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Extraction and Characterization of Cellulose Nanofibers from *Phyllostachys nidularia* Munro *via* a Combination of Acid Treatment and Ultrasonication

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In this work, α-cellulose was extracted from *Phyllostachys nidularia* Munro using an acidified sodium chlorite treatment followed by alkali treatments, and cellulose nanofibers (CNFs) were then extracted from α-cellulose *via* the combination of sulfuric acid (64 wt%) and low-intensity ultrasonication. The results showed that superior CNFs were successfully extracted and their diameters were in the range of 5 to 20 nm. Fourier transform infrared spectroscopy (FTIR) suggested that a majority of the hemicellulose and lignin were removed from the original material and that the chemical constituents of α-cellulose and CNFs were similar. X-ray diffraction (XRD) analysis indicated that the relative crystallinity of CNFs was significantly increased to approximately 69.32% and all specimens presented a typical cellulose I crystal form. Thermogravimetric analysis (TGA) showed that the thermostability of the CNFs was greatly increased.

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INTRODUCTION

For some decades now, cellulose has attracted extensive interest because of its biocompatibility, biodegradability, thermal stability, and sustainability, *etc.* (Sakurada *et al.* 1962; Nishino *et al.* 2004; Bergenstråhle *et al.* 2007). In nature, cellulose is a linear homopolymer of glucose $(C_6H_{10}O_5)_n$ consisting of D-glucose in a $^4C_1$ conformation, and a large number of nano-sized single cellulose nanofibers are self-assembled into microfibrils by hydrogen bonds between the hydroxyl groups of adjacent cellulose (Chen *et al.* 2011). The nanocelluloses mainly include cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF). CNC also has been called nanocrystalline cellulose, whiskers, and nanowhiskers; while CNF has been called nanofibrillated cellulose and microfibrillated cellulose as well (Eichhorn *et al.* 2010; Siró and Plackett 2010). Recently, nanocelluloses have been noticed because of their superior properties such as little thermal expansion, outstanding mechanical properties, high surface area-to-volume ratio, and large surface area, as well as their sustainability, biocompatibility, and assembly capacity (Nishino *et al.* 2004; Orts *et al.* 2005; Bergenstråhle *et al.* 2007; Eichhorn *et al.* 2010; Habibi *et al.* 2010). Generally, they have been extensively used as a reinforcing agent in composite materials (*e.g.*, Siqueira *et al.* 2008), substrates for electronic displays or electrical condensers (Nogi and Yano 2008; Nogi *et al.* 2009), and oxygen-barrier layers in food packaging (Fukuzumi *et al.* 2009), as well as functional aerogels (Lu *et al.*

2014), *etc.* Consequently, the extraction of CNFs from renewable sources has gained much interest during the past few years.

A number of extraction methods have been used to isolate nanocellulose from various cellulosic materials. Many reports indicate that mechanical treatments are the conventional methods; they include homogenizing (Herrick *et al.* 1983; Turbak *et al.* 1983), grinding (Abe *et al.* 2007; Iwamoto *et al.* 2008), cryocrushing (Chakraborty *et al.* 2005), and ultrasonication processing (Cheng *et al.* 2007, 2009). Despite these successful methods, there are still many problems such as low efficiency, high energy consumption, and high cost. To decrease energy consumption during mechanical treatments, pre-treatments have generally been applied prior to the mechanical process, including sulfuric acid hydrolysis (Beck-Candanedo *et al.* 2005; Elazzouzi-Hafraoui *et al.* 2007), TEMPO-mediated oxidation (Saito *et al.* 2007; Isogai *et al.* 2011), and enzyme-assisted hydrolysis (Pääkkö *et al.* 2007, 2008). In essence, in addition to the properties of raw materials, the characteristics of nanocelluloses are primarily decided by the different disintegration processes and pretreatments.

