Carbohydrate Polymers 95 (2013) 32–40

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Chemically and mechanically isolated nanocellulose and their self-assembled structures

Feng Jiang, You-Lo Hsieh*

Fiber and Polymer Science, University of California, Davis, CA 95616, USA

ARTICLE INFO

Article history:
Received 16 November 2012
Received in revised form 5 January 2013
Accepted 9 February 2013
Available online xxx

Keywords:
Cellulose nanocrystals
Cellulose nanofibrils
Rice straw
Self-assembly
Cellulose Iβ

ABSTRACT

Cellulose nanocrystals (CNCs) and nanofibrils (CNFs) have been isolated from pure rice straw cellulose via sulfuric acid hydrolysis, mechanical blending and TEMPO-mediated oxidation to 16.9%, 12% and 19.7% yields, respectively. Sulfuric acid hydrolysis produced highly crystalline (up to 90.7% CrI) rod-like (3.96–6.74 nm wide, 116.6–166 nm long) CNCs with similarly negative surface charges (−67 to −57 mV) and sulfate contents but decreasing yields and dimensions with longer hydrolysis time. Mechanical defibrillated CNFs were 82.5% crystalline and bimodally distributed in sizes (2.7 nm wide and 100–200 nm long; 8.5 nm wide and micrometers long). TEMPO mediated oxidation liberated the most uniform, finest (1.7 nm) and micrometer long, but least crystalline (64.4% CrI) CNFs. These nanocellulose self-assembled into submicron (153–440 nm wide) fibers of highly crystalline (up to 90.9% CrI) cellulose Iβ structure upon rapid freezing (−196 °C) and freeze-drying. The self-assembling behaviors were analyzed based on nanocellulose dimensions, specific surfaces and surface chemistries.

1. Introduction

Cellulose, synthesized by many organisms including plants, marine animals, fungi and bacteria as an important structural component, is the most abundant polymer in nature and has long been a major renewable source of materials. In the native forms, the long poly(β-1,4-glucopyranose) chains are organized in highly crystalline 1.5–3.5 nm wide nanofibrils with intramolecular and intermolecular hydrogen bonds as part of larger microfibrils and macroscopic fibers (Habibi, Lucia, & Rojas, 2010; Klemm, Heublein, Fink, & Bohn, 2005). The nanofibrillar domains, generally referred as nanocellulose, can be separated from each other by overcoming the extensive and strong inter-fibrillar hydrogen bonds with harsh caustic chemicals, specific enzymes and/or intense mechanical forces. Nanocellulose, either in rod-like cellulose nanocrystals (CNCs) or longer cellulose nanofibrils (CNFs), has generated significant interest due to its nanoscale dimensions and superior properties including extraordinary elastic modulus of 150 GPa (Iwamoto, Kai, Isogai, & Iwata, 2009), low axial thermal expansion coefficient of 10^{-7} K^{-1} (Nishino, Matsuda, & Hirao, 2004) and high specific surface area (Heath & Thielemans, 2010; Saito, Uematsu, Kimura, Enomae, & Isogai, 2011).

Acid hydrolysis has been the primary method for isolating rod-like CNCs since early reports in the late 1940s (Nickerson & Habrle, 1947). Sulfuric acid hydrolysis has shown to produce relatively uniformly sized CNCs from a single source under a fixed condition, however, widely varied dimensions of 3–70 nm widths and 35–3000 nm lengths have been reported from different cellulose sources and hydrolysis conditions (Beck-Candanedo, Roman, & Gray, 2005; Elazzouzi-Hafraoui et al., 2008; Habibi et al., 2010). Other acids such as hydrochloric acid, hydrobromic acid as well as mixed acetic and nitric acids are also capable of hydrolyzing cellulose into CNCs, without esterifying the surfaces as in the case with sulfuric acid while in higher yields (Jiang, Esker, & Roman, 2010; Sadeghifar, Filpponen, Clarke, Brougham, & Argyropoulos, 2011; Zuluaga, Putaux, Restrepo, Mondragon, & Ganan, 2007). Strong acids hydrolyze cellulose chains in the less ordered regions, producing CNCs with higher crystallinities than the original source but usually at low yields of less than 30% (Bondeson, Mathew, & Oksman, 2006; Lu & Hsieh, 2012). A variety of mechanical defibrillation methods including high-pressure homogenization (Zimmermann, Bordeanu, & Strub, 2010), grinding (Abe & Yano, 2009), ultrasonication (Chen, Yu, & Liu, 2011), cryocrushing (Alemdar & Sain, 2008) and high-speed blending (Uetani & Yano, 2011) have shown to improve the yields, some to as high as 100% (Isogai, Saito, & Fukuzumi, 2011). These mechanical processes produce longer (several micrometers) but less uniformly sized (5–100 nm wide) (Siro & Plackett, 2010) and less crystalline (Iwamoto, Nakagaito, & Yano, 2007) CNFs. More uniform CNFs with 1–5 nm diameters have been isolated through oxidation using nitroxyl radical 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO) (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006). The TEMPO oxidized CNFs have been reported to have the same crystallinity as the starting materials (Saito, Kimura, Nishiyama, &

