



A comparative study of cellulose nanofibrils disintegrated via multiple processing approaches



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ABSTRACT

Various cellulose nanofibrils (CNFs) created by refining and microfluidization, in combination with enzymatic or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidized pretreatment were compared. The morphological properties, degree of polymerization, and crystallinity for the obtained nanofibrils, as well as physical and mechanical properties of the corresponding films were evaluated. Compared to refining, intense microfluidization contributed greater separation of nanofibril bundles, which led to an enhancement of mechanical strength and transparency for the resultant film. The selected enzymatic pre-treatments produced shortened fibers due to preferential hydrolysis of amorphous cellulose and, in combination with mechanical treatments, resulted in short and stiff cellulose nanocrystal (CNC)-like materials. Despite films from these CNC-like fibrils having inferior tensile strength, their tensile modulus and transparency were significantly improved compared to CNFs prepared without pre-treatment. The unique fiber morphology and high crystallinity potentially offer a green and ecologically friendly alternative for the preparation of CNCs and CNFs as part of an integrated biorefinery approach.

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1. Introduction

Because of its abundance and sustainability, plant cellulose and cellulosic nanomaterials have attracted growing interest as an alternative to synthetic materials, especially as a filler and reinforcement for composites. Cellulose nanofibrils (CNFs), the class of cellulosic nanomaterials examined in this work, have a diverse range of reported applications including paper additives (Sehaqui, Allais, Zhou, & Berglund, 2011), barrier packaging (Aulin, Gällstedt, & Lindström, 2010), pharmaceutical carrier (Czaja, Young, Kawecki, & Brown, 2007), reinforcements for polymer composites (Qing, Sabo, Wu, & Cai, 2012; Qing, Sabo, Cai, & Wu, 2013; Srithip, Turng, Sabo, & Clemons, 2012; Tingaut, Zimmermann, & Lopez-Suevos, 2010), conductive nanopaper (Nyström et al., 2010), electronic substrates (Okahisa, Yoshida, Miyaguchi, & Yano, 2009; Sabo, Seo, & Ma, 2012), and multi-functional magnetic materials (Olsson et al., 2010). However, efficient production of cellulose nanofibril is still challenging with respect to energy consumption, commercial scale, and high capacity.

Numerous methods for creating cellulose nanofibrils have been reported since early studies (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983), but nearly

all involve some type of chemical or enzymatic pre-treatment of the plant fibers followed by intensive mechanical disintegration. Various types of mechanical operations have been applied to produce cellulose nanofibrils including homogenization (Herrick et al., 1983; Nakagaito & Yano, 2004; Stelte & Sanadi, 2009; Turbak et al., 1983), ultrafine grinding or refining (Stelte & Sanadi, 2009; Wang, Zhu, Gleisner, et al., 2012), microfluidization (Spence, Venditti, Rojas, Habibi, & Pawlak, 2011; Zhu, Sabo, & Luo, 2011; Zimmermann, Bordeanu, & Sturb, 2010), intense ultrasonication (Chen et al., 2011; Cheng, Wang, & Rials, 2009; Tonoli et al., 2012), cryocrushing in liquid nitrogen (Alemdar & Sain, 2008; Chakraborty, Sain, & Kortschot, 2005; Wang & Sain, 2007), and high-speed blending (Uetani & Yano, 2011). Due to different shear mechanisms and intensity, the energy requirement and morphologies of obtained nanofibers also vary widely. For instance, grinding or refining is considered more effective in removing external layers of the cell wall through abrasive actions, which promotes the thicker secondary cell wall to efficient fibrillation (Iwamoto, Nakagaito, & Yano, 2007; Stelte & Sanadi, 2009). Microfluidization provides significantly higher shear than others (Microfluidics Corporation, 2012), and is able to create high-performance nanofibrils (Spence et al., 2011). However, depending on the flexibility of raw material and pretreatment, fiber suspensions sometimes clog in the reaction chamber during high-pressure microfluidization (Henriksson, Henriksson, Berglund, & Lindström, 2007; Spence et al., 2011; Stelte & Sanadi, 2009).

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Various chemical (Saito & Isogai, 2004; Saito et al., 2009) and enzymatic pretreatments (Henriksson et al., 2007; Janardhan & Sain, 2006; Pääkkö et al., 2007; Siddiqui, Mills, Gardner, & Bousfield, 2011; Zhu et al., 2011) have been employed to facilitate the disintegration of cellulose into nanofibrils and thus reduce energy consumption. A common chemical treatment involving 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) oxidation generated interfibrillar repulsive forces between fibrils by the conversion of primary hydroxyls in cellulose into carboxylate groups, which contribute to an easy and fast fibrillation (Saito et al., 2009; Siró & Plackett, 2010). Henriksson et al. (2007) proposed that endoglucanase treatment of softwood pulp fibers made it possible to create CNFs using a microfluidizer. Zhu, Sabo, and Luo (2011) showed that extensive enzymatic treatment of cellulose fibers yielded both sugar streams (for production of fuels and chemicals) and hydrolyzed cellulose fibers, and that the enzymatic treatment facilitated the production of CNFs. Such integrated approaches may be of importance to future biorefineries which might produce a multitude of varied product streams, including cellulosic nanomaterials, fuels and chemicals. Due to their environment friendliness, enzymatic pretreatment seems to be a promising approach for industrial applications (Engström, Ek, & Henriksson, 2006; Lavoine, Desloges, Dufresne, & Bras, 2012).