Bamboo is a vital component of plant and forest resources of the world. There are over 70 genera and 1200 species of bamboo in the world. In previous works, cellulose nanocrystals were extracted from *Bambusa rigida* with a combination of low-concentration sulphuric acid (33%) treatment and high-intensity ultrasonication (800W) processing (He *et al.* 2013); The result showed that the diameters of the nanocrystals were in the range of 30 to 60 nm. However, the *Ph. nidularia* Munro is different from the *Bambusa rigida.* The *Bambusa rigida* belongs to Bambusa (Sympodial bamboo), while the *Ph. nidularia* Munro belongs to Gramineae Bambusoideae Phyllostachys (Scattered bamboo). The *Bambusa rigida* has closely parenchymal tissue and longer vascular bundles compared to the *Ph. nidularia* Munro. Moreover, the chemical compositions of both are significantly different; in general, the hemicellulose, lignin, and α-cellulose of *Bambusa rigida* are around 28.1%, 23.81%, and 45.50%, respectively; while the hemicellulose, lignin, and α-cellulose of *Ph. nidularia* Munro are approximately 21.91%, 20.20%, and 58.55%, respectively (Jiang 2002). On the other hand, the acid solution concentration and ultrasonic power have a big effect on the characterization and properties of nanocelluloses isolated from biomaterials (Chen *et al.* 2011). Therefore, in this work, the authors attempt to extract superior CNFs from *Phyllostachys nidularia* Munro using a combination of high-concentration sulphuric acid (64%) treatment and low-intensity ultrasonication (400W) processing. The morphology, crystallinity, thermal properties, and their intermediate products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Ph. nidularia Munro was collected from Yibing County in Sichuan province, China. First, bamboo green and tabasheer were removed and ground into particles (using 80 to 100-mesh) for the original material; then, the particles were oven-dried at 105 °C for 24 h and stored in a desiccator at room temperature until further use. Benzene, ethanol, sodium chlorite, acetic acid, sodium hydroxide, sulfuric acid, and other chemicals were of laboratory grade and were used without further purification.

Preparation of α-Cellulose

Ph. nidularia Munro particles were first treated for 6 h to remove part of the extractives in a Soxhlet apparatus with a 2:1 (v/v) mixture of benzene and ethanol, then the treated particles were washed five times with distilled water and dried for 12 h at 100 °C in a vacuum-drying oven. Next, the dewaxed particles were treated with an acidified sodium chlorite solution at 75 °C for 1 h, and the process was repeated six times; then, these delignified particles (or holo-celluloses) were washed multiple times with distilled water until neutral. Finally, the delignified particles after washed and dried were immersed in a 5 wt% sodium hydroxide solution for 24 h and vigorously stirred at 80 °C for 2 h to remove hemicellulose, residual starch, and pectin. After these chemical treatments, the particles (or α-cellulose) were filtered and cleaned repeatedly with distilled water until neutral.

Extraction of CNFs

CNFs were isolated by the combination of strong acid hydrolysis and low-intensity ultrasonication from the α-cellulose obtained. Six g of α-cellulose were hydrolyzed in a 64% H_2SO_4 (96% purity) solution at 40 °C for 30 min with intense agitation, in which the ratio of acid and α-cellulose was 15 mL/g; the hydrolysis reaction was terminated by adding cold distilled water (about 400 mL).

The diluted hydrolysis suspension was centrifuged by a centrifugal apparatus (GT10-1, China) at 8000 rpm for 12 min to obtain the precipitates. Then, the precipitates were re-suspended and centrifuged with the same process until the pH level was between 4 and 5. Next, dialysis was carried out with a cellulose membrane until the suspension became neutral. Finally, the suspension obtained was sonicated for 15 min using an ultrasonic processor (JY98-IIID, Ningbo Scientz Biotechnology, China) at 20 to 25 kHz and an output power of 400 W to isolate the CNFs. The whole ultrasonication process was carried out in an ice bath. Finally, the white suspension obtained was freeze-dried with a freeze-dryer (CKG1B63-100SMS, China), and the products of lyophilization (namely CNFs) were collected and stored in a refrigerator at 4 to 5 °C for investigation.

Characterization

Scanning electron microscopy (SEM)

All specimens were coated with gold for 60 s using a vacuum sputter coater (Quorum Q150TES, UK), then observed with an SEM (JSM-7600F, Japan) operating at 12.5 and 20 kV.

Transmission electron microscopy (TEM)

TEM observation of CNFs was performed on a JEM-2100 (Japan) electron microscope at an acceleration voltage of 80 kV. The suspension of CNFs was diluted with distilled water and dropped on carbon-coated electron microscopy grids, and then negatively stained by a 1% phosphotungstic acid solution. Image software was applied for analysis of diameter distributions of more than 100 CNFs randomly selected from the TEM images.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of all specimens were investigated with a Fourier transform infrared spectrometer (Nicolet Magna 560, USA). These specimens were dried at 85 °C in a vacuum-dryer for 12 h before detection. Then a small quantity of each specimen was

blended with KBr powder and compressed to form a disk. The spectra for each specimen were detected in the range of 4000 to 500 cm^{-1} at a resolution of 2 cm^{-1}.

