



# Ionic liquid-mediated technology to produce cellulose nanocrystals directly from wood



Hatem Abushammala<sup>a,b</sup>, Ingo Krossing<sup>b,c</sup>, Marie-Pierre Laborie<sup>a,b,\*</sup>

<sup>a</sup> Chair of Forest Biomaterials, University of Freiburg, Werthmannstr. 6, 79085 Freiburg, Germany

<sup>b</sup> Freiburg Materials Research Center, University of Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg, Germany

<sup>c</sup> Institute of Inorganic and Analytical Chemistry, University of Freiburg, Albertstr. 21, 79104 Freiburg, Germany

## ARTICLE INFO

### Article history:

Received 10 April 2015

Received in revised form 18 June 2015

Accepted 22 July 2015

Available online 26 July 2015

### Keywords:

Ionic liquids

Wood pulping

Cellulose nanocrystals

Hydrolysis

## ABSTRACT

We report for the first time the direct extraction of cellulose nanocrystals (CNCs) from wood by means of a 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) treatment. A native cellulosic product could be recovered in 44% yield with respect to wood cellulose content. The product was analyzed for morphological (TEM, AFM, XRD), chemical (FTIR, <sup>13</sup>C CP/MAS NMR), thermal (DSC, TGA) and surface properties (Zeta potential, contact angle). These analyses evidenced the presence of partially acetylated (surface DS = 0.28) nanocrystals of native cellulose I microstructure, with a crystallinity index of about 75% and aspect ratio of 65. Direct production of CNCs from wood is ascribed to the simultaneous capability of [EMIM][OAc] to (1) dissolve lignin in situ while only swelling cellulose, (2) decrease intermolecular cohesion in wood via acetylation, and (3) to catalyze cellulose hydrolysis.

© 2015 Published by Elsevier Ltd.

## 1. Introduction

Cellulose nanocrystals (CNCs), rod like nanoparticles, have shown a great potential in a wide range of applications due to their high mechanical properties, low density, and biodegradability (Eichhorn, 2011; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Zadorecki & Michell, 1989). CNCs are traditionally extracted by hydrolysis of cellulosic materials with strong acids (Ranby, 1949) in yields ranging from 20 to 60% (Bondeson, Mathew, & Oksman, 2006; Fan & Li, 2012). While CNCs are commonly produced from pure cellulosic materials such as wood pulp or microcrystalline cellulose, two groups have explored approaches for extracting CNCs from more complex lignocellulosic biomass. Namely, Mathew et al. converted a cellulosic-rich residue of wood bioethanol production into CNCs by successively conducting mild acid hydrolysis, bleaching and high pressure homogenization (Herrera, Mathew, & Oksman, 2012; Oksman, Etang, Mathew, & Jonoobi, 2011; Mathew et al., 2014). Likewise, Leung et al. (2010, 2011) patented an inorganic persulfate treatment of vegetable biomass for producing

CNCs. In both cases, the starting lignocellulosic material displayed low lignin content as either a delignified residue (Herrera et al., 2012; Mathew et al., 2014) or as a naturally low lignin-content (5–7%) hemp fiber (Bismarck, Mishra, & Lampke, 2005). In lignocellulosic biomass, lignin is particularly recalcitrant to removal due to its bonding to heteropolysaccharides in lignin-carbohydrate complexes (LCC) (Glasser, 1981; Glasser & Barnett, 1979) and its maintained reactivity and propensity for condensations. Wood comprises high lignin content, ranging from 20 to 40%. Not surprisingly, the direct extraction of CNCs from wood has never been demonstrated to date. Therefore, the need remains for a technology to directly extract CNCs from wood. Such a technology should simultaneously induce (i) wood delignification, (ii) hydrolysis of cellulose amorphous regions in situ while (iii) leaving cellulose native crystalline regions intact. Finding a single reagent, which could perform these multiple functions is challenging. Ionic liquids (ILs) appear as the most likely candidates. Indeed, the interaction of ionic liquids with wood structural polymers can be easily modulated based on the hydrophilicity/hydrophobicity (Jiang et al., 2011; Kilpeläinen et al., 2007), size (Pinkert, Goetze, Marsh, & Pang, 2011), and acidity/basicity of their constituting ions (Brandt, Hallett, Leak, Murphy, & Welton, 2010), and viscosity (Sun et al., 2009). Accordingly, ILs have been successfully used for multiple purposes including notably complete dissolution of wood and sugar recovery (Fadeev & Meagher, 2001; Mäki-Arvela, Anugwom, Virtanen, Sjöholm, & Mikkola, 2010; Vancov, Alston,

\* Corresponding author at: Chair of Forest Biomaterials, University of Freiburg, Faculty of Environment and Natural Resources, Werthmannstr. 6, 79085 Freiburg, Germany. Fax: +49 761 203 3763.

