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# Extraction of cellulose nanofibrils from dry softwood pulp using high shear homogenization

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ABSTRACT

The objective of this study was to extract cellulose nanofibrils (CNFs) from dry softwood pulp through a simple and environmentally friendly physical method of refining pretreatment coupled with high shear homogenization. An optical microscopy (OM) clearly showed the morphological development from the cellulose fibers to CNFs under repeated shear forces. The morphology, structure and properties of the obtained CNFs were comprehensively investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transformed infrared (FTIR) spectra, X-ray diffraction (XRD) and thermogravimetric (TG) analysis. The results indicated that the CNFs had diameters mainly ranged from 16 to 28 nm. Compared with the pulp fibers, the CNFs exhibited a slightly higher crystallinity and a lower thermal stability. Moreover, a novel nanopaper with high optical transparency was prepared from the obtained CNFs, and a possible mechanism for the high optical transparency was discussed.


## 1. Introduction

Cellulose is one of the most abundant natural polymers on the earth. It has a lot of extraordinary properties in terms of biocompatibility, biological degradability, and sustainability (Chen et al., 2011a; Li et al., 2012). Cellulose can be obtained from various sources, such as wood (Chen et al., 2011a), cotton (de Morais Teixeira et al., 2010), pineapple leaves (Cherian et al., 2010), sisal fibers (Madera-Santana, Soto Valdez, & Richardson, 2012), straws (Chen, Yu, Zhang, & Lu, 2011; Kaushik & Singh, 2011), sugarcane bagasse (Mandal & Chakrabarty, 2011). In nature, cellulose fibers are composed of many nanometer-sized single fibers which are bound together by hydrogen bonds. These nanofibers are usually named as nanocrystals, nanowhiskers or nanofibrils. The term "nanowhiskers" is usually used to designate elongated crystalline rod-like nanoparticles, whereas "nanofibrils" should be used to designate long flexible nanostrings consisting of alternating crystalline and amorphous regions (Eichhorn et al., 2010). The dimensions of nanocellulose are dependent on the initial source (Eichhorn, 2011). In addition to the above-mentioned advantages of cellulose, the cellulose nanofibrils (CNFs) have many other unique characteristics, such as a very large surface-to-volume ratio, high mechanical properties, and the ability to form highly porous mesh (Abraham et al., 2011). They have been extensively applied as reinforcement components in composite materials (Abraham et al., 2013b), functional fibers (Walther, Timonen, Díez, Laukkanen, & Ikkala, 2011), photoelectric materials (Nogi & Yano, 2008), as well as functional aerogels (Wu, Li, Liang, Chen, & Yu, 2013), etc. Consequently, the preparation and utilization of CNFs from renewable sources have gained much attention during the past few years.

There are several approaches to prepare nanocellulose. Concentrated acid hydrolysis is one method to extract cellulose nanowhiskers from various cellulose resources (Satyamurthy & Vigneshwaran, 2013). However, a large amount of waste acidic liquid is generated after processing. The waste leads to potential hazards to the environment. This approach is also time-consuming due to the repeated centrifuge and dialysis procedures. Furthermore, string-like nanofibrils with high aspect ratio cannot be obtained this way. Some bacteria such as *acetobacter xylinum* are able to synthesize CNFs (Klemm et al., 2009), but using bacteria can be very expensive. Recently, physical approaches such as grinding (Jonoobi, Mathew, & Oksman, 2012), cryo-crushing (Chakraborty, Sain, & Kortschot, 2005), high pressure homogenizing (Li et al., 2012; Sehaqui, Morimune, Nishino, & Berglund, 2012), became popular for extracting CNFs. A combination of two or several methods has also been tried to improve the efficiency of CNFs extraction. For instance, Fujisawa, Okita, Fukuzumi, Saito, and Isogai (2011) used TEMPO-oxidation combined with ultrasonic homogenization to make CNFs from softwood pulp. Abraham et al. (2013a) reported steam explosion followed by acid treatment could be very effective to isolate CNFs from coir fiber. Despite these successful

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experiments, there are still many problems such as low efficiency, high energy consumption, high cost, which have not been solved yet.

In this study, a chemical-free refining pretreatment with high shear homogenization was used to extract CNFs. The morphology, structure and properties of the obtained nanofibrils were analyzed by optical microscope (OM), scanning electron microscope (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The mechanism for preparing CNFs from original cellulose fibers using high shear homogenization is discussed for the first time. Furthermore, a nanopaper with high optical transparency was fabricated via simple casting.

## 2. Experimental

### 2.1. Materials

Bleached softwood pulp with cellulose content above 95%, kindly provided by the Institute of Paper Science and Technology at Georgia Tech, USA, was used as the starting materials to skip the matrix removal processes of pulping and bleaching. The pulp we used was in dry condition due to the convenience of transportation, though some researchers claimed that non-dried pulp are easier for micro-/nanofibrillation because hydrogen bonds can be regenerated between CNFs upon drying (Syverud, Chinga-Carrasco, Toledo, & Toledo, 2011). Deionized water was used throughout the experiment. No chemical reagent was involved in the experiment.