X-ray diffraction analysis (XRD)

The X-ray diffraction (XRD) analysis of all specimens was performed with an X-ray diffractometer (D/max 2200, Rigaku, Japan) using Ni-filtered CuKa radiation (k=1.5406 Å) at 40 kV and 30 mA. Scattered radiation was recorded in the range of 2θ=5 to 35° at a scan rate of 5°/min. The crystallinity index (C$_I$) was calculated from the height of the 200 peak (I$_{200}$, 2 h=22.6°) and the intensity minimum between the 200 and 110 peaks (I$_{am}$, 2 h=18°) using the Segal method (Segal and Meshulam 1979), as shown in Eq. 2:

$$C_I(\%) = \left(1 - \frac{I_{am}}{I_{200}}\right) \times 100 \qquad (1)$$

I_{200} represents both crystalline and amorphous material and I_{am} represents the amorphous material.

Thermal analysis

Thermogravimetric curves (TGA) were investigated with a synchronous thermal analysis system (Pyris 6, Perkin-Elmer, USA). Approximately 8 mg of specimen was used for each testing and every specimen was repeated three times. Testing temperature was performed from 30 °C to 600 °C at a heating rate of 10 °C /min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Morphological Analysis

Figure 1a shows optical images of the *Ph. nidularia* Munro particles after extraction; obviously, the color of the original fibers became light yellow after Soxhlet extraction. This is because the aliphatic acid, pigment, and other extracts were removed from the original materials. The CNFs with a solid content of *ca*. 1 mg/mL became uniformly dispersed in water, as shown in Fig. 1b. This kind of phenomenon is in accordance with the results of isolation of CNFs from different plants (Wenshuai *et al.* 2011). Figures 1c and d show the morphology of holo-cellulose and α-cellulose. After chemical purification, the original fibers were separated into distinguishably different types of cells: fibrous cells and rectangular cells, which can be regarded as fiber and parenchyma cells, respectively. These fibers were separated into individual micro-sized fibers—which were composed of nanofibers—by strong hydrogen bonding. SEM and TEM micrographs of CNFs are shown in Fig. 1e and f, respectively; both micrographs display a classical web-like network structure in which the fibers occur as very long entangled cellulosic filaments (Abe and Yano 2009). Also, the darker areas could be observed in Fig. 1f, which may be ascribed to the agglomeration of cellulose nanocrystals. The diameter distribution of CNFs obtained is shown in Fig. 2; noticeably, the diameter of the CNFs is mainly in the range of 5 to 10 nm and accounted for 52% of the mass. Comparatively, the amount of diameter in the range of 10 to 20 nm is about 34%. Generally, the diameter of a single microfibril is reported to be about 3 to 5 nm in