* Corresponding author. Tel.: +1 530 752 0843.
E-mail address: ylhsieh@ucdavis.edu (Y.-L. Hsieh).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.02.022

Isogai, 2007) and, when aided with mechanical means, over 90% yield (Isogai et al., 2011).

Rice straw is the largest crop residue globally and, with relatively high cellulose contents of ca. 40% (Lu & Hsieh, 2012), is a significantly under-utilized, non-wood cellulose source. Rice straw cellulose has been mechanically ground to 12–35 nm wide and several micrometer long nanofibrils with very similar crystal structures and mechanical properties as those from grinding wood and potato tuber (Abe & Yano, 2009). Sulfuric acid hydrolysis of rice straw cellulose, on the other hand, produced more uniformly sized CNCs, i.e., averaged 11.2 nm wide, 5.06 nm thick and 117 nm long, but at a very low 6% yield (Lu & Hsieh, 2012).

Furthermore, in freeze-drying these CNC suspensions to solid forms, cellulose nanocrystals were observed to self-assemble into micrometer-long, highly crystalline (91.2%) and nonporous or macroporous fibers with an average diameter of 386 nm that remained in the assembled fibrous form in suspensions with hand shaking and mechanical stirring for prolonged time (Lu & Hsieh, 2012). Cellulose nanofibers have been generated by electrospinning of cellulose and cellulose derivative solutions (Liu & Hsieh, 2002), a process relying on chemicals in dissolution and derivatization of cellulose which resulting in the loss of the native cellulose Iβ crystalline structure. The intriguing self-assembling behavior of CNCs suggests this cryogenic process to be an attractive non-chemical alternative for fabricating ultra-fine cellulose fibers from aqueous nanocellulose suspensions while achieving highest crystallinity surpassing even its source.

This study was to isolate nanocellulose from rice straw cellulose by different individual isolation approaches, to characterize nanocellulose structures in relationship to each isolation method as well as with each other and to investigate their self-assembling behaviors during rapid freezing and freeze-drying. Sulfuric acid hydrolysis, TEMPO-mediated oxidization and mechanical blending were individually applied to pure rice straw cellulose to isolate nanocellulose. The different forms of nanocellulose, i.e., CNCs and CNFs, and their yields, chemical and crystalline structures, thermal stability, physical dimensions, morphologies and surface properties were analyzed and compared. This represented the first report of TEMPO oxidation of rice straw cellulose as well as systematic comparisons of nanocellulose from a single and significant rice straw feedstock.

2. Experimental

2.1. Materials

Pure cellulose was isolated from rice straw (Calrose variety) by a three-step process of 2:1 v/v toluene/ethanol extraction, acidified $NaClO_2$ dissolution of lignin (1.4%, 70 °C, 5 h) and alkaline dissolution of hemicellulose and silica (5% KOH, 90 °C for 2 h) to a 36% yield (Lu & Hsieh, 2012). Sulfuric acid (H_2SO_4, 95–98%, ACS GR, EMD), hydrochloric acid (HCl, 1 N, Certified, Fisher Scientific), sodium hydroxide (NaOH, 1 N, Certified, Fisher Scientific), sodium hypochlorite (NaClO, 11.9%, reagent grade, Sigma–Aldrich), 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO, 99.9%, Sigma–Aldrich), sodium bromide (NaBr, BioXtra, 99.6%, Sigma–Aldrich) were used as received without further purification. All water used was purified by Milli-Q plus water purification system (Millipore Corporate, Billerica, MA).

