



Preparation and characterization of nanocomposite films containing starch and cellulose nanofibers



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ARTICLE INFO

Keywords:

Starch
Cellulose nanofibers
Composite films
Morphology
Mechanical properties

ABSTRACT

Starch nanocomposites films were successfully prepared using the isolated cellulose nanofibers (CNFs) at loading from 5 to 20% by solution casting. The morphology, crystallinity, surface hydrophobicity, water vapor permeability, opacity, and mechanical test of nanocomposites films were studied. The CNFs were uniformly distributed within these films up to 15% of CNFs. The incorporation of 20% CNFs in the composite film produced selective aggregation and, thus, inhomogeneity of the CNFs. The contact angle values increased from 49.46° (starch-only films) to 88.57° (CNFs loading at 20%). The incorporation of CNFs hinders the diffusion or permeability of water vapor through the composite. Addition of CNFs resulted in significant improvement in glass transition temperature (T_g), tensile strength and modulus of elasticity of nanocomposites films.

1. Introduction

With the growing awareness of environmental issues and the depletion of non-renewable resources, it is urgent to develop a new kind of bio-based, biodegradable, and environment-friendly packaging material having good mechanical and thermal performance (Kargarzadeh et al., 2017). Biorefinery is a new technique which uses the agriculture waste, plant starch and lignocellulose substance as raw materials to produce various chemicals, fuel and biomaterials (Cherubini, 2010). Some researchers have studied glycerol biorefining by using chemocatalytic method, with low-cost and less environmental pollution (Lari et al., 2018). In recent years, the biomass-based packaging material derived from renewable raw materials, agricultural waste, and agro-industrial by-products have drawn more and more attention due to its low price, easy availability and eco-friendliness, compared to synthetic ones (Baishya and Maji, 2017).

Starch is one of the most abundant natural biopolymers, it is made from glucose polymerization. In recent years, considering the low cost, degradability, edibility, and ease of chemical modification of starch, many studies have focused on its application to packaging field (such as cheese and meat) to replace the conventional petroleum plastic (Yang et al., 2018; Chandra Mohan et al., 2016; Avella et al., 2005; Laohakunjit and Noomhorm, 2004; Mohanty et al., 2000). Incorporating plasticizer such as water and glycerol, starch can be made

thermoplastic called thermoplastic starch (TPS) or plasticized starch (PS) (Carvalho et al., 2003). However, much broader applications of starch-based composites in packaging have been restricted because of its disadvantages such as water sensibility, poor mechanical properties, low heat distortion temperature, brittleness, and low melt viscosity for further process (Curvelo et al., 2001; Li et al., 2012). The poor resistance to water can be ascribed to the presence of numerous hydroxyl groups in nature of starch. As a result, several methods (physical and chemical modification) have been carried out to improve positive properties of starch films, such as chemical modification, graft copolymerization, and the addition of other polymers (polylactic acid, polyethylene, and polyvinyl) to the starch matrix (Muller et al., 2017; Biduski et al., 2017; Noshirvani et al., 2018; Shen et al., 2016). Some researchers proposed that cellulose nanofibers (CNFs) obtained from renewable resources can also improve the mechanical and thermal properties of the starch-based nanocomposites while preserving the biodegradability (Pelissari et al., 2017). Various types of CNFs can be produced from wood (Abe et al., 2007), soy hulls (Alemдар and Sain, 2008), corn cob (Silvério et al., 2013), areca husk (Soman et al., 2018), and waste mango wood scrap (Yadav et al., 2018). Babae et al. (2015) reported that the composite films containing starch and CNFs can be completely degraded by white rot fungi after 60 days.

Cellulose nanofibers (CNFs) is a new type of polymer functional material, which is derived from agricultural crop-residues. In recent

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<https://doi.org/10.1016/j.indcrop.2018.07.043>

Received 18 March 2018; Received in revised form 11 July 2018; Accepted 16 July 2018

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years, CNFs as a reinforcing agent has been widely used in different natural and synthetic polymer matrices for different application due to its high aspect ratio, high tensile strength, high Young's modulus, high crystalline, and low coefficient of thermal expansion (Faruk et al., 2012).

In our previous work, we have produced nanocomposite films containing maize starch and sugar beet pulp cellulose nanofibrils (CNFs) and investigated the viscoelastic property of the plasticized starch (PS)/CNFs nanocomposite films (Li et al., 2015, 2014). In this context, this work was aimed at characterization of the nanocomposite films in terms of water vapor permeability, opacity, and mechanical properties. The morphological features, contact angle, thermal properties and crystal structure of the PS/CNFs nanocomposite films were investigated using scanning electron microscopic (SEM), contact angle meter, differential scanning calorimeter (DSC) and X-ray diffraction (XRD) techniques.

2. Materials and methods

2.1. Materials

Sugar beet pulp (SBP) was obtained from Xinjiang province of China. Corn starch (28% amylose content) was supplied from Hebei Zhangjiakou Yujing Food Co. Ltd. (Hebei, China). Xylitol (food grade) was purchased from Tianjin Jinguigu Science & Technology Development Co. Ltd (Tianjin, China). Sodium chlorite (NaClO₂) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Benzene, absolute ethanol, sodium hydroxide (NaOH), glycerol and other chemicals were of analytical grade and were supplied by Beijing Chemical Works (Beijing, China).

