$) were used to compare the differences among films.

3. Results and discussion

3.1. MCC and CNC morphology

SEM images of MCC and CNC after freeze drying are shown in Fig. 2a and b, respectively. MCC has a rod-like structure with ~20 μm diameter. After hydrolysis, the MCC became nanosized as shown in Fig. 2b. The TEM image of CNC is shown in Fig. 2c. CNC