



Reducing water sensitivity of alginate bio-nanocomposite film using cellulose nanoparticles

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ABSTRACT

A bio-based nanocomposite was developed by incorporation of cellulose nanoparticles (CN) obtained from sulfuric acid hydrolysis into alginate biopolymer using solution casting method. The effect of CN loading content (1, 3, 5 and 10 wt%) on microstructural, physical, mechanical and optical properties of the nanocomposites were characterized. The results showed that water solubility and water vapor permeability of the nanocomposites decreased by about 40% and 17%, respectively, upon increasing the CN content to 10%. In addition, the crystalline structure of the CN increased surface hydrophobicity of the alginate film by about 98%. The tensile strength value of the composite films increased from 18.03 to 22.4 MPa with increasing NC content from 0 to 5%; but, it decreased with further increase of the filler content. Nevertheless, film transparency decreased with CN incorporation, especially in high level (10%), which suggested the occurrence of partial agglomeration of the fillers at 10% that coincided with microstructural and mechanical results.

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1. Introduction

Biopolymers and their biodegradable films have become a topic of great interest all over the world because they present a viable solution for environmental problems caused by petroleum-based packaging materials and post-consumption disposal of wastes. These polymers are considered renewable, environmentally friendly and attractive materials with interesting properties and functionalities, which can improve food shelf life in the film form [1]. Nevertheless, packaging materials made by biopolymers have constituted only about 1–2% of the food packaging market although food packaging accounts for about 40% of the \$460 billion global packaging industry [2]. However, recent research has reported that the current capacity of bio-based packaging materials will have increased from about 0.185 million tons annually to 0.545 million tons by 2012 [3]. Among them, carbohydrates like alginate are the most attractive materials for food packaging and coating applications because of their good film-forming ability, related to their unique colloidal properties.

Sodium alginate (SA) is a water-soluble hydrocolloid which is extracted from brown seaweed and is composed mainly of (1–4)-linked β -D-mannuronic acid units and α -L-guluronic acid units [4]. It is the only polysaccharide that naturally contains carboxyl groups in each constituent residue and possesses various functionalities for

applications as functional materials [5,6]. Its key properties, such as nontoxicity, biocompatibility, biodegradability and reproducibility, have led to its usage in many areas including food, pharmaceutical additives, biology or enzyme carrier and tissue engineering materials [7]. Several authors [6,8,9] have reported that SA also has meaningful potential to be developed as a source for biodegradable or edible films. However, poor mechanical and gas barrier properties and high water sensitivity limit its application, particularly in the presence of water and humidity [6,7].

Various strategies can overcome these challenges in the application of biopolymers such as alginate in food packaging. One of the most recent methods is the addition of nanoreinforcing fillers. Fillers with at least 1 dimension in the nanometric scale are called nanoparticles or nanoreinforcements and their composites with biopolymers are bionanocomposites [10]. In this way, cellulose nanowhiskers (CNW) or cellulose nanocrystals have attracted significant interest as potential nanoreinforcements during the last decade [11,12]. CNWs are crystalline, spherical or rod-shaped nanomaterials obtained by treating native microfibrils or microfibrillated cellulose with high strong acids such as sulfuric acid. Several research teams [11,13,14] have reviewed the CNW's potential for improving composite properties through its interesting characteristics such as the abundance of cellulose, its biocompatibility, good mechanical properties and the large specific surface area of the nanowhiskers.

Although some works have studied the effects of CNW on the mechanical and thermal properties of natural biopolymers [12,15–20], very little is known about the effect of CNW on the

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properties of bionanocomposites in general [21] and carbohydrates, especially sodium alginate. Thus, the focus of the present study was on preparing a bionanocomposite film from alginate reinforced with CNW and comprehensively evaluating the effects of cellulose nanoparticle on the physical, mechanical and barrier properties of the film.

2. Materials and methods

2.1. Materials

Sodium alginate (medium viscosity) and microcrystalline cellulose with dimensions of 10–15 μm and density of 0.600 g/cm^3) were obtained from Sigma–Aldrich Chemical Co., USA. Sulfuric acid and glycerol were purchased from Merck Co. with analytical grade.

2.2. Isolation of cellulose nanoparticles

Cellulose nanoparticles were prepared from microcrystalline cellulose (MCC) by sulfuric acid hydrolysis according to the method described by Rahimi and Behrooz [22] with some modifications. In order to prepare cellulose nanoparticles, MCC was hydrolyzed by sulfuric acid (64% w/w) at 45 °C for 120 min. The excess sulfuric acid was removed by washing with deionized water for 10 min at 12000 rpm using repeated centrifugation (Wiggen Hauser, D-500, Germany). Each time, the supernatant was removed from the sediment and was replaced with deionized water. The centrifugation continued until the supernatant became turbid. After centrifugation, the suspension containing nanocrystalline cellulose was dialyzed against deionized water until achieving the pH of 5.5. In order to achieve homogeneous suspension, it was sonicated (Misonix, S-4000, USA) for 20 min. The final concentration of the nanowhisker dispersions was approximately 0.5% (w/w).

