PREPARATION AND CHARACTERIZATION OF BAMBOO NANOCRYSTALLINE CELLULOSE

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Nanocrystalline cellulose (NCC) has many potential applications because of its special properties. In this paper, NCC was prepared from bamboo pulp. Bamboo pulp was first pretreated with sodium hydroxide, followed by hydrolysis with sulfuric acid. The concentration of sulfuric acid and the hydrolysis time on the yield of NCC were studied. The results showed that sulfuric acid concentration had larger influence than the hydrolysis time on the yield of NCC. When the temperature was 50°C, the concentration of sulfuric acid was 48wt% and the reaction time was 30 minutes, a high quality of nanocrystalline cellulose was obtained; under these conditions, the length of the nanocrystalline cellulose ranged from 200 nm to 500 nm, the diameter was less than 20 nm, the yield was 15.67wt%, and the crystallinity was 71.98%, which is not only higher than those of cellulose nanocrystals prepared from some non-wood materials, but also higher than bamboo cellulose nanocrystals prepared by other methods.

Keywords: Nanocrystalline cellulose (NCC); Bamboo pulp; Sulfuric acid hydrolysis; Pretreatment

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INTRODUCTION

Nanocrystalline cellulose (NCC) is a kind of the natural green renewable resource. It is typically rod-shaped monocrystalline cellulose with tens to hundreds of nanometers in length and 1 to 100 nm in diameter (Ruiz et al. 2000). NCC has received a great deal of attention in the last two decades, particularly for its potential applications as reinforcement and retention in polymer composites and paper-making (Habibi et al. 2010; Roman and Winter 2006; Wu et al. 2007) because of its high Young's modulus and unique tensile strength (Ruiz et al. 2000; Samir et al. 2005; Sakurada et al. 1962). Moreover, due to its distinctive optical properties, highly crystalline structure, and high surface area (Bai et al. 2009), NCC can be used for many applications such as optical devices (Revol et al. 1998), regenerative medicine (Fleming et al. 2001), automotive applications (Dahlke et al. 1998; Hill 1997), and so on. NCC suspensions can be used to form films having potential applications as ink pigments and optically variable films for security papers, since the optical properties cannot be reproduced by printing or photocopying (Pan et al. 2010; Revol et al. 1998).

Cellulose contains both amorphous and crystalline structures. The amorphous regions can be removed to form highly crystalline cellulose. Different methods for producing NCC have been attempted, such as acid hydrolysis (Beck-Candanedo et al. 2005; Elazzouzi-Hafraoui et al. 2008), enzymolysis (Henriksson et al. 2007; Pääkkö et al. 2008), and chlorine oxidation degradation (Fan et al. 2011), as well as a combination of two or several of these methods. All these methods lead to different types of NCC, depending on the raw material and pretreatment. Although various means of generating NCC have been attempted in recent years, the method of acid hydrolysis is well-known process used to dissolve amorphous regions effectively (Bai et al. 2009; Elazzouzi-Hafraoui et al. 2008; Hirai et al. 2009). The use of sulfuric acid to produce NCC imparts sulfate ester groups to the cellulose nanocrystal surfaces, resulting in electrostatically stabilized aqueous NCC suspensions (Beck et al. 2011).

Previous studies have shown that NCC can be produced from acid hydrolysis of various natural cellulose fibers such as cotton (Elazzouzi-Hafraoui et al. 2008), wood (Beck et al. 2011; Pan et al. 2010), and MCC (microcrystalline cellulose) (Agblevor et al. 2007; Bai et al. 2009). However, the limited sources of these raw materials restrict the application and promotion of NCC, and the size and shape of NCC particles are also determined to a certain extent by the nature of the cellulose source and the hydrolysis conditions (Elazzouzi-Hafraoui et al. 2008). The degree of crystallinity of the cellulose varies widely from species to species.

