Carbohydrate Polymers 150 (2016) 187–200

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Isolation of cellulose nanocrystals from grain straws and their use for the preparation of carboxymethyl cellulose-based nanocomposite films

Ahmed A. Oun[a,b], Jong-Whan Rhim[a,*]

[a] Department of Food Engineering and Bionanocomposite Research Institute, Mokpo National University, 61 Dorimri, Chungkyemyon, Muangun, 534-729 Jeonnam, Republic of Korea
[b] Food Engineering and Packaging Department, Food Technology Research Institute, Agricultural Research Center, Giza, Egypt

ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form 4 May 2016
Accepted 7 May 2016
Available online 10 May 2016

Keywords:
Rice straw
Wheat straw
Barley straw
Cellulose nanocrystals
Carboxymethyl cellulose
Bio-nanocomposite

ABSTRACT

Cellulose nanocrystals (CNCs) were isolated from rice straw (RS), wheat straw (WS), and barley straw (BS) by using acid hydrolysis method. They were fibrous in shape with length (L) of 120–800 nm and width (W) of 10–25 nm, aspect ratio (L/W) of 18, 16 and 19, crystallinity index (CI) of 0.663, 0.710, and 0.634, and yield of 64, 75, and 69 wt% for RS, WS, and BS respectively. Carboxymethyl cellulose (CMC)/CNC composite films were prepared with various concentration of the CNCs. SEM results showed that the CNCs were evenly distributed in the polymer to form homogeneous films. Mechanical and water vapor barrier properties were varied depending on the type of CNCs and their concentration. Tensile strength (TS) increased by 45.7%, 25.2%, and 42.6%, and the water vapor permeability (WVP) decreased by 26.3%, 19.1%, and 20.4% after forming composite with 5 wt% of CNCs obtained from RS, WS, and BS, respectively.

1. Introduction

Cellulose nanocrystals (CNCs) have been emerging as a new class of nanomaterials that can be used as a reinforcing component for the preparation of high performance nanocomposites due to their unique properties such as biodegradability, renewability, non-toxicity, high modulus and mechanical strength, high specific surface area, with interesting surface chemistry and optical properties (Habibi, Lucia, & Rojas, 2010; Peng, Dhar, Liu, & Tam, 2011; Zhou & Wu, 2012). Nanocellulose materials are generally produced by mechanical methods (Silva, Couturier, Berrin, Buléon, & Rouau, 2012), chemical methods (Jiang & Hsieh, 2013; Reddy & Rhim, 2014), chemo-mechanical (Alemdar & Sain, 2008b), and a combination of the methods. CNCs are usually produced by strong acid hydrolysis of cellulose to remove amorphous parts to obtain highly crystalline forms of cellulose (Lu & Hsieh, 2012). On the contrary, cellulose nanofibrils are usually obtained by mechanical method, TEMPO-mediate oxidation method or enzymatic hydrolysis (Lavoine, Desloges, Dufresne, & Bras, 2012). The properties of nanocellulose materials are affected by the source of cellulose, pretreatment, isolation method and isolation conditions (Chen et al., 2011; Jiang & Hsieh, 2013; Li et al., 2014; Oun & Rhim, 2015a).

CNCs are obtained from a variety of renewable bioresources such as wood, cotton, bacterial cellulose, agricultural crops, and agricultural cellulosic wastes (Li, Mascheroni, & Piergiovanni, 2015). Wood or cotton have been considered as the most important source of cellulosic fibers, however, concerns on the environment and diminishing of forest caused by the increased demand for wood resources led to the increased interest in the exploitation of non-wooden cellulosic materials (Ashori & Nourbakhsh, 2010; Tang, Kumar, Alavi, & Sandeep, 2012). Recently, ligno-cellulosic materials derived from food processing and agricultural processing waste or by-products such as grain straws, coconut fibers, maize cobs, bagasse fibers, peanut shells, stalks of cereal crops and sugar palm tree have been used for the preparation of CNCs (Ashori & Nourbakhsh, 2010; Hassan, Fadel, El-Wakil, & Oksman, 2011; Panthapulakkal, Zereshkian, & Sain, 2006; Sahari, Sapuan, Zainudin, & Maleque, 2013). The ligno-cellulosic resources derived from agricultural wastes or by-products are of particular interest due to their abundance, low cost, hollow cellular structure, renewability, and biodegradability (John & Thomas, 2008). One of such agricultural wastes or by-products with high potential for the use