E-mail addresses: [hatem.abushammala@biomat.uni-freiburg.de](mailto:hatem.abushammala@biomat.uni-freiburg.de) (H. Abushammala), [krossing@uni-freiburg.de](mailto:krossing@uni-freiburg.de) (I. Krossing), [marie-pierre.laborie@biomat.uni-freiburg.de](mailto:marie-pierre.laborie@biomat.uni-freiburg.de) (M.-P. Laborie).

Brown, & McIntosh, 2012), delignification and recovery of cellulose (Anugwom et al., 2011; Brandt et al., 2011; Hou, Smith, Li, & Zong, 2012; Leskinen, King, Kilpeläinen, & Argyropoulos, 2013; Pinkert et al., 2011; Shamsuri & Abdullah, 2010; Tan et al., 2009). Among ILs commonly used with lignocellulose, 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) is known to display specificity for lignin dissolution (Brandt et al., 2010; Hauru et al., 2013; Hossain & Aldous, 2012; Lee, Doherty, Linhardt, & Dordick, 2009). It has been utilized for ionic liquid-assisted fractionation (ILAF) of wood under homogeneous conditions thereby producing a cellulose II pulp (Sun et al., 2009). Its potential for heterogeneous ILAF to recover a native cellulose I pulp has also been proposed (Hauru et al., 2013). Moreover, [EMIM][OAc] has been shown to hydrolyze cellulose under mild conditions (Gazit & Katz, 2012). [EMIM][OAc] might therefore be an IL of choice to specifically delignify wood while selectively hydrolyzing cellulose amorphous fractions and preserving its native crystalline regions. Here, we demonstrate for the first time that wood treatment with [EMIM][OAc] can be optimized to simultaneously pulp wood and extract native cellulose I nanocrystals.

## 2. Materials and methods

### 2.1. Materials

Angelim vermelho (*Dinizia excelsa*) wood from the Amazonian rain forests was milled to 150  $\mu\text{m}$  particle size using disc mill RS 200 (Retsch, Düsseldorf, Germany) and dewaxed with an ethanol:acetone:toluene mixture (1:1:4 volume ratio) in a soxhlet operating at 120 °C for 8 h. The dewaxed wood powder (ca. 9% mass loss) was then washed with hot water and oven-dried overnight at 60 °C under vacuum and kept in a vacuum desiccator until use.

1-Ethyl-3-methylimidazolium acetate [EMIM][OAc] (97%), acetyl bromide (99%), hydroxylamine hydrochloride (98%), hydrogen peroxide (30 wt.% in water), pyridine (99.8%), phenyl isocyanate ( $\geq 98\%$ ), sodium hydroxide ( $\geq 98\%$ ), phenolphthalein (98–102%), sodium chloride (80%) were purchased from Sigma–Aldrich. These chemicals were mainly used for the pulping process, chemical composition analysis of the biomass, and GPC analysis of the CNCs. Acetone (technical grade), ethanol (technical grade), toluene (ACS grade), chloroform (ACS grade), dimethyl sulfoxide (ACS grade), acetic acid ( $>98\%$ ), tetrahydrofuran ( $\geq 99.9\%$ ), methanol (technical grade), hydrochloric acid (37 wt.% in water) were purchased from VWR. Most of these chemicals were used for the CNC dispersibility study.

