CELLULOSE CHEMISTRY AND TECHNOLOGY

CELLULOSE NANOCRYSTALS FROM COTTON STALK FOR REINFORCEMENT OF POLY(VINYL ALCOHOL) COMPOSITES

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This paper presents an efficient method for extracting cellulose and cellulose nanocrystals (CNCs) from waste cotton stalks. The chemical composition, crystallization, spectroscopic, thermal and morphological analyses of the cotton stalks in every step were performed by relevant tests. Results indicated that the cotton stalks, which were treated by 12.5% sodium hydroxide concentration at 160 °C for 1 hour, retained the highest contents of cellulose (68.5%), while maintaining the cellulose crystal type I. An acidified $NaClO_2$ bleaching was subsequently introduced to remove the residual lignin component. Finally, cellulose nanocrystals were successfully extracted from cotton stalks by 65 wt% sulfuric acid hydrolysis at 50 °C. The reinforcing efficiency of the extracted CNCs in poly(vinyl alcohol) (PVA) composites was also investigated. Results showed that 3 wt% of CNCs could improve both the tensile strength and modulus of PVA by 48.3% and 21.1%, respectively. The work offers a promising approach to utilizing an abundant agricultural waste, such as cotton stalks.

Keywords: cellulose nanocrystals, renewable polymers, poly(vinyl alcohol), biomaterials, nanoparticles

INTRODUCTION

Cotton, the so-called 'white gold', is an important commercial crop that plays a key role in economic, political and social affairs of the world. It accounts for nearly 40% of the global fiber production. While approximately 80 countries worldwide produce cotton, China, India and the U.S. together provide over half of the world's cotton.[1] As important by-products of cotton, cotton stalks (stem and branches) generally consist of three main components: cellulose (36%), hemicelluloses (21%), and lignin (28%).[2]

China is the largest cotton producing country in the world, which produces more than 9 million tons cotton stalks per year.[3] Most of this by-product is burned, thereby resulting in serious environment pollution problems and waste of resources. Fortunately, the government and researchers have realized the importance of solving this problem. Over the past ten years, increasing research efforts have been directed towards the reutilization of cotton stalks. One of the most important methods of valorization to be considered is to utilize cotton stalks for obtaining cellulose nanocrystals, which have high strength, recyclability, and environmental sustainability.[4] Cellulose nanocrystals (CNCs) have great potential to be used as reinforcement in biocomposites,[5,6,7] in antibacterial packaging,[8] biomedical implants,[9] drug delivery,[10,11] electroconductive materials,[12] *etc.*

Extensive researches on extracting nanocellulose from different sources have been reported. Many common plants available worldwide have been used as feedstock for nanocellulose, including cotton,[4] rice,[13] corn,[14] bamboo,[15] sisal,[16] jute,[17] kenaf[18] *etc.* In addition, many indigenous crops have also been studied, such as *Helicteres isora* plant,[19] mulberry,[20] sugarcane,[21] banana pseudostem,[22] pineapple leaf fiber,[23] *Phormium tenax*,[24] coir fiber,[25] Okra fibers,[26] etc. Massive newer studies[27-31] indicate that this is still a significant and hot research topic.

Based on these researches, we summarized some principles for selecting a suitable feedstock for CNCs as follows:

(1) stable and abundant sources, such as agricultural wastes,[22,25] are good choices due to the low cost and environmental friendliness;

(2) high cellulose contents; for instance, many non-wood feedstocks (*e.g.* cotton, rice straw, flax, *etc.*) are chosen due to the fact that they require less usage of some strong chemical reagents to remove lignin;[32,33]

(3) high axis ratio (L/d) of cellulose crystals. As we know, the morphology and dimensions of cellulose nanocrystals are dependent on the raw cellulose source and on the disintegration process.[18,20] It has been reported that rod-like cellulose particles from different sources have the diameter and length ranging from 5 to 20 nm and 100 nm to several micrometers.[34] Moreover, cellulose nanocrystals with higher axis ratio (L/d) always show better reinforcing effects on composites.[35]

To obtain cellulose from raw fiber, a pretreatment, which can remove most of the hemicelluloses and lignin, is always necessary. One of the most efficient approaches is the alkali treatment, sometimes named as mercerization.[36] Ma *et al.*[37] have also found that the alkali treatment at high temperature (140~160 °C) appears to be more effective than at normal temperature (25~100 °C). Another treatment, which is used in cellulose industries after alkali treatment, is the bleaching with hydrogen peroxide. It aims to degrade lignin and hemicelluloses, and release the cellulose fibers. Meanwhile, chlorine dioxide (ClO_2) treatment is also used after alkali treatment, due to its excellent ability to separate lignin.[13,26,34]

