



Soy protein isolate nanocomposites reinforced with nanocellulose isolated from licorice residue: Water sensitivity and mechanical strength

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ARTICLE INFO

Keywords:

Licorice residue nanocellulose
Soy protein isolate
Nanocomposite
Water sensitivity
Mechanical properties

ABSTRACT

The cellulose-rich residues of licorice are usually discarded as waste in many medicine factories, resulting in serious wastage of biomass. In this work, nanocellulose was extracted from licorice residue and the microstructure, particle size, crystallinity, and stability were investigated. The prepared licorice residue nanocellulose (LNC) was incorporated to soy protein isolate (SPI) for the production of eco-friendly nanocomposites. The effects of LNC content (0, 2, 4, 6, and 8 wt%) on the water sensitivity, mechanical and barrier properties of SPI films were characterized. The results revealed that LNC had a short rod-like structure (100–400 nm in length and 10–35 nm in diameter) and had high stability in aqueous media. LNC had a higher crystallinity degree than licorice residue cellulose. The addition of LNC significantly improved the properties of SPI films, especially at 6 wt%. At 6 wt% LNC, tensile strength and contact angle of SPI films increased by 35.4% and 20.3%, respectively, and monolayer moisture content, water vapor permeability, and oxygen permeability decreased by 44.4%, 27.2%, and 55.5%, respectively.

1. Introduction

Polymer nanocomposites are generated by dispersing nanoparticles (nanofillers) in polymer matrices (Cho and Park, 2011). The addition of a small amount of nanoparticles results in composites with enhanced properties suitable for industrial and technological applications. Inorganic nanoparticles such as montmorillonite (Echeverría et al., 2014), TiO₂ (Feng et al., 2007), and nano-graphene (Ashori and Bahrami, 2014) have been used to improve the mechanical, thermal, and gas barrier properties of polymers. However, environmental awareness and economic concerns have increased interest towards the use of bio-based fillers.

Cellulose is one of the most ubiquitous and abundant biopolymers in the world. Cellulose is present in wood, cotton, hemp, and other plant-based materials. Additionally, cellulose can be synthesized by some bacteria and animals (Bondeson et al., 2006). Nanocellulose, a cellulose derivative, has been widely utilized as a reinforcement agent in polymer matrices due to its mechanical characteristics (stiffness, tensile strength, and high Young's modulus), low cost, biodegradability, and eco-friendliness (Qazanfarzadeh and Kadivar, 2016). Moreover, it exhibits good compatibility with hydrophilic polymers. The use of nanocellulose yields polymers with superior mechanical and barrier properties due to strong hydrogen-bond interactions (Jiang and Hsieh, 2015;

Khan et al., 2014). Recently, there has been increasing interest in the derivation of nanocellulose from cellulosic waste such as rice husk (Hassan et al., 2010), wheat straw (Rahimi and Behrooz, 2011), pineapple leaf (Santos et al., 2013), beer industrial residues (Shahabi-Ghahfarrokhi et al., 2015), and sweet potato residues (Lu et al., 2013). Several methods have been reported for the preparation of cellulose nanocrystals, including acid hydrolysis, oxidation method, mechanical refining, ionic liquid treatment, enzymatic hydrolysis, subcritical water hydrolysis, and combined processes (Trache et al., 2017). Among them, acid hydrolysis is the mainstream way to prepare cellulose nanocrystals for the sulfate-modified surface, high crystallinity and good colloidal stability in water (El Achaby et al., 2018).

Traditional Chinese medicine, which has been prevalent in China for thousands of years, has considerable effects on the treatment and prevention of diseases (Chen et al., 2012). Licorice, commonly used in traditional Chinese medicine, has been used in over-the-counter drugs, throat pastilles, cough syrups, and licorice tea (Isbrucker and Burdock, 2006). The remaining cellulose-rich residue of licorice is discarded as waste, resulting in environmental problems. Mujtaba et al. (2016), who successfully isolated cellulose from licorice root using bleaching and alkali treatments (Samples were treated with 4.0% sodium hypochlorite at 100 °C for 20 min to remove the lignin, followed by treating with 2 M NaOH solution at room temperature for 20 h to remove most of the

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noncellulosic materials), reported that cellulose content of licorice (*Glycyrrhiza glabra*) root is 48.51%. Therefore, licorice residue can be used as a source of nanocellulose. The utilization of the licorice residue nanocellulose as a reinforcement agent in bio-polymer matrices has not only benefits to the waste reuse, but also certain economic values.

