Carbohydrate Polymers 136 (2016) 485–492

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Preparation of highly charged cellulose nanofibrils using high-pressure homogenization coupled with strong acid hydrolysis pretreatments

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ARTICLE INFO

Article history:
Received 3 August 2015
Received in revised form
17 September 2015
Accepted 18 September 2015

Keywords:
Cellulose nanofibrils
High-pressure homogenization
Acid hydrolysis pretreatment
Surface charge

ABSTRACT

Cellulose nanofibrils (CNFs) are attracting much attention for the advantages of excellent mechanical strength, good optical transparency, and high surface area. An eco-friendly and energy-saving method was created in this work to produce highly negative charged CNFs using high-pressure mechanical defibrillation coupled with strong acid hydrolysis pretreatments. The morphological development, zeta potential, crystal structure, chemical composition and thermal degradation behavior of the resultant materials were evaluated by transmission electron microscopy (TEM), zeta potential analysis, X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), and thermogravimetric analysis (TGA). These CNFs were fully separated, surface-charged, and highly entangled. They showed a large fiber aspect ratio compared to traditional cellulose nanocrystrals that are produced by strong acid hydrolysis. Compared to hydrochloric acid hydrolysis, the CNFs produced by sulfuric acid pretreatments were completely defibrillated and presented stable suspensions (or gels) even at low fiber content. On the other hand, CNFs pretreated by hydrochloric acid hydrolysis trended to aggregate because of the absence of surface charge. The crystallinity index (CI) of CNFs decreased because of mechanical defibrillation, and then increased dramatically with increased sulfuric acid concentration and reaction time. FTIR analysis showed that the C—O—SO_3 group was introduced on the surfaces of CNFs during sulfuric acid hydrolysis. These sulfate groups accelerated the thermal degradation of CNFs, which occurred at lower temperature than wood pulp, indicating that the thermal stability of sulfuric acid hydrolyzed CNFs was decreased. The temperature of the maximum decomposition rate (T_{max}) and the maximum weight-loss rates ($MWLR_{max}$) were much lower than for wood pulp because of the retardant effect of sulfuric acid during the combustion of CNFs. By contrast, the CNFs treated with hydrochloric acid had better thermal stability, because no functional groups were introduced on the surface.

1. Introduction

Biomaterials are attracting much attention because they are environmentally friendly and sustainable. One biomaterial, cellulose is widely used for papermaking and garments, and is beginning to find application in bioenergy, and reinforcing agents in composites (Henriksson & Berglund, 2007; Iwamoto, Nakagaito, &Yano, 2007; Klemm et al., 2006). Cellulose consists of β-1,4 linked glucopyranose units (Azizi Samir, Alloin, & Dufresne, 2005; Chirayil, Mathew, Hassan, Mozetic, & Thomas, 2014; Khalil et al., 2014). Primary and secondary hydroxyl groups in cellulose result in intramolecular and intermolecular hydrogen bonding and provide abundant sites for surface modifications (Xu et al., 2013). Various novel materials including nanocrystals, whiskers, nanofibrils, and nanofibers have been produced from wood cellulose (Klemm et al., 2011). These sustainable nano-scale celluloses possess high mechanical strength, excellent optical transparency, high specific surface area, low weight, and biodegradability. These superior properties make nanocelluloses desirable candidates for tailoring materials properties and further broaden the scope of applications (Henrique et al., 2015; Tingaut, Zimmermann, & Sèbe, 2012; Xu, Liu, Jiang, Zhu, Haagenson, & Wiesenborn, 2013).

Cellulose nanocrystals (CNCs), the generally rod-like cellulose nanocrystals of 10–20 nm in width and several hundred nanometers in length (Xu et al., 2013), were firstly produced with sulfuric

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http://dx.doi.org/10.1016/j.carbpol.2015.09.055
0144-8617/

acid hydrolysis by Mukherjee and Woods (1953). Strong acid hydrolysis is the primary method used to produce highly crystalline CNCs, because the cellulose in amorphous regions is more accessible for hydrolysis in comparison with the chains in crystalline regions (Henrique et al., 2015; Tang, Yang, Zhang, & Zhang, 2014). Sulfate groups are introduced on the surface of CNCs during the hydrolysis process through the esterification of surface hydroxyl groups, and form negatively charged surfaces (Roman, & Winter, 2004). Even small amounts of sulfate groups on CNCs surfaces will cause electrostatic repulsion among CNCs, resulting the excellent dispersion and stability of the aqueous suspension (Yu et al., 2013). The presence of these negative charges are crucial factors for the self-assembling (Habibi, Lucia, & Rojas, 2010; Han, Zhou, Wu, Liu, & Wu, 2013; Qing, Sabo, Wu, Zhu, & Cai, 2015), rheological properties (Boluk, Lahiji, Zhao, & McDermott, 2011) and thermal stability (Araki, Wada, Kuga, & Okano, 1998) of the resultant cellulose nanocrystals (CNCs). Therefore, surface charges play important roles for obtaining excellent surface functionality, which determines the manner of interactions of nanocelluloses with other nanocellulose molecules and with other kinds of polymers (Kalia, Boufi, Celli, & Kango, 2014; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011).