Despite all the studies describing CNFs, the effect of pretreatments and mechanical disintegration processes on the morphology and properties of cellulose nanofibrils is still not clear. For example, Siddiqui et al. (2011) concluded that enzyme pretreatment did not have a significant effect on the nanofibril size distribution, although they only measured the diameters of the fibers and did not show any comparative images of the CNFs prepared under different conditions. However, enzymatic treatments are known to affect fiber morphology, and we demonstrate such effects in this work. Here, we aim to further understand the effects of pretreatments and mechanical defibrillations on the properties of nanofibrils and films made from them. Grinding and high-shear homogenization, combined with chemical or extensive enzymatic pretreatment, are applied to produce various nanofibrils. The morphology and crystallinity of the cellulose nanofibrils, as well as mechanical and optical properties of their neat films are reported and compared.

2. Experimental

2.1. Materials

Commercially supplied bleached eucalyptus Kraft pulp (Aracruz Cellulose, Brazil) was received in dry form and used for the raw materials. After soaking in distilled water for at least 24 h, the pulp was disintegrated by shear mixing in a blender for 10 min. The mixture of pulp fiber and water were centrifuged and concentrated to 1.5 wt% consistency, which were employed in the subsequent pretreatments or mechanical disintegrations.

2.2. Preparation of cellulose nanofibrils

2.2.1. Enzyme pretreatment

The disintegrated eucalyptus pulp fibers were enzymatically pretreated using two formulations before mechanical fibrillation. The first enzyme formulation was simply a commercial grade endoglucanase of FiberCare® from Novozymes (Franklin, NC). The second enzyme formulation was a mixture of FiberCare® and another complex enzyme cocktail, Cellulclast 1.5 L from Novozymes. The enzyme loading for both pretreatments was 3 FPU/g fiber. However, in the multiplex enzyme pretreatment, the loadings for FiberCare® and Cellulclast 1.5 L were 2 and 1 FPU/g fiber, respectively. Fibers were separately mixed with each enzyme

Table 1
Preparation approaches for various cellulose nanofibrils.

Materials	Preparation approach		
	Pretreatment	Refining	Microfluidization
Pulp fiber	No	No	No
R	No	Yes	No
RM	No	Yes	Yes
ER	Enzyme	Yes	No
ERM	Enzyme	Yes	Yes
TEMPO	TEMPO	Yes	Yes

formulation at 10% solids and incubated in a 1-L flask on a shaker (Thermo Fisher Scientific, Model 4450, Waltham, MA) at 50 °C and 200 rpm for 24 h. The resultant solids after enzymatic pretreatment were washed and then used for mechanical fibrillation.

2.2.2. Mechanical fibrillation by the SuperMassCollider

The pulp fibers with or without enzymatic treatment were mechanically fibrillated at initial solids loading of 1.5% (w/w) using a MKZA6-2 SuperMassColloider (Masuko Sangyo Co. Ltd, Saitama, Japan) at 1500 rpm as described previously (Wang, Zhu, Gleisner, et al., 2012). The SuperMassCollider is equipped with two stone grinding disks (Disk Model: MKGA6-80#) and positioned on top of each other. The bottom disk rotates while the top disk is stationary. Pulp fiber suspension was fed into the disk grinder continuously by gravity using a loop consisting of a peristaltic pump (Cole Parmer, Chicago, IL) and plastic tubing. The gap of the two disks was adjusted to $-100\ \mu\text{m}$ from motion zero position after pulp fibers were loaded. The motion zero position was determined right at the contact position between the two grinding disks before loading pulp fibers. Due to the presence of pulp fibers, there was no direct contact between the two grinding stones even at a negative setting of disk position. Approximately 100 g pulp fibers (on a dry basis) were ground for 6 h before use.

2.2.3. TEMPO oxidation

TEMPO-oxidized cellulose nanofibrils used in this study were prepared according to the work reported by Saito et al. (2009). The same bleached eucalyptus pulp fibers were carboxylated using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), sodium chlorite, and sodium hypochlorite as the reactants at 60 °C for 48 h. TEMPO oxidized pulp fibers were then washed thoroughly using distilled water and homogenized in a disk refiner to break apart fibril bundles. The fiber slurry was diluted to facilitate separation of coarse and fine fractions by centrifugation at $12,000\times g$, and the coarse fraction was rejected. The nanofiber suspension was concentrated to a solid content of approximately 0.4% using ultrafiltration. A final clarification step was performed, in which the nanofiber suspension was passed once through an M-110EH-30 microfluidizer (Microfluidics, Newton, MA) with 200- and 87- μm chambers in series. The carboxylate content of reacted pulp fibers was measured via titration based on TAPPI Test Method T237cm-98 and found to be 0.46 mmol COONa per gram of pulp.

2.2.4. Microfluidization

A portion of the pulp refined for 6 h in the SuperMassCollider was further refined in the microfluidizer. The refined pulp fiber suspensions were diluted to 1% solids consistency and passed through the 87 μm chamber of the microfluidizer 15 times. The pressure of the acting chamber was adjusted to 150 MPa.

All cellulose nanofiber suspensions were stored in 4 °C room until further characterization or processing into films. The samples were given label designations of R, RM, ER, ERM, TEMPO (seen in Table 1), where “R” and “M” correspond to mechanical fibrillations of refining in the SuperMassColloider and microfluidizer,

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