* Corresponding author.
E-mail addresses: jwrhim@mokpo.ac.kr, jwrhim@hanmail.net (J.-W. Rhim).

http://dx.doi.org/10.1016/j.carbpol.2016.05.020
0144-8617/

of renewable cellulosic resources is straw of cereal grains such as rice, wheat, and barley. Rice straw is composed of cellulose (38.3%), hemicellulose (31.6%), lignin (11.8%), and silica (18.3%) (Hessien, Rashad, Zaky, Abdel-Aal, & El-Barawy, 2009), while wheat straw is composed of cellulose (30–40%), hemicellulose (20–35%) and lignin (15–25%) (Ruiz et al., 2013), and barley straw contains 35–40% of cellulose, 20–30% of hemicellulose, and 8–15% of lignin (Garcia-Aparicio, 2007). Annually, billions of tons of grain straws have been produced in the world, but only a small portion of them is used for animal feed, production of biogas, biofuel, extraction of hemicellulose and lignin, and isolation of cellulose, whereas most of them are burned, especially in the developing countries (Hassan et al., 2011; Saha & Cotta, 2010; Sun, Jing, Fowler, Wu, & Rajaratnam, 2011).

In order for the value-added utilization of such under-utilized grain straws, efforts have been made to develop environmentally-friendly composite materials using celluloses obtained from agricultural processing by-products (John & Thomas, 2008). However, most of previous works have been focused on the preparation of nanofibers from grain straws by mechanical methods (ultra-high friction grinding and high-pressure homogenization) and sonication method for use as filler for making composites with biopolymers such as chitosan (Hassan et al., 2011), thermoplastic starch (Alemdar & Sain, 2008a), poly(vinyl chloride) (Kamel, 2004), and wheat gluten (Montano-Leyva et al., 2013). Only a few works on the isolation and characterization of cellulose nanocrystals from rice, wheat, and barley straws for the value-added utilization of them are available in the literature (Alemdar & Sain, 2008b; Jiang & Hsieh, 2013; Jiang, Kondo, & Hsieh, 2016; Jonoobi et al., 2015).

In order for the value-added utilization of the grain straws, CNCs were isolated from the grain straws and tested their reinforcing effect by preparation of carboxymethyl cellulose (CMC)/CNC composite films in the present study. CMC, as a polymer matrix, was chosen because it has a similar structure as the CNC thereby is expected to form compatible composite films. In fact, CMC is one of the most widely used cellulose derivatives which has been used in the food processing industries as a viscosity modifier, edible coating, and films as a carrier of functional materials and a barrier against oxygen and carbon dioxide, cosmetics as a thickener and emulsion stabilizer (Kono, 2014; Oun & Rhim, 2015b). Moreover, CMC has been used to produce hydrogel for wound dressing, drug delivery, agriculture, and sanitary pads (Saha, Saarai, Roy, Kitano, & Saha, 2011).

The objectives of the present work were isolation and characterization of CNCs from grain straws of rice, wheat, and barley, and preparation of CMC/CNC composite films to test the effect of incorporation of CNCs on the properties of CMC films such as morphology, mechanical, transparency and water vapor barrier properties.

2. Materials and methods

2.1. Materials

Rice straw (RS), wheat straw (WS), and barley straw (BS) were collected from local farms at Muan, Korea. Potassium hydroxide (KOH, 85%) and toluene (99.8%) were purchased from Sigma-Aldrich Co. (St Louis, MO, USA). Sodium chlorite ($NaClO_2$, 80%), sulfuric acid (H_2SO_4, 98%), acetic acid glacial (CH_3COOH, 99.7%), glycerol and ethanol (C_2H_6O, 99.9%) were procured from Daejung Chemicals & Metals Co. Ltd. (Siheung, Gyonggi-do, Korea). All chemicals were used as received without further purification. Sodium carboxymethyl cellulose (CMC) was obtained from Junsei Chemical Co., Ltd. (Tokyo, Japan).

