Carbohydrate Polymers 174 (2017) 291–298

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Research paper

Effect of oxidation time on the properties of cellulose nanocrystals from hybrid poplar residues using the ammonium persulfate

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ARTICLE INFO

Article history:
Received 14 May 2017
Received in revised form 18 June 2017
Accepted 20 June 2017
Available online 23 June 2017

Keywords:
Cellulose nanocrystal
Crystal structure
Regioselectivity
Size uniformity

ABSTRACT

This work was to investigate the influence of time on the properties of cellulose nanocrystals (CNCs) during the ammonium persulfate (APS) oxidation of hybrid poplar residues (HPHL). The CNCs at the different times were characterized by different techniques. The results showed that CNCs were thinned and shortened with increased oxidation time, and their yield, crystallinity index and zeta potential increased, however, these properties stayed constant after the APS oxidation for 16 h. At this time, the CNC yield was more than 50%, and the CNCs had a zeta potential of –48.84 mV and a CrI of 86.8%. More than 95% of CNCs had a width of 16.87 ± 5.92 nm, and 86.4% of them had a length-to-width ratio from 10 to 30. The primary hydroxyl groups were regioselectively oxidized during the APS treatment. Therefore, the CNCs with stable properties could be extracted from HPHL using APS oxidation.

1. Introduction

Cellulose nanocrystals (CNCs) are ideal and potential materials on which a new biopolymer composite industry would be based owing to their exceptionally high mechanical strength (modulus of 100–140 GPa), low density (1.6 g cm^{-3}), environmental sustainability, and anticipated low cost. CNCs have a high aspect ratio and a reactive surface of —OH groups that facilitates grafting chemical species to achieve different surface properties (Leung et al., 2011; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Apart from their potential use as reinforcing agents for industrial biocomposites, CNCs have also been fostered for a lot of applications including enzyme immobilization, drug delivery, biomedical applications, green catalysis, and metallic reaction templates (Klemm et al., 2011; Lin, Huang, & Dufresne, 2012; Peng, Dhar, Liu, & Tam, 2011). In order to generate CNCs, the amorphous segments in native cellulose have to be eliminated with acids, enzymes, oxidants, mechanical means, or a combination of these in multiple steps (Lin et al., 2012). Of all these methods, hydrolysis with mineral acids (H_2SO_4 or HCl) and TEMPO-mediated oxidation have been investigated most extensively (Habibi, Lucia, & Rojas, 2010). Recently, ammonium persulfate (APS), an oxidant with low long-term toxicity, high water solubility and low cost, has been used to produce highly crystalline carboxylated CNCs (Leung et al., 2011). Spherical CNCs with narrow distribution have been extracted from lyocell fibers using APS oxidation (Cheng et al., 2014). More uniform rod-like CNCs with a diameter of 5 nm and a length of 150 nm have been prepared using APS from microcrystalline cellulose (Lam et al., 2013). The APS oxidation is simple, amenable to scale-up because the procedure can be used to prepare CNCs directly from a variety of cellulosic biomass without any need to remove noncellulosic components such as lignin and hemicelluloses (Kargarzadeh et al., 2012; Leung et al., 2011). Hence, this method appears to be a promising alternative in comparison with thermos-catalytic method, TEMPO-oxidation, and the acid hydrolysis (Rozenberga et al., 2016).

Hybrid poplar is extensively planted for paper and plywood in China, and there are huge amounts of residues such as twigs, wood shaving and sawdust during the processing hybrid poplar wood. These residues provide a good source for hemicelluloses. Meanwhile, the residual solid fractions after the extraction of hemicelluloses (HPHL) from these hybrid poplar residues are rich in cellulose, and a good source for CNCs. However, no report has been found about the preparation of CNCs from HPHL by the APS oxidation so far.

