

Homogeneous Isolation of Nanocellulose from Cotton Cellulose by High Pressure Homogenization

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ABSTRACT

Nano-cellulose materials are widely believed to have the potential to push polymer mechanical properties. The cotton cellulose was dissolved in ionic liquid (1-butyl-3-methylimidazolium chloride ([Bmim]Cl)), and then was isolated by high pressure homogenization in a homogeneous media. The nano-cellulose was obtained at 80 MPa for 30 cycles. The geometry and microstructure of the cellulose nano-fibres were observed by SEM and their particle size analysis. FTIR, XRD and TGA were used to characterize changes to chemical functionality. Particular emphasis is given to the physical and chemical characterization of these nano-fibres together with their thermal stability and crystallinity, in order to develop their suitability.

Keywords: Ionic Liquid; Particle Size; High Pressure Homogenization; Thermal Stability; Crystallinity

1. Introduction

Science and technology continue to move toward renewable raw materials and more environmentally friendly and sustainable resources and processes [2]. Cellulose, as a whole is of growing importance in the development and application of polymer materials, represents a potentially sustainable source to create fuels, chemicals, composites, and a host of other products to replace fossil-based products [8]. The nanomaterial landscape is vast, which is widely believed to have the potential to push polymer mechanical properties to extreme values [6]. Production of nanocellulose has different methods, such as acid hydrolysis [9] alkali hydrolysis ball milling and so on. And the weakness of these methods limit the development.

Homogeneous isolation of nanocellulose by high pressure homogenization is a new and comparatively green method due to without pretreatment by adding catalytic amount of sulfuric acid and cellulose solution under mild condition [5].

We report the structural and physicochemical properties of the nanocellulose caused by the whole process, using Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy, and XPS measure-

ments.

2. Experimental

2.1. Materials

Cotton cellulose was purchased by local factory in Zhanjiang, China. The ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was synthesized according to the previous work [4]. All other chemicals were of analytical grade, come from Guangzhou Chemical Reagent Factory (Guangzhou, China).

2.2. Preparation of Nanocellulose

Cotton cellulose was pretreated by 1% (w/v) sodium hydroxyl solution to remove hemicellulose and lignin, respectively. It was washed with distilled water until the solution was neutral, and then air dried. Pretreated cotton cellulose was dissolved in [Bmim]Cl by microwave (Qpro-M, Questron Inc., Canada) heating until it formed a clear and viscous solution after completely dissolved in ILs. Then it was homogenized by a high pressure homogenizer (AH100D, ATS Engineering Inc., Canada) at pressure levels ranging from 40 to 120 MPa and for up to 50 HPH cycles. Finally, the regenerated SBC was dried in a vacuum freeze drying equipment.

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2.3. Characterization

2.3.1. TEM Analysis

The morphology of the nanocellulose was studied by TEM (JEM-100, JEOL, Tokyo, Japan), operated at 100 keV.

2.3.2. Infrared Spectroscopy (IR) Analysis

The FTIR spectra of original cellulose, IL pretreated cellulose and nanocellulose was measured in the range from 4000 to 400 cm^{-1} (Spectrum GX-1, PerkinElmer, USA).

2.3.3. Thermal Analysis

Thermal analysis measurements (TG) were carried out with a Synchronous Thermal Analysis (STA449C/4/G, Netzsch, Germany). Original cellulose, IL treated cellulose, and nanocellulose were heated from 50°C to 700°C at a heating rate of 10°C min^{-1} . Under a nitrogen atmosphere with a gas flow of 20 $\text{ml}\cdot\text{min}^{-1}$.

2.3.4. X-Ray Diffraction (XRD) Analysis

X-ray diffractometry in reflection mode was carried out using a diffractometer (DLMAX-2550, Japan), with monochromatic Cu K α radiation ($\lambda = 0.15418 \text{ nm}$), generated at 40 kV and 40 mA, at room temperature. The samples were scanned within 5.00 - 45.00° 2 θ in step mode with a step of 0.01° and a rate of 1 min^{-1} . The crystallite index of cellulose was calculated using the kim's empirical method [1].

3. Results and Discussion

Dissolution process was performed at 110°C, 120°C, 130°C, 140°C and 150°C. As expected, the dissolution time of cellulose decreased with increasing temperature. However, the yield of cellulose always increased with increasing temperature. Finally, we found experimentally that the best solubilisation could be achieved in 1% (g/g) cellulose/[Bmim]Cl during 150°C for 6mins at 400 W of microwave.

The pretreated cotton cellulose was dissolved in [Bmim] Cl to form a homogeneous solution. And the mixed solution was passed through high pressure homogenizer to gain the nanocellulose. Considered the particle sizes and economical factor, the optimum of HPH process condition was at a pressure of 80MPa with 30 cycles.

3.1. TEM Analysis

The TEM micrograph of a dilute suspension of nanocellulose was shown in **Figure 1**. The particles of nanocellulose was about 20 nm. This result indicates that the diameter of cellulose treated by HPH could be reached on the scale of a nanometer.

3.2. Infrared Spectroscopy (IR) Analysis

FT-IR spectra of original cellulose, IL treated cellulose and nanocellulose was carried out in **Figure 2**. We observed between 3700 cm^{-1} and 3000 cm^{-1} corresponding to O-H stretching, decrease and become broader after treated with ILs, which can be correlated with a disruption of intra-molecular and intermolecular hydrogen bonds. The absorption band at 1452 cm^{-1} in cotton cellulose, assigned to CH₂ motion [11], became very weak and shifted to a low wave number after treated with ILs in different temperature, responding to the breaking of an intra-molecular hydrogen bond involving O6 [13]. The band at 880 cm^{-1} belongs to β -glucosidic bond, and the absorption peak in regeneration cotton cellulose shifted to a high wave number than the corresponding one in the cotton cellulose, which is a characteristic of transition from cellulose I to cellulose II [3].