Bamboo is a kind of natural and abundant cellulose with excellent toughness, hygroscopicity, and high crystallinity (Li and Bai 2007), and it has a great potential for producing NCC (Wang et al. 2006). Bamboo fiber may play an important role in forming future organic structures and composites, and is recognized as an attractive candidate as a strengthening natural fiber (Liu et al. 2010). In 2010, Zhang et al. (2010) reported that microfibrillated cellulose (MFC) was obtained by disintegrating bleached kraft bamboo pulp with a procedure of chemical pretreatment and high-pressure homogenization. Abe has isolated cellulose microfibril aggregates from fiber and parenchyma cells of Moso bamboo (Abe et al. 2010). In 2011, Chen et al. (2011) reported that cellulose I nanofibers (CNFs) were successfully prepared from bamboo fibers, by using chemical pretreatment combined with high intensity ultrasonication. In 2012, Chang et al. attempted to separate cellulose nanofibers (CNFs) from bamboo using hot-compressed water (HCW) treatment followed by disk milling. However, there is still a lack of research in manufacture and use of nanocrystalline cellulose from bamboo.

Therefore, in this study, the method of NaOH pretreatment and sulfuric acid hydrolysis were used to obtain NCC from bamboo pulp. NaOH pretreatment is known as a very effective method of removing fatty acids, the residual lignin, and some other impurities from bamboo pulp. Moreover, NaOH has the function of saponification of bamboo pulp, as well as accelerating the hydrolysis of fiber when it is subsequently treated with sulfuric acid. Geometrical characteristics of NCC depend on the source of cellulose and the hydrolysis conditions, the influence of the sulfuric acid concentration, and the duration of hydrolysis. The yield and size of NCC were studied to determine the optimum reaction conditions. Nanocrystalline cellulose was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Materials

Bleached kraft bamboo pulp samples with 84.2% α-cellulose were obtained from a local pulp mill in Thailand. The sodium hydroxide and concentrated sulfuric acid (98%) both were of analysis grade commercial products and purchased from Guangzhou Chemical Reagent Factory, China. Dialysis membranes having a molecular weight cutoff of 14,000 were provided by Union Carbide of USA. All water utilized throughout the experimental procedures was deionized (DI) water at room temperature.

Methods

Pretreatment of bamboo pulp

3 wt% NaOH aqueous solution was used to pretreat the bamboo pulp to remove the fatty acids, the residual lignin, and some other impurities at 50 ^{o}C for 2 hours. The amorphous cellulose can be sufficiently swelled up so that sulfuric acid subsequently can easily penetrate into the fiber interior during the process of hydrolysis.

Preparation of NCC suspensions

Bamboo pulp (10.0 g) with pretreatment was hydrolyzed by diluted sulfuric acid (46%, 250 mL, at 55 ^{o}C) with continuous stirring. After several minutes, when the color of suspension became dark yellow, the cellulose suspension was diluted with deionized (DI) H_2O to stop the hydrolysis reaction and allowed to settle for several hours until the suspensions were layered, and the clear top layer was decanted off, then repeatedly washed with DI H_2O until they were not layered. The suspensions were then washed with deionized water using repeated centrifuge cycles of (10 min at 5,000 rpm, Sorvall RC-5B). The supernatant was removed from the sediment and replaced with new deionized water and mixed. The centrifuge step was stopped until the supernatant became turbid (Bondeson et al. 2006). The final wash was conducted using dialysis with DI H_2O for several days until the water pH remained constant. Afterwards, the ultrasonication was conducted for 20 min at an output power of 1200W, resulting in a stabilized aqueous NCC suspension (Chen et al. 2011; Dong et al. 1996). The nanocrystalline cellulose suspension samples were subjected to freeze-drying; thus NCC powders were prepared after grinding.

Suspension analysis

The sample of NCC suspension was stained with uranyl acetate (around 5wt%) for 3 min (Zimmermann et al. 2006), prior to being placed on a copper grid and dried at room temperature (25 ^{o}C). TEM graphs were acquired with TEM JEM-100 CXII type (Japanese electronic company) at 36 kV.

Yield analysis

The weight of the bamboo pulp with pretreatment was designated as M_2, the NCC suspension was freeze dried at -45 ^{o}C for 12 hrs, and then the dry weight was determined as M_1. The yield of NCC suspensions is given as follows.

$$Yield(\%) = \frac{M_1}{M_2} \times 100\% \quad (1)$$

FTIR analysis

The dried NCC powders were embedded in KBr pellets, and were analyzed by using a Shimadzu FTIR spectrometer (model 8201PC). The spectra were recorded in the absorption band mode in the range of 4,000 to 400 cm^{-1}.