It is well known that reaction time has been recognized as one of the most significant parameters to influence the CNC properties during the acid hydrolysis process (Kargarzadeh et al., 2012). The effect of the reaction time on the properties of CNCs has also been investigated using the acid hydrolysis (Bondeson, Mathew, & Oksman, 2006; Chen, Liu, Chang, Cao, & Anderson, 2009; Rosa et al., 2010). However, little has been known about the changes in the CNCs properties, about the oxidation regioselectivity to hydroxyl

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http://dx.doi.org/10.1016/j.carbpol.2017.06.080
0144-8617/

groups during the APS oxidation. All these information was very important for the efficient extraction of CNCs directly from lignocellulosic with APS oxidation.

Therefore, based on our previous result that the time is the most significant of all the factors during the APS oxidation of HPHL for CNCs, the present study is to examine the effects of APS oxidation time on the surface zeta potential, the crystal structure, the particle size and its distribution, and the morphology of the extracted CNCs. Moreover, the regioselectivity to hydroxyl groups in CNCs was examined at different oxidation times.

2. Materials and methods

2.1. Preparation of CNCs

HPHL was prepared (Jiang et al., 2014Jiang, Chen, Ge, & Zhang, 2014). Briefly, the dried and ground hybrid poplar sample was first extracted with toluene-ethanol for 6 h. The dewaxed sample was treated with 70% ethanol solution containing 1% NaOH aided by ultrasound. After filtration, the partially delignified solid residue was treated with 8% NaOH solution for polymeric hemicellulose at 90 °C, then was filtrated. The solid residue was dried at 40 °C under vacuum for 24 h, and ground. The fraction between 1.8 and 0.7 mm, defined as HPHL, was collected and sealed in a zipper-lock plastic bag and kept in a 4 °Cfor the next experimental work. It's main components were as follows: glucan (60.45%), xylan (4.74%), mannan (1.26%) and Klason lignin (29.85%) on a dry weight basis (Jiang et al., 2014). Cellulose content was based on the glucan in it.

2.5 g of the particulate HPHL was placed into a 500 ml round-bottomed flask and 250 ml of 1 mol l^{-1} APS solution was added. The resulting suspension was stirred with a magnetic stirrer and kept at 70 °C for a given time to yield a white suspension containing CNCs. After the given time, the suspension was immediately cooled to ambient temperature with tap water, and then it was centrifuged at Allegra 64R centrifugator (Beckman Coulter, USA.) with 16,000 rpm (relative centrifugal force (RCF) = 32,000) for 15 min. The supernatant was decanted, and 120 ml of water was added to the ensuing precipitate, followed by mixing up with Vortex (Scientific Industries, USA) and repeated centrifugation. The centrifugation/washing cycles were repeated 4 times until the solution conductivity was about 5 μS cm^{-1}, close to that of deionized water.

All the resulting precipitate was pooled and 100 ml of water was added to it, and stirred for 30 min. Then, the suspension was transferred to a 500-ml separatory funnel. 100 ml of water was added to the suspension again, and it was shaken violently. The suspension was settled and the large particles precipitated in 60 s were removed from it. The suspension exclusive of large particles was centrifuged at Allegra 64R centrifugator with 16,000 rpm for 15 min, and about 150 ml of supernatant was removed. Finally, all the remains (about 60 ml) were ultrasonicated using the Sonic System Scientz-IID (NingBo, Zhejiang) with the sonic power of 800 W. The ultrasound irradiated for 2 s every 2-s pause, and the total irradiation times were 60 s so that uniform and translucent colloid was formed. The colloidal suspension was lyophilized with Heto Powerdry LL3000 freeze dryer (Thermo, Denmark). The CNC yield was defined as the ratio of the mass of the obtained CNCs to the one of cellulose in HPHL.

2.2. Periodate oxidation of 12-h CNCs

In order to investigate if the hydroxyl groups at C2 and C3 in cellulose were oxidized during the APS oxidation of HPHL. Periodate oxidation of 12-h CNCs was conducted.

