



# Homogeneous isolation of nanocelluloses by controlling the shearing force and pressure in microenvironment



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## ARTICLE INFO

### Article history:

Received 1 April 2014

Received in revised form 17 June 2014

Accepted 24 June 2014

Available online 11 July 2014

### Keywords:

Dynamic high pressure microfluidization

High pressure homogenization

Homogeneous isolation

Microenvironment

Nanocellulose

### Chemical compounds studied in this article:

1-Butyl-3-methylimidazolium chloride

(PubChem CID: 2734161)

1-Methylimidazole (PubChem CID: 1390)

1-Chlorobutane (PubChem CID: 8005)

Sodium hydroxide (PubChem CID: 14798)

Nitric acid (PubChem CID: 944)

Potassium bromide (PubChem CID:

253877)

N, N-dimethylacetamide (PubChem CID:

31374)

Lithium chloride (PubChem CID: 433294)

Methanol (PubChem CID: 887)

Sulfuric acid (PubChem CID: 1118)

## ABSTRACT

Nanocelluloses were prepared from sugarcane bagasse celluloses by dynamic high pressure microfluidization (DHPM), aiming at achieving a homogeneous isolation through the controlling of shearing force and pressure within a microenvironment. In the DHPM process, the homogeneous cellulose solution passed through chambers at a higher pressure in fewer cycles, compared with the high pressure homogenization (HPH) process. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) demonstrated that entangled network structures of celluloses were well dispersed in the microenvironment, which provided proper shearing forces and pressure to fracture the hydrogen bonds. Gel permeation chromatography (GPC), CP/MAS <sup>13</sup>C NMR and Fourier transform infrared spectroscopy (FT-IR) measurements suggested that intra-molecular hydrogen bonds were maintained. These nanocelluloses of smaller particle size, good dispersion and lower thermal stability will have great potential to be applied in electronics devices, electrochemistry, medicine, and package and printing industry.

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## 1. Introduction

Celluloses are considered to be a typical kind of biopolymers that are inexhaustible, environmentally friendly and biocompatible to meet the increasing demand for biomaterials (Klemm, Heublein, Fink, & Bohn, 2005) and electronic devices. Due to their extensive

hydrogen bonds between polymer backbone and their high crystallinity (Hinterstoisser, Åkerholm, & Salme'n, 2003), the celluloses are chemically stable and insoluble in acidic, alkaline or organic solvents. This high stability presents a challenge for the fine celluloses to be processed and used in a wide range of applications. Therefore, challenges and future opportunities of celluloses will be focused on the processes that can improve the productivity.

Nanocelluloses are normally isolated by means of chemical (Zhang, Ruan, & Zhou, 2001), physical (Ikeda, Holtman, Kadla, Chang, & Jameel, 2002), and biological methods (Lavoine, Desloges, Dufresne, & Bras, 2012). Among them, physical process has been the most widely used method but requires a lot of energy to destroy

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the tangles between the molecular chains under solid condition. Recently, ionic liquids have been used as nonderivatizing solvents for the production of celluloses as the extensive hydrogen bonds between cellulose chains can be easily broken by anionic ionic liquids in the homogeneous dissolution process (Swatloski, Spear, Holbrey, & Rogers, 2002). The entangled molecular chain networks are scattered into single molecular chains and form a microenvironment system that facilitates the isolation of nanocelluloses from the dispersed cellulose molecular chains.

In our previous study (Li et al., 2012), the nanocelluloses were successfully prepared with a high pressure homogenization (HPH) process in homogeneous media. Nanocelluloses with a particle size of 10–20 nm were obtained at 80 MPa in 30 cycles. However, the celluloses were degraded to a certain degree during the processing due to too many cycles being used, resulted in the deterioration of materials properties.

Contrary to high pressure homogenization technology, dynamic high pressure microfluidization (DHPM) can produce finer emulsion particles and avoid the occurrence of coalescence or aggregation because of the high shearing force and high stress during the ultra-high pressure homogenization and head-on collision (Hu, Zhao, Sun, Zhao, & Ren, 2011). DHPM has been used to improve the functional properties of peanut proteins, and extend the shelf life of milk (Hu et al., 2011; Pereda, Perragut, Quevedo, Guamis, & Trujillo, 2008) because of the unnoticeable damage to the molecular structures. However, to our knowledge, the DHPM process has not been explored for the fabrication of polymer materials, as the mechanism of the process and its effects on the structure of materials are not well understood.

The objective of this study was to evaluate the effect of homogenization forces on the structural changes of celluloses. In this study, DHPM was applied to isolate nanocelluloses from sugarcane bagasse in a microenvironment. The optimal conditions of the DHPM process were investigated. Compared with the HPH process, the effects of DHPM process were characterized by rheological property, Fourier transform infrared spectroscopy (FT-IR) analysis, X-ray photoelectron spectroscopy, and solid-state CP/MAS  $^{13}\text{C}$  NMR.

