Preparation and Characterizations of Nanocellulose from Wood Pulp using Hydrolysis Method

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Abstract

Nanocellulose was prepared from wood pulp by hydrolysis method using H_2SO_4 60% wt at 45°C for 60 minutes with ratio solid/solution of 1/10. Suspension was cleaned into neutral by centrifuge followed by ultrasonication treatment at room temperature for 2 hours. Nanocellulose was characterized by X-ray diffraction (XRD), Scan electron microscopy (SEM) and Fourier Transform Infrared (FT-IR). Obtained nanocellulose is cellulose nanocrystal (CNC) with dimensions of 20-30 nm x 100-300 nm and crystallinity index of 90%.

Keywords: cellulose, nanocellulose, acid hydrolysis

1. Introduction

Cellulose is one of the most abundant renewable material in the world, it has been using in various industries, such as papermaking and clothing. Almost cellulose is produced as wood pulp for papermaking and for the production of modified cellulose materials, such as esters and ethers.

Recently, nanocellulose - a new generation of cellulose materials is an interesting research field. The most important nanocelluloses are cellulose nanofibril (CNF) and cellulose nanocrystal (CNC) [1], both prepared by chemical, physical or physicochemical methods. The geometrical dimensions of CNC can be with diameter in the range of 5-50 nm and length in the range of 100-500 nm while the CNF can be 20-50nm in width and 500-2000nm in length.

Sulfuric acid is the most commonly used acid for CNC preparation by hydrolysis process, amorphous domains and local interfibrillar contacts of cellulose are preferentially hydrolyzed, whereas stable crystallites remain intact and can be isolated as nanocrystalline particles [2]. The hydrolyze suspension CNC can be neutralized by additional steps such as filtration and centrifugation.

In this report, nanocellulose was prepared from bleached wood pulp by hydrolysis used acid sulfuric solution, effects of time and temperature on yield and structure of nanocellulose were investigated.

2. Experimental

2.1. Materials

Bleached *wood pulp* was supplied by Bai Bang paper company, Phu Tho, Vietnam. The other chemicals were purchased from Aldrich or Merck used as received without further purification.

The dry pulp was stored in plastic bags at room temperature. Chemical compositions (w/w) of the material was determined by TAPPI methods as follow: cellulose content by TAPPI T201 wd-76; pentosane content by TAPPI T223 cm-84.

2.2. Preparation of nanocellulose

10g of the wood pulp was dispersed in 54 mL water and stirred at room temperature for 2 hours. The mixture was added by 46 mL of sulfuric acid 96% to get acid hydrolysis concentration of 60%. The temperature of the mixture was adjusted to 25-100°C with stirring for 30-80 mins. Washing was repeated until the pH of the suspensions in the centrifuge was almost neutral.

The treated pulp was poured into a cup of 100 mL water in an ultrasonic bath at room temperature for 2 hours. The treated suspension was kept in glass bottle for analytical.

2.3. Characterization of nanocellulose

The morphology of the nanocellulose after each treatment was investigated using a JEOL JSM-7600F FESEM microscopes and Hitachi S4800 FESEM.

The samples were characterized crystallinity by X-ray diffraction (XRD) on D8 Advance - Bruker using Cu-Kα radiation source (λ= 0.1540 nm) at an accelerating voltage of 40 kV and the current of 30 mA. The data were collected from 2θ= 5-50°. The

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crystallinity index was determined by the method reported by Wang [5].

$$CrI\ (\%) = (I_{002} - I_{am})/I_{002}\ x\ 100;$$

Where I_{002} is the maximum intensity of the crystal lattice diffraction peak and I_{am} is the intensity of the amorphous region of the sample. The diffraction peak for I_{002} is located at a diffraction angle of around $2\theta = 22.5^o$ and the intensity of the amorphous part was measured as the lowest intensity at a diffraction angle of around $2\theta = 18^o$.

Fourier transform infrared spectrum (FT-IR) was obtained on a FT-IR 6700 NRX Raman Module-Thermo Nicolet to examine the changes in the functional groups after treatments.

3. Results and discussion

3.1. Chemical composition of material

The chemical compositions of bleached *Wood pulp* were determined by TAPPI methods, results were showed on table 1.

Bleached *Wood pulp* is obtained from wood chips by sulfate pulping followed by bleaching process. As shown in table 1, in bleached *Wood pulp*, a small amount of pentose remained and main component of the material was cellulose. In hydrolysis process, cellulose will be hydrolyzed to obtain nanocellulose, whereas pentose will be hydrolyzed into dissolve phase.