Crystalline degree analysis

The degree of crystallization was determined using the method of X-ray Crystallinity Index (Yang 2001). The formula below was used in calculating degree of crystallization,

$$\text{X-ray Crystallinity Index} = \frac{I_{002} - I_{am}}{I_{002}} \quad (2)$$

where I_{002} represents the diffraction intensity of crystallization at the 002 peak and I_{am} represents the diffraction intensity of amorphous regions at 2θ=18 °.

RESULTS AND DISCUSSION

After pretreatment, NaOH removed much of the impurities from the bamboo pulp; the α-cellulose content of the bamboo pulp increased from 84.2% to 93.5% due to pretreatment. The cellulose content played an important and vital role in the different morphologies of NCC (Elazzouzi-Hafraoui et al. 2008). The pretreatment step was indispensable for producing nanocrystalline cellulose.

Preparation of Nanocrystalline Cellulose

The hydrolysis conditions were known to affect the properties of the resulting nanocrystalline cellulose (Beck-Candanedo et al. 2005). Among the factors of influencing the yield of NCC, sulfuric acid concentration, and the hydrolysis time were found to be the most important (Beck-Candanedo et al. 2005; Zhang et al. 2008). Therefore, these two factors were taken into account in the process of the hydrolysis.

Effect of sulfuric acid concentration on yields of NCC

The pretreated bamboo pulp was treated at 50 ^{o}C during 30 min at six different sulfuric acid concentrations, as shown in Table 1. The yield of NCC treated with different concentration of sulfuric acid can be observed in Fig. 1.

As the sulfuric acid concentration increased, the color of suspension changed from white to yellow (as shown in Table 1). And from Fig. 1, when the concentration of sulfuric acid increased, the yield of NCC also increased. When the sulfuric acid concentration was 48wt%, the highest yield was 15.67wt%. However, with further increase of the concentration of the sulfuric acid, the yields gradually decreased and finally went down to zero, which was a consequence of the reaction going too far and the cellulose being totally degraded. The results showed that 48 wt% of sulfuric acid was the best condition.

Table 1. Effect of Sulfuric Acid Concentration on Yields of NCC

sample	Weight of sample (g)	Sulfuric acid concentration (wt%)	Observation
A	10.005	42	White, with obvious fiber
B	10.025	44	Light yellow, with large fiber particles
C	10.002	46	Light yellow, translucent solution
D	10.007	48	Yellow, translucent solution
E	10.012	50	Deep yellow, transparent solution
F	10.007	52	Deep yellow, transparent solution

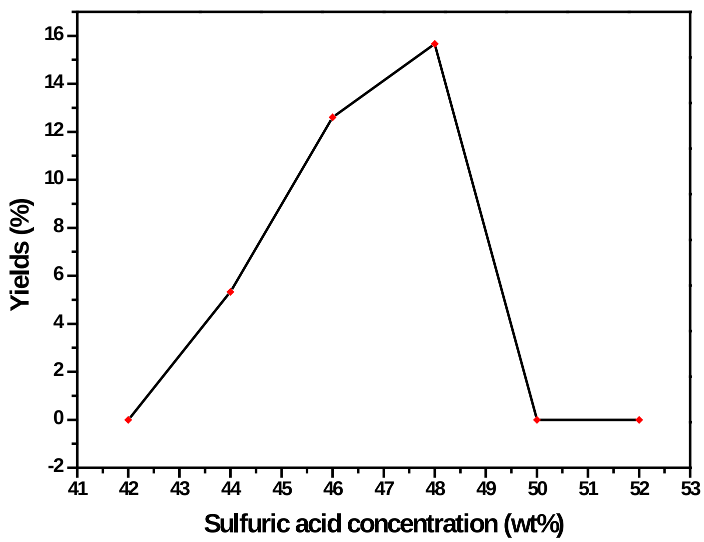

Fig.1. Effect of sulfuric acid concentration on yields

Effect of hydrolysis time on yields of NCC

The pretreated bamboo pulp was subjected to a sulfuric acid concentration of 48wt% at 50^{o}C for different hydrolysis time periods. The color of the suspension changed from light yellow to black as the reaction time was extended (see Table 2). Figure 2 shows that when the reaction time was increased, the yield increased a little. When the hydrolysis time was 30 min, the yield reached a maximum of 15.67wt%. However, when the hydrolysis time continued to extend, the yield dramatically declined. This was due to bamboo fiber's irregular microcrystalline regions. Therefore, the hydrolysis time of the bamboo pulp would need to be controlled within the range 20 to 30 min.

