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Preparation and characterization of sodium carboxymethyl cellulose/cotton linter cellulose nanofibril composite films

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ABSTRACT

Crystalline cellulose nanofibril (CNF) was isolated from cotton linter pulp using an acid hydrolysis method and used as a filler to reinforce sodium carboxymethyl cellulose (CMC) film. The CNF was in rod shape with the diameter of 23–38 nm and the length of 125–217 nm and crystallinity index (CI) was 0.89. The effect of CNF concentration (1, 3, 5, and 10 wt% based on CMC) on the optical, morphological, mechanical, water vapor barrier, surface hydrophobicity, and thermal properties of the nanocomposites were studied. The CNF was evenly distributed in the polymer matrix to form smooth and flexible films indicating the CNF is highly compatible with the CMC. The tensile strength (TS) and elastic modulus (EM) of CMC film increased by 23% and 27%, respectively, while the elongation (E) decreased by 28% with 5 wt% of CNF inclusion. The WVP of CMC film decreased at low content of CNF, and increased with increase in CNF content, then decreased but to the same level of the control CMC film with the inclusion of 10 wt% of CNF. Transparency of CMC film decreased slightly from 87.7% to 86.2% with 5 wt% of CNF. The CMC/CNF composite films have a high potential to be used as an edible coating or packaging films for the extension of shelf life of fresh and minimally processed fruits and vegetables.

1. Introduction

Recently, there has been an increasing interest in development and application of sustainable bio-based polymer films instead of petroleum-based plastic films due to the concerns on the exhaust of natural resources and environmental problems caused by the plastic films (Khan, Huq, Khan, Riedl, & Lacroix, 2014; Reddy, Vivekanandhan, Misra, Bhatia, & Mohanty, 2013). Thus the suitability of biomaterials, especially biopolymers, for film production have been intensively studied. Various biopolymers such as polysaccharides, proteins, and lipids obtained from plant and animal resources have been studied as an alternative or reduced use of non-biodegradable packaging materials since they are abundant, renewable, inexpensive, environmentally friendly as well as biodegradable and biocompatible (Tang, Kumar, Alavi, & Sandeep, 2012). Among those materials, polysaccharides are considered attractive source due to their good film forming property, good mechanical and gas barrier properties compared to other biodegradable materials (Rhim, Park, & Ha, 2013). Various polysaccharides such as chitosan (Li, Zhou, & Zhang, 2009), thermoplastic starch (Savadekar, Karande, Vigneshwaran, Kadam, & Mhaske, 2014), agar (Reddy & Rhim, 2014), carrageenan (Rhim & Wang, 2014), and carboxymethyl cellulose (Ghanbarzadeh & Almasi, 2011) have been studied to make biodegradable packaging films. However, the industrial utilization of natural biopolymer-based packaging films has not been materialized due to their poor mechanical and barrier properties (Rhim & Ng, 2007). One of the methods to overcome such problems of biopolymer-based packaging materials is to make composite with other filler materials. With the advent of nanotechnology, various types of nano-sized filler materials such as nanoclays, nanometals, and cellulosic nanofibers have been utilized to improve the physical, mechanical, and gas barrier properties of biopolymer films (Rhim et al., 2013). These are mainly due to the strong interfacial interaction between the nano-sized filler and polymer matrix as well as the formation of tortuous pathway of gas diffusion induced by the impervious nanofillers. Among the nanofillers, natural cellulosic nanofibers isolated from various natural resources, such as stems of plants like jute, flax, ramie, and hemp, and byproducts of agricultural crops, have been gaining considerable attention due to their unique and attractive features such as biodegradability, biocompatibility, renewability, abundance, high aspect ratio, and light weight (Kalia et al., 2011).

In the present work, we focused on the preparation of cellulose nanofibrils (CNF) from cotton linter and its application

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in the preparation of carboxymethyl cellulose (CMC)-based nanocomposite films. CMC is the most widely used cellulose derivative, which composed of ß-D-glucose and ß-D-glucopyranosyl-2-*O*-(carboxymethyl)-monosodium salt connected via β-(1,4-glycosidic) bonds (Rachtanapun, Luangkami, Tanprasert, & Suriyatem, 2012). CMC has been widely used in the pharmaceutical and food processing industries (Ghanbarzadeh & Almasi, 2011; Schmitt, Sanchez, Desobry-Banon, & Hardy, 1998) since it is abundantly available biopolymer with non-toxic, biodegradable, biocompatible, and good film forming properties (Almasi, Ghanbarzadeh, & Entezami, 2010). Moreover, CMC film is known to be a very efficient barrier against oxygen, carbon dioxide, and lipid (Li, Shoemaker, Ma, Shen, & Zhong, 2008). For these reasons, CMC has been used as highly effective additive to improve polymer film properties (Almasi et al., 2010), and as edible coating to improve quality and shelf life of fresh fruits and vegetables (Togrul & Arslan, 2004).