2.2. Preparation of nanocomposites films

Cellulose nanofibers were produced by the method in our previous study (Li et al., 2014), and the PS/CNFs nanocomposites films were produced based on a convenient solution-casting process on polycarbonate petri dishes (Shi et al., 2013).

Corn starch, plasticizers (glycerol and xylitol, 1:1), CNFs and deionized water were mixed together to form starch-plasticizer-CNFs dispersions with 5.0 wt% (w/v) solid concentration. The plasticizers content was fixed at 30% based on the total solid content. The dispersion batches were heated at 100 °C for 1 h. After cooling down to 70 °C, the resulting paste was degassed under vacuum. Then 13 mL of the dispersions were casted into a 9 cm diameter petri dish, followed by drying at 45 °C for 6 h. By changing the content of CNFs over a range of 5, 10, 15, 20 wt%, a series of nanocomposites films with a thickness of 0.01–0.05 mm were prepared coded as PS/CNFs-5, PS/CNFs-10, PS/CNFs-15 and PS/CNFs-20, respectively in which the CNFs content was expressed on a water-free matrix. As a control, a neat matrix film which did not contain the CNFs was obtained with the same fabrication process. In order to ensure the equilibration of the water content, these resulting films were preserved in a controlled desiccator (20 °C, RH = 43%) for one week.

2.3. Characterization of morphological features

The morphology and microstructure of these nanocomposite films were characterized using scanning electron microscope (SEM) (JSM-6010LA, JEOL Co., Ltd., Tokyo, Japan). Samples were fixed on a metal stub with double-sided adhesive tape and the surface of these samples was coated with a thin layer of platinum. SEM micrographs were taken at 10 KV accelerating voltage.

2.4. X-ray diffraction (XRD) analysis

The crystallinity of the starch films in the presence and absence of

the CNFs was examined by using an X-ray diffractometer (XD-2, Beijing Purkinje General Instrument Co., Ltd., China) under the following conditions: Nickel filtered Cu K α radiation ($\lambda = 0.15406$ nm) at an operating voltage of 36 KV and a filament current of 20 mA. The samples were scanned in 2 θ angles ranging from 5° to 40° with a scanning rate of 1°/min and sampling interval of 0.02° at room temperature.

2.5. Contact angle determination

To determine the surface hydrophobicity of the nanocomposites films, water contact angle measurements were performed using a contact angle meter (JCD2000D, Shanghai zhongchen digital technic apparatus Co. Ltd., China) equipped with a type of diffuse light and a Charge-coupled Device (CCD) camera (6 photo/s). The film was fixed on a stainless-steel sheet with double-sided adhesive tape. The drop (4 μ l) of distilled water was carefully placed on the surface of the film by an auto pipette. Images were captured immediately after a drop of distilled water was deposited on the surface of the nanocomposites films. The gypsometry was used to determine the contact angle (θ) which was calculated from the shape of the drop according to the following equation:

$$\theta = 2 \tan^{-1} (2h/d) \quad (1)$$

Where h is the height of water droplet, d is the diameter of bottom of water droplet.

The reported contact angle values are the mean value of three measurements taken at least three different positions on the film.

2.6. Water vapor permeability (WVP)

The water vapor permeability of the samples was conducted based on the ASTM method E96-80 with some modifications (American Society for Testing and Materials, 1987). Each sample was sealed over a circular opening in a permeation cell which was stored at 25 °C in a desiccator under 75% relative humidity (saturated sodium chloride solution). To maintain a 75% RH gradient across the film that the water vapor can continuously diffuse through the film, anhydrous calcium chloride (0% RH) was placed inside the cell. The extent of water vapor transport across the film was determined from the weight gain of the permeation cell. The change in the weight of the cell was recorded to the nearest 0.0001 g and weighed every 24 h over a week. Film thickness was measured after the permeation tests. Changes in the weight of the cell were plotted as a function of time and the slope of line was calculated by linear regression. Then, the water vapor transmission rate (WVTR) was calculated from the slope divided by the cell area. WVTR ($\text{g s}^{-1} \text{m}^{-2}$) and WVP ($\text{g Pa}^{-1} \text{h}^{-1} \text{m}^{-1}$) were calculated using Eqs. (2) and (3):

$$WVTR = \frac{1}{A} \left(\frac{\Delta m}{t} \right) \quad (2)$$

$$WVP = \frac{WVTR \times h}{P \times (R_1 - R_2)} \quad (3)$$

where A is the area of circular opening (m^2), Δm is the mass change of the cell (g), t is the time (h), h is the film thickness (m), P is the saturation vapor pressure of water (3.169×103 Pa) at 25 °C, R₁ and R₂ are the relative humidity (RH) in the desiccator and the permeation cell, respectively. All the tests were carried out in triplicate.

2.7. Opacity

The opacity of the nanocomposites films was determined using a modified BSI standard procedure (Mali et al., 2004) using an UV-vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd., Beijing, China). Films samples were cut into 40 mm \times 10 mm and

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