



Preparation of nanocellulose from micro-crystalline cellulose: The effect on the performance and properties of agar-based composite films



Shiv Shankar, Jong-Whan Rhim*

Department of Food Engineering and Bionanocomposite Research Institute, Mokpo National University, 61 Dorimri, Chungkyemyon, Muangun, 534729 Jeonnam, Republic of Korea

ARTICLE INFO

Article history:

Received 23 July 2015

Received in revised form 15 August 2015

Accepted 25 August 2015

Available online 29 August 2015

Keywords:

Nanocellulose

Micro-crystalline

Cellulose

Agar

Composite films

ABSTRACT

A facile approach has been performed to prepare nanocellulose (NC) from micro-crystalline cellulose (MCC) and test their effect on the performance properties of agar-based composite films. The NC was characterized by STEM, XRD, FTIR, and TGA. The NC was well dispersed in distilled water after sonication and their size was in the range of 100–500 nm. The XRD results revealed the crystallinity of NC. The crystallinity index of NC (0.71) was decreased compared to the MCC (0.81). The effect of NC or MCC content (1, 3, 5 and 10 wt% based on agar) on the mechanical, water vapor permeability (WVP), and thermal properties of the composites were studied. The NC obtained from MCC can be used as a reinforcing agent for the preparation of biodegradable composites films for their potential use in the development of biodegradable food packaging materials.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, the demands of products made from renewable and sustainable resources that are biodegradable, carbon neutral, non-petroleum based, and have low environmental, animal/human health and safety risks are increasing by the consumers, industry, and the government (Duncan, 2011; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Rhim, Park, & Ha, 2013). Thus the suitability of biomaterials, especially biopolymers, for film production have been intensively studied. Various biopolymers such as polysaccharides, proteins, and lipids have been considered as an alternative biodegradable packaging materials because of their abundant availability, renewable, inexpensive, environmentally friendly, biodegradable, and biocompatible nature (Duncan, 2011; Rhim et al., 2013; Tang, Kumar, Alavi, & Sandeep, 2012). Among these materials, polysaccharides are most widely utilized and studied for food packaging applications due to their good film forming property and good mechanical and gas barrier properties compared with other biopolymeric materials (Rhim et al., 2013). Various polysaccharides such as agar (Shankar, Teng, & Rhim, 2014), carboxymethyl cellulose (Ghanbarzadeh & Almasi, 2011), carrageenan

(Paula et al., 2015), chitosan (Li, Zhou, & Zhang, 2009), and thermoplastic starch (Savadekar, Karande, Vigneshwaran, Kadam, & Mhaske, 2015) have been studied to make biodegradable packaging films. However, owing to the poor mechanical and barrier properties of biopolymer-based packaging films, the industrial utilization has not been materialized (Rhim et al., 2013). With the advent of nanotechnology, various types of nano-sized filler materials such as nanoclays, metallic nanoparticles, and nanocelluloses have been utilized to improve the physical, mechanical, and gas barrier properties of biopolymer films (Rhim et al., 2013). Among the nanofillers, nanocellulose isolated from various natural resources, such as jute, flax, rice straw, paper mulberry pulp, and by-products 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). However, acid hydrolysis techniques has been utilized to prepare nanocellulose from cellulose microfiber (Reddy & Rhim, 2014). In the present study, nanocellulose (NC) was prepared from micro-crystalline cellulose using facile approach without using any harmful chemicals like sulfuric acid and hydrochloric acid.

Among the biopolymers, agar has a potential for making biodegradable films for packaging applications (Kanmani & Rhim, 2014; Shankar et al., 2014). Agar is a polysaccharide derived from red algae contains two components such as agarose and

* Corresponding author.

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

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 clay, silver, and copper nanoparticles and reported that the mechanical and water vapor permeability have been improved with the addition of nanofillers (Rhim et al., 2013; Shankar et al., 2014; Shankar & Rhim, 2015). However, there are no reports on reinforcement of nanocellulose from regenerated MCC into agar based composites available in the literature. Therefore, in the present study, nanocellulose prepared from MCC was reinforced into agar polymer film and the films were characterized using various techniques.

2. Materials and methods

2.1. Materials

All chemicals were procured from Sigma–Aldrich (St. Louis, MO, USA) unless otherwise stated. Food grade agar was procured from Gel Tec Co., Ltd. (Seoul, Korea).

2.2. Preparation of cellulose nanoparticles

Nanocellulose (NC) was prepared from microcrystalline cellulose (MCC) by the method of Adsul, Soni, Bhargava, and Bansal (2012). For this, 5 g of microcrystalline cellulose (MCC) was added into 100 mL solution of 7% (w/w) NaOH and 12% (w/w) urea and the solution was stirred for 30 min at room temperature, then kept in a freezer at -20°C for 16 h. The content was stirred using a magnetic stirrer at 1000 rpm for 10 min until the MCC dissolved completely. The dissolved MCC was regenerated by adding an excess amount (~ 1000 mL) of double distilled water (DDW). The regenerated cellulose was separated by centrifugation at 3000 rpm for 10 min. The regenerated cellulose was washed with double distilled water for 6–7 times to remove the remnant of urea and NaOH and bring down the pH around 7–9. The regenerated MCC was suspended in DDW and ultrasonicated for 5 min using a 2 mm probe at 75% amplitude (SONICS Vibra cell; model VC 130, Sonic & Materials, Inc., Newtown, CT, USA). The dispersed cellulose, nanocellulose (NC), was kept at 4°C until further used.

