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Homogeneous isolation of nanocellulose from eucalyptus pulp by high pressure homogenization

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ABSTRACT

Nanocellulose from eucalyptus (*Eucalyptus robusta Smith*) pulp was extracted by simply disrupting the hydrogen bond network of celluloses with high pressure homogenization (HPH). It was found that nanocellulose was 20–100 nm in diameter, and presented a narrower molecular weight distribution, lower thermal stability and crystallinity index. Fourier transform infrared (FT-IR) and solid state cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ^{13}C NMR) were used to confirm the physicochemical properties of nanocellulose, suggesting that intra-molecular hydrogen bonds are entirely maintained. Meanwhile, the feasibility of high pressure homogenization for different cellulosic biomass materials was investigated using comparison of eucalyptus pulp nanocellulose, sugarcane (*Saccharum officinarum*) bagasse nanocellulose and cotton (*Gossypium* spp) nanocellulose. Results showed that eucalyptus pulp chains could be interrupted easily by the shearing forces for its harder texture, which was suited for high pressure homogenization. Other kinds of cellulose could also be well suited through controlling key parameters such as mechanical forces and treatment temperature in the process.

1. Introduction

Eucalyptus is genus of tall, evergreen and magnificent trees cultivated all over the world. It is well famous for its various extracts, such as essential oils (Xiong et al., 2004), insecticidal constituent, ethanol (Castro et al., 2013) and xylose (Canettieri et al., 2007), which are extensively used in the cosmetics (Yang et al., 2004), perfumery, food and pharmaceutical industry. Besides the extractives, the main components of the plants are celluloses (the holocellulose content is about 74.2%) (Casas et al., 2013), which can be employed in many other applications capable of upgrading the value of eucalyptus utilization. For example, several authors have been reported that the extraction of *eucalyptus globulus* bark and a concentration strategy to obtain a phenolic-rich extract for application in the leather tanning industry (Pinto et al., 2013). Among the applications, the development of nanocellulose have been attracted much attention due to its super functionalities, such as its high aspect ratio, high surface area and good mechanical properties (Brinchi et al., 2013). It may provide value-added materials with superior performance and extensive applications, such as in paper, polymer, textile, pharmaceutical, biomedical applications and food industries (Chen et al., 2014).

Extensive investigations indicated that nanocellulose are normally isolated by means of physical treatments (Ikeda et al., 2002), chemical treatments (Peng et al., 2011) and biological treatments (Penttilä et al., 2013), so that the bonds of the cellulose–hemicellulose–lignin complex can be broken. There are some disadvantages among these methods that restrict the applications of nanocellulose. For example, by chemical treatments, due to the harsh reaction conditions used and the resulting acid degradation of the amorphous region, the production is time consuming and the yield is low (Conte et al., 2009). The enzymatic hydrolysis is an expensive technique and therefore requires more elaborate components (Brinchi et al., 2013). The mechanical treatments is the most well-known and widely used (Avolio et al., 2012; Hu et al., 2011). However, due to the highly crystalline of celluloses and the presence of strong intermolecular hydrogen bonds between chains and intra-molecular hydrogen bonds within a single chain, it need extensive energies to overcome the resistance of celluloses chains in the solid phase. In previous studies, liquid homogenous nanotechnology (First,

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cellulose is dissolved in a homogeneous solution. Then it is restructured through the high pressure shearing during the whole homogeneous solution, And thus the nanocellulose was obtained after regeneration) is proved to have a significant effect on structure of fibers of several different sources (sugarcane bagasse celluloses and cotton celluloses) (Li et al., 2012, 2014; Wang et al., 2015), which can be considered a promising and sustainable alternative for its simplicity, high efficiency and conquering huge resistance between celluloses chains (Saelee et al., 2016). However, the applicability about liquid homogenous nanotechnology is unclear now.

As we known that fiber clusters of sugarcane bagasse cellulose (SCB) have characteristics including high stiffness, short fibers clusters and weak interlacing of fibers bundles (Oliveira et al., 2016). Furthermore, interior of SCB is filled with pores or vessels or holes. On the contrary, the ones of cotton cellulose possess opposite characteristics, covering high softness, long fibers clusters and strong interlacing of fibers bundles (Rahbar Shamskar et al., 2016). Experimental results show that the nanocellulose from cotton cellulose aggregated to a far greater extent than the ones from SCB (Li et al., 2012; Wang et al., 2015), which could be that chemical composition, refining treatments, structure, and properties of fibers influenced the nanocellulose, mean particle size and so on. Therefore, nanocellulose from eucalyptus pulp was extracted by HPH in order to study the suitability of liquid homogenous nanotechnology for fibers with different structure.

