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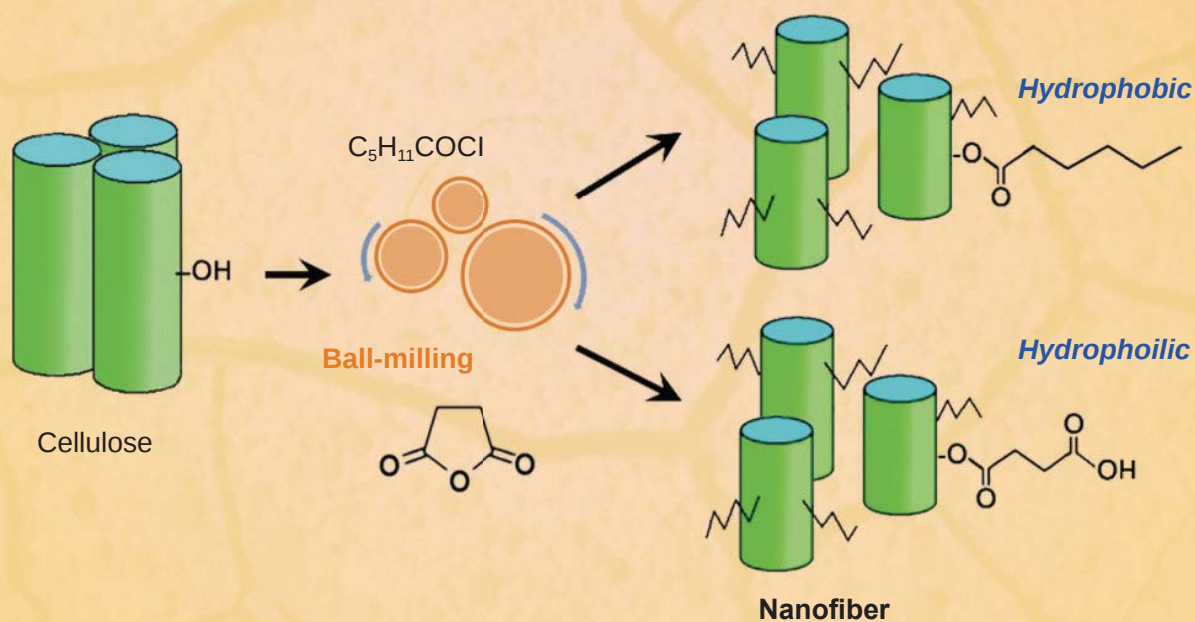
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Toward Sustainable, Economic, and Tailored Production of Cellulose Nanomaterials

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Abstract: This paper introduces a concentrated di-carboxylic acid (DCA) hydrolysis process for the integrated production of thermally stable and carboxylated cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). The DCA hydrolysis process addressed several issues associated with mineral acid hydrolysis for CNC production, such as cellulose loss and acid recovery. The surface and morphological properties of the cellulose nanomaterials resulting from the DCA hydrolysis process can be tailored simply by controlling the severity of DCA hydrolysis. To further reduce cost, a low-temperature ($\leq 80^{\circ}\text{C}$) hydrotropic chemical process using *p*-toluenesulfonic acid (*p*-TsOH) was also introduced to rapidly fractionate raw lignocelluloses for the production of lignin containing cellulose nanofibrils (LCNFs) and lignin nanoparticles (LNPs). The LCNF surface hydrophobicity and morphology can be tailored by controlling the fractionation severity, i.e., the extent of delignification. The lignin also improved the thermal stability of LCNFs. LNPs can be easily separated by diluting the spent acid liquor to below the *p*-TsOH minimal hydrotropic concentration of approximately 10%. *p*-TsOH can also be easily recovered by re-concentrating the diluted spent liquor after lignin precipitation. We believe that these two novel processes presented here have the potential to achieve true sustainable, economic, and tailored production of cellulose nanomaterials, suitable for a variety of applications.