The effect of sulfuric acid concentration and the hydrolysis time on the properties of materials were considered. The results showed that when the bamboo pulp that pretreated by NaOH was hydrolyzed with 48 wt% sulfuric acid at 50 ^{o}C for 30 min, the maximum yields of NCC were obtained.

Table 2. Effect of Different Hydrolysis Time on Yields of NCC

sample	Weight of sample (g)	hydrolysis times (min)	Observation
G	10.002	10	Light yellow, with residual fiber
H	10.009	20	Light yellow, translucent solution
I	10.013	30	yellow, translucent solution
J	10.015	40	yellowish-brown
K	10.010	50	black

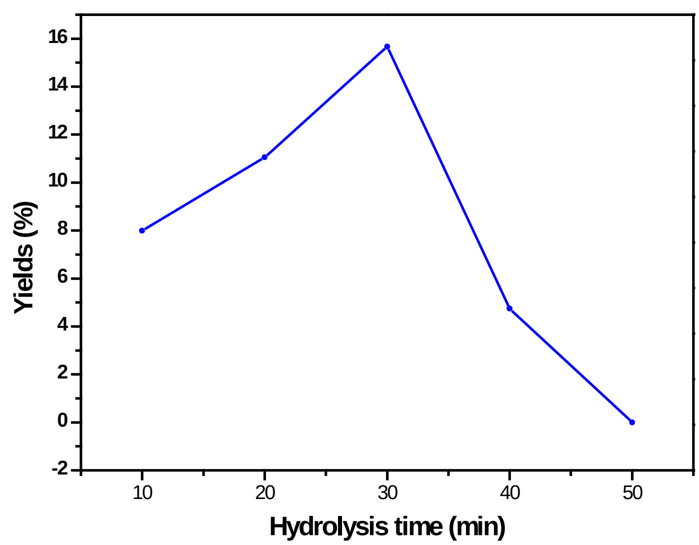

Fig. 2. Effect of various hydrolysis times on yields

Morphology of NCC

As shown in Fig. 3, NCC suspensions having three different concentrations were light blue, clear, and transparent. These suspensions displayed a colloidal nature. In the hydrolysis conditions of 44wt%, 46wt%, and 48 wt% sulfuric acid, NCC concentrations were 1.5%, 3%, and 5%, respectively. It was shown that to some extent, as sulfuric acid concentration increased, the concentration of NCC also increased accordingly. TEM images of NCC revealed that the rod-like structure (De Souza and Borsali 2004) of the crystallite had a length ranging from 200 nm to 500 nm, and the crystals had diameters less than 20 nm, similar to wood and cotton cellulose nanocrystals (Beck-Candanedo et al. 2005).

FTIR Spectra of Nanocrystalline Cellulose

Figure 4 shows the FT-IR spectra of nanocrystalline cellulose and of the bamboo pulp following pretreatment with NaOH. As shown in Fig. 4, the spectrum of NCC was similar to that of pretreated bamboo pulp with respect to characteristic of cellulose peaks. A more satisfactory indication of the crystallinity parameter was the ratio of the absorptivity at 1372 cm^{-1}(C—H bending) and 2900 cm^{-1}(C—H stretching) (Wang et al. 2007). The peaks at 1644 and 897 cm^{-1} were attributed to the H–O–H stretching vibration of absorbed water in carbohydrate and the C_1–H deformation vibrations of cellulose, respectively. The acid hydrolysis removed the amorphous cellulose on the surface; therefore, more C–OH, C–O-C, and C–C bonds were exposed, resulting in the increases in the stretching absorbency (Sun et al. 2008). The FTIR spectrum of NCC showed broadening of the OH absorption band at 3342 cm^{-1} shifted to 3409 cm^{-1} not only because of sulfuric acid hydrolysis, but also because of water adsorption. What's more, the broadening of the absorption band at 3342 cm^{-1} was attributed to the presence of the amorphous fraction of the cellulose.