Up to now, there is a little information available on structure and properties of fibrous raw material and their impact on the subsequent HPH. As a consequence, the current research is specifically focused on this aspect. In the paper, nanocellulose from eucalyptus pulp was isolated by HPH associated with ILs (liquid homogenous nanotechnology), which could overcome enormous resistance of celluloses chains in the solid state (Cerruti et al., 2008). The performance of the nanocellulose was characterized using gel permeation chromatography (GPC), X-ray diffraction (XRD) and thermal gravimetric (TG) analysis. Furthermore, we present a quantitative analysis of the mechanism of fabricating nanocellulose by FT-IR spectra and CP/MAS ^{13}C NMR measurements. The present work was also focused on assessment of liquid homogenous nanotechnology for the applicability from eucalyptus.

2. Experimental

2.1. Materials

A bleached soda-anthraquinone pulp of *eucalyptus citriodora* produced was kindly provided by Zhanjiang Chenming Pulp & Paper Co., Ltd., and pretreated by acid treatment. The contents of celluloses, hemicellulose and lignin content were 93.09%, 0.38% and 5.82%, respectively. Ionic liquids 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was prepared by following the procedures reported in literature (Li et al., 2014). All other reagents and chemicals were of analytical grade.

2.2. Preparation of nanocellulose

Samples were dissolved with 1% (w/w) [Bmim]Cl under microwave heating (150 °C, 400 W). They were then homogenized by a high pressure homogenizer (AH100D, ATS Engineering Inc., Canada) at pressure levels from 40 to 120 MPa and for up to 50 cycles. Eucalyptus pulp were then precipitated from the ILs solution by adding distilled water (distilled water-to-ILs solution ratio of 5:1). After that, [Bmim]Cl were removed by repeated centrifugation at 12,000 rpm. Finally, the regenerated eucalyptus nanocellulose was dried in a vacuum freeze dryer.

2.3. Mean particle size

Mean particle size and the polydispersity index of ILs treated eucalyptus pulp and nanocellulose from eucalyptus pulp were analyzed by a photon correlation spectroscopy with a Nano-ZS (Malvern Instruments, UK), to ascertain the impact of high pressure homogenization on nanocellulose. The nanocellulose was diluted in deionized water at pH 7.0 at room temperature. The scattering angle was fixed at 90°, and the temperature was maintained at 25 °C.

2.4. Microscopic analysis

To observe the structure of nanoparticles from eucalyptus pulp, morphological characterization of nanocellulose from eucalyptus pulp was analyzed with transmission electron microscopy (JEM-100, JEOL, Tokyo, Japan) operated at 100 keV. Drop of whisker suspension in water, were mounted onto carbon coated grids and then allowed to dry at 20 °C. Observations were carried out with TEM without further staining.

2.5. Gel permeation chromatography (GPC) analysis

Eucalyptus pulp, ILs treated eucalyptus pulp and nanocellulose from eucalyptus pulp were dissolved in LiCl-DMAc. The solution and mobile phases (DMAc/0.5% LiCl) were filtered through a polytetrafluoroethylene (PTFE) membrane filter. The sample volume was 200 µl. The columns used were a series of two PL gel mixed bed columns (300 × 7.8 mm; particle size 10 µm). A G1311B 1260 Quat Pump and a differential refractometer detector (Agilent Technologies, USA) were used. Eight pullulan standards of narrow polydispersity were used to calibrate the columns. The linear coefficient of determination (R^2) was 0.99.

2.6. X-ray diffraction (XRD) analysis

X-ray diffractometry in reflection mode was carried out using a diffractometer (Bruker D8 Advance, Germany). Each sample was scanned within the 2θ range of 0–50°. Instrumental line broadening was calibrated with α-alumina. Specimen line broadening for the major equatorial peaks was modeled by Lorentzian profiles, following the delft line-broadening model. The crystallinity index (CI) was calculated based on the Segal's empirical method (Segal et al., 1959), with the equation as follows:

$$C_{I_r}(\%) = \frac{(I_{200} - I_{am}) \times 100\%}{I_{200}} \quad (1)$$

where I_{200} is the maximum intensity of the principal peak lattice diffraction, and I_{am} is the intensity of diffraction attributed to amorphous celluloses.

2.7. Thermal gravimetric (TG) analysis

The thermogravimetric experiment of samples was performed by using a differential thermal analyzer (STA449C/4/G, Netzsch, Germany). TG measurements were carried out from 25 to 700 °C at a constant heating rate of 10 °C min^{-1}. All of the measurements were performed under a pure nitrogen gas flow of 50 ml min^{-1}.

2.8. Molecular analysis

Effects of HPH on the structure of nanocellulose were discussed by FT-IR and NMR analysis. The FT-IR spectra were obtained using Spectrum GX-1, PerkinElmer, USA spectrometer. The spectra were operated with a resolution of 1 cm^{-1}, 64 scans, and a signal gain of 8. The test specimens were prepared by the KBr disk method.

Solid state ^{13}C NMR spectra were recorded on an infinity plus 400 spectrometer (Varian; magnetic field: 9.4 T, ^{13}C frequency: 100 MHz) with a CP-MAS unit at room temperature. The spinning rate and contact