Several researches have indicated that the cellulose molecular chains are biosynthesized and self-assembled into microfibrils, which are composed of crystalline domains (the most are nanoscale) and amorphous parts.[16,23,38] However, nanocellulose extraction is just the opposite, which means that cellulose nanocrystals are extracted by disintegrating the amorphous parts. There are three types of disintegration processes: i) mechanical methods, such as compression (CMT) and roller (RMT) mechanical techniques,[39] homogenization,[40] cryocrushing,[40] and steam explosion[41] (ultrasonication combined with chemical treatment has been also employed to prepare cellulose nanocrystals in recent researches);[42,43] ii) enzyme hydrolysis;[44] iii) chemical treatments. Acid hydrolysis has been the most common method for isolating rod-like CNCs, since it was reported in the late 1940s[45] because the amorphous regions in native cellulose are more susceptible to the acid's hydrolytic action than the crystalline domains.[35] The characteristics of CNCs are basically dependent on the acid species, acid concentration, time and temperature of the hydrolysis reaction. However, few studies have been focused on the effects of the hydrolysis conditions.[34]

This study presents an effective and economic way to isolate cellulose nanocrystals from cotton stalks by two main steps: isolating pure cellulose from cotton stalks and extracting CNCs from the obtained cellulose. To the best of our knowledge, it is the premier research to extract CNCs from cotton stalks. In the first step, the effects of alkali treatment at high temperature (160 °C), which has been reported to be more effective in removing lignin and hemicelluloses compared to normal temperature (25~100 °C), and subsequent acidified $NaClO_2$ or alkaline hydrogen peroxide (H_2O_2) treatment on the cotton stalks compositional variation, crystallinity and thermal stability were studied. Subsequently, high purity cellulose was obtained. In the second step, the obtained cellulose underwent a sulfuric acid hydrolysis to produce CNCs. The effects of acid concentration and hydrolysis time on the morphological behavior of CNCs were characterized by transmission electron microscopy (TEM). To investigate the reinforcing effects of the resulting CNCs on polymer, PVA/CNC composite films were finally prepared by the solution casting technique.

EXPERIMENTAL

Materials

Shanxi Gerui Equipment Co. Ltd. (China) kindly supplied raw cotton stalk fibers. The fibers were ground and the fraction passing through an 80 mesh screen (less than 0.178 mm size) was collected. Poly(vinyl alcohol) was purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai.

Other chemical reagents used were sodium hydroxide (Tianjin, China); sodium chlorite (Shanghai, China); hydrogen peroxide (Shanghai, China); acetic acid (Shanghai, China); absolute ethyl alcohol (Guangzhou, China); sulfuric acid (Guangzhou, China). All the chemicals were reagent grade and used as received.

Methods

Isolation of cellulose from cotton stalks

The cotton stalk powders were first dried at 105 °C for 1 hour before soaking them in a sodium hydroxide solution of 5%, 7.5%, 10%, 12.5%, 15%, 17.5% (w/w), liquor to fiber ratio of 5 ml/g, and then the suspension was transferred to a sealed and rotating digester for 3 h at 160 °C (1 °C/min from 25 °C to 160 °C). The residue was subsequently washed by distilled water, and then dried for component analysis.

Secondly, the alkali treated cotton stalks were bleached by two methods to remove the lignin completely:

i) 2 g of dried pretreated cotton stalk was heated at 75 °C in 65 ml of water containing 0.667 g sodium chlorite and 0.5 ml glacial acetic acid. The mixture was stirred for 1 h before cooling in an ice bath, and the residue was washed by deionized water. This step was repeated twice with component analysis after each time.

ii) a certain amount of pretreated cotton stalk was soaked in 1.5 wt% hydrogen peroxide for 6 h at 20 °C and 80 °C respectively, then the components of the residue were analyzed.

Preparation of CNCs

Cellulose nanocrystals were prepared by sulfuric acid hydrolysis, and the effects of acid concentration and hydrolysis time were studied as follows.

The extracted cotton stalk cellulose was treated in sulfuric acid solution (45, 50, 55, 60, 65 wt%, liquor to fiber ratio of 15 ml/g) at 50 °C for 1 h under constant agitation.

Another group of cellulose was treated at 50 °C for 1, 2, 3, 4, 5 hours in sulfuric acid solution (55 wt%, liquor to fiber ratio of 15 ml/g) under constant agitation.

Hydrolysis was terminated by adding a 10-fold amount of cold water, and then the mixture was allowed to rest for a few hours until two layers could be distinguished. The lower turbid liquid was collected and centrifuged twice (8,000 rpm, 15 min). Then the precipitates were continuously dialyzed against water for 3 days until constant pH was reached. Subsequently, the precipitate was dispersed in water again to obtain nanocrystal suspensions for further characterization. The CNC yields of the suspension were calculated by weighing the CNCs in a certain volume of suspension after drying.