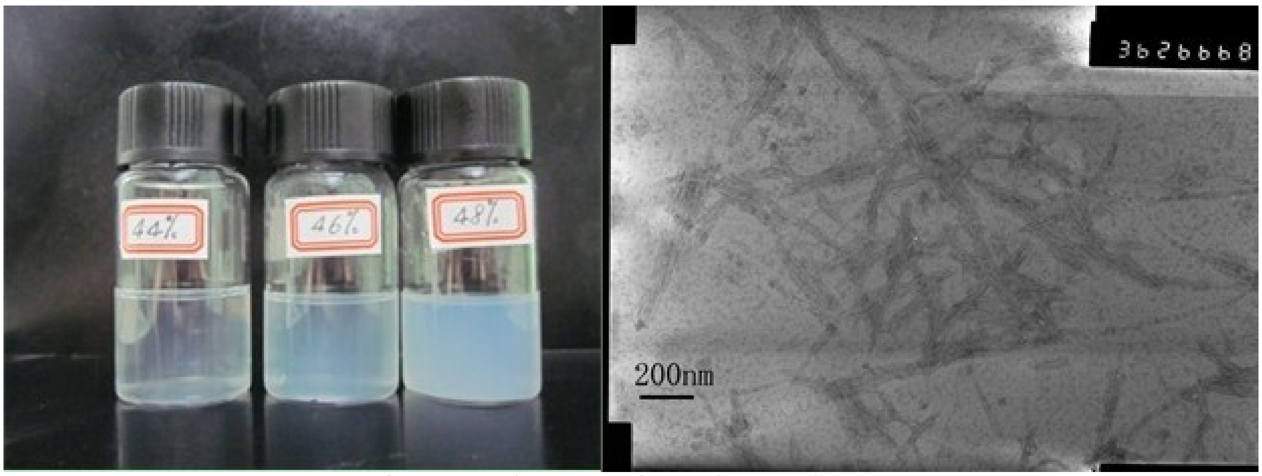

Fig. 3. Morphology and TEM image of NCC

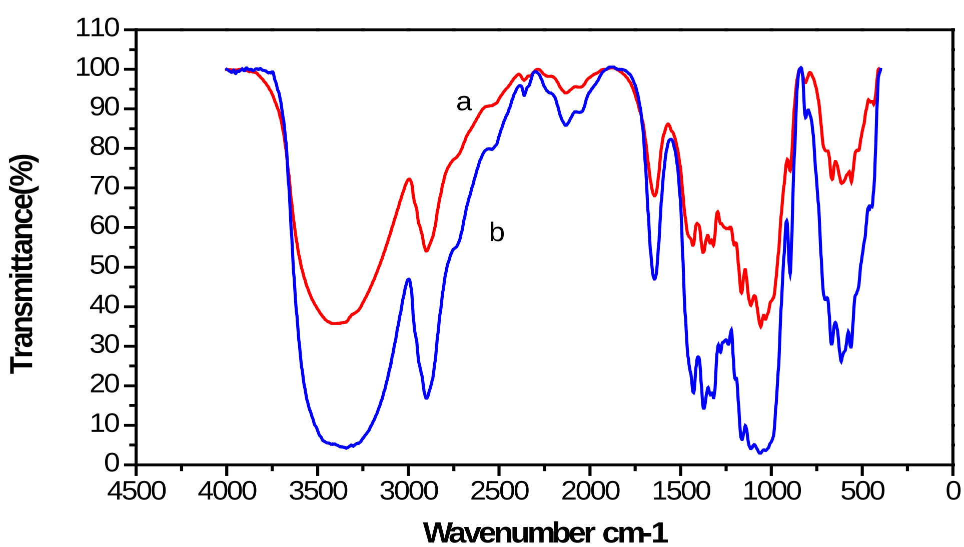

Fig. 4. FTIR spectra of bamboo nanocrystalline cellulose (a), and bamboo pulp with NaOH pretreatment (b)