Keywords: cellulose nanomaterials; cellulose nanocrystals; lignocellulosic nanofibrils; sustainability; tailored properties; economic production



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1 Introduction

Cellulose nanomaterials (CNMs), such as cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) have attracted significant attention in recent years for producing many biodegradable and functional bioproducts for a variety of applications. This is reflected by several recent high-profile reviews on the subject^[1-3]. CNMs are embedded in the cell walls of high plants with a hierarchical structure. Efficient and sustainable fractionation or separation technologies are the key to achieve the economic production of CNMs as a truly green biomaterial for a sustainable future.

As discussed in a recent seminal review^[1], CNCs refer to those crystalline CNMs resulting from the concentrated acid hydrolysis of cellulosic materials, such as commercial bleached pulp fibers, after hydrolyzing some disordered cellulose and amorphous hemicelluloses; this is despite the fact that accurate cellulose crystallinity measurements using the commonly used X-Ray diffraction method remain questionable. CNCs often have the morphology of nano-whiskers with diameters of approximately 10 nm and a length of approximately 150 nm, and have a certain degree of crystallinity. Sulfuric acid is commonly used to produce CNCs^[4-6]. The main problems associated with the conventional concentrated mineral acid hydrolysis process are as follows: ①low CNC yield of approximately 30%~50%; ②low CNC thermal stability; ③difficulties in economic recovery of the acid; ④high capital cost due to the corrosive nature of the acids at high concentrations; and ⑤environmental concerns over the disposal of large amounts of mineral salts and the consumption of a large amount of water for dialysis for CNC separation. Recently, we found that acid concentration is the key to dictating the CNC yield and morphologies^[4,7]. By controlling the acid concentration at approximately 58 wt%, we were able to achieve a CNC yield of approximately 90% based on the cellulose content in the starting bleached kraft pulp fibers^[4], and were able to tailor the morphological and surface properties of the resultant CNC^[4]. For example, the length of CNCs can be increased by a factor of two

at an acid concentration of 58 wt%. We also proposed to reduce the severity of acid hydrolysis by using an acid concentration below the commonly practiced concentration of 64 wt%. This can achieve a cellulose loss close to zero and the integrated production of CNC with CNF^[8]. Despite these advances, CNC production using mineral acid hydrolysis remains unsustainable, expensive, and beyond the reach of most applications.

CNFs are currently produced through mechanical fibrillation of commercial pulp fibers but with substantial energy cost^[9-11]. Chemical pretreatments^[12-13], including oxidation^[14-15], or enzymatic^[16-17] pretreatments of pulp fibers were often applied to loosen the cell wall structure to reduce energy consumption. TEMPO-mediated oxidation is very effective in reducing fibrillation energy input. However, the economic recovery of TEMPO still needs to be addressed.

In view of the above discussions, we would like to present some recent studies in our laboratory on achieving the sustainable, economic, and tailored production of CNMs. Specifically, we introduce the concentrated di-carboxylic acid (DCA) hydrolysis process^[18-19] for integrated production of thermally stable CNCs with CNFs. The DCA hydrolysis process addresses several issues associated with concentrated mineral acid hydrolysis, such as low CNC thermal stability, and acid recovery. Certain DCAs such as oxalic and maleic acids have low solubility at ambient temperatures, which ease acid recovery through mature and proven crystallization technology. The DCA hydrolysis process also produces carboxylated CNMs for easy dispersion in aqueous solutions. Because they are weak acids, the DCAs are incapable of depolymerizing all the cellulose into CNCs, which results in a low CNC yield. However, the remaining partially hydrolyzed fibrous cellulosic solid residue (FCSR) can be used to produce CNFs through mechanical fibrillation with low energy input^[18,20]. Lignin-containing CNCs (LCNCs) and CNFs (LCNFs) can also be produced when using unbleached chemical pulp fibers^[21] as well as mechanical pulp fibers^[22].

2 Experimental

2.1 Materials

Anhydrous oxalic acid (O), anhydrous maleic acid (M), and *p*-toluenesulfonic acid (P) were purchased from Sigma-Aldrich (St. Louis, MO). Dialysis bags with a typical cut-off molecular weight of 14000 Da were also obtained from Sigma-Aldrich (Product No. D9402-100FT). The filter paper (15 cm, slow) was obtained from Fisher Scientific Inc. (Pittsburgh, PA).

