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Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose

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ABSTRACT

Crystallized nanocellulose (CNC) was separated from paper-mulberry (*Broussonetia kazinoki* Siebold) bast pulp by sulfuric acid hydrolysis method and they were blended with agar to prepare bionanocomposite films. The effect of CNC content (1, 3, 5 and 10 wt% based on agar) on the mechanical, water vapor permeability (WVP), and thermal properties of the nanocomposites were studied. Changes of the cellulose fibers in structure, morphology, crystallinity, and thermal properties of the films were evaluated using FT-IR, TEM, SEM, XRD, and TGA analysis methods. The CNC was composed of fibrous and spherical or elliptic granules of nano-cellulose with sizes of 50–60 nm. Properties of agar film such as mechanical and water vapor barrier properties were improved significantly ($p < 0.05$) by blending with the CNC. The tensile modulus and tensile strength of agar film increased by 40% and 25%, respectively, in the composite film with 5 wt% of CNC, and the WVP of agar film decreased by 25% after formation of nanocomposite with 3 wt% of CNC. The CNC obtained from the paper-mulberry bast pulp can be used as a reinforcing agent for the preparation of bio-nanocomposites, and they have a high potential for the development of completely biodegradable food packaging materials.

1. Introduction

Not only concerns on the exhaust of natural resources and soaring oil price, but also environmental awareness caused by non-biodegradable plastic packaging materials have attracted considerable attention on the development of entirely biodegradable packaging materials from renewable and sustainable resources (Abdul Khalil, Bhat, & Ireana Yusra, 2012; Khan, Huq, Khan, Riedl, & Lacroix, 2014; Reddy, Vivekanandhan, Misra, Bhatia, & Mohanty, 2013; Sorrentino, Gorrasi, & Vittoria, 2007). Biodegradable packaging materials are usually produced from renewable, biological raw materials such as starch, cellulose, and other biopolymers (Tang, Kumar, Alavi, & Sandeep, 2012). Among them, cellulose is the most abundant natural biopolymers in the world and it is increasingly being used for the preparation of composites with other biopolymers (Faruk, Bledzki, Fink, & Sain, 2012; Jawaid & Abdul Khalil, 2011; John & Thomas, 2008; Khan et al., 2014; Siqueira, Bras, & Dufresene, 2010). Cellulose is a semicrystalline linear polysaccharide composed of β-1,4 linked glucopyranose units, with polymer chains associated by hydrogen bonds forming bundles of fibrils, which consist of highly ordered crystalline domains and disordered amorphous domains. The crystalline domains can be isolated in nanoscale with highly ordered and regular rod-like nanocrystals, after removing the amorphous domains by acid hydrolysis, which is called cellulose nanofiber, crystalline nanocellulose, or nanowhisker (De Souza Lima & Borsali, 2004). The production of cellulose nanofibers and their application in nanocomposite materials has gained increasing attention due to the profound improvement of properties of the composites such as increased mechanical and decreased gas barrier properties (Lavoine, Desloges, Dufresne, & Bras, 2012; Siró & Plackett, 2010). Such benefits of nanocellulose as nanofiller are mainly caused by their high strength and stiffness combined with low weight, as well as their biodegradability, biocompatibility, and renewability (Peng, Dhar, Liu, & Tam, 2011). Compared with microsized cellulose, cellulose nanofibers are more effective to reinforce polymers due to interactions between the nanosized elements that form a percolated network connected by hydrogen bonds when the nanofibers are well dispersed in the polymer matrix (Khan et al., 2014). In addition, nanocellulose can be obtained from cheap and abundant renewable natural resources such as wood, plants, vegetables, and other agricultural residues and agricultural processing wastes (Klemm et al., 2011). The properties of nanocellulose are known to be strongly dependent not only on the isolation method but also on

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the source of the nanofibers (Azizi Samir, Alloin, & Dufresne, 2005). Nanocelluloses have been separated from various source of plant materials and demonstrated that they were good fillers to improve the mechanical properties of biopolymer films such as starch (Da Silva, Pereira, & Druzian, 2012), alginate (Huq et al., 2012), and chitosan (Khan et al., 2012) films.

As one of the renewable and sustainable resources of cellulose fibers, mulberry bast fiber has attracted as an environmentally-friendly new fiber source (Li et al., 2009; Lim & Choi, 2008; Qu & Wang, 2011; Walia, 2013). Mulberry (*Broussonetia kazinoki* Siebold) trees are extensively grown in Asian countries like China and India for feeding silk worms with their leaves. Thousands tons of mulberry branches consisting of bast and stalk are produced for firewood or agro-wastes every year. The bast of the mulberry tree has been used for paper manufacturing since the mulberry fibers are very long (6–20 mm; average 10 mm) and provide great strength to the paper (Lim & Choi, 2008; Walia, 2013). The chemical composition and the structural characterization of the mulberry pulp fibers and the chemically treated fibers were reported (Qu & Wang, 2011). The extraction and characterization of nanowhiskers from mulberry bark fibers were also reported in the literature (Li et al., 2009). However, few studies on the isolation of nanocellulose from mulberry pulp and its application in the preparation of nanocomposites with biopolymers have been appeared in the literature.