Crystalline Structure of NCC

A representative X-ray diffraction image of NCC is shown in Fig. 5. It is evident that the three strongest peaks respectively were 15.77°, 21.79°, and 33.81 °. These results suggested that the crystalline structure of bamboo nanocrystalline cellulose is like that of cotton nanocrystalline cellulose, and they both belong to cellulose-I. What's more, bamboo pulp pretreatment with sodium hydroxide didn't cause a transformation of the cellulose crystalline structure. In the process of hydrolysis, the amorphous and microcrystalline areas were destroyed, while crystalline areas were retained; thus highly crystalline samples were obtained. According to the formula of crystallinity index, the crystallinity was 71.98%, which was higher than that of bamboo nanocrystalline cellulose prepared by using chemical pretreatment combined with high intensity ultrasonication (61.25%) (Chen et al. 2011). It also appeared that the crystallinity of bamboo nano-crystalline cellulose was higher than that of flax and rutabaga nanofibrils (59% and 64%, respectively) (Bhatnagar and Sain 2005). Therefore, the high crystalline NCC could be more effective in providing better reinforcement for composite materials.

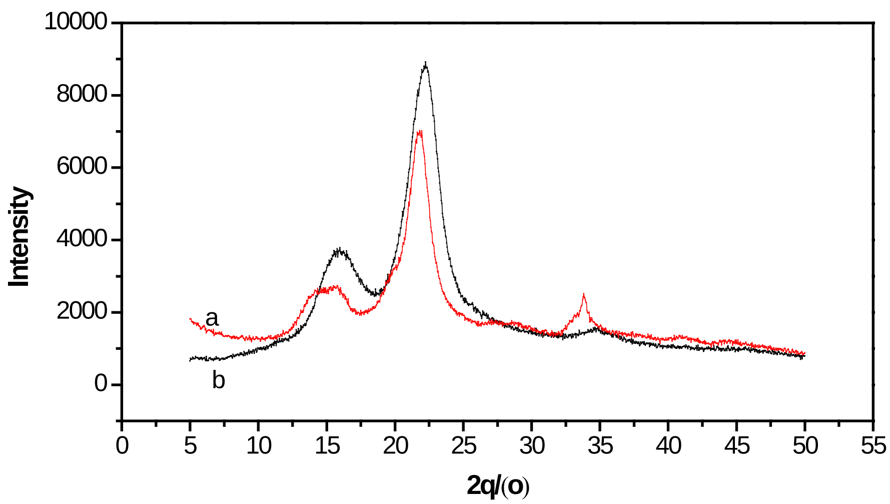

Fig. 5. X-ray diffraction image of bamboo nanocrystalline cellulose (a) and cotton nanocrystalline cellulose (b)

CONCLUSIONS

1. When the bamboo pulp with pretreatment was hydrolyzed with 48wt% of sulfuric acid at 50 ^{o}C for 30 minutes, NCC was obtained. The biggest difference of hydrolysis condition between bamboo and cotton nanocrystalline cellulose is the sulfuric acid concentration. The sulfuric acid concentration for producing bamboo nanocrystalline cellulose must be no more than 48%, or NCC won't be obtained, while that of cotton nanocrystalline cellulose has a wider range. TEM images showed that the crystallites

had a rod-like structure, in which the length ranged from 200 nm to 500 nm, and the diameter was less than 20 nm.

2. With pretreatment using 3 wt% NaOH at 50 ^{o}C for 2 hours, the bamboo pulp lost 9.3wt% of its original mass. NaOH swelled up the amorphous cellulose and let sulfuric acid easily penetrate into the fiber interior to accelerate the hydrolysis.
3. XRD measurements showed that high quality nanocrystalline cellulose from bamboo pulp belongs to cellulose-I. Based on the initial bamboo pulp, the yield of NCC suspension was 15.67wt% and its crystallinity was 71.98%. These results indicate that the material had much higher crystallinity compared with that from some non-wood materials, such as flax and rutabaga. This demonstrates that the origin of the starting raw material governs the resulting reinforcing effect via its degree of crystallinity. NCC from bamboo pulp was judged to be suitable for use as a reinforcing material.

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