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higher plants; therefore, the observed nanofibers are similar to the single microfibrils. This result indicates that fine nanofibers are successfully obtained from *Ph. nidularia* Munro.
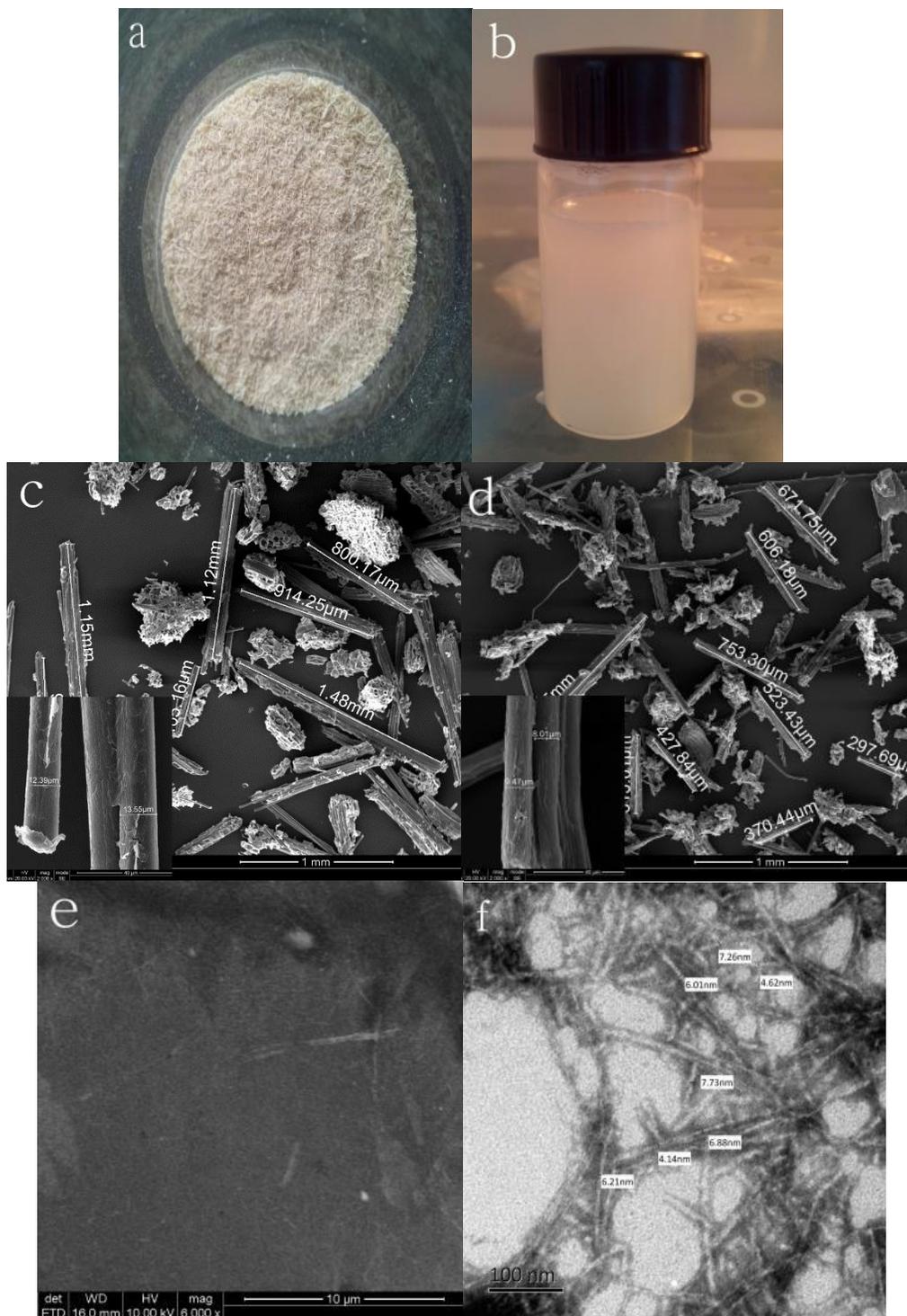
Fig. 1. Optical images of (a) the original *Ph. nidularia* Munro particles and (b) CNFs dispersed in water; (c) SEM micrographs of holo-cellulose, (d) α-cellulose, and (e) CNFs; (f) TEM micrograph of CNFs
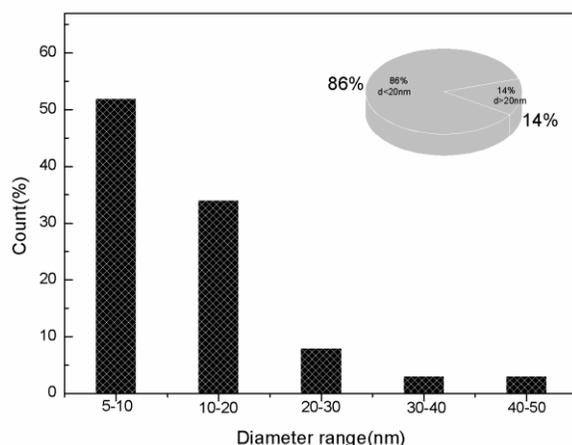
Fig. 2. Diameter distribution of the CNFs after a combination of acid treatment and ultrasonication

FTIR Analysis

      FTIR spectra of the CNFs, original bamboo particles, and their intermediate products are shown in Fig. 3.
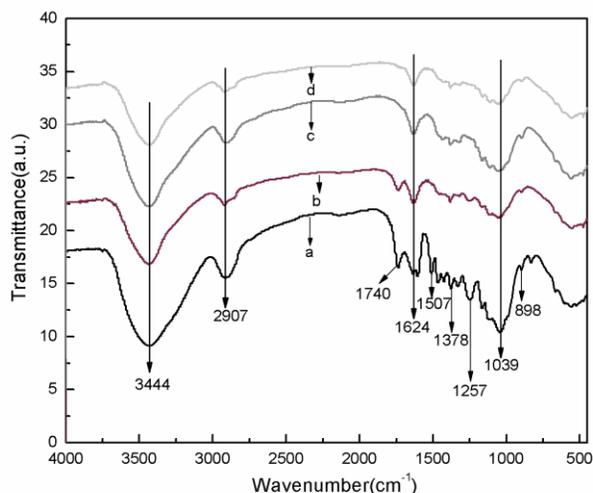
Fig. 3. FTIR spectra of the original particles (a), holo-cellulose (b), α-cellulose (c), and CNFs (d)