Preparation of PVA/CNC nanocomposites

Composite films of PVA and cellulose nanofibers were prepared by solution casting to yield an approximate thickness of 200 µm. To this end, PVA powder was first dissolved in distilled water and stirred at 90 °C for 1 h to produce a 10 wt% PVA solution. The cellulose suspension was subsequently mixed with the PVA solution at ambient temperature for 30 min to produce mixtures with increasing CNC loadings. Each mixture was then cast onto a polystyrene dish and was left standing at ambient temperature until the water evaporated and the sample weight was constant. The samples were then dried at 40 °C overnight to avoid the plasticizing effect of moisture during characterization.[4]

Characterization

The cellulose, hemicelluloses and lignin of cotton stalks (before and after alkali treatment) were analyzed as follows. First, the samples were extracted for 24 h in ethanol–benzene of 1:2 (v/v of biomass to the solvent) in a Soxhlet apparatus, according to ASTM Standard D1107-96. Then, holocellulose (cellulose and hemicelluloses) was determined according to ASTM Standard D1104-56. The α-cellulose content was calculated based on ASTM D1103-55T. The content of hemicelluloses was calculated by deducting the α-cellulose from the value of holocellulose. The content of the acid insoluble lignin (known as ‘‘Klason lignin’’, extracting the residue in sulfuric acid of 72%) was determined according to ASTM Standard D1106-96. All of the specific operations have been stated by Hanieh Kargarzadeh *et al.*[18] Every reported value of the chemical analyses represents the mean of three replicates.

XRD spectra for cotton stalks (before and after alkali treatment) were collected on a Rigaku Dmax/III diffractometer (Rigaku Corporation, Tokyo, Japan) using Cu Kα radiation (λ = 1.54 Å). The generator was operated at 40 kV and 30 mA. The samples were scanned from 5° to 45°, with a step length of 0.02°.

Crystallinity index (CrI) was determined by an empirical method using the following equation:[46]

$$CrI(\%)=(I_{002}-I_{am})/I_{002}*100\% \qquad (1)$$

where I_{002} is the maximum intensity of the (002) lattice diffraction peak and I_{am} is the intensity scattered by the amorphous part of the sample. The diffraction peak for plane (002) is located at a diffraction angle of around $2\theta = 22.5°$ and the intensity scattered by the amorphous part is measured as the lowest intensity at a diffraction angle of around $2\theta = 18.0°$.

FTIR spectra were recorded in the transmission mode with a Bruker Vertex 70 FTIR spectrometer at a spectral resolution of 2 cm^{-1} and 32 scans. KBr pellets of raw and 12.5% NaOH treated cotton stalks were prepared (200 mg KBr:1.5 mg sample) under pressure.

The thermal stabilities of raw and alkali treated cotton stalks and cellulose whiskers were characterized using a thermogravimetric analyzer (TA Instruments Q2000, USA).

The amount of sample for each measurement was of about 5~8 mg. All of the measurements were performed under a nitrogen atmosphere with a gas flow of 20 ml/min. Samples were heated up to 700 °C at a heating rate of 20 °C/min.

The morphologies of raw cotton stalks, high-temperature alkali-treated fibers, acidified $NaClO_2$-bleached fibers and freeze-dried nanocellulose were observed by a Nova Nano SEM 430 instrument (FEI, Netherlands) at an acceleration voltage of 10 kV. The sample powder was held on a sample holder with adhesive tape and then sputter-coated with gold to prevent the buildup of electrostatic charge.

The microstructure and morphology of CNCs were visualized by a Hitachi H-7650 transmission electron microscope at an accelerating voltage of 80 kV. The samples for TEM measurement were prepared by dropping the sample solution on Cu grids of 200 meshes.

Tensile tests were performed at room temperature with an Instron 5560 mechanical tester equipped with an 100 N load cell, and at a cross-head speed of 10 mm/min. Dog-bone shaped specimens of 25 mm × 4 mm× t mm (t = thickness) were punched out from the sheet, using the standard mode. The samples were conditioned at 40 °C and 50% humidity before testing.

RESULTS AND DISCUSSION

Chemical composition

The main chemical composition of the cotton stalks treated by alkali of different concentration is shown in Table 1. As expected, the raw cotton stalks had the lowest percentage of cellulose (37.1±1.2 wt%) and the highest percentage of hemicelluloses (32.6±1.2 wt%) and lignin (25.0±0.8 wt%), compared to the alkali treated samples. After the treatment by a low concentration (5%) of NaOH at 160 °C for 1 h, the contents of hemicelluloses and lignin decreased significantly, reaching 15.6±0.6 wt% and 16.3±0.5 wt%, respectively, whereas the cellulose content increased to 61.9±1.5 wt%, so that it nearly doubled the content of the raw cotton stalks. It indicated that the alkali treatment could remove the hemicelluloses and lignin from cotton stalks efficiently, and the values corresponded well to the broad range of values reported in the literature.[20,47,48] With the increase of alkali concentration from 5% to 17.5%, the cellulose contents increased gradually from 61.9±1.5% to 79.1±1.5%, while the hemicelluloses and lignin were just the reverse, decreasing from 15.6±0.6% and 16.3±0.5% to 8.3±0.3% and 6.5±0.3%. It was due to the higher concentration of alkali, which could penetrate into the deeper region of the fiber structure, and then dissolve more lignin and hemicelluloses.