Dry lap bleached eucalyptus kraft pulp (BEP) was obtained from Aracruz Cellulose (Brazil). Two unbleached never dried virgin mixed hardwood (mainly birch and maple) kraft pulps (in suspension) with high (UHP-LL) and low (UHP-HL) lignin contents, or kappa numbers, were complementarily provided by the International Paper Company (Loveland, OH). Medium density fiberboard fibers (MDFs) were produced by refining birch wood chips in a 30.5 cm pressurized disk refiner (Sprout-Bauer, model 1210P, Muncy, PA, USA) with disk plate patterns of D2B505 and a diskgap of 0.178 mm.

2.2 CNM production

Concentrated aqueous acid solutions were prepared by heating a desired amount of DI water in a multiple-neck flask submerged in a liquid glycerol bath on a heating plate. An appropriate amount of the selected anhydrous organic acid was added to obtain a solution of the desired concentration with the aid of magnetic stirring. At high acid concentrations, the solution temperature can be raised to the desired hydrolysis temperature between 80°C and 120°C without boiling. BEP (or UHP-LL, or UHP-HL, or MDF) fibers (10 g, in oven dry (OD) weight) were added to the acid solution with continuous stirring. The reactions were quenched by adding 200 mL of DI water to the suspensions at the end of each reaction. The suspension was washed, and repeatedly diluted and centrifuged at 10000 r/min for 10 min to separate the solids and the supernatant which was decanted to remove the acid. The slurry was then dialyzed for a week or until the conductivity of

the dialysis water no longer changed. CNCs or LCNCs were finally obtained by centrifuging the dialyzed and turbid sample at 10000 r/min for 10 min to separate FCSR from CNCs or LCNCs, which remained in the aqueous phase. The amount of CNCs or LCNCs in the dispersion was measured using a COD method described previously^[8].

The precipitated FCSR was mechanically fibrillated at a solid consistency of approximately 1% using a microfluidizer (M-110EH, Microfluidics Corp., Westwood, MA) to produce CNFs or LCNFs after passing through two chambers with diameters of 200 and 87 µm in series at an operating pressure of 120 MPa.

2.3 Morphology analyses

The morphologies of the CNM samples were observed using atomic force microscopy (CS-3230, AFM Workshop, Signal Hill, CA, USA). Samples were diluted to a solid consistency of 0.01 wt% and deposited onto clean mica substrates and air dried overnight at room temperature. A silicon cantilever was used to image samples in vibrating tapping mode at 160~225 kHz with a tip curvature radius of less than 10 nm. Crystal and fibril heights were measured using Gwyddion (Department of Nanometrology, Czech Metrology Institute, Czech Republic, 64-bit).

2.4 Crystallinity

Wide-angle X-ray diffraction measurements of CNM samples were carried out on a Bruker D8 130 Discover system with Cu-Kα radiation (Bruker Corp., Billerica, MA). Freeze-dried samples were pressed into pellets at 180 MPa as described previously. The crystallinity index (CrI) of a sample was calculated using the Segal method (without base line subtraction).

2.5 Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) absorption measurements were carried out to identify ester groups in the resultant CNM samples. The original BEP, UHP-LL, and UHP-HL fibers were also analyzed as control samples. A commercial FT-IR spectrophotometer

(Spectrum 100, PerkinElmer, Waltham, MA) equipped with a universal attenuated-total-reflection (ATR) probe was used.

2.6 Thermogravimetric analysis

Thermogravimetric analyses (TGA) of different CNM samples were carried out on a thermogravimetric analyzer (Pyris 1, PerkinElmer, Inc., Waltham, MA). Samples of approximately 5 mg were heated from ambient temperature to 600°C under a 20 mL/min high purity nitrogen stream using a heating rate of 10°C/min.