2.3. Characterization of cellulose nanoparticles

The morphology and size of MCC were determined by FE-SEM (S-4800, Hitachi Co., Ltd., Matsuda, Japan). The size and shape of NC was determined by scanning transmission electron microscopy (STEM, FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan). The aqueous suspension of NC was dropped on a carbon coated copper grid, air dried and image was analyzed using FE-SEM in the transmission mode.

Fourier transform infrared (FTIR) spectra of MCC and NC were collected using a FTIR spectroscopy (SENSOR 37 Spectrophotometer with OPUS 6.0 software, Billerica, MA, USA) at a resolution of 4 cm^{-1} in the range of $500\text{--}4000\text{ cm}^{-1}$. The crystalline nature of MCC and NC was determined by XRD (PANalytical Xpert pro MRD diffractometer, Amsterdam, Netherlands) by placing MCC and NC powders on a glass slide and spectra were recorded using $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA with scanning at $2\theta = 5\text{--}50^{\circ}$. The degree of crystallinity (DC) of MCC and NC was calculated using following equation (Shankar & Rhim, 2015):

$$\text{DC} = \frac{I_{200} - I_{\text{am}}}{I_{200}}$$

where I_{200} is the intensity of the peak at (200) lattice and I_{am} is the intensity of the peak at amorphous region. The crystallite size

(D) of the MCC and NC was calculated in nm using the Scherrer's equation (Reddy & Rhim, 2014):

$$D = \frac{K\lambda}{\beta_{1/2} \cos \theta}$$

where K is the Scherrer constant (0.94), λ is the X-ray wavelength ($\lambda = 0.154056\text{ nm}$), $\beta_{1/2}$ is the full width at the half maximum of the deflection peak (FWHM), and θ is Bragg's angle.

2.4. Preparation of agar/cellulose nanocomposite film

Agar, agar/MCC, and agar/NC composite films were prepared using a solution casting method following the method of Shankar et al. (2014). For the preparation of agar film, 3 g of agar powder was dissolved into 150 mL of distilled water including 0.9 g of glycerol (a plasticizer) while mixing vigorously for 30 min at 95°C using a magnetic stirrer. The solubilized film forming solution was cast evenly onto a leveled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plate ($24\text{ cm} \times 30\text{ cm}$), then dried for about 48 h at room temperature. In addition, agar/MCC and agar/NC composite films were prepared with different concentration of MCC and NC (1, 3, 5, and 10 wt% based on agar weight). For this, predetermined amount of MCC or NC was dispersed in 150 mL of distilled water and stirred vigorously for 1 h using a magnetic stirrer. The fully dispersed suspensions were homogenized using a high shear mixer (T25 basic, Ika Labortechnik, Janke & Kunkel GmbH & Co., KG Staufen, Germany) at 12,000 rpm for 10 min. Then, 0.9 g of glycerol were dissolved into the suspension while mixing vigorously for about 20 min. Finally, 3 g of agar was added slowly into the solution and mixed vigorously at 95°C using a hot plate stirrer and followed the same procedure for the preparation of the neat agar film. The dried films were peeled off from the casting plate and conditioned in a constant temperature–humidity chamber set at 25°C and 50% relative humidity (RH) for at least 48 h before further characterization.

2.5. Characterization of agar/AgNPs nanocomposite films

2.5.1. Morphological observation, FTIR, and XRD

Scanning electron microscopy (SEM) analysis was used to observe surface microstructure of agar and agar-based composite films. Film sample was cut into small pieces and directly mounted on a specimen holder and analyzed using a field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan) with an accelerating voltage of 5.0 kV.

Fourier transform infrared (FTIR) spectra of the films were obtained using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrophotometer (SENSOR 37 Spectrophotometer with OPUS 6.0 software, Billerica, MA, USA) operated at a resolution of 4 cm^{-1} . Film samples were cut into rectangular shapes ($5\text{ cm} \times 5\text{ cm}$) and directly placed on the ray exposing stage. The spectrum was recorded at wave number of $500\text{--}4000\text{ cm}^{-1}$.

X-ray diffraction (XRD) pattern of the films was analyzed by X-ray diffractometer (PANalytical X'pert pro MRD diffractometer, Amsterdam, Netherlands). Rectangular film samples ($2.5\text{ cm} \times 2.5\text{ cm}$) were placed on a glass slide and the spectra were recorded using $\text{Cu K}\alpha$ radiation (wavelength of 0.1541 nm) and a nickel monochromator filtering wave at 40 kV and 30 mA. The diffraction pattern was obtained at diffraction angles between $2\theta = 30$ and 80° with scanning speed of $0.4^{\circ}/\text{min}$ at room temperature.

2.5.2. Surface color and optical properties

The surface color of the films was measured using a Chroma meter (Konica Minolta, CR-400, Tokyo, Japan). A white standard color plate ($L = 97.75$, $a = -0.49$, and $b = 1.96$) was used as a

Download English Version:

<https://daneshyari.com/en/article/1383539>

Download Persian Version:

<https://daneshyari.com/article/1383539>

[Daneshyari.com](https://daneshyari.com)