Some bleaching treatments were applied to remove the lignin residues after alkali treatment. As shown in Table 2, after two bleaching processes by acidified $NaClO_2$, the contents of lignin in the cotton stalks decreased from 9.7±0.4% to 3.2±0.2%, and then to 0.5%. It demonstrated that acidified $NaClO_2$ bleaching had a strong ability to remove lignin. Since lignin can react with $NaClO_2$, an oxidative fragmentation of lignin will take place and some parts of lignin will dissolve out as lignin chloride.[23,25] Meanwhile, the bleaching with alkaline H_2O_2 could also remove the lignin of cotton stalks, but higher temperature and more time were required compared to the acidified $NaClO_2$. In a word, these findings strongly indicated that there was still a significant amount of residual lignin after the alkali treatment, and the second bleaching treatment was necessary. The morphology images of cotton stalk fiber at different stages are shown in Figure 1 a-d.

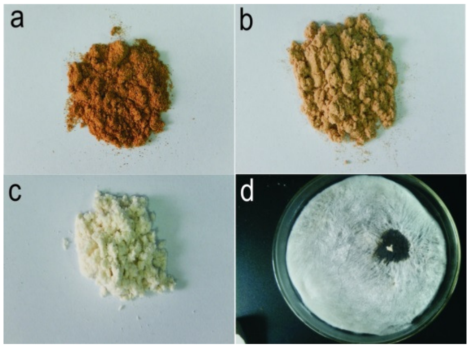

Figure 1: Optical images of (a) raw cotton stalk fiber; (b) CSB after high-temperature alkali treatment; (c) CSB after bleaching treatment; (d) CNC fibers obtained by freeze-drying

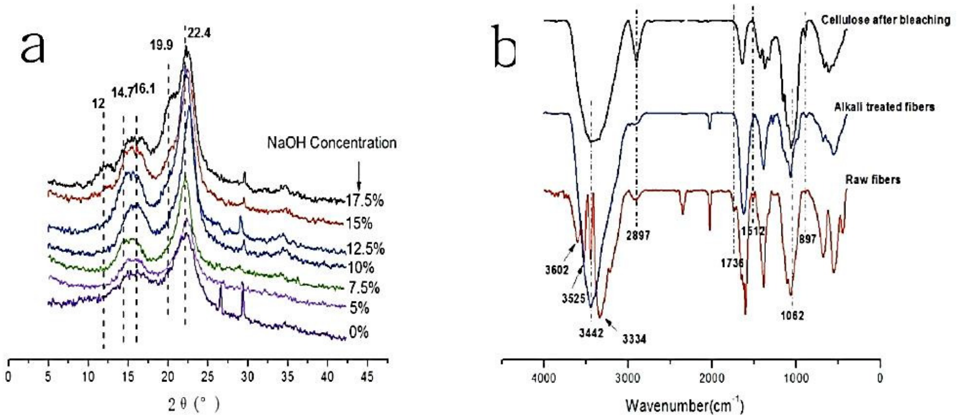

Figure 2: (a) X-ray diffraction patterns of raw cotton stalks, cotton stalks pretreated with 5%, 7.5%, 10%, 12.5%, 15%, 17.5% of sodium hydroxide (NaOH) at high temperature; (b) FT-IR spectra of raw cotton stalks, 12.5% NaOH treated cotton stalks and cellulose extracted after bleaching

Table 1
Chemical composition and crystallinity of cotton stalks after high-temperature alkali treatment of different concentration

Number (#)	Samples*	Cellulose (wt%)	Hemicelluloses (wt%)	Lignin (wt%)	Crystallinity (%)
1	Raw cotton stalks (CS)	37.1±1.2	32.6±1.2	25.0±0.8	35.3
2	5%NaOH-treated CS	61.9±1.5	15.6±0.6	16.3±0.5	47.9
3	7.5%NaOH-treated CS	68.1±2.6	11.9±1.7	12.7±0.5	60.7
4	10%NaOH-treated CS	66.7±1.2	14.1±0.5	11.9±0.6	62.3
5	12.5%NaOH-treated CS	68.5±0.9	13.6±0.6	9.7±0.4	64.9
6	15%NaOH-treated CS	73.5±1.3	9.9±0.5	7.6±0.3	60.2
7	17.5%NaOH-treated CS	79.1±1.5	8.3±0.3	6.5±0.3	54.7

*alkali treatment at 160 °C for 1 h

Table 2
Chemical composition of alkali treated cotton stalks after bleaching treatment

Samples*	Cellulose (wt%)	Lignin (wt%)
Unbleached	68.5±0.9	9.7±0.4
Bleached with acidified $NaClO_2$ once	73.4±0.6	3.2±0.2
Bleached with acidified $NaClO_2$ twice	75.9±0.5	<0.5
Bleached with alkaline H_2O_2 at 20°C	68.5±0.5	9.6±0.2
Bleached with alkaline H_2O_2 at 80°C	72.9±0.5	3.9±0.2