3 Results and discussion

3.1 CNM yields

To facilitate discussion, samples were labeled using their abbreviated conditions as (AxxTxxTxx) to represent the acid loading in wt%, reaction temperature in °C, and duration in min. The FCSR from acid hydrolysis was separated after filtration and washing coupled with centrifugation. Due to the weak acidity of oxalic and maleic acid and insufficient hydrolysis, the FCSR yield was high of approximately 90% and the CNC (or LCNC) yield was very low at only a few percent. With respect to *p*-toluenesulfonic acid, approximately 85% of the birch wood lignin and 70% of xylan were solubilized at P80T80t20 with an FCSR yield of approximately 51%. The great selectivity of solubilizing lignin over the dissolution of cellulose resulted in cellulose-rich FCSR and a spent acid liquor primarily containing dissolved lignin and acid. These acids can be recovered through crystallization after cooling to ambient temperature. Yields of FCSR and CNC (or LCNC) from organic acid treatments under various conditions are shown in Table 1.

3.2 CNM morphologies

AFM images of (L)CNC and (L)CNF from different lignocellulosic sources are shown in Fig.1 and Fig.2, respectively. Crystal height (*H*) was determined by Gwyddion (Department of Nanometrology, Czech Metrology Institute, Czech Republic, 64-bit) and used as the sample diameter in Table 2.

Table 1 Yields of FCSR and CNC (or LCNC) from organic acid treatments under various conditions

Raw material	Condition*	FCSR yield	CNC (or LCNC)
		/%	yield/%
BEP	O60T100t45	89.1	9.0
	O70T100t45	80.8	11.4
	M50T100t45	95.9	1.1
	M60T120t120	94.2	3.0
UHP-LL	M60T120t120	94.2	5.9
UHP-HL	M60T120t120	92.9	2.1
MDF	P65T80t20	54.2	ND
	P80T80t20	51.3	ND

*O, M and P denote oxalic, maleic, and *p*-toluenesulfonic acids, respectively. Data from the literatures [18] and [21-22].

Compared with CNC produced from BEP (Fig.1a and Fig.1b), lignin particles were clearly visible in the LCNF samples produced from the unbleached mixed hardwood pulp of UHP-LL and UHP-HL and MDF (Fig.1c~Fig.1f). The height values determined by AFM indicated that high lignin content resulted in crystals with greater height (Table 2), suggesting that lignin protected against cellulose depolymerization to result in crystals with large diameters. Subsequent mechanical fibrillation of various partially acid hydrolyzed FCSR samples using microfluidization produced (L) CNF with varied morphologies as shown in Fig.2. The number-averaged fibril heights (*H*) were 13.4, 9.6, and 7.1 nm for BEP, UHP-LL, and UHP-HL under condition M60T120t120, which suggested that residual lignin promoted fibrillation (Fig.2b~Fig.2d). However, the higher lignin content of 11.6% for MDF-P65T80t20 impeded mechanical fibrillation, contradictory to the above-mentioned results. Perhaps lignin may have undergone some degree of condensation compared to other processes after *p*-TsOH acid hydrolysis.

3.3 Crystallinity

The crystallinity index (CrI) of selected (L)CNC and (L)CNF samples were analyzed using wide-angle X-ray diffraction (Table 2). The BEP-CNF had the highest CrI of 80.3%, with the LCNF samples having lower values, which is most likely due to the presence of lignin in the LCNF samples. The MDF-P65T80t20-LCNF with

a lignin content of 11.6% had the lowest CrI of 67.5%. Due to the low yield of LCNC with limited samples available, CrI measurements of the LCNC samples were not carried out. The CrI of these samples would be expected to be higher than those of their corresponding LCNF samples.

3.4 FT-IR

FT-IR spectroscopy was used to characterize the chemical structure of the lignocellulosic materials. As shown in Fig.3 and Fig.4, the absorption around 1160 and 896 cm^{-1} in each sample are interpreted as being those of typical cellulose structures. The bands at 1507 and 1596 cm^{-1} are associated with the aromatic skeletal vibration of lignin and are only observed for the lignin-containing samples. Furthermore, a weak band was observed around 1722 cm^{-1} in the BEP-CNF and UHP-LL-LCNF samples (Fig.3). This peak corresponds to the C=O vibrations in the carboxyl group from esterification by maleic acid. However, the 1722 cm^{-1} peak is not observable in Fig.4, which suggests *p*-TsOH has no effects on cellulose structure^[22].