2.2. Nanocellulose isolation

2.2.1. Cellulose nanocrystals (CNCs) by sulfuric acid hydrolysis

Rice straw cellulose was added to preheated (45 °C) sulfuric acid (64 wt%) at a 8.75 mL/g acid-to-cellulose ratio and proceeded at 45 °C under constant stirring for 15, 45 and 60 min. Hydrolysis was terminated by quenching with 10-fold cold water and the suspension was centrifuged (5000 rpm, 15 min) to collect the sediment which was dialyzed against water until neutral. Further centrifugation (5000 rpm, 30 min) yielded the supernatant as CNC suspension and the sediments consisting cellulose fragments from incomplete hydrolysis. The CNC suspension was then ultrasonicated in an ice bath for 5 min at 40% amplitude to disperse CNCs (Misonix ultrasonic liquid processors S4000), then filtered through 2 μm pore size syringe filter (Whatman Puradisc™ 25GD). The yields of CNCs were calculated gravimetrically based on the original pure rice straw cellulose and reported as percentages. The CNCs were referred as CNC15, CNC45 and CNC60 for the 15, 45 and 60 min reactions, respectively.

2.2.2. Cellulose nanofibrils by high-speed blending (CNF-B)

Cellulose nanofibrils were mechanically defibrillated from rice straw cellulose using a high-speed blender (Vitamix 5200) in three consecutive blending and separation steps. Cellulose (0.5 g) was added to 200 mL water and mixed with magnetic stirring bar for 5 min. The cellulose suspension was transferred to a 2L blender beaker and blended at 37,000 rpm for 60 min, reaching 97 °C. The suspension was cooled to room temperature, then centrifuged (1500 rpm, 15 min) to collect the first CNF-containing supernatant, referred as CNF-B60. The first precipitate was re-dispersed in 200 mL water and blended for another 30 min and centrifuged to obtain a second CNF-containing supernatant that was blended for a total of 90 min, referred as CNF-B90. The second precipitate was re-dispersed, blended for 30 min and centrifuged to obtain a third CNF-containing supernatant or CNF-B120. The final precipitate was referred as blended cellulose fibers (CF-B). The yields were calculated gravimetrically and cumulative yields were used to for CNF-B90 and CNF-B120. All three CNF-B supernatant were combined, concentrated in a rotary evaporator and designated as CNF-B for further characterization.

2.2.3. Cellulose nanofibrils by TEMPO mediated oxidation (CNF-T)

Cellulose (1.0 g) was added to 100 mL water and mixed with a magnetic stirrer for 5 min, then 2 mL of an aqueous mixture of TEMPO (0.016 g) and sodium bromide (0.1 g) was added and stirred for another 5 min. Oxidation reaction was initiated by adding 11.9% NaClO solution drop-wisely to reach 5 mmol NaClO per gram of cellulose. The pH decreased as oxidation proceeded and was adjusted to 10 ± 0.2 with 0.5 M NaOH. The oxidation reaction ended when no acid was produced or pH ceased to lower, lasting approximately 65 min. The pH was adjusted to 7 with 0.5 M HCl. The suspension was centrifuged (5000 rpm, 15 min), dialyzed against water and centrifuged (1500 rpm, 15 min) again to obtain the CNF-containing supernatant which was then concentrated using a rotary evaporator, ultrasonicated at 40% amplitude for 5 min in an ice bath, then filtered (Whatman 541) to remove large particulates. It should be noted that TEMPO oxidation was conducted without being aided by any other means of mechanical forces to study its sole ability to isolate cellulose nanofibrils. CNF prepared by TEMPO oxidation was named as CNF-T, and the yield was calculated gravimetrically. The final precipitate was also collected and referred as TEMPO oxidized cellulose fiber (CF-T).

2.3. Characterization

All aqueous suspensions were stored at 4 °C before surface charge and zeta potential characterization and imaging upon drying on specified substrates. Rapid freezing of 20 mL of dilute aqueous suspensions and precipitates, i.e., 0.1 wt% CNCs, CF-Ts, CNF-Ts and CF-Bs or 0.05 wt% CNF-Bs, was conducted by immersing each in 50 mL centrifuge tube in liquid nitrogen (−196 °C) and lyophilized