*all samples are cotton stalk treated by 12.5 wt% of sodium hydroxide (5# in Table 1)

X-ray diffraction (XRD) analysis

Figure 2a shows the peaks and changes in the X-ray diffraction pattern of raw and alkali treated cotton stalks. First, it is worth noting that on all X-ray diffraction patterns of the samples, three typical peaks of cellulose I are present at 2θ = 14.7°, 16.1° and 22.4°. Meanwhile, more intense crystalline peaks of cellulose are observed with increasing alkali concentration. Another matter of concern is that three typical peaks of cellulose II (2θ = 12.1°, 19.9° and 22.0°) appears with the increase of the NaOH solution concentration (>15%). A probable explanation is that when the cellulose was treated by the alkali solution, the cellulose swelled to various extents depending on the type and the concentration of alkali as well as on the temperature. The path from cellulose type I to cellulose type II went by the way of Na-cellulose I. At low concentrations, only the large pores in the cellulose structure were occupied. With increasing concentration, the small cation Na^+ ($Na^+ = 0.276$ nm) can advance more easily into smaller pores. Na^+ seemed to have a favorable diameter, which was able to widen the smallest pores down to the space between the lattice planes and advanced into them. During intensive washing, the linked Na^+ were removed and another lattice, the cellulose II lattice was formed.[33]

The crystallinity of each sample was also calculated and listed in Table 1. With the increase of alkali concentration, the crystallinity of the samples firstly increased from 35.3% (untreated sample) to 64.9% (sample treated by 12.5 wt% NaOH solution), then decreased to 54.7% (sample treated by 17.5 wt% NaOH solution). This result was due to the dissolution of the amorphous components like lignin and hemicelluloses, followed by the destruction of the crystalline regions.

Owing to the better mechanical properties of cellulose type I,[49] and seeking to obtain higher contents of cellulose, the cotton stalks treated by 12.5 wt% NaOH solution have been selected for further bleaching in this study.

FTIR spectroscopy analysis

Figure 2b shows the FTIR spectra of raw cotton stalks, 12.5 wt% sodium hydroxide treated cotton stalks and bleached cellulose. The peak present at 1736 cm^{-1} in the spectrum of raw cotton stalks was attributed to the C=O stretching of the acetyl and uranic ester groups of hemicelluloses or the ester linkage of carboxylic group in the ferulic and p-coumaric acids of lignin and hemicelluloses. However, it almost disappeared in the spectra of alkali-treated cotton stalks and bleached cellulose.[48,50] Similarly, the characteristic peak at 1512 cm^{-1}, which was the contribution of the aromatic C=C stretch of the aromatic ring in the lignin, also decreased in the spectrum of alkali-treated cotton stalks and then disappeared in the spectrum of bleached cellulose.[51] Other two peaks at 1061 and 897 cm^{-1} were associated with the C–O stretching and C–H rock vibrations of cellulose, which appeared in all the spectra.[52] The absorbance peaks between 3330 and 3605 cm^{-1} in the spectrum of raw cotton stalks were related to the stretching of the hydroxy from different components (*e.g.* cellulose, hemicelluloses, lignin, *etc.*) in raw cotton stalks. After the alkali and bleaching treatments, a broad peak of hydroxy appeared at 3442 cm^{-1}, because of the enhanced hydrogen bond between the cellulose hydroxy after the removal of lignin. In general, these findings clearly indicate that most of the hemicelluloses and lignin were removed by the 12.5 wt% NaOH treatment and bleaching.

Thermogravimetric analysis (TGA)

The thermal stability was a key factor for fillers to be used as effective reinforcing materials, since the typical processing temperature of thermoplastics often exceeded 200 °C.[53]

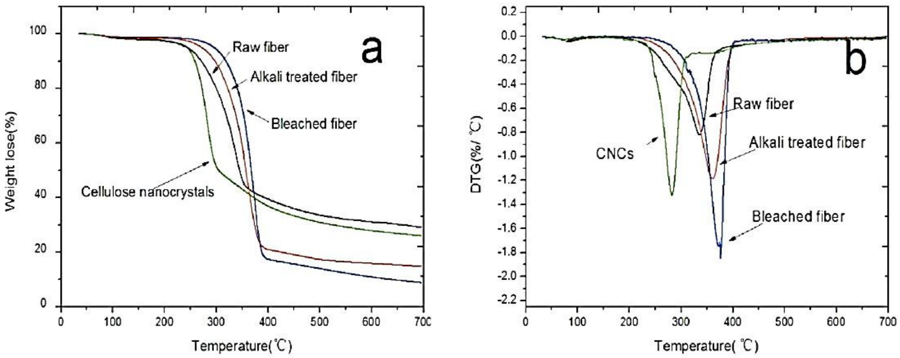

Figure 3: (a) TGA and (b) DTG curves of the raw, alkali treated and bleached cotton stalk fibers and CNCs