Soy protein isolate (SPI), the main by-product of soybean oil, consists of at least 90% protein (Hu et al., 2013). SPI has been widely used in the food industry due to its nutritional value, low cost, eco-friendliness, and functional properties (Koshy et al., 2015). Moreover, SPI has suitable film-forming capacity. SPI films with excellent oxygen and oil barrier properties have potential applications in food packaging and coating fields. However, the poor strength and high water sensitivity of SPI films have limited their commercial applications. Most of previous works have been focused on the performance enhancement of biopolymers by using nanocellulose as filler. Jensen et al. (2015) have reported that the incorporation of cellulose nanofibers extracted from soy cellulosic waste improved the mechanical and barrier properties of SPI nanocomposite films by using hot surface solvent casting method. Agustin et al. (2013) have studied starch-based biocomposite films reinforced with nanocrystal cellulose isolated from garlic stalks. Oun and Rhim (2016) have isolated nanocrystal cellulose from grain straws and utilized them to prepare the carboxymethyl cellulose-based nanocomposite. Thus, the incorporation of licorice residue nanocellulose (LNC) to SPI films may result in an eco-friendly nanocomposite with excellent mechanical and water barrier properties due to strong hydrogen bonding interactions between the LNC and SPI.

The objective of this study was to extract nanocellulose from licorice residue using acid hydrolysis and study its potential use in the preparation of nanocomposites as a reinforcement agent. The effects of LNC addition on the microstructure, thermal stability, mechanical properties, water sensitivity (water sorption, surface hydrophobicity, and water vapor permeability), oxygen permeability, and light barrier properties of SPI nanocomposites were investigated.

2. Materials and methods

2.1. Film-forming materials

Licorice roots were purchased from Yixiaotang Chinese medicine pharmacy (Bozhou, China). SPI powder (90% protein) was supplied by Harbin High Technology Soy Protein Co. Ltd. (Harbin, China). Sodium hypochlorite, sodium hydroxide and sulfuric acid used were purchased from Yongda Chemical Reagent Co. Ltd. (Tianjin, China)

2.2. Isolation of cellulose and nanocellulose from licorice residue

2.2.1. Cellulose isolation

Cellulose isolation from licorice residue was performed as reported by Mujtaba et al. (2016). Licorice (300 g) was mixed three times with boiling water (2000 mL) for 2 h each time and dried at 60 °C to obtain licorice residue. Dried licorice residue was peeled and milled to a 60-mesh sieve size. Licorice residue powder (10 g) was mixed twice with 4% (w/w) sodium hypochlorite under constant stirring at 100 °C for 20 min to remove lignin and washed with distilled water. De-lignified fiber was treated with 2 M NaOH at room temperature for 20 h and heated at 90 °C for 2 h to remove hemicellulose. Licorice residue cellulose (LC) was washed repeatedly with distilled water to attain a neutral pH and dried at 60 °C for 10 h.

2.2.2. Preparation of LNC

LNC was prepared from LC by acid hydrolysis. Hydrolysis was initiated with 64% (w/w) sulfuric acid (10 mL/g cellulose) under vigorous stirring at 45 °C for 45 min and terminated with a 10-fold cold water dilution. The resulting suspension was centrifuged at 10,000 rpm for 10 min to remove excess sulfuric acid. The precipitate was washed and centrifuged repeatedly to remove the supernatant until the

supernatant became turbid. The turbid supernatant was collected as LNC suspension. Centrifugation and collection were stopped when the supernatant became clear. The LNC suspension was dialyzed against distilled water until a neutral pH was obtained. Finally, the suspension was sonicated (Ultrasonic processor model JY99-IIDN, Ningbo Scientz Biotechnology Co., Ningbo, China) at 1000 W for 30 min and stored at 4 °C. An aliquot of the suspension was frozen and freeze-dried (Scientz-18N, Ningbo Xinzhi Co., Ningbo, China) to calculate LNC content. The final LNC content was approximately 0.42% (w/v).