### 2.2. Preparation of CNFs

The dry softwood pulp board was cut into small pieces and soaked in deionized water for 24 h. A disintegrator was then used to disintegrate the softwood pulp. After the filtration of most water, the pulp was beaten for 30,000 revolutions in a PFI mill. A certain amount of deionized water was then added to dilute the pulp dispersion until a concentration of 0.5 wt%. Finally, the dispersion was processed with a high shear homogenizer (T18, IKA, Germany). The homogenization was set at a rotation speed of 22,000 rpm for 2 h. It has been found that 2 h is an optimal processing time because no further fibrillation of CNFs can be detected by SEM when the homogenization time is over 2 h, and over-homogenization (more than 2 h homogenization) will cause a decreased crystalline of CNFs and a waste of power. The homogenizing process was cooled every 5 min to prevent overheat.

### 2.3. Preparation of cellulose nanopaper

The cellulose nanopaper was prepared following Dufresne's method (Dufresne, Cavaillé, & Vignon, 1997). Briefly, the obtained CNFs suspension was ultrasonically treated for 10 min to evenly disperse nanofibrils. Air in the suspension was removed by pumping under vacuum in order to eliminate bubbles which can be formed in the material during drying. The dispersion was then cast into a polystyrene petri dish and stored in a fume hood at room temperature. After 48 h, the air-dried sample was stored in the desiccator for at least a week.

### 2.4. Characterization

#### 2.4.1. Optical microscopy (OM)

The suspensions of treated fibers were obtained during the high shear homogenization and diluted to a concentration of 0.1 wt%. One drop of the diluted sample was dropped on a glass slide and stamped with a coverslip. An optical microscope (Leica DMLM) was used to observe the samples, and the morphology of fibers was captured by a digital imaging system.

#### 2.4.2. Scanning electron microscopy (SEM)

The suspensions of the cellulose fibers before and after the high shear homogenization were air-dried to form sheets. The obtained thin sheets were coated with gold for 60 s using a vacuum sputter coater (Quorum Q150T ES, UK) and then observed with SEM (LEO 1530, Germany) at 10 kV. ImageJ software was used for analysis of diameter distributions of more than 100 cellulose fibers or CNFs selected randomly from the SEM images.

#### 2.4.3. Transmission electron microscopy (TEM)

A drop of diluted aqueous CNFs suspension was deposited on the carbon-coated grids, which was then dried under table lamp. After the specimen has been completely dried, it was observed using TEM (Tecnai $G^2$ F20, Holland) with an acceleration voltage of 80 kV.

#### 2.4.4. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of CNFs and raw cellulose fibers were recorded on a Fourier transform infrared spectrometer (Nicolet Magna-IR 550, USA). The samples were dried at 80 °C under vacuum for 12 h before analysis. Then a small quantity (2 mg) of sample was blended with KBr powder (300 mg) and compressed to form a disk. The spectra for each sample were recorded as an average of 100 scans in the range from 4000 to 400 $cm^{-1}$ at a resolution of 2 $cm^{-1}$.

#### 2.4.5. X-ray diffraction (XRD)

The crystallinity of softwood cellulose fibers and CNFs was examined by high resolution X-ray diffractometer (Philips Analytical X'Pert, Netherlands) with nickel filtered Cu Kα radiation ($\lambda = 0.1540$ nm) at 40 kV and 40 mA. Scattered radiation was detected in the range $2\theta = 5–30°$ with a step interval of 0.02°. The crystallinity index (CrI) was calculated by Segal's method (Segal, Creely, Martin, & Conra, 1959) using the equation given by

$$\mathrm{CrI} = \frac{(I_{002} - I_{\mathrm{am}})}{I_{002}} \times 100 \quad (1)$$

where $I_{200}$ is the intensity value for the crystalline cellulose close to 22°, and $I_{\mathrm{am}}$ is the intensity value for the amorphous cellulose close to 18°.

#### 2.4.6. Thermal analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were carried out with a synchronous thermal analysis system (STA 6000, Perkin Elmer, USA). Approximately 10 mg of sample was used for each testing. Temperature programs for dynamic tests were from 30 °C to 500 °C at four different heating rates (5, 20 and 30 °C/min) under an air flow of 40 mL/min.

## 3. Results and discussion

### 3.1. Morphology observation by OM

OM analysis was carried out to observe the morphological development of softwood nanofibers during high shear homogenization at micron level. Fig. 1(a) shows that the diameters of pristine softwood cellulose fibers are between 20 and 50 μm. It has been well known that the refining process prior to homogenization is a key step to reduce energy consumption for the isolation of CNFs, because it helps to soften and to loosen the structure of cellulose fibers. This process not only produces external fibrillation by raising fine fibers on the surface layers (P and S1 layers) via abrasive action, but also makes internal fibrillation by breaking links between CNFs (Stelte & Sanadi, 2009). From Fig. 1(b), it is evident that the refining treatment by PFI mill made the fibers much looser, and generated