Table 3
Onset decomposition temperature (Td onset), degradation temperature at maximum weight loss rate (Td max) and char yield for the samples under analysis

Samples	Td onset (°C)	Td max (°C)	Char at 500 °C (%)
Raw fiber	224±2.2	338±3.4	32.6
Alkali treated fiber	255±2.6	362±3.6	16.9
Bleached fiber	295±2.9	376±3.8	13.9
CNCs	245±2.5	283±2.9	30.8

The thermogravimetric (TGA) and differential thermogravimetry (DTG) curves of the raw, alkali treated and bleached cotton stalk fiber, and those of the CNCs after sulfuric acid hydrolysis are shown in Figure 3a and Figure 3b, respectively. The corresponding data are listed in Table 3.

For all samples, a main weight loss was found in the range of 200-400 °C due to the decomposition of the lignocellulosic components in the cotton stalk fiber. Yang *et al.*[54] have shown that cellulose decomposition mainly ranges from 315 °C to 400 °C with a maximum weight loss rate at 355 °C, hemicelluloses decomposition starts at 220 °C and continues up to 315 °C with a maximum weight loss rate at 268 °C, while lignin decomposition occurs in a wide range from 200 °C to 700 °C. As a consequence, the raw cotton stalk fiber decomposed in the range from 200 °C to 400 °C, which mainly resulted from the decomposition of the cellulose and hemicelluloses, and the decomposition between 400 °C and 700 °C was attributed to the lignin component. As observed from the DTG curves, the decomposition peak of cotton stalks after alkali treatment took place over a narrower range, compared to that of raw fiber. The onset (Td onset) and maximum (Td max) decomposition temperatures were also shifted to a higher temperature, from 224±2.2 °C to 255±2.6 °C and from 338±3.4 °C to 362±3.6 °C, respectively. This was due to the decrease of lower thermally stable hemicelluloses contents caused by the alkali treatment. After bleaching, the decomposition temperature was further shifted to a typical cellulose range between 300 °C and 400 °C, which indicated that the complete elimination of hemicelluloses and lignin occurred. Meanwhile, the char residue was also decreased from 32.6% to 13.9%, corresponding with the removal of high char residual lignin (46 wt%) and hemicelluloses (20 wt%), compared to cellulose (6.5 wt%).[54]

However, it was observed that there was a significant decline in the decomposition profile after applying the sulfuric acid hydrolysis. The Td onset and Td max of CNCs were 245±2.5 °C and 283±2.9 °C, respectively, which are much lower than those of the cellulose after bleaching (Td onset and Td max at 295±2.9 °C and 376±3.8 °C, respectively). This behavior was expected given the introduction of sulfate groups, which diminished the thermal stability of the CNCs, because of the dehydration reaction of cellulose catalyzed by sulfuric acid.[53]

According to the results, approaches such as neutralizing with sodium hydroxide, which could reduce the sulfate groups present on the surface of the CNCs, seemed to be effective for improving the thermal stability of CNCs.[55]

Scanning electron micrographs (SEM)

Figure 4 shows the surface morphology of cotton stalks before (Fig. 4a) and after (Fig. 4b) high-temperature alkali, and bleaching (Fig. 4c) treatments, and of freeze-dried nanocellulose (Fig. 4d) after acid hydrolysis. The raw cotton stalk fibers (Fig. 4a) were clearly bonded together by massive cementing materials, like hemicelluloses and lignin. After the high-temperature alkali treatment (Fig. 4b), most of the hemicelluloses were hydrolyzed and became water soluble. Meanwhile, the lignin was also partially depolymerized, which exposed the cellulose microfibrils from the fiber bundles. Figure 4c shows the morphology of the bleached cotton stalk fibers. The bleaching process helped to remove the residual lignin present in the fibers, leading to further defibrillation. Just as the photograph shows, several cellulose microfibrils with diameters in the range of 3-12 μm were separated from each other. Figure 4d shows the freeze-dried nanocellulose after acid hydrolysis, where several cellulose crystal films with the thickness less than 100 nm can be observed. The probable explanation is that the rod-like cellulose nanocrystals were self-assembled into films due to the intermolecular hydrogen-bond interaction, while the solvent evaporated. However, during the freeze-drying, the frozen water forced cellulose nanocrystals to self-assemble in a limited direction, which led to a one-dimensional nanocellulose film at micro level.