Table 1. Chemical composition of material

Material and method	Cellulose (wt%)	Pentose (wt%)
Bleached *Wood pulp*	92.5	5.8

3.2. Effects of hydrolysis conditions on yield of nanocellulose

During hydrolysis by sulfuric acid, pentose, amorphous regions and local internal contacts of cellulose are firstly hydrolyzed, whereas crystal regions remain and can be isolated as nanocellulose particles.

Effect of various acid concentrations on yield of nanocellulose have been studied in many literatures [6-8]. It shows that hydrolysis with 60%wt sulfuric is optimal condition for a high nanocellulose yield and a uniform of nanocellulose morphology. The cellulose sample was completely dissolved when the acid concentration was above 65%wt [6], otherwise with concentrations from 40 to 55%wt, mostly particles size of obtained solid were bigger than nano size.

In this research, hydrolysis with acid concentration of 60%wt was used for studied. The effect of hydrolysis time and temperature on yield and morphology of obtained nanocellulose have studied.

Hydrolysis of cellulose was carried out as follow conditions: acid concentration 60%wt, solid/liquid ratio of 1/10, temperature 45°C and time 30-80 mins. The results were showed on Fig. 1.

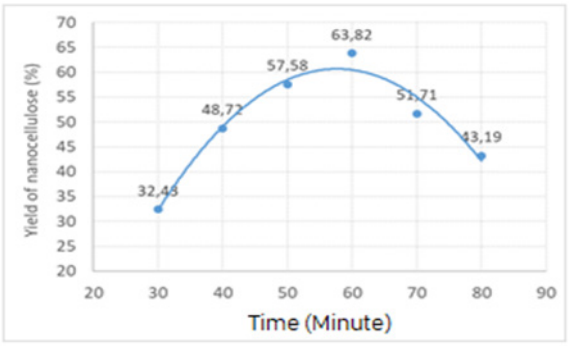

Fig. 1. Effect of hydrolysis time on yield of nanocellulose.

Fig.1 showed that, yield of nanocellulose was increasing as hydrolysis time was reached from 30-60 mins, while the yield was decreasing when hydrolysis time longer than 60 mins.

When hydrolysis time lower than 60 mins, pentose, amorphous part of cellulose was hydrolyzed completely, while the hydrolysis process of cellulose was being continued. It causes the nanocellulose yield to increase.

Electron microscopic observation (Fig.2) of the samples with hydrolysis time lower than 60 mins showed that, beside nanocellulose particles, in the samples was remain particles which bigger than nano size.

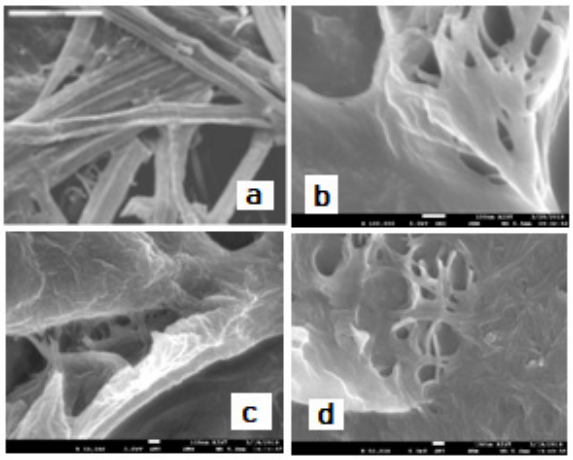

Fig. 2. SEM of (a) raw material, (b) 40 mins hydrolysis, (c) 50 mins hydrolysis and (d) 60 mins hydrolysis.

When hydrolysis time longer than 60 mins, cellulose was completely hydrolyzed and obtained nanocellulose was also started to be hydrolyzed unceasingly. This causes a decrease of nanocellulose yield. The appropriate hydrolysis time is 60 mins, with 63.82 % yield of nanocellulose.

Hydrolysis was carried out hydrolysis with acid concentration of 60%wt, solid/liquid ratio of 1/10, time of 60 mins and temperature from 25-100°C. The results were showed on table 2.

The results showed that, the best hydrolysis temperature was 45°C. The yield of nanocellulose was decreasing when temperature increase from 45-100°C and at a temperature higher than 85°C, almost cellulose was completely hydrolyzed. When the hydrolysis temperature was lower than 45° C, obtained solid contain nanocellulose and some particles was bigger than nanocellulose (Fig. 3). It causes of the decreasing nanocellulose yield.

Table 2. Effect of hydrolysis temperature on yield of nanocellulose.