Cotton linters are short, thick-walled, curly and cylindrical fibers adhered to cottonseed after ginning, which is obtained as by-products in the textile industry (Lu, Weng, & Cao, 2005). Cotton linters are produced about 2.5 million metric tons annually in the world, which is comparable to the production of 42 million metric tons of cotton lint in 2010 (FAOSTAT, 2012; Morais et al., 2013). Cotton linter is considered as one of the most attractive cellulose nanofiber sources since it contains higher content of cellulose (80% of holocellulose with 75% of α-cellulose) (Morais et al., 2013) compared with other natural resources such as sisal (67–78%) (Oksman, Mathew, Långström, Nyström, & Joseph, 2009), bagasse of sugarcane (44.9–45%) (Cerqueira, Filho, & Meireles, 2007), and bamboo (41.8–54.0%) (Ardanuy, Claramunt, García-Hortal, & Barra, 2011). Cellulose nanofibers isolated from cotton linter have been tested as a reinforcing nanofiller to improve the film properties of various biopolymers such as fish gelatin (Santos et al., 2014), starch (Lu et al., 2005; Savadekar et al., 2014), soy protein isolate (Wang, Cao, & Zhang, 2006), and chitosan (Li et al., 2009) films. However, no works on the use of cotton linter nanofiber composited with CMC are available.

Therefore, the main objective of the present study was to isolate cellulose nanofibril from cotton linter and prepare CMC/cellulose nanofibril composite film to test the potential use of the biopolymer film. Isolated cellulose nanofibrils were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA), and the properties of nanocomposite films were evaluated by measuring mechanical properties, water vapor permeability (WVP), water contact angle (CA), surface color, transparency as well as SEM and TGA analysis.

2. Materials and methods

2.1. Materials

Sodium carboxymethyl cellulose (CMC) was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). Glycerol and sulfuric acid were procured from Daejung Chemicals & Metals Co., Ltd. (Siheung, Gyeonggi-do, Korea) and Duksan Pure Chemicals Co., Ltd (Ansan, Gyeonggi-do, Korea), respectively. Cotton linter pulp (CLP-A; α-cellulose 99.1%, viscosity 8.4 cPs, DPn 465, DPw 1745) was generously donated from COMSCO (Korea Minting and Security Printing Corporation, Daejeon, Korea).

2.2. Isolation of cellulose nanofibril (CNF)

Crystalline cellulose nanofibril (CNF) was isolated from cotton linter pulp by acid hydrolysis method (Morais et al., 2013; Reddy & Rhim, 2014) with slight modification. Fiber of the cotton linter pulp was separated by using a laboratory scale blender (Green Mix, model DA700-G) to separate fibers, and then dried in a hot air oven at 70 °C for at least 2 h and ground to powder. Five grams of the dried cotton linter pulp powder was hydrolyzed with 100 mL of pre-heated sulfuric acid (60%) at 50 °C for 90 min with strong agitation. The reaction was quenched by adding abundant cold distilled water to the mixture and the resulting mixture was then cooled to the room temperature. The suspension was centrifuged at 4000 rpm for 20 min using a bench-top centrifuge (Hanil Scientific Centrifuge, Incheon, Gyeonggi-do, Korea) and repeated 3 times to remove the excess sulfuric acid. The precipitate was re-suspended in distilled water and dialyzed against water using dialysis tubing (cellulose membrane with molecular cut-off of 14,000, Sigma-Aldrich, St Louis, MO, USA) until neutrality was attained. The suspension was homogenized using a high shear mixer (T25 basic, Ika Labotechnik, Janke & Kunkel Gmbh & Co., KG Staufen, Germany) at 7000 rpm for 5 min in an ice water bath, and then was sonicated using a high intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., New-Town, CT, USA) at 75% amplitude with pulse of 5 s on and 2 s off for 10 min in an ice water bath. The suspension was centrifuged at 4000 rpm for 30 min to remove aggregated and incompletely hydrolyzed fibers. The suspension of CNF was collected and stored in a refrigerator at 3 °C before further characterization and use for the preparation of nanocomposite film with CMC.

2.3. Preparation of nanocomposite film

Sodium-carboxymethyl cellulose (CMC) and CMC/CNF composite films were prepared using casting method following the method of (Reddy & Rhim, 2014) with minor modification. Control film was prepared by adding 3 g (2% w/v) CMC and 0.9 g glycerol (30% of CMC weight) to 150 mL distilled water. The solution was heated at 90 °C for about 20 min until completely dissolve. CMC solution was casting onto a balance leveled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plate (24 cm × 30 cm) and dried at room temperature. Before peeling, the films were dried in oven for 2 h/40 °C. For preparation of CNF composite film, amount of CNF (1, 3, 5 and 10% according to CMC weight) was mixed with 150 ml distilled water and stirring for 2 h at room temperature. After that, the suspension was homogenized (T25 basic, Ika Labotechnik, Janke & Kunkel Gmbh & Co., KG Staufen, Germany) at 8,000 rpm/10 min. Then, 3 g of CMC and 0.9 g of glycerol were added to the CNF suspension and heated at 90 °C/20 min then casting as same as control film. Before characterization, films were kept in a humidity chamber condition 25 °C/50 RH for 4 days.

2.4. Characterization

Microstructure of cotton linter fiber and CMC/nanocomposite films were tested 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. The morphology and dimensions of cotton linter nanofibrils were determined by scanning transmission electron microscopy (STEM) using the FE-SEM instrument with transmission mode. For this, the CNF suspension was diluted to 0.01 wt% in distilled water and then 10 μL of the solution was dropped onto a 300 mesh nickel grid. After 20 min, the excess liquid was removed by blotting with a filter paper and allowed to dry under the ambient condition.

Fourier transform infrared (FT-IR) spectra of fiber samples were obtained using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrophotometer (TENSOR 37