Among the natural biopolymers, agar has a potential for making biodegradable films for packaging applications (Rhim & Wang, 2013). Agar is a polysaccharide derived from red algae. Agar contains two components such as agarose and agaropectin. Agar is soluble in hot water and it forms biodegradable film when added with proper plasticizer. Agar has been also successfully used to make nanocomposites with nanoclay and reported that the mechanical and water vapor permeability have been improved with the addition nanoclay (Rhim, 2011; Rhim, Lee, & Hong, 2011). However, no reports on crystallized nanocellulose reinforced agar-based composites are available in the literature.

The main objective of the present study was therefore to prepare agar-based bionanocomposite films reinforced with crystallized nanocellulose isolated from paper mulberry bast pulp. For this, crystallized nanocelluloses were isolated from mulberry pulp fibers and characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA). In addition, the agar-based nanocomposite films with nanocellulose were prepared by the solution casting method and their film properties were evaluated.

2. Materials and methods

2.1. Materials

Food grade agar was obtained from Fine Agar Co., Ltd. (Damyang, Jeonnam, Korea). Glycerol, sulfuric acid and sodium hydroxide were obtained from Sigma Aldrich (St Louis, MO, USA). Bleached pulp of paper mulberry bast with a cellulose content of 85% was obtained from Chunyang Paper Co., Ltd. (Jeonju, Korea).

2.2. Isolation of nanocellulose

For the pretreatment, the mulberry pulp was immersed in water after cut into small pieces (5 cm long) and the cellulose fibers were separated using a laboratory scale valley beater for 60 min. The separated fibers were dried in a drying oven at 105 °C for 24 h.

The mulberry cellulose fibers were subjected to acid hydrolysis for the isolation of nanocellulose. For this, 5 g of mulberry cellulose fiber was hydrolyzed with sulfuric acid (47% H_2SO_4 with fiber to solution ratio of 1:20) by refluxing for 3 h at 60 °C under strong agitation. The reaction was quenched by adding an excess of distilled water to the reaction mixture and the resulting mixture was then cooled to the room temperature. Then, the suspension was centrifuged at 4000 rpm for 20 min using a bench-top centrifuge (Hanil Scientific Centrifuge, Incheon, Kyonggido, Korea) repeatedly and the supernatant was discarded until it became turbid. Subsequently, the fractions were washed with distilled water by centrifugation. Under this condition, the pH of the suspension was above 5. The suspension was then sonicated using a high intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., Newtown, CT, USA) for 5 min in an ice bath. Then the suspension was subjected to dialysis with water until neutrality was attained. After this, the suspension was freeze-dried to get crystalline nanocellulose (CNC) of the mulberry pulp fiber.

2.3. Characterization

FT-IR spectra of fiber samples were obtained using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrophotometer (TENSOR 37 spectrophotometer with OPUS 6.0 software, Billerica, MA, USA) in the range of 4000–500 cm^{-1}.

X-ray diffraction (XRD) pattern of the CNC was analyzed using a PANalytical Xpert pro MRD diffractometer (Amsterdam, Netherlands). The XRD spectra were recorded using Cu-Kα radiation (wavelength of 0.1546 nm) and a nickel monochromator filtering wave at a voltage and current of 40 kV and 30 mA, respectively. The diffraction patterns were obtained at diffraction angles between 5° and 50° with a scanning rate of 0.4°/min at room temperature. The degree of crystallinity (DC) of mulberry fiber and its CNC was calculated using following equation (Gumuskaya, Usta, & Kirci, 2003):

$$DC = (I_{002} - I_{am})/I_{002} \quad (1)$$

where I_{002} is the intensity of the 0 0 2 peak (at $2\theta = 22°$) and I_{am} is the intensity of the peak at $2\theta = 16°$. And the crystallite size (D) of the fiber was calculated by using the Scherrer equation (Das et al., 2009)

$$D = K\lambda/\beta_{1/2} \cos\theta \quad (2)$$

where K is a constant (0.94), λ is the X-ray wavelength ($\lambda = 0.1546$ nm), $\beta_{1/2}$ is the full width at the half maximum of the deflection peak (FWHM), and θ is Bragg's angle.

The microstructure of mulberry fiber and the surface morphology of bionanocomposite films were observed using a field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan) operated with an acceleration voltage of 10 kV and current of 10 μA after coating the samples with osmium (Os) using a vacuum sputter coater.

For the TEM observation, the CNC was dispersed in distilled water (0.01 wt%) and about 8 μL of the CNC solution was deposited onto a glow-discharged carbon-coated TEM grid (Farmvar film on 200 square mesh copper grid, Ted Pella Inc., Redding, CA, USA). After 10 min, the excess liquid was removed by blotting with a filter paper and allowed to dry under the ambient condition. The microstructure of CNC was observed using a transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Tokyo, Japan). The length and diameter of CNC were determined using the internal scale of the TEM images.

2.4. Preparation of films

Agar and agar-based nanocomoposite films were prepared using a solution casting method following the method of Rhim et al. (2011). Agar film was prepared by dissolving 4 g of agar powder