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Effect of post-treatments and concentration of cotton linter cellulose nanocrystals on the properties of agar-based nanocomposite films

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ABSTRACT

Cellulose nanocrystals (CNCs) were prepared by acid hydrolysis of cotton linter pulp fibers and three different purification methods, i.e., without post purification (CNC1), dialyzed against distilled water (CNC2), and neutralized with NaOH (CNC3), and their effect on film properties was evaluated by preparation of agar/CNCs composite films. All the CNCs were rod in shape with diameter of 15–50 nm and length of 210–480 nm. FTIR result indicated that there was no distinctive differences in the chemical structure between CNCs and cotton linter cellulose fiber. No significant relationship was observed between the sulfate content and crystallinity index of CNCs. The CNC3 showed higher thermal stability than the other type of CNCs due to the less adverse effect on the thermal stability of sulfate groups induced by the neutralization with NaOH. The tensile strength (*TS*) of agar film increased by 15% with incorporation of 5 wt% of CNC3, on the contrary, it decreased by 10% and 15% with incorporation of CNC1 and CNC2, respectively. Other performance properties of agar/CNCs composite films such as optical and water vapor barrier properties showed that the CNC3 was more effective filler than the other CNCs. In the range of concentration of CNC3 tested (1–10 wt%), inclusion of 5 wt% of CNC3 was the maximum concentration for improving or maintaining film properties of the composite films. The neutralization of acid hydrolyzed cellulose using NaOH was simple and convenient for the preparation of CNC and bionanocomposite films.

1. Introduction

As the advent of nanotechnology, various types of nano-sized filler materials such as nanoclays, metallic nanoparticles, and nanocellulose have been exploited to improve properties of packaging materials such as physical, mechanical, and gas barrier properties (Rhim, Park, & Ha, 2013). Among the nanofiller materials, nanocellulose has attracted interest due to their unique features such as biodegradability, renewability, abundance with high modulus and mechanical strength, high specific surface area, and low density (Azizi Samir, Alloin, & Dufresne, 2005). Such properties made them attractive for their use in nanocomposite materials (Xu et al., 2013). Nanocellulose can be isolated from any cellulose-containing materials by various mechanical methods such as high-pressure homogenization, grinding, ultrasonication or high-speed blending (Li et al., 2012; Li et al., 2014), chemical methods including sulfuric acid, hydrochloric acid, or TEMPO (2,2,6,6-tetramethylpyperidine-L-oxyl) oxidation (Jiang & Hsieh, 2013; Rhim, Reddy, & Luo, 2015), enzyme-assisted hydrolysis (Henriksson, Henriksson, Berglund, & Lindstrorn, 2007), as well as a combination of two or several of the above mentioned methods (Alemdar & Sain, 2008; Chen et al., 2011). Nanocellulose materials obtained by the chemical methods are relatively uniform in size with high crystallinity (Jiang & Hsieh, 2013). Among the chemical methods, acid hydrolysis is the most widely used method to prepare cellulose nanocrystals (Jiang & Hsieh, 2013; Rhim et al., 2015). Strong acids such as hydrochloric acid and sulfuric acid can be used to prepare crystal forms of nanocelluose. Hydrolysis of cellulose fiber using hydrochloric acid produces nanocellulose with minimal surface charge, and the nanocrystals formed are inclined to aggregate due to lack of the electrostatic repulsion force between crystal particles (Wang, Ding, & Cheng, 2007). On the contrary, hydrolysis of cellulose fiber using sulfuric acid produces cellulose nanocrystals in a more stable colloidal suspension (Teixeira, Correa, Manzoli, Leite, Oliveira, & Mattoso, 2010) since the surface hydroxyl groups of cellulose fibers are esterified to form anionic sulfate ester groups (Beck-Candanedo, Roman, & Gray, 2005), however, the high sulfate content of the cellulose nanocrystals causes a decreased thermal

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stability. Therefore, sulfuric acid hydrolysis have been widely used with various cellulose materials such as coconut husk fibers (Rosa et al., 2010), cotton linter (Morais et al., 2013), rice straw (Jiang & Hsieh, 2013), bacterial cellulose (Roman & Winter, 2004), wood (Beck-Candanedo et al., 2005), and agricultural processing waste (Rhim et al., 2015). However, the presently used acid hydrolysis method for the isolation of cellulose nanofiber has some limitations, such as prolonged time and cost to remove free sulfuric acid in the cellulose nanofiber after hydrolysis process, for their use in industrial scale. The free sulfuric acid in the cellulose nanofibers are usually removed by dialysis against water until they reach to neutral pH, which is costly and takes long time (more than two or three days). The presence of sulfate groups, the divalent group or anionic SO_4^{2-} or $-OSO_2O-$ of sulfuric acid and sulfates, on the surface of nanocellulose reduces interaction of the cellulose with other polymeric materials (Kontturi, Tammelin, & Osterberg, 2006). In addition, even low levels of sulfate groups onto the surface of fibers cause a significant decrease in the thermal stability of nanocellulose (Roman & Winter, 2004). To overcome such problem, cellulose nanocrystal suspension produced by mixed sulfuric acid and hydrochloric acid was adjusted to pH about 9 using sodium hydroxide, then washed with distilled water until to reach the neutrality (Wang et al., 2007). However, this process also took a long time. Compared with the time-consuming dialysis method, the chemical neutralization method is simple with less processing steps to prepare cellulose nanocrystals, especially this method is efficient when the cellulose nanofibers are used to make composite with other polymer and biopolymer materials. To the best of our knowledge, no work on the preparation of bionanocomposite blended with cellulose nanocrystals produced by this method has been reported.