The cellulose nanofibrils (CNFs) are another series of common nanocelluloses. Different from the CNCs, CNFs are usually produced by mechanical methods, which are not negatively charged (Haafiz, Eichhorn, Hassan, & Jawaid, 2013; Mandal & Chakrabarty, 2011). Also CNFs are longer and highly entangled (Sacui et al., 2014). Those nano-scale fibrils imparts higher mechanical strength and modulus than CNCs owing to their much larger aspect ratio and their percolation networks (Sakurada, Nukushina, Ito, 1962; Siqueira, Bras, & Dufresne, 2010; Xu et al., 2013). Xu et al. (2013), compared the properties of CNCs/PEO (cellulose nanocrystals/polyethylene oxide) and CNFs/PEO (cellulose nanofibrials/polyethylene oxide) films, finding that the Young's modulus, yield strength, and stress-at-failure of PEO/CNFs film were much higher (Xu et al., 2013). The highly entangled CNFs provide a stronger reinforcing effect (Zimmermann, Bordeanu, & Strub, 2010). Although TEMPO-mediated oxidation can produce the negatively charged CNFs, the oxidation process and system is rather complicated (Benhamou, Dufresne, Magnin, Mortha, & Kaddami, 2014). The common method, high-pressure homogenization, was originally used by Herrick and Turbak (Herrick, Casebier, Hamilton, & Sandberg 1983; Turbak, Snyder, Sandberg, 1983) to produce CNFs. Generally, cellulose is cycled through the high pressure homogenizer. With increasing number of homogenization cycles, particles are generally smaller and more uniform (Siró, & Plackett, 2010), but high-pressure mechanical treatment tends to reduce the crystallinity and damage the structure by separating the molecular mass, or instead fails to defibrillate pulp fiber sufficiently (Henriksson & Berglund, 2007; Iwamoto, Nakagaito, & Yano, 2007). Also the energy demands increases greatly with increased of treatment times. High energy demands may be the main limitation on application for CNFs. As no electric charge is introduced on the surface, CNFs trend to aggregate. Extensive clogging of the homogenizer is often a problem (Khalil et al., 2014). Numerous studies have reported that when negative charges are introduced on the surfaces of CNFs, the resulting electrostatic repulsion can decrease the friction between CNFs dramatically (Klemm et al., 2011; Mandal & Chakrabarty, 2011). Therefore there is less flocculation and clogging by CNFs, and the energy consumption is decreased (Horvath, & Lindström, 2007). Besides the decrease of flocculation and clogging, the introduction of negative charge also can provide more sites for surface modification and is an effective approach to reduce energy consumption (Klemm et al., 2011). Thus, a better understanding of negative charges on CNFs should be useful.

Table 1
The experimental conditions of acid hydrolysis.

Sample	Acid type and concentration	Reaction time	Temperature
CNFs-1	45 wt% H_2SO_4	10 min	45 °C
CNFs-2	45 wt% H_2SO_4	20 min	45 °C
CNFs-3	45 wt% H_2SO_4	30 min	45 °C
CNFs-4	50 wt% H_2SO_4	10 min	45 °C
CNFs-5	50 wt% H_2SO_4	20 min	45 °C
CNFs-6	50 wt% H_2SO_4	30 min	45 °C
CNFs-7	55 wt% H_2SO_4	10 min	45 °C
CNFs-8	55 wt% H_2SO_4	20 min	45 °C
CNFs-9	55 wt% H_2SO_4	30 min	45 °C
CNFs-10	64 wt% H_2SO_4	30 min	45 °C
CNFs-H	37wt% HCl	30 min	45 °C

In this work, wood fibers were pretreated with lower concentrations of acid and shorter hydrolysis times, an eco-friendly way to obtain negative charged surfaces, and then treated with a homogenizer under lower pressure, also energy-saving, to obtain CNFs. To study the properties of the resulting materials, the morphology was detected by transmission electron microscopy (TEM), negative charges of the CNFs were evaluated with zetasizer nano-ZS, and crystallinity was investigated by X-ray diffraction (XRD). The chemical composition was inferred from Fourier transform infrared spectroscopy (FTIR), and thermal degradation behavior was characterized by thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

Bleached eucalyptus wood pulp, mainly consists of cellulose and hemicellulose with moisture content 4–5%, was kindly supplied by a papermaking company (Chenzhou Yulong Paper Co., LTD), Sulfuric acid (GR, 95–98 wt%, Zhuzhou Star Glass Co., Ltd) was diluted to concentrations of 45, 50, 55 and 64 wt% before use. Hydrochloric acid (AR, 36–38 wt%, Hengyang Kaixin Chemical Reagent Co., LTD) was analytical grade and used without further treatment. All water used was deionized.

2.2. Preparation of CNFs

Bleached eucalyptus wood pulp (30 g) was pretreated using sulfuric acid and hydrochloric acid for obtaining the CNFs with eleven experimental conditions (Table 1).

The acid hydrolysis was stopped immediately by 15-folds dilution with deionized water. The mixture was centrifuged at room temperature with the speed of 3000 rpm (the relative centrifugal force was 1580 × *g*) for 10 min (TD5A, Hunan Kaida Sientific Istruments C., LTD). The separated particles were washed with distilled water. This washed mixture was centrifuged again. After three centrifugation cycles, the precipitate was then placed in regenerated cellulose dialysis tubing (Viskase with nominal flat width 77 mm and diameter 49 mm) with a molecular weight cutoff of 14,000 and dialyzed against distilled water for 3 days until pH reached a value of 7.0. To obtain the nanosized cellulose fibers, each suspension was passed through a high-pressure homogenizer (M-110EH-30, American Microfluidics International Corporation) five times with the Z-shaped 200 μm chambers, and 20 times with the Z-shaped 87 μm chamber under the pressure of 600 bar.

2.3. Characterization

2.3.1. Transmission electron microscopy (TEM) measurement

The CNFs were observed with an FEI Fei tecnai 20 under an acceleration voltage of 80 kV. A drop of 0.1–0.3 wt% CNFs suspension was