2.3. Formation of SPI films

SPI (6 g) was dissolved in a certain volume of distilled water containing glycerol (50% w/w SPI) as plasticizer. Different amounts of LNC (0, 2, 4, 6, and 8 wt%, based on SPI weight) were added to the solution to enhance the SPI. The blending solution was stirred gently to get a uniform solution. Next, the pH was adjusted to 9.0 with 2 M NaOH and heated at 85 °C for 20 min. Then the mixture was casted to a Plexiglas plate (0.0676 m²) and dried at 55 °C for 12 h. After drying, the film was peeled off and stored in a 43 ± 2% RH for 24 h for testing. The nanocomposites containing 0, 2, 4, 6, and 8 wt% LNC were labeled as LNC0, LNC2, LNC4, LNC6, and LNC8, respectively

2.4. Characterization of LNC and SPI/LNC films

Surface microstructure of LNC and cross sections of SPI-based films were observed by with a Philips-FEI scanning electron microscope (SEM) (The Netherlands) at an accelerating voltage of 10.0 kV with gold coating. The cross sections of film samples were obtained by fracturing in liquid nitrogen. Transmission electron microscopy (TEM) was obtained using a JEOL JEM-2100 transmission electron microscopy at 200 kV. The particle size and zeta potential of nanocellulose were determined by a Malvern Zetasizer Nano ZS (ZEN 3600, Malvern Instruments, UK). Fourier transform infrared (FT-IR) spectra were recorded by an ATR-FTIR spectrometer (Nicolet 6700, Thermo Fisher Scientific Co., Ltd., MA, USA) ranging from 4000 to 650 cm⁻¹. X-ray diffraction (XRD) analysis was carried out with a D/max 2200 X-ray diffractometer (Rigaku Rotaflex, Japan) at 50 kV and 30 mA from 5° to 50°. Thermal stability was determined by using a thermogravimetric analyzer (Q500, Newcastle, USA) with heating from 35 °C to 600 °C at a rate of 20 °C min⁻¹. The derivative thermo-gravimetric (DTG) curves were recorded in each test.

Water sorption isotherms of the films were carried out as reported by Xiao, Lim, and Tong (2012). The films were dried at 60 °C for 24 h and conditioned in desiccators with 0.11, 0.22, 0.33, 0.53, 0.75, 0.84, and 0.90 equilibrium water activity (*a_w*) provided by saturated salts solutions of LiCl, CH₃COOK, MgCl₂, Mg(NO₃)₂, NaCl, KCl, and BaCl₂, respectively. Samples were weighed periodically until an equilibrium moisture content was achieved. The Guggenheim–Anderson–de Boer (GAB) model (Eq. (1)) was used to fit the resulting data (Version 8.0 Origin software, Origin Lab Corporation, Northampton, USA),

$$X_{eq} = \frac{X_0 C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

where X_{eq} represents the equilibrium moisture content (g H₂O/g dry film), X_0 is the monolayer moisture content (g H₂O/g dry film), a_w is water activity, and C and K are associated with the sorption heat of monolayers and multilayers, respectively.

The water vapor permeability (WVP) of the films was measured by the cup method according to a method previously developed (Han and Wang, 2016). The samples were sealed to the bottles (4.6 cm in inner diameter × 3.0 cm in depth) containing anhydrous calcium chloride [0% RH]. Then, the bottles were conditioned at room temperature and 75% RH and weighed periodically for 2 days. The static contact angles (CA) of the films were measured using an OCA20 goniometer (Data-physics Company, Germany). Oxygen permeability (OP) of the films

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