      The dominant peaks of OH-stretching and CH-stretching at approximately 3444 cm^{-1} and 2907 cm^{-1}, respectively were observed in the entire spectra (Sain and Panthapulakkal 2006; Alemdar and Sain 2008). At the same time, the peaks at 1624, 1039, and 898 cm^{-1} could also be found in all spectra. These peaks were associated with the H–O–H stretching vibration of absorbed water in carbohydrates, the C–O stretching, and the C1-H deformation vibrations of cellulose, respectively (Herrick *et al.* 1983; Turbak *et al.* 1983). The peak at 1740 cm^{-1} in the spectrum of holo-cellulose represented either the acetyl and uronic ester groups or the ester linkage of the carboxylic group of the ferulic and p-coumeric acids of the hemicelluloses (Sun *et al.* 2000). However, this peak disappeared completely in the spectra of α-cellulose and CNFs, which could be attributed

to the removal of most of the hemicellulose after NaOH treatment. The peaks at 1507 and 1378 cm^{-1} in the spectrum of the original particles, which were attributed to the C=C stretching vibration and C–H deformation vibration in the aromatic ring of lignin (Sun *et al.* 2000; Sain and Panthapulakkal 2006), respectively, disappeared completely on the remaining spectra. This indicates that lignin was removed from the newly-prepared holo-cellulose by acid $NaClO_2$ treatment. Interestingly, the spectrum of the CNFs was similar to that of α-cellulose. These facts indicate that hemicellulose and lignin were to a large degree removed after chemical purification and that the original molecular structure of the cellulose was maintained even after the removal of the matrix components and after acid treatments.

X-ray Diffraction Analysis

Figure 4 and Table 1 present comparisons of the corresponding X-ray diffraction patterns and the relative degree of crystallinity of the original material, holo-cellulose, α-cellulose, and CNFs.
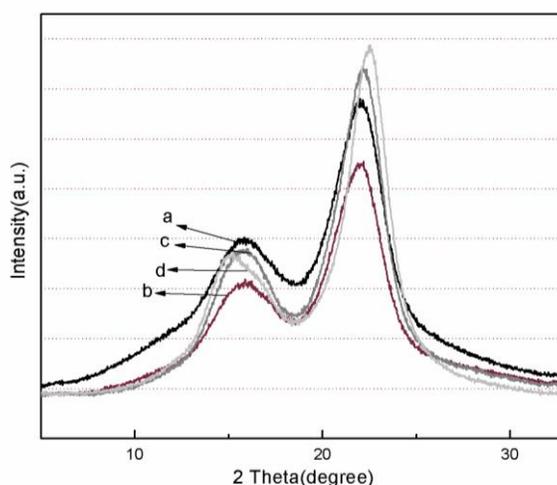
Fig. 4. X-ray diffraction patterns of (a) the original particles, (b) holo-cellulose, (c) α-cellulose, and (d) CNFs

All specimens had diffraction peaks at $2\theta = 16.5°$ and $22.5°$, which are believed to represent the typical cellulose I structure (Nishiyama *et al.* 2002, 2003). This indicates that the crystal integrity was maintained during chemical purification and ultrasonic treatment. As shown in Table 1, the relative degree of crystallinity in the original materials, holo-cellulose, and α-cellulose was 40.51%, 44.13%, and 51.25%, respectively. The increase of crystallinity in the specimens was primarily attributed to the removal of lignin and hemicellulose in the amorphous regions, which led to the realignment of cellulose molecules (Li *et al.* 2009). The crystallinity of CNFs exhibited a significant increase, with a value of about 69.32%. In general, the degree of crystallinity of CNFs is decreased due to the high mechanical treatment; therefore, the increase of crystallinity could be ascribed to the production of part cellulose nanocrystals (CNCs) during the acid hydrolysis, in which the non-crystalline regions of cellulose were removed. The highly crystalline nanofibers could be more effective for providing better reinforcement and thermal stability for composite materials.