2.2. Chemical analysis and isolation of cellulose

The chemical compositions (α-cellulose, hemicelluloses and lignin) of the straws were determined according to quantitative analysis method (Reddy & Rhim, 2014; Reddy, Maheswari, Reddy, Guduri, & Rajulu, 2010).

Cellulose was isolated from RS, WS, and BS following the method described by Lu and Hsieh (2012) and Reddy et al. (2010). Each straw was cut into small pieces with the length of 3–5 cm, and washed several times with hot water to remove dirt and aqueous soluble substances, then they were dried in an air oven at 60 °C for 48 h. Dried straw was ground into fine powder using a laboratory blender (Green Mix, model DA700-G, Artlon, Seoul, Korea) and passed through a sieve with 300 μm aperture to obtain a fine powder of the straw. Thirty grams of dried straw powder were dispersed into 450 mL of a mixed solvent of toluene and ethanol (2:1) for 20 h at room temperature and filtered using a filter paper (Whatman #41) and washed the residue with ethanol to get rid of extractives such as wax, pectin, and pigments, then dried using a hot air oven at 100 °C for 24 h. The percentage of extractives was calculated from the difference in weight before and after drying. The dewaxed samples were dispersed into 1000 mL of 1.4% (w/v) sodium chlorite solution and adjusted pH to 4 using 5% acetic acid and heated at 70 °C for 5 h to remove lignin. After the color of the solution turned into yellow, cold water was added to stop the reaction and washed with distilled water several times until the filtrate became neutral, then the residues were dried in a hot air oven until constant weight reached to obtain holocellulose (hemicellulose and α-cellulose). Lignin content was determined by the weight difference in this step. To remove hemicellulose, the dried holocellulose was dispersed into 600 mL of 5% KOH solution with stirring at room temperature for 24 h, and heated at 90 °C for 2 h, and then centrifuged at 4000 rpm for 20 min to get white cellulose slurry. The cellulose slurry was washed with copious amount of water until filtrate reached neutral and dried the cellulose at 105 °C using a dry oven to obtain α-cellulose. Hemicellulose content was determined by the weight difference.

2.3. Isolation of cellulose nanocrystals (CNCs)

Cellulose nanocrystals were isolated from cellulose obtained from RS, WS, and BS using an acid hydrolysis method (Oun & Rhim, 2015a). The dried cellulose was disintegrated using a laboratory scale blender (Green Mix, model DA700-G, Artlon Co., Ltd., Seoul, Korea) to get fine powder, and then 5 g of the powder was hydrolyzed using pre-heated 64% sulfuric acid with fiber to acid ratio of 1:20 at 50 °C for 75 min with strong agitation. The reaction was stopped by adding 10-fold of cold water and centrifuged at 4000 rpm for 20 min using a bench-top centrifuge (Hanil Scientific Centrifuge, Incheon, Gyonggi-do, Korea), which was repeated until the pH reached above 5. The precipitate was resuspended in 500 mL of distilled water using a homogenizer (T25 basic, Ika Labotechnik, Janke & Kunkel Gmbh & Co., KG Staufen, Germany) at 7000 rpm for 2 min, and then neutralized with 0.1 M NaOH solution. The suspension was sonicated using a high intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., New Town, CT, USA) for 10 min (pulses of 2 s on and 1 s off) with an amplitude of 65% using a plastic beaker in an ice water bath to avoid overheating, and followed by homogenization at 7000 rpm for 1 min to obtain CNCs. The CNCs were filtered through stainless steel mesh with an aperture of 75 μm to remove aggregated large particles, and stored in a refrigerator at 4 °C before further characterization. To determine the yield of CNCs, 35 mL aliquots of the suspension was weighed and dried at 40 °C until to reach the constant weight.