2.3. Nanocomposite preparation

Alginate films were prepared by modifying the method used by Rhim [6]. A solution of sodium alginate was prepared by dissolving the sodium alginate (1 w/v) in distilled water at 70 °C under stirring for 30 min. After complete dissolution, glycerol (0.25 g/g of alginate) as a plasticizer was added to enhance film flexibility, decrease brittleness and facilitate their detachment from the petri dishes. The film-forming solution was cast onto petri dishes which were 9 cm in diameter and oven dried at 40 °C for approximately 24 h. The dried films were then removed from the petri dishes and stored in desiccators containing saturated magnesium nitrate solution at 25 °C and 52.89% relative humidity until being used.

In order to prepare the nanocomposite films, different amounts of the cellulose nanowhisker (CNW) (1, 3, 5 and 10% (w/w) on solid sodium alginate) were added to 50 mL of deionized water and sonicated for 5 min. Afterwards, the alginate solution (prepared according to the explained method) was added slowly to the pretreated CNW solutions. The mixture was stirred for 1 h. Then, the mixture was homogenized using a homogenizer at 10,000 rpm for 5 min at room temperature (Wiggen Hauser, D-500.). This step was followed by sonication using ultrasound equipment (Misonix, S-4000, USA) for 5 min at 50% amplitude (sequence 1 min). The resulting solution was degassed under vacuum for 30 min followed by slow stirring for 4 h to remove all the bubbles. Finally, the films were prepared and stored, as described previously.

2.4. Samples characterization

2.4.1. X-ray diffraction (XRD) characterization

The crystallinity of cellulose nanoparticles and MCC was evaluated by XRD measurement. XRD patterns were taken with a Philips

X'Pert MPD Diffractometer (Eindhoven, Netherlands) with Co Ka radiation at the wavelength of 1.544 nm at 40 kV and 30 mA. The powder samples were scanned over the range of diffraction angle $2\theta = 5\text{--}40^\circ$ by the scan speed of $1^\circ/\text{min}$ at room temperature. Crystalline index ($C_{\text{I}r}$) of MCC and CN was determined according to the empirical method described by Segal et al. [23] using the following equation:

$$C_{\text{I}r}(\%) = \frac{I_{\text{cry}} - I_{\text{am}}}{I_{200}} \times 100 \quad (1)$$

where I_{cry} is the peak intensity corresponding to cellulose I and I_{am} is the peak intensity of the amorphous fraction.

2.4.2. Scanning electron microscopy (SEM)

Surface microstructure of the MCC, CN and alginate-based films was examined by a Philips XL 30 scanning electron microscope (Philips, Eindhoven, the Netherlands) under high vacuum condition at the accelerating voltage of 20.0 kV. The mounted samples on the holder were frozen in liquid nitrogen and then sputtered with gold in a Bal-Tec SCD 005 sputter coater (Bal-Tec AG, Balzers, Liechtenstein).

2.4.3. Film thickness

A manual digital micrometer (0.001 mm, Mitutoyo, Mizonokuchi, Japan) was used to measure thickness of the alginate-based films. Average values of ten measurements in different regions of each sample were calculated and used in the calculation of water vapor permeability and tensile properties.

2.4.4. Moisture content (MC)

MC of the films was determined after drying in an oven at 105 °C for 24 h. The small specimens of films (4 cm \times 4 cm) collected after conditioning were cut and placed on glass petri dishes that were weighed before and after oven drying. MC values were measured in triplicate for each film and calculated as the percentage of weight loss based on the original weight.

2.4.5. Total soluble matter of films in water

The solubility of the films in water was determined as described by Tunc et al. [24]. The cut samples in rectangular (4 cm \times 4 cm) form were dried at 105 °C for 24 h to measure initial dry matter of the films (W_i). After 24 h agitation (250 rpm) in 50 mL distilled water at 25 °C, the samples were filtered through Whatman No. 1 filter paper. Then, the filter papers were dried at 105 °C for 24 h to achieve final dry weight (W_f) and the film solubility (%) was calculated using Equation (2).

$$\text{Solubility in water}(\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (2)$$

2.4.6. Surface hydrophobicity of films

The surface hydrophobicity of the films was determined by measuring water contact angle by a PG-X goniometer (Thwing-Albert Instrument Co., USA) at room temperature. A 5 μL drop of distilled water was placed on the film surface and the contact angle was automatically calculated using the goniometer software. For each film type, at least 5 measurements were made and the mean value was calculated.

2.4.7. Water vapor permeability measurement

The films' water vapor permeability (WVP) was determined gravimetrically according to the ASTM E96-92 method as described by Abdollahi et al. [25]. Glass permeation cups with internal diameter of 30 mm containing distilled water were covered with films and then placed in a desiccator. It was maintained at 20 °C and 1.5% RH (28.044 Pa water vapor pressure) with silica gel and the air

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