Table 1. Crystallinities of Cellulose Fibers at Different Stages

Specimens	I_{am} (a.u.)	I_{200} (a.u.)	Relative Crystallinity (%)
Original Particles	3.9483×10^4	6.6419×10^4	40.51
Holo-cellulose	3.0734×10^4	5.4868×10^4	44.13
α-cellulose	3.5370×10^4	7.3055×10^4	51.25
Cellulose Nanofiber	3.3387×10^4	10.9353×10^4	69.32

Thermostability Analysis

Thermogravimetric curves of the original material, intermediate products, and CNFs are shown in Fig. 5. First of all, all specimens showed an initial small mass loss (about 2.5%) on the TG curves at about 100 °C, which could be attributed to the evaporation of absorbed moisture. It is evident that the original material had a lower initial decomposition temperature (about 215 °C) because of the presence of hemicellulose and lignin (Morán *et al.* 2008). Similarly, the curve of the holo-cellulose also showed a lower initial decomposition temperature (approximately 210 °C) because of the presence of hemicellulose. However, with increasing temperature, the thermostability of the holo-cellulose was significant higher than that of the original material; this could be ascribed to the removal of lignin. Apparently, the pyrolysis temperature of α-cellulose was increased to 304 °C, which could have been caused by the removal of hemicellulose and lignin.
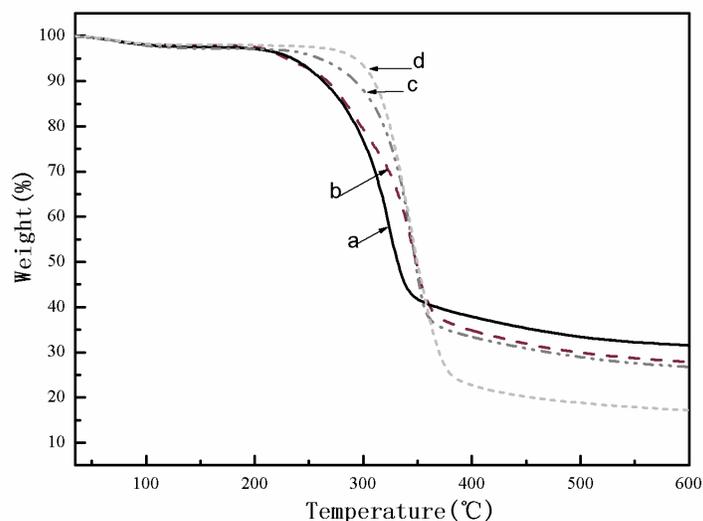
Fig. 5. TG curves of (a) the original material, (b) holo-cellulose, (c) α-cellulose, and (d) CNFs

It is worthwhile to note that the pyrolysis temperature of CNFs rose to 318 °C, which could have been caused by the removal of the alkali-insoluble matrix that existed in α-cellulose after treatment with sulfuric acid (Alemdar and Sain 2008). These findings are completely in accordance with the results obtained from FTIR and X-ray

measurements. The higher thermal stability of the CNFs compared with the original material may broaden the application area of cellulose fibers for biocomposite processing.

CONCLUSIONS

Nano-sized fibers were successfully extracted from *Ph. nidularia* Munro using acid hydrolysis combined with low-intensity ultrasonication processing.

1. The average diameters of the CNFs ranged from 5 to 20 nm.

2. Hemicellulose and lignin were shown to be removed from the original material after the chemical process, and the original molecular structure of the cellulose was maintained even after the removal of the matrix components and after acid treatments.

3. All specimens still presented a typical cellulose I crystal form; furthermore, the relative crystallinity of the CNFs was increased to 69.32%.

4. Thermogravimetric curves analysis indicated that the thermostability of CNFs was significantly enhanced with the removal of hemicellulose and lignin.

These facts show that superior CNFs were isolated from *Ph. nidularia* Munro using the described processes. Moreover, the results prove that the characteristics and properties of nanocellulose obtained in this work are different from the previous results obtained from *Bambusa rigida*. Next, we intend to manufacture flexible electronic displays using this material as substrate.

ACKNOWLEDGEMENTS

REFERENCES CITED

Abe, K., and Yano, H. (2009). "Comparison of the characteristics of cellulose microfibril aggregates of wood, rice straw and potato tuber," *Cellulose* 16(6), 1017-1023. DOI: 10.1007/s10570-009-9334-9

Abe, K., Iwamoto, S., and Yano, H. (2007). "Obtaining cellulose nanofibers with a uniform width of 15 nm from wood," *Biomacromol.* 8(10), 3276-3278.