0.5 g 12-h CNCs, 0.66 g $NaIO_4$, 1.93 g NaCl and 32.5 ml water were mixed together and gently stirred at room temperature in the dark for 24 and 36 h, respectively. When the reaction was finished, excess periodate was decomposed with ethylene glycol and the treated CNCs was filtered and washed with deionized water until all periodate, salt and iodate ions were removed (Chen and van de Ven, 2016Chen & van de Ven, 2016). The periodate-oxidized CNCs were lyophilized with Heto Powerdry LL3000 freeze dryer (Thermo, Denmark) for next use.

All the experiment was carried out three times at the same conditions. All chemicals used in the study were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.3. Characterization of the CNCs

Conductometric titrations were conducted to determine the carboxylic acid content on the CNCs (Habibi, Chanzy, & Vignon, 2006), Briefly, CNCs (50 mg) were suspended in 10 ml of 0.01 mol l^{-1} HCl and ultrasonicated for 5 min to disperse them. The suspension was then titrated against 0.01 mol l^{-1} NaOH, and the carboxylic acid contents were determined from the resulting conductivity curves. Degree of oxidation (DO, mol hydroxyl groups per mol glucose) of the CNCs was calculated using the following equation:

$$DO = \frac{162 \times C \times (V_2 - V_1)}{w - 36 \times C \times (V_2 - V_1)} \qquad (1)$$

where C is the NaOH concentration (mol l^{-1}), V_1 and V_2 are the amount of NaOH (ml), corresponding to the first and the second inflection points in the titration curve, respectively; w the weight of the oven-dried sample (g); 162 and 36 correspond to the molecular weight of an anhydro-glucose unit (AGU) and the molecular weight difference between an AGU and the sodium salt of a glucuronic acid moiety, respectively.

Fourier transform infrared (FT-IR) spectra were collected from 4000 to 400 cm^{-1} for 64 scans at a resolution of 4 cm^{-1} using an FT-IR spectrophotometer (Nicolet 6700, USA). Samples were run as KBr pellets containing 1% finely ground samples.

The particle size distribution and zeta potential were determined on Zetasizer ZEN 3600 (Malvern, UK). The colloidal CNC suspension was diluted to 0.02 wt% with 5 mmol l^{-1} NaCl solution. Measurements were performed in triplicate at 25 °C. Particle size was determined by photon correlation spectroscopy (PCS). PCS is a light-scattering method. The measured CNC particle size values are the hydrodynamic diameters of equivalent spheres and do not represent actual physical dimensions of the rod-like CNC particles. However, they are valid for comparison purposes.

The X-ray diffraction was recorded at room temperature from 5° to 50° at a scanning speed of 0.02°/s with a Rigaku-D/Max-2550PC diffractometer (Rigaku, Japan) using Ni-filtered Cu K_α radiation of wavelength 0.1542 nm. The operating voltage and current were 40 kV and 20 mA, respectively.

Crystallinity index (CrI) was calculated from the ratio of the sum area of all crystalline peaks to the total area (Garvey, Parker, & Simon, 2005; Park, Baker, Himmel, Parilla, & Johnson, 2010). The average size of crystallite and the d-spacing were calculated from the Scherrer's and Bragg's equations, respectively.

$$L_{(hkl)} = \frac{k\lambda}{B_{(hkl)}\cos\theta} \qquad (2)$$

$$d_{(hkl)} = \frac{\lambda}{2\sin\theta} \qquad (3)$$

where (*hkl*) is the lattice plane, L(*hkl*) is the size of crystallite, k is the Scherrer's constant (0.94), λ is the X-ray wavelength (0.154 nm), B(*hkl*) is the FWHM (full width half maximum) of the measured *hkl* reflection and 2θ is the corresponding Bragg's angle. $d_{(hkl)}$ is the d-spacing of the lattice plane (*hkl*) (Garvey et al., 2005).