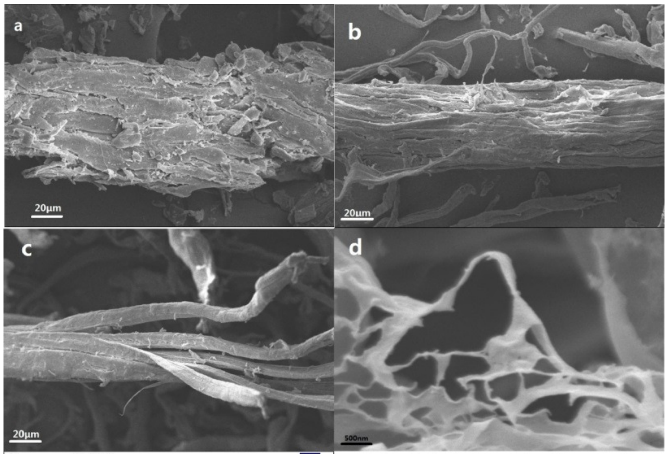

Figure 4: Scanning electron micrographs (SEM) of (a) raw cotton stalks; (b) high-temperature alkali-treated fibers; (c) acidified $NaClO_2$-bleached fibers; (d) freeze-dried nanocellulose

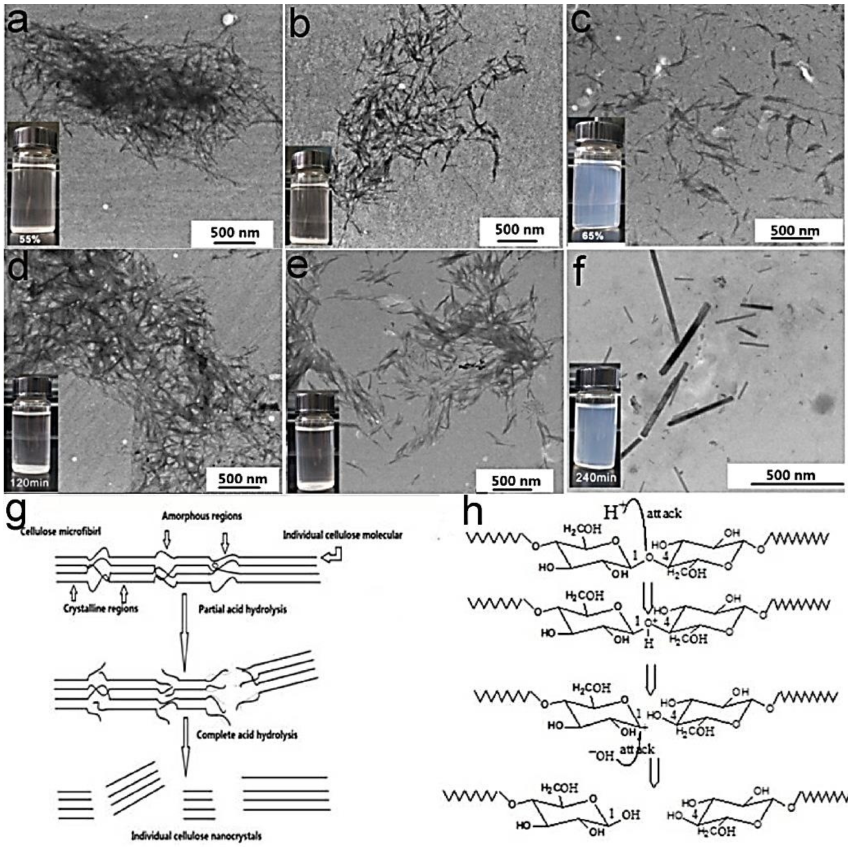

Figure 5: TEM images of CNCs obtained for (a) 55 wt%, (b) 60 wt%, (c) 65 wt% of H_2SO_4 treatment at 50 °C in 60 min, and (d) 120 min, (e) 180 min, (f) 240 min of hydrolysis time treatment by 55 wt% H_2SO_4 at 50 °C; schematic of cellulose treated by acid hydrolysis at microfiber level (g) and molecular level (h)

Transmission electron micrographs (TEM)

The effect of hydrolysis conditions on the microstructure of CNCs could be further explained by the TEM images in Figure 5. It is well known that the amorphous parts of cellulose underwent preferential acidic hydrolysis when compared to crystalline domains.[17] As shown in Figure 5a, the crystalline domains were coated by the amorphous parts of cellulose or residual lignin, resulting in a blurred morphology of the cellulose fiber. It indicates that most of the amorphous parts are still retained when the acid concentration is less than 55% (under the conditions of 50 °C, 60 min). The reason is that there is no sufficient concentration of H^+ to attack the β-glycosidic bond in the amorphous region. When the acid concentration reached 60%, a clearer cellulose crystal morphology appeared (Fig. 5b), which indicated that the majority of the amorphous parts had been destroyed. However, most of the cellulose nanocrystals were still not fully stripped off. After improving the acid concentration to 65%, the amorphous domains of cellulose were mostly degraded and most of the nano-sized cellulose crystals were spread out from each other (Fig. 5c). Thus, a well-dispersed nanocellulose solution was obtained. The dimensions of CNCs had also been previously determined from TEM images, which ranged from 10 to 50 nm in width and 100 to 300 nm in length.