### 2.2. Treatment of Angelim Vermelho using [EMIM][OAc]

4.0 g of the extractive-free wood flour (WR-0) was stirred in open atmosphere with 80.0 g of [EMIM][OAc] pre-heated at 60 °C. After two hours of mixing, the mixture was centrifuged at 12,000 rpm for 10 min (F156  $\times$  100Y Multifuge, Thermo Scientific, USA), yielding a precipitate and a supernatant. The supernatant (*Pulping Liquor 1*) was decanted into a 200 mL Erlenmeyer flask. The precipitate (*Wood Residue 1*, WR-1) was washed multiple times with DMSO then deionized water to remove residual dissolved wood and residual ionic liquid. It was subsequently oven-dried at 60 °C under vacuum overnight and kept in a desiccator until characterization. In this process, the pulping liquor and the washing eluents (*Washing 1*) were also generated and collected for analysis (Fig. 1). A second identical treatment using a fresh [EMIM][OAc] was repeated on Wood Residue 1. This second treatment cycle similarly generated 3 fractions, named *Wood Residue 2* (WR-2), *Pulping Liquor 2*, and *Washing 2*. WR-2 was bleached with 5%  $\text{H}_2\text{O}_2$  at 60 °C for 2 h, washed with DI water and oven-dried at 60 °C under vacuum.

The pulping liquors and washings of the two treatment cycles were separately treated to collect the dissolved wood polymers. Each pulping liquor was mixed with an equivalent weight of 52% (w/w) acetone/water solution as anti-solvent. A brownish material was precipitated and filtered off (Polysaccharide-Rich Residue). The filtrate was diluted with water and kept for one day to settle down. Another brown material (Lignin-Rich Residue) was also precipitated using water as antisolvent. The precipitate was filtered off and oven-dried (Washing Residue). The ionic liquid was collected after distilling the other liquids under vacuum (DMSO at 80 °C and water at 50 °C). All wood fractions were oven-dried under vacuum overnight and weighed for mass balance purposes. Both pulping cycles and subsequent treatments were performed in duplicate to ascertain reproducibility.

### 2.3. Compositional analysis of raw wood (WR-0) and wood residues (WR-1 and WR-2) upon pulping with [EMIM][OAc]

The composition of the pulping products was analyzed with traditional wet chemistry methods. Lignin content was measured with the acetyl bromide method of Foster, Martin, and Pauly (2010) with some modifications. The absorbance of the final solutions was determined using UV spectrophotometer TIDAS (J&M Analytik AG, Germany). The lignin content was then computed from the absorbance of the solution based on a UV calibration curve previously built with wood-milled lignin solutions of known concentrations. The wood-milled lignin was obtained from Angelim vermelho by the method of Björkman (1956). Holocellulose and cellulose contents were determined following the method of Ona et al. (1995). The extracted cellulose was used as a reference for comparison (CELL-0).

Additionally, FT-IR was performed on KBr pellets comprising 2 mg of sample. Spectra were collected in transmittance mode on a FT-IR spectrometer 65 (PerkinElmer, USA) using 64 scans at a resolution of 2  $\text{cm}^{-1}$ . For elemental analysis, 2 mg of dried material was analyzed on a Vario elemental analyzer (Elementar Analysensysteme GmbH, Germany).

### 2.4. Morphological and structural analysis of the supernatant obtained from wood residues

Upon redispersion of WR-2 in deionized water (after bleaching using 5%  $\text{H}_2\text{O}_2$ ) and rapid sonication (30 s in ultrasonicator UW 2200, Bandelin Electronic, Germany), a turbid supernatant formed, which was collected and then subjected to further characterization either directly as a dispersion or after freeze-drying.

Zeta potential: the zeta potential of about 0.01% (w/w) supernatant was measured using a Zetasizer Nano-ZS90 (Malvern Instruments Ltd., UK).

Transmission Electron Microscopy: a droplet of diluted sample from the supernatants was placed on a carbon-coated TEM grid and allowed to dry overnight at ambient temperature. The sample was observed under TEM (Zeiss LEO CEM 912) operating at an accelerating voltage of 100 kV.

#### 2.4.1. Atomic force microscopy (AFM)

A droplet of a diluted sample from the supernatant was allowed to dry overnight on a fresh surface of mica. The sample was then observed in tapping mode with an atomic force microscope (Nanoscope III) equipped with a tube scanner (Veeco Santa Barbara, USA) using silicon tips (PPP-NCH, Nanoandmore, Germany). Resonance frequency of 360 kHz and a spring constant of 50  $\text{N m}^{-1}$  were used. The particle dimensions (height and length) were assessed using Nanoscope Analysis software (version 1.40) on about 100 particles.

Download English Version:

<https://daneshyari.com/en/article/7787228>

Download Persian Version:

<https://daneshyari.com/article/7787228>

[Daneshyari.com](https://daneshyari.com)