



Properties of alginate-based films reinforced with cellulose fibers and cellulose nanowhiskers isolated from mulberry pulp



Long-Feng Wang, Shiv Shankar, Jong-Whan Rhim*

Department of Food Engineering and Bionanocomposite Research Institute, Mokpo National University, 61 Dorimri, Chungkyemyon, Muangun, 534-729, Jeonnam, Republic of Korea

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ABSTRACT

Cellulose fibers (CF) and cellulose nanowhiskers (CNW) were isolated from the mulberry pulp and blended with alginate to prepare alginate-based composite films. Different concentrations (2, 4, and 6 wt % based on alginate) of CF and CNW were used to test the effect of filler concentrations on the mechanical, water vapor barrier, and thermal properties of the alginate-based composite films. The CNW was in needle shape with the length of 200–400 nm and the diameter of 15–30 nm. The mechanical properties of alginate films were improved by blending with the CNW. The elastic modulus and tensile strength of alginate films were increased by 35% and 25%, respectively, however, water vapor permeability remained at the same level as the neat alginate films by blending 4 wt% of CNW. The CNW obtained from the mulberry pulp can be used as a reinforcing filler for the preparation of bionanocomposites for the development of completely biodegradable food packaging materials.

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1. Introduction

Environmental concerns and exhaust of natural resources caused by the petroleum-based non-biodegradable plastics aroused renewed interest in the development of completely biodegradable green packaging materials using biopolymers derived from agricultural or biological products (Duncan, 2011; Rhim, Park, & Ha, 2013). Various carbohydrates, proteins, and lipids based materials have been considered for the use as alternative biodegradable packaging materials because of their eco-friendly, biodegradable, biocompatible, abundant availability, and renewable nature (Rhim, Park et al., 2013). Among such biopolymers, carbohydrates have been used extensively for the preparation of biopolymer films because of their excellent film forming properties with good gas barrier and mechanical properties (Rhim, Park et al., 2013; Shankar, Teng, & Rhim, 2014). As one of such carbohydrate polymers, alginate has frequently been exploited in the development of biodegradable food packaging films (Abdollahi, Alboofetileh, Rezaei, & Behrooz, 2013; Norajit, Kim, & Ryu, 2010). Alginate is an anionic polysaccharide derived from brown seaweed (*Phaeophyceae*) such as *Laminaria hyperborea*, *Macrocystis pirifera*, *Laminaria digitata*, and *Ascophyllum nodosum*, and composed of β -D-

mannuronic acid and α -L-glucuronic acid, which are linked together in varying proportions by 1–4-linkages (Rehm & Valla, 1997). Since alginate is abundantly available, biodegradable, and biocompatible with gelling and stabilizing properties, it has been widely used industrially as non-toxic food additives for thickening and gelling agents, emulsifier, and colloidal stabilizer (Carneiro-da-Cunha et al., 2010). Owing to its good film forming property, alginate has been used in the food industry in the form of films or hydrogels (Norajit et al., 2010; Pereda, Amica, Racz, & Marcovich, 2011). Alginate films are highly transparent with high mechanical strength, (Abdollahi et al., 2013; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011), however, they have poor water vapor barrier property with low flexibility like other biopolymer-based films (Huq et al., 2012). In order to improve the mechanical and gas barrier properties of biopolymer films, various methods of blending biopolymers with different types of metallic, inorganic, or organic nanofillers have been used (Rhim, Park et al., 2013; Shankar & Rhim, 2015). Among such organic nanofillers, nanocellulose isolated from various natural cellulosic resources have gained significant attention due to their unique and attractive features such as biocompatibility, biodegradability, abundance, renewability, light weight, and high aspect ratio (Siró & Plackett, 2010).

Both biodegradable and nonbiodegradable polymeric matrices have been reinforced with cellulose nanowhiskers, nanocrystals, or nanofibers to prepare nanocomposites films to improve film properties (Chang, Jian, Zheng, Yu, & Ma, 2010; Fortunati et al.,

* Corresponding author.

E-mail address: jwrhim@mokpo.ac.kr (J.-W. Rhim).

2012). Cellulose nanofibers and cellulose nanocrystals have been isolated from microcrystalline cellulose (Shankar & Rhim, 2016), cotton (Oun & Rhim, 2015), flax (Cao, Dong, & Li, 2007), hemp (Cao, Chen, Chang, Stumborg, & Huneault, 2008), ramie (Lu, Weng, & Cao, 2006), wheat straw, and soy hulls (Alemdar & Sain, 2007) using various methods including physical, chemical or a combination of them. Reddy and Rhim (2014) isolated and characterized the cellulose nanocrystals from paper-mulberry pulp and demonstrated that the paper-mulberry pulp was an excellent source for the preparation of cellulose nanocrystals. The properties of nanocellulose are known to depend not only on the sources of cellulose but also on the isolation methods and their conditions. Extraction conditions such as acid concentration, time and temperature in the acid hydrolysis process play an important role to obtain nanocellulose with the desired shape, size, and crystallinity. Reddy and Rhim (2014) obtained spherical type nanocrystals by hydrolysis of mulberry pulp fibers using 47% H₂SO₄ (fibers to solution ratio of 1:20) with refluxing and strong agitation for 3 h at 60 °C. Cellulose nanowhiskers (CNW) with high aspect ratio are desirable for enhancing the film properties when blended with polymeric film material. In the present study, cellulose nanowhiskers (CNW) were isolated from the mulberry pulp fibers using a higher concentration of H₂SO₄ (50%) at a lower temperature (50 °C) than the previously reported one (Reddy & Rhim, 2014).