## 2. Experimental

### 2.1. Materials

Sugarcane bagasse was purchased from Guangdong Fengshou Sugar Industry Co., Ltd, Zhanjiang, China, and pretreated by acid and alkali treatment (Adsul, Soni, Bhargava, & Bansal, 2012; Weng, Zhang, Ruan, Shi, & Xu, 2004). Ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was prepared by following the procedures reported in the literature (Li et al., 2012). All other reagents and chemicals were of analytical grade.

### 2.2. Preparation of nanocelluloses

Sugarcane bagasse celluloses (SBC) with a content of celluloses up to 93.53% were dissolved in [Bmim]Cl under microwave heating (130 °C, 500 W). They were then homogenized by dynamic high pressure microfluidization (S/N8425, Micro DeBEE Inc., USA) at pressure levels from 34 to 172 MPa and for up to 6 cycles. SBC were precipitated from the ILs solution by water. After that [Bmim]Cl were removed by centrifugal separation. Finally, the regenerated SBC were dried in a vacuum freeze dryer. For comparison purpose, nanocellulose samples treated with high pressure homogenization were also prepared at 80 MPa for 30 cycles under the optimum operating conditions.

### 2.3. Characterization of supramolecular structures

#### 2.3.1. Particle size distribution

The particle size and size distribution were measured by a photon correlation spectroscopy with a Nano-ZS (Malvern Instruments, UK) in order to characterize the supramolecular structures of the nanocelluloses. The nanocelluloses were diluted in deionized water at pH 7.0 at room temperature. The mean diameter (*z*-average) was calculated by analyzing the intensity autocorrelation function. The data reported are the average of three replicates.

#### 2.3.2. Morphological analysis

The morphology measurements of the nanocelluloses were carried out on a TEM (JEM-100, JEOL, Tokyo, Japan) operated at 100 keV. The nanocelluloses were deposited from an aqueous dilute dispersion and cast one drop onto copper grid with carbon film support. Samples were observed directly with TEM after they were dried at 20 °C without further staining.

#### 2.3.3. Rheological properties analysis

Dynamic viscoelasticity of celluloses/[Bmim]Cl solution was measured using an AR2000 stress-controlled rheometer (TA Instruments, USA) with 40 mm parallel-plate geometry. The gap chosen was about 1000  $\mu\text{m}$  for all measurements. The experimental temperature was set at 40 °C. The measurements were performed by embedding with a thin layer of standard viscosity silicon oil on the free surface of the solution.

#### 2.3.4. X-ray diffraction (XRD) analysis

X-ray diffractometry in reflection mode were carried out using a diffractometer (Bruker D8 Advance, Germany), with monochromatic Cu K $\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ), generated at 40 kV and 40 mA, at room temperature. Diffractograms were made by continuous scanning over the range of diffraction angle from  $2\theta = 5^\circ$  to  $2\theta = 45^\circ$ . Crystallinity index was calculated based on the Segal's empirical method (Sasaki, Adschiri, & Araai, 2003), using the equation:

$$C_{\text{I}}(\%) = (I_{200} - I_{\text{am}}) \times 100\% / I_{200} \quad (1)$$

where  $I_{200}$  is the maximum intensity of the principal peak lattice diffraction, and  $I_{\text{am}}$  is the intensity of diffraction attributed to amorphous celluloses. Integration of crystalline reflection was carried out with Origin Pro software.

#### 2.3.5. X-ray photoelectron spectroscopy (XPS) analysis

XPS measurements were performed to investigate the surface chemical changes of the samples using VG Multilab 2000 (Thermo Electron Corporation, USA) X-ray Photoelectron Spectrometer with Al source. A spot size of 100  $\mu\text{m}$  and a power of 25 W were used. All binding energy values were calculated relative to the carbon (C 1s) photoelectron at 285 eV by applying a linear background subtraction method followed by C 1s curve deconvolution into three Gaussian's curves.

#### 2.3.6. Fourier transform infrared spectroscopy (FT-IR) analysis

The cellulose samples were subjected to Fourier transform infrared (FT-IR) analysis (model: Spectrum GX-1, PerkinElmer, USA spectrometer) to investigate the changes in functional groups. The spectra (4000–400  $\text{cm}^{-1}$ ) were recorded with a resolution of 1  $\text{cm}^{-1}$  and 64 scans per sample. About 2 mg samples were prepared by mixing with 120 mg of spectroscopic grade KBr then compressed to form a disk.

#### 2.3.7. Solid-state CP/MAS $^{13}\text{C}$ NMR analysis

Solid-state  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature on an Infinity Plus 400 spectrometer ( $^{13}\text{C}$  frequency =

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