3.5 Thermal stability

Thermogravimetric analyses were conducted to investigate the differences in the decomposition behavior and thermal stability of samples. Since the (L)

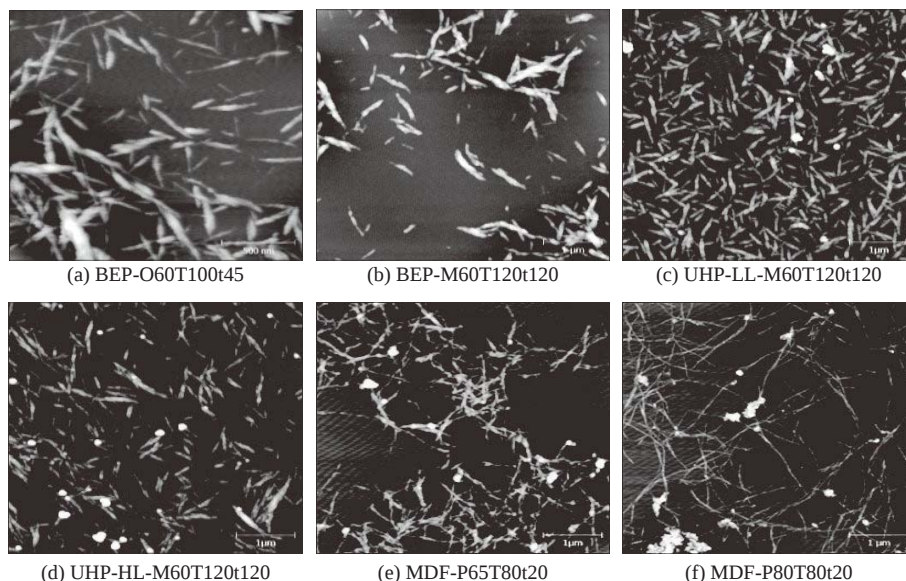


Fig.1 AFM images of CNC and LCNC from different raw materials and conditions
Images from literatyres [18] (a), [21] (b~d) and [22] (e and f). With permission from Royal Society of Chemistry for reproduction.

Fig.1 AFM images of CNC and LCNC from different raw materials and conditions

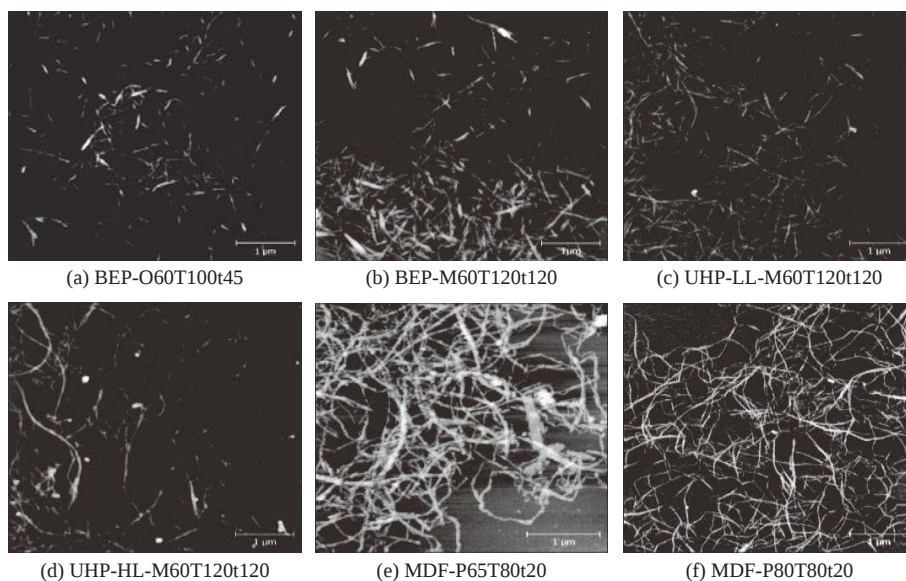


Fig.2 AFM images of CNF and LCNF from different raw materials and conditions
Images from the literatures [18] (a), [21] (b, c and d), and [22] (e and f). With permission from Elsevier Science for reproduction.