Alemdar, A., and Sain, M. (2008). "Isolation and characterization of nanofibers from agricultural residues–Wheat straw and soy hulls," *Bioresource Technology* 99(6), 1664-1671. DOI: 10.1016/j.biortech.2007.04.029

Beck-Candanedo, S., Roman, M., and Gray, D. G. (2005). "Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions," *Biomacromolecules* 6(2), 1048-1054. DOI: 10.1021/bm049300p

Bergenstråhle, M., Berglund, L. A., and Mazeau, K. (2007). "Thermal response in crystalline I cellulose: A molecular dynamics study," *The Journal of Physical Chemistry B* 111(30), 9138-9145. DOI: 10.1021/jp072258i

Chakraborty, A., Sain, M., and Kortschot, M. (2005). "Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing," *Holzforschung* 59(1), 102-107. DOI: 10.1515/HF.2005.016

Chen, W., Yu, H., and Liu, Y. (2011). "Preparation of millimeter-long cellulose I nanofibers with diameters of 30–80 nm from bamboo fibers," *Carbohydrate Polymers* 86, 453-461. DOI: 10.1016/j.carbpol.2011.04.061

Cheng, Q., Wang, S., Rials, T., and Lee, S. (2007). "Physical and mechanical properties of polyvinyl alcohol and polypropylene composite materials reinforced with fibril aggregates isolated from regenerated cellulose fibers," *Cellulose* 14(6), 593-602. DOI: 10.1007/s10570-007-9141-0

Cheng, Q., Wang, S., and Rials, T. G. (2009). "Poly(vinyl alcohol) nanocomposites reinforced with cellulose fibrils isolated by high intensity ultrasonication," *Composites Part A: Applied Science and Manufacturing* 40(2), 218-224. DOI: 10.1016/j.compositesa.2008.11.009

Eichhorn, S. J., Dufresne, A., Aranguren, M., Marcovich, N. E., Capadona, J. R., Rowan, S. J., Weder, C., Thielemans, W., Roman, S., Renneckar, S., *et al.* (2010). "Review: Current international research into cellulose nanofibres and nanocomposites," *Journal of Materials Science* 45(1), 1-33. DOI: 10.1007/s10853-009-3874-0

Elazzouzi-Hafraoui, S., Nishiyama, Y., Putaux, J. L., Heux, L., Dubreuil, F., and Rochas, C. (2007). "The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose," *Biomacromolecules* 9(1), 57-65. DOI: 10.1021/bm700769p

Fukuzumi, H., Saito, T., Iwata, T., Kumamoto, Y., and Isogai, A. (2009). "Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation," *Biomacromolecules* 10(1), 162-165. DOI: 10.1021/bm801065u

Habibi, Y., Lucia, L. A., and Rojas, O. J. (2010). "Cellulose nanocrystals: Chemistry, self-assembly, and applications," *Chemical Reviews* 110(6), 3479-3500. DOI: 10.1021/cr900339w

He, W., Jiang, S., Zhang, Q., and Pan, M. (2013). "Isolation and characterization of cellulose nanofibers from *Bambusa rigida*," *BioResources* 8(4), 5678-5689.

Herrick, F. W., Casebier, R. L., and Hamilton, J. K. (1983). "Microfibrillated cellulose: Morphology and accessibility," *Journal of Applied Polymer Science: Applied Polymer Symposium* 37, 797-813.

Isogai, A., Saito, T., and Fukuzumi, H. (2011). "TEMPO-oxidized cellulose nanofibers," *Nanoscale* 3(1), 71-85. DOI: 10.1039/c0nr00583e

Iwamoto, S., Abe, K., and Yano, H. (2008). "The effect of hemicelluloses on wood pulp nanofibrillation and nanofiber network characteristics," *Biomacromolecules* 9(3), 1022-1026. DOI: 10.1021/bm701157n

Jiang, Z. (2002). "Structure and properties of bamboo," in: *Bamboo and Rattan in the World*, Science and Technology (ed.), Shen Yang and Liao Ning (eds.).

bioresources.com

Li, R., Fei, J., Cai, Y., Li, Y., Feng, J., and Yao, J. (2009). "Cellulose whiskers extracted from mulberry: A novel biomass production," *Carbohydrate Polymers* 76(1), 94-99. DOI: 10.1016/j.carbpol.2008.09.034