Significantly, no difference was found between the spectrum of nanocellulose and IL treated cellulose. The result indicates that no other derivational reaction occurred during the processes of dissolution and refining.

3.3. Thermal Analysis

The TGA and DTG curves of three kinds of cellulose were shown in **Figure 3**. The onset decomposition temperature of original cellulose was about 339°C. Whereas IL treated cellulose and homogenized cellulose was

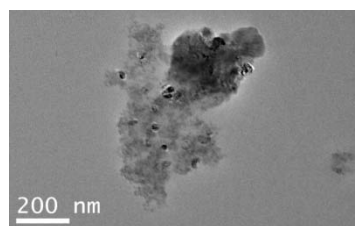


Figure 1. TEM of nanocellulose.

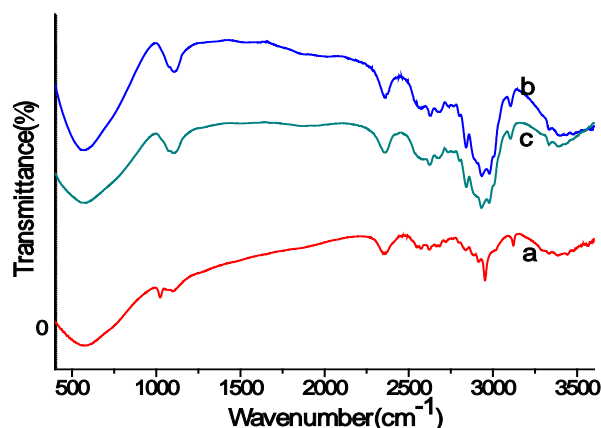


Figure 2. IR spectra of original cellulose (a), IL treated cellulose (b) and nanocellulose (c).

326°C and 286°C respectively. It implied that the nanocellulose exhibited the lowest thermal stability. Possible explain was that crystal region between cellulose were destroyed in the process.

3.4. X-Ray Diffraction (XRD) Analysis

The X-ray diffraction patterns of original cellulose, IL treated cellulose as well as nanocellulose was shown in Figure 4. shown in °C. The diffraction peaks on about

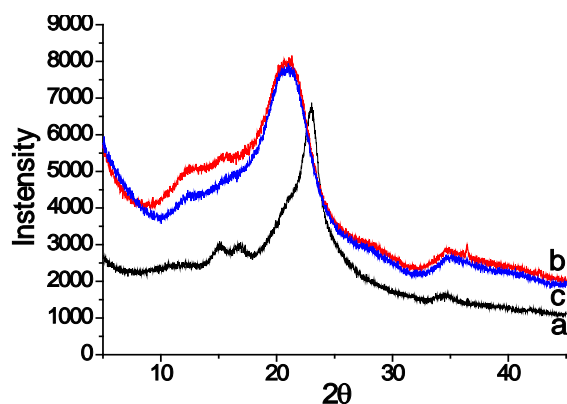


Figure 3. X-ray diffraction patterns of original cellulose (a), IL treated cellulose (b) and nanocellulose (c).

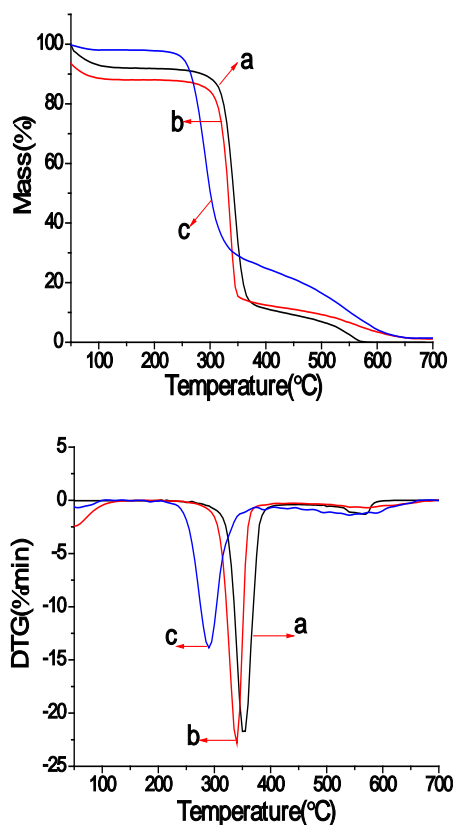


Figure 4. TG and DTG curves of original cellulose (a), IL treated cellulose (b) and nanocellulose (c).

15.1° ($1\bar{1}\bar{0}$), 16.9° (110), and 23.0° (200), confirmed that only cellulose I was present in it [12]. During the dissolution process, the cellulose chains are separated and became random [7], which are indicated by the crystalline form of regenerated cotton cellulose II [10]. The crystallinity index of original cellulose, IL treated cellulose and homogenized cellulose was 43.1%, 15.8% and 14.66% respectively. The crystallinity index decreased because the intermolecular and intra-molecular hydrogen bonds of cellulose were broken by ionic liquids and HPH [7]. It was suggested that the hydrogen bonds of cellulose were broken, which cause the collapse of crystal structure during the whole process.

4. Conclusion

The present work has demonstrated that nano-cellulose could be prepared by high pressure homogenization. Nanocellulose with dimensions of 20 nm in diameter was served under TEM. The FTIR spectra confirmed that the basic structure of cellulose nanocrystals was maintained and no derivative was formed. The nanocellulose had a lower thermal stability and crystallinity index. These results showed significant modifications in the structure and the texture treated by HPH. A possible explanation was that numbers of hydrogen bonds decreased by HPH. The applications of nano-cellulose will be explored.

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