Fig.2 AFM images of CNF and LCNF from different raw materials and conditions

CNC yield was very low, TG measurements were not carried out. LCNFs have better thermal stability than CNFs based on thermogravimetric analysis (TGA) because lignin is more thermally stable than cellulose. The maximum degradation temperatures T_{max} of (L) CNF derived from the derivative TGA data are listed in Table 2. The T_{max} of the UHP-HL-M60T120t120-

Table 2 List of morphological, physical, chemical, and thermal properties of the (L)CNC and (L)CNF

Sample	Condition	<i>H</i> /nm	<i>CrI</i> /%	<i>T</i> _{max} /°C
(L)CNC	BEP-O60T100t45	12.0	82.4	—
	BEP-M60T120t120	15.9	—	—
	UHP-LL-M60T120t120	20.7	76.6	—
	UHP-HL-M60T120t120	25.0	—	—
	MDF-P65T80t20	51.0	—	—
	MDF-P80T80t20	28.2	—	—
(L)CNF	BEP-O60T100t45	—	—	—
	BEP-M60T120t120	13.4	80.3	361
	UHP-LL-M60T120t120	9.6	76.2	376
	UHP-HL-M60T120t120	7.1	69.0	393
	MDF-P65T80t20	29.4	67.5	358
	MDF-P80T80t20	15.3	68.8	338

Data from literatures [18, 21-22].

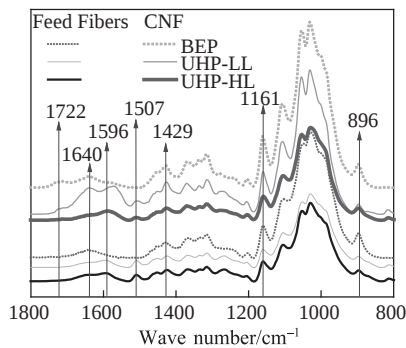


Fig.3 FT-IR spectra of BEP, UHP-LL, and UHP-HL fibers and their corresponding LCNF samples

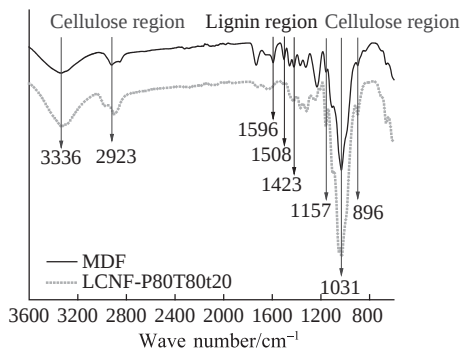


Fig.4 Comparison of FT-IR absorption spectra between the MDF fiber and LCNF from the most severe *p*-TsOH treatment with lignin removal of approximately 85%^[22]

LCNF and MDF-P65T80t20-LCNF were 376°C and 393°C, which were higher than those of UHP-LL-M60T120T120-LCNF and MDF-P80T80t20-LCNF. The increased surface area from nanofibrillation

increased thermal degradation. These results clearly demonstrate the (L)CNF samples produced with organic acids exhibit good thermal stability, which is an extraordinary advantage for thermal processing such as extrusion at high temperatures.

4 Conclusions

4.1 A di-carboxylic acid (DCA) hydrolysis process for producing thermally stable and carboxylated cellulose nanocrystals and fibrils from chemical pulp was introduced. Using solid DCA addressed the acid recovery problem associated with using mineral acid hydrolysis. The cellulose loss was minimal. The esterification of cellulose by the DCA produced carboxylated cellulose nanomaterials with surface charge to facilitate dispersion in aqueous systems.

4.2 A low-temperature (80°C) fractionation process using *p*-toluenesulfonic acid (*p*-TsOH) was introduced to produce lignin-containing CNFs directly from raw lignocelluloses to substantially reduce cost. *p*-TsOH is a solid acid, and it can be recovered through mature crystallization technology without involving any chemical processes.

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