Temperature (°C)	Yield of nanocellulose (%)
25	37.43
35	49.72
45	63.84
55	57.38
65	45.72
75	23.19
85	1.24
100	0.16

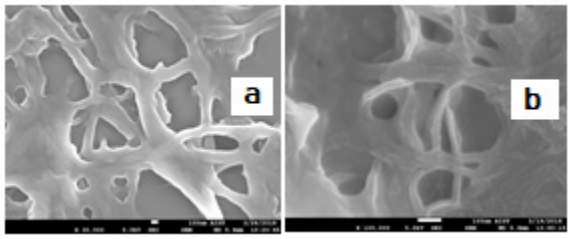

Fig. 3. SEM of (a) hydrolysis at 35°C, (b) hydrolysis at 45°C.

3.3. Characterization of nanocellulose

The FTIR spectra presented in Fig. 4 shows the function groups of raw material and nanocellulose. The strong peaks around 3450 cm^{-1} (in range 3550-3200 cm^{-1}) and 3200-2700 cm^{-1} (around 2800 cm^{-1}) correspond to OH groups of cellulose which are creating hydrogen bonds in the materials. The peaks around 1640 cm^{-1} corresponds to the C-H groups of the pyranose ring of cellulose. Finally, the absorbance peaks observed in the 1028-1161 cm^{-1} range were attributed to C-O stretching of the pyranose ring.

No significant changes were observed in the FTIR spectrum of the raw material and the nanocellulose obtained after hydrolysis shows that hydrolysis process did not change the chemical structure of cellulose.

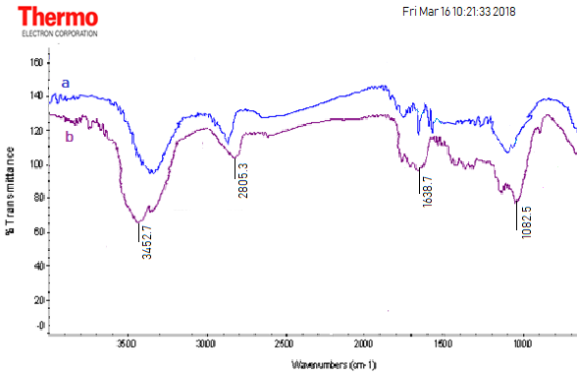

Fig. 4. FTIR spectra of (a) bleached *Wood pulp* and (b) nanocellulose.

XRD was used to analyze the crystallinity of the raw material as well as nanocellulose obtained after hydrolysis. Three crystalline peaks typical of cellulose were present at around 2θ = 16°, 22.5°, and 35°. The magnitudes of these crystalline peaks increased after hydrolysis process, in which removal of amorphous parts of cellulose and pentose. The crystallinity index was found to be approximately 74% for the raw material and 90% for nanocellulose.

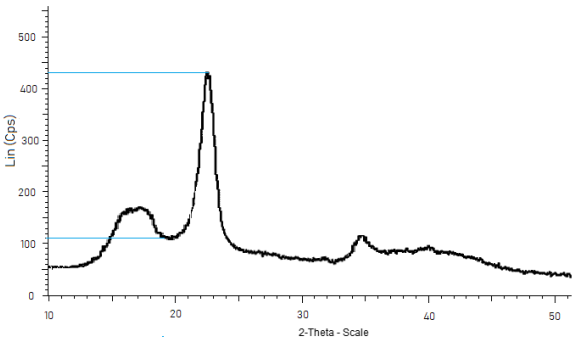

Fig. 5. X-ray diffraction patterns of bleached *Wood pulp*

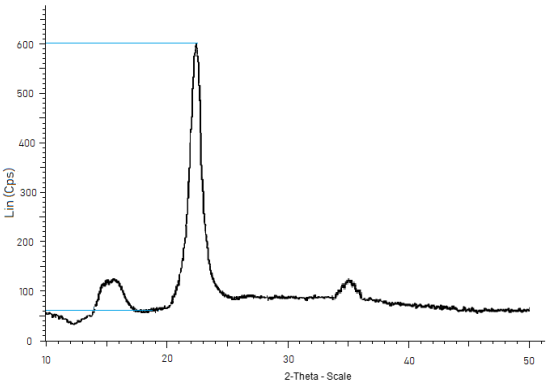

Fig. 6. X-ray diffraction patterns of nanocellulose

Combine the results from SEM, FTIR and XRD showed that obtained nanocellulose was cellulose nanocrystal (CNC) with dimension 20-30nm x 100-300 nm and crystallinity index around 90%.

4. Conclusions

Successfully fabricated cellulose nanocrystal (CNC) from bleached *Wood pulp* by hydrolysis process using acid sulfuric 60%wt, at 45ºC for 60 mins with solid/liquid ratio of 1/10. Yield of CNC was around 64%.

Obtained CNC has dimension of 20-30nm x 100-300 nm with crystallinity index of 90%.

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