In the present study, agar-based nanocomposite films were prepared by blending agar with cellulose nanocrystals isolated from cotton linter pulp using the acid hydrolysis and neutralization with NaOH. Agar has been chosen because it is not only renewable, biodegradable, biocompatible, and abundantly available, but also it has good film forming ability with high mechanical strength and moderate water resistance (Gimenez, Lopez de Lacey, Perez-Santín, Lopez-Caballero, & Montero, 2013). Agar has been used to form composite films with various biopolymers such as carrageenan and konjac glucomannan (Rhim & Wang, 2013), and gelatin (Gimenez et al., 2013) to improve physical and mechanical properties of the films. It has also been used as a carrier or matrix of antimicrobial materials such as grapefruit seed extract (Kanmani & Rhim, 2014), silver nanoparticles (Rhim, Wang, Lee, & Hong, 2014), copper nanoparticles (Shankar, Teng, & Rhim, 2014), and clay (Rhim, 2011). Cellulose nanocrystals have been used to improve mechanical and gas barrier properties of agar-based films (Reddy & Rhim, 2014). Cotton linters are short fibers adhered to cottonseed after ginning and obtained as leftover in the textile industry as they are too short for normal uses (Lu, Weng, & Cao, 2005; Savadekar, Karande, Vigneshwaran, Kadam, & Mhaske, 2014). Cotton linter contains high cellulose content (80% of holocellulose with 75% of α-cellulose) (Morais et al., 2013) compared with other natural resources. Cellulose nanocrystals isolated from cotton linter have been used as nanofiller to improve the properties of fish gelatin (Santos et al., 2014), chitosan (Li, Zhou, & Zhang, 2009), and thermoplastic starch (Savadekar et al., 2014) films.

Therefore the main objective of the present study was to test the efficiency of the proposed method of acid hydrolysis of cellulose fiber followed by neutralization with NaOH without tedious process of dialysis. Isolated cellulose nanocrystals were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The effect of sulfate content and concentration of nanocrystals on the mechanical properties, water vapor permeability (WVP), water contact angle (CA), surface color, transparency as well as SEM and XRD analysis of agar/cellulose nanocrystals composite films were also tested.

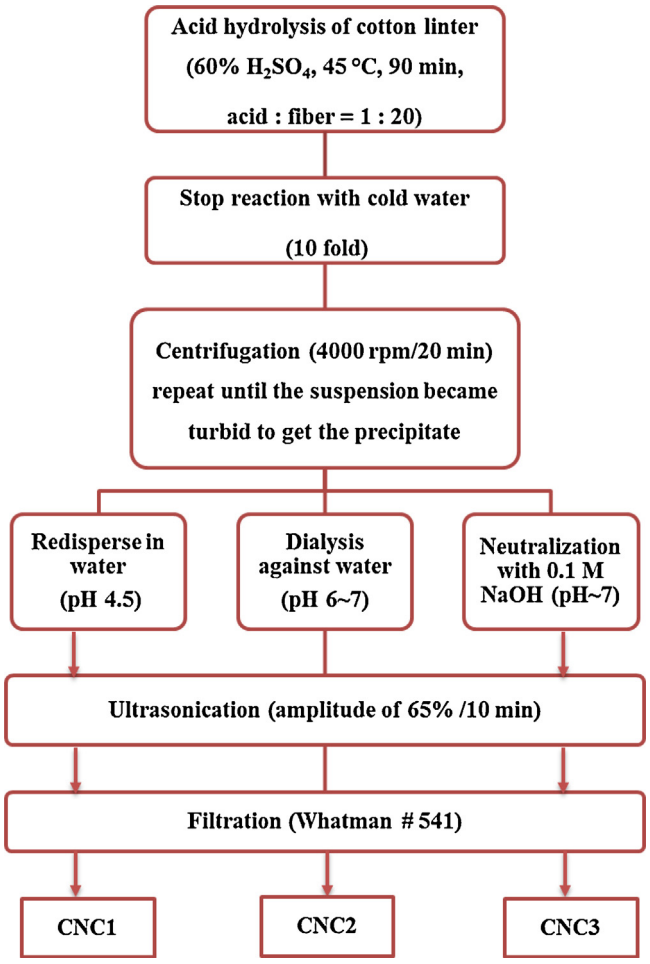

Fig. 1. Procedure for the preparation of cellulose nanocrystals (CNCs) from cotton linter pulp fiber.

2. Materials and methods

2.1. Materials

Food grade agar was obtained from Fine Agar Co., Ltd. (Damyang, Jeonnam, Korea). Glycerol was procured from Daejung Chemicals & Metals Co., Ltd. (Siheung, Gyeonggi-do, Korea). Sulfuric acid and sodium hydroxide were purchased from Duksan Pure Chemicals Co., Ltd (Ansan-city, Gyeonggi-do, South Korea). Cotton linter pulp (CLP-A; α-cellulose 99.1%, viscosity 8.4 cP, DPn 465, DPw 1745) was generously donated from COMSCO (Korea Minting and Security Printing Corporation, Daejeon, Korea).

2.2. Preparation of cellulose nanocrystals (CNCs)

Cotton linter pulp was ground to fine powder using a laboratory scale blender (Green Mix, model DA700-G, Artlon, Seoul, Korea), then cellulose nanocrystals (CNCs) were isolated from the fiber using acid hydrolysis and post-purification methods as shown in Fig. 1. The finely disintegrated cotton linter fiber was hydrolyzed with pre-heated 60% sulfuric acid with fiber to acid ratio of 1:20 at 45 °C for 90 min with strong agitation. The reaction was quenched by adding 10-fold of cold water and the suspension was centrifuged at 4000 rpm for 20 min using a bench–top centrifuge (Hanil