The main objective of the present study was to prepare alginate-based bionanocomposite films reinforced with CNW isolated from mulberry pulp cellulose fibers to test their potential application for food packaging. Alginate was chosen as a polymer matrix since it has good film forming property being compatible with the nanocellulose owing to their hydroxyl groups. The alginate-based nanocomposite films were characterized by SEM, XRD, and FTIR methods and film properties such as optical, mechanical, water vapor barrier, and thermal stability were also evaluated.

2. Materials and methods

2.1. Materials

Sodium alginate was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Glycerol and sulfuric acid were procured from Daejung Chemicals & Metals Co., Ltd. (Siheung, Gyeonggi-do, Korea). Bleached pulp of mulberry inner bark composed of 85% of cellulose was obtained from Chunyang Paper Co., Ltd. (Jeonju, Korea).

2.2. Preparation of cellulose fibers and nanowhiskers

Fibers from mulberry pulp were separated using a laboratory scale valley beater and a disintegrator (Disintegrator DM-826, Daeil Machinery Co., Ltd, Daejeon, Korea). First, the inner bark pulp of mulberry (*Broussonetia kazinoki* Siebold) was cut into short pieces and soaked into water, followed by beating for 1 h using the valley beater. The separated fibers were collected and dried at 105 °C for 24 h to obtain mulberry pulp cellulose fibers (CF).

Cellulose nanowhiskers (CNW) were isolated from the CF using the acid hydrolysis method as described by Reddy and Rhim (2014). Briefly, 10 g of CF were mixed into 200 mL of 50% sulfuric acid solution and heated at 50 °C for 3 h with constant stirring. Excess of distilled water was added to stop the reaction, and the suspension was centrifuged at 4000 rpm for 20 min. The precipitated fibers were repeatedly washed with distilled water until the supernatant become turbid. The samples were sonicated using a high-intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., Newtown, CT, USA) for 5 min followed by dialysis against distilled water to reach neutrality to obtain mulberry pulp cellulose nanowhiskers (CNW). Then the CNW in suspension form was collected

and stored at 4 °C before further use.

2.3. Characterization of cellulose fibers and nanowhiskers

The microstructure of the CF was observed using a scanning electron microscope (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan) after coating the sample with platinum (Pt). The microstructure of the CNW was observed by a scanning transmission electron microscope (STEM) using the FE-SEM instrument in the transmission mode. The sample was prepared by putting a drop of the diluted CNW suspension on a carbon coated Cu-grid and air dried.

Fourier transform infrared (FTIR) spectroscopy of CF and CNW was performed using an attenuated total reflectance-FTIR (ATR-FTIR) spectrophotometer (SENSOR 37 Spectrophotometer with OPUS 6.0 software, Billerica, MA, USA).

The crystallinity of the CF and CNW was determined by X-ray diffraction (XRD) using an XRD diffractometer (PANalytical Xpert pro MRD diffractometer, Amsterdam, Netherlands). The crystallinity index (CI) of the samples was calculated according to the following equation (Gumuskaya, Usta, & Kirici, 2003):

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

where I_{002} and I_{am} represent the maximum intensity of diffraction of 002 peak ($2\theta = 22.7^\circ$) and amorphous peak (the minimum between the 002 and 101 peaks ($2\theta = 16^\circ$), respectively (Park, Baker, Himmel, Perilla, & Johnson, 2010).

The thermal stability of the CF and CNW were evaluated using a TGA (thermogravimetric analysis) analyzer (TGA; Hi-Res TGA 2950, TA Instrument, New Castle, DE, USA). For analysis, 5 mg of each sample was put in an aluminium pan, and the samples were heated at a rate of 10 °C/min from 30 to 600 °C under a nitrogen flow of 50 cm³/min with an empty pan as a reference. The derivative of TGA (DTG) was determined by the central finite difference method (Reddy & Rhim, 2014):

$$DTG = (W_{t + \Delta t} - W_{t - \Delta t})/2\Delta t \quad (2)$$

where $W_{t + \Delta t}$ and $W_{t - \Delta t}$ are the residual weight of sample at time $t + \Delta t$ and $t - \Delta t$, respectively, and Δt is the time interval for reading residual sample weight.

2.4. Preparation of alginate-based composite films

Alginate, alginate/CF, and alginate/CNW composite films were prepared using a solution casting method (Rhim, Wang, & Hong, 2013). Alginate film solutions were prepared by dissolving 3 g of sodium alginate into 150 mL of distilled water with 1.2 g of glycerol with vigorous mixing at 90 °C for 30 min using a magnetic stirrer. In addition, alginate/CF and alginate/CNW film solutions with different filler concentration (2, 4, and 6 wt% based on alginate) were prepared by dispersing predetermined amount of CF or CNW (i.e., 0.06, 0.12, and 0.18 g) into 150 mL of distilled water with 1.2 g of glycerol and homogenized for 10 min at 8000 rpm using a high shear mixer (T25 basic, Ika Labortechnik, Janke & Kunkel GmbH & Co., KG Staufen, Germany) and sonicated using a high intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., New Town, CT, USA) for 5 min to get homogeneously dispersed filler solution. Then 3 g of alginate was dissolved into the filler solution and followed the same procedure for the preparation of alginate film solutions. The film forming solution was cast onto a leveled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plates (24 cm × 30 cm) and dried for about 24 h at room

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