Similar changes could also be observed from the TEM images (Fig. 5d-f) of CNCs obtained after various hydrolysis time. The amorphous regions were found to decrease gradually with the increase of hydrolysis time. Nano-sized cellulose crystals were successfully produced by 65 wt% of H_2SO_4 hydrolysis at 50 °C for 1 hour or 55 wt% of H_2SO_4 at 50 °C for 4 hours.

The considered hydrolysis process of cellulose microfiber and molecular chain from partial to complete is described simply in Figure 5 (g) and (h).

Mechanical behavior of PVA/CNC composites

The mechanical behavior of neat PVA and PVA/CNC nanocomposites was evaluated and tensile test results were reported in Figure 6. First, the ultimate tensile strength (UTS) and elongation at break (εb) tended to improve, but then followed a decrease with an increase of CNC loadings. When the CNC loading reached 3 wt%, the UTS and εb of the composite increased to 40±2 MPa and 660±30%, respectively, which increased by 48.3% and 63.8% compared to those of the neat PVA (Fig. 6a, c). This indicated that only a small amount of CNCs (3 wt%) was needed for a great improvement in the strength and toughness of PVA. The inherent high strength and modulus of the CNCs, combined with a strong hydrogen bonding between the cellulose molecule and the PVA matrix, were considered to be responsible for the significant enhancement in the mechanical properties of these composites.

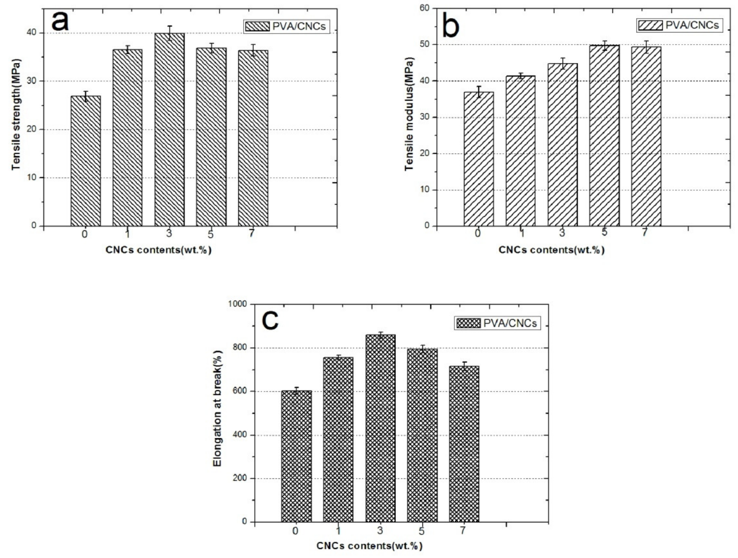

Figure 6: Tensile properties of PVA/CNC composites (0, 1, 3, 5, 7 wt%): (a) tensile strength; (b) tensile modulus; (c) elongation at break

However, the UTS and εb tended to decrease when the CNC loadings exceeded 3 wt%. This was probably due to the aggregation of CNCs that formed by the strong hydrogen-bond interaction between cellulose molecule. Secondly, regarding the tensile modulus, it increased slightly with the addition of CNCs. As it is well known, the stiffness of materials mainly depends on the composition of the composite, which indicates that the introduction of high stiffness CNCs could improve the modulus of PVA efficiently even at low loadings. Some further property researches of CNC reinforced PVA composites will be reported in a subsequent article.

CONCLUSION

The aim of the work was to suggest a simple and economical method to extract cellulose and cellulose nanocrystals from an agricultural waste, such as cotton stalks. Chemical components and FTIR spectra analysis of the fibers indicated the effective removal of hemicellulose and lignin due to the high-temperature alkali treatment. With an increasing concentration of alkali from 0% to 17.5%, the cellulose content was found to rise gradually from 37.1% to 79.1%. However, the cellulose crystal type I began to convert into cellulose type II once the concentration of alkali reached 15%, according to the XRD. The crystallinity of the fibers also increased to the highest percentage of 64.9% at an alkali concentration of 12.5%. A further bleaching with acidified $NaClO_2$ could remove more residual contents of lignin than alkaline H_2O_2. TGA analysis showed that the thermal stability of cotton stalks improved greatly after alkali and bleaching treatments, while the sulfuric acid hydrolysis reduced the thermal stability of CNCs due to the catalytic dehydration of cellulose. Finally, the purified cotton stalk cellulose was obtained after this two-step pretreatment. TEM analysis showed that the increased acid concentration and extended acid hydrolysis time were both conductive to removing the amorphous parts of the cellulose molecules. Considering that the increase of acid concentration was more efficient than the extension of hydrolysis time, we extracted CNCs from cotton stalks at 50 °C by 65% sulfuric acid hydrolysis for 1 hour. The prepared CNCs from cotton stalks have been proved to be an efficient reinforcement in the poly(vinyl alcohol) based composites.

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