Lu, T. H., Li, Q., Chen, W. S., and Yu, H. P. (2014). "Composite aerogels based on dialdehyde nanocellulose and collagen for potential applications as wound dressing and tissue engineering scaffold," *Composites Science and Technology* 94, 132-138. DOI: 10.1016/j.compscitech.2014.01.020

Morán, J., Alvarez, V., Cyras, V., and Vázquez, A. (2008). "Extraction of cellulose and preparation of nanocellulose from sisal fibers," *Cellulose* 15(1), 149-159. DOI: 10.1007/s10570-007-9145-9

Nishino, T., Matsuda, I., and Hirao, K. (2004). "All cellulose composite," *Macromolecules* 37(20), 7683-7687. DOI: 10.1021/ma049300h

Nishiyama, Y., Langan, P., and Chanzy, H. (2002). "Crystal structure and hydrogen-bonding system in cellulose I$_\beta$ from synchrotron X-ray and neutron fiber diffraction," *Journal of the American Chemical Society* 124(31), 9074-9082. DOI: 10.1021/ja0257319

Nishiyama, Y., Sugiyama, J., Chanzy, H., and Langan, P. (2003). "Crystal structure and hydrogen bonding system in cellulose I$_\alpha$ from synchrotron X-ray and neutron fiber diffraction," *Journal of the American Chemical Society* 125(47), 14300-14306. DOI: 10.1021/ja037055w

Nogi, M., and Yano, H. (2008). "Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics device industry," *Advanced Materials* 20(10), 1849-1852. DOI: 10.1002/adma.200702559

Nogi, M., Iwamoto, S., Nakagaito, A. N., and Yano, H. (2009). "Optically transparent nanofiber paper," *Advanced Materials* 21(16), 1595-1598. DOI: 10.1002/adma.200803174

Orts, W. J., Shey, J., Imam, S. H., Glenn, G. M., Guttman, M. E., and Revol, J. F. (2005). "Application of cellulose microfibrils in polymer nanocomposites," *Journal of Polymers and the Environment* 13(4), 301-306. DOI: 10.1007/s10924-005-5514-3

Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O., *et al.* (2007). "Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels," *Biomacromolecules* 8(6), 1934-1941. DOI: 10.1021/bm061215p

Pääkkö, M., Vapaavuori, J., Silvennoinen, R., Kosonen, H., Ankerfors, M., Lindstrom, T., Berglund, L. A., and Ikkala, O. (2008). "Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically Porous templates for functionalities," *Soft Matter* 4(12), 2492-2499. DOI: 10.1039/b810371b

Sain, M., and Panthapulakkal, S. (2006). "Bioprocess preparation of wheat straw fibers and their characterization," *Industrial Crops and Products* 23(1), 1-8. DOI: 10.1016/j.indcrop.2005.01.006

Saito, T., Kimura, S., Nishiyama, Y., and Isogai, A. (2007). "Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose," *Biomacromolecules* 8(8), 2485-2491. DOI: 10.1021/bm0703970

Sakurada, I., Nukushina, Y., and Ito, T. (1962). "Experimental determination of the elastic modulus of crystalline regions in oriented polymers," *Journal of Polymer Science* 57(165), 651-660. DOI: 10.1002/pol.1962.1205716551

Segal, A. W., and Meshulam, T. (1979). "Production of superoxide by neutrophils: A reappraisal," *FEBS Letters* 100, 27-32. DOI: 10.1016/0014-5793(79)81124-2

Siqueira, G., Bras, J., and Dufresne, A. (2008). "Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites," *Biomacromolecules* 10(2), 425-432. DOI: 10.1021/bm801193d

Siró, I., and Plackett, D. (2010). "Microfibrillated cellulose and new nanocomposite materials: A review," *Cellulose* 17(3), 459-494. DOI: 10.1007/s10570-010-9405-y

Sun, R. C., Tomkinson, J., Wang, Y. X., and Xiao, B. (2000). "Physicochemical and structural characterization of hemicelluloses from wheat straw by alkaline peroxide extraction," *Polymer* 41(7), 2647-2656. DOI: 10.1016/S0032-3861(99)00436-X

Turbak, A. F., Snyder, F. W., and Sandberg, K. R. (1983). "Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential," *Journal of Applied Polymer Science: Applied Polymer Symposium* 37, 815-827.