

Preparation and Characterization of Nanocellulose Fibers from NaOH/Urea Pretreatment of Oil Palm Fibers

Xianxing Luo and Xiwen Wang *

A facile method is reported to prepare nanocellulose fibers from oil palm trunk fibers. The fibers were pretreated 2 hours with NaOH/urea solution, and the fully swelled fibers were mechanically treated through high-pressure homogenization to obtain nanocellulose. The nanocellulose fibers were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). FTIR results revealed that there was no obvious difference between the spectra of the bleached fibers (BF), pretreated cellulose fibers (PCF), and cellulose nanofibers (NCF), which indicated that the pretreatment process is a non-derivative reaction. The crystallinity of PCF and NCF decreased and contained the cellulose I crystal structure. The PCF presented both a distorted structure and a coarser surface. The resulting NCF were approximately 10 nm to 100 nm in diameter with the length varying from hundreds of nanometers to several micrometers, as observed by SEM. The thermal degradation of NCF was 223 °C with about 20% weight loss, and the maximum degradation temperature was 338 °C. NaOH/urea showed potential as a mild solvent for preparing nanocellulose fibers.

Keywords: Oil palm fiber; Nanocellulose fibers; NaOH/urea; High-pressure homogenization

Contact information: State Key Laboratory of Pulp and Paper Engineering School of Light Industry Science and engineering, South China University of Technology, Guangzhou, 510640, China;

* *Corresponding author:* wangxw@scut.edu.cn

INTRODUCTION

Cellulose in plant-based materials is the most ubiquitous green, renewable, and biodegradable natural biopolymer (Klemm *et al.* 2005; Abraham *et al.* 2011; Fatah *et al.* 2014). Cellulose is a high molecular-weight linear homopolymer, consisting of β -D-glucopyranosyl repeating units joined by (1 \rightarrow 4) glycosidic linkages (Lima and Borsali 2004; Khalil *et al.* 2014). The molecular chains of cellulose are self-assembled into elemental microfibrils, with diameter ranges of 2 nm to 5 nm, composed of finely oriented crystalline and randomly oriented amorphous domains (Nishiyama 2009; Fernandes *et al.* 2011; Hiden *et al.* 2014). The term nanocellulose fibers usually refers to fibers within a general size range of 10 nm to 1000 nm, basically consisting of nanocrystalline cellulose, nanofibrillated cellulose, and bacterial cellulose. Due to its excellent properties, such as thermal stability, environmental benefits, optical transparency, and hydroxyl groups on the surfaces, nanocellulose fibers have become a precursor in a variety of new functional biomaterials, including transparent films (Zhu *et al.* 2014), aerogels (Chen *et al.* 2014), reinforcing agents (Tibolla *et al.* 2014), and separation membranes (Metreveli *et al.* 2014).

As for the source of cellulose to prepare nanocellulose fibers, it can be obtained from several raw materials such as cotton, orange peel, rubberwood, softwood, and so on (Nickerson and Habrle 1947; Jonoobi *et al.* 2011; Li *et al.* 2011; Hiden *et al.* 2014). As

an abundant plant resource, oil palm is also used for preparation nanocellulose in many studies. Fahma *et al.* (2010) isolated cellulose nanocrystals from the empty fruit bunch by acid hydrolysis. Jonoobi *et al.* (2011) isolated nanocrystals using the chemo-mechanical process. The synthesis and characterization of cellulose phosphate from oil palm empty fruit bunch derived microcrystalline cellulose has been reported (Wanrosli *et al.* 2011). Haafiz *et al.* (2014) compared the effect of two different isolation techniques on the properties of oil palm cellulose nanowhiskers. Ching and Ng (2014) investigated the effect of bleaching duration on the properties of the cellulose derived from oil palm.

There are two types of methods for preparing nanocellulose fibers: mechanical and chemical. Mechanical methods include high-pressure homogenization, micro-grinding, high intensity ultrasonication, and PFI milling. However, this method requires high-energy consumption (Spence *et al.* 2011). Alternatively, chemical pretreatments, include acid hydrolysis, enzyme hydrolysis, and TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl] oxidation. The drawbacks of the chemical method are its time-consuming nature and low-yield results (Tang *et al.* 2011). To reduce energy consumption, chemical and mechanical methods are usually combined; fibers are pretreated by chemical reagent prior to preparing nanocellulose by mechanical methods (Li *et al.* 2011). There have been a large number of studies on the preparation of nanocellulose fibers with lignocellulosic biomass. Nanocellulose was first prepared in 1947 using sulfuric acid and hydrochloric acid hydrolysis from wood fibers and cotton fibers (Nickerson and Habrle 1947). Malainine *et al.* (2005) prepared cellulose microfibril suspensions using a pressure homogenizer under alkaline conditions. Abe *et al.* (2007) obtained nanocellulose fibers with a uniform width of approximately 15 nm using a grinding treatment. These methods were followed by Iwamoto *et al.* (2007) with a grinder modification. Cheng *et al.* (2009) used high intensity ultrasonication. Surface carboxylated cellulose nanocrystals were prepared from cotton linters by TEMPO-mediated oxidation followed by mechanical treatment (Montanari *et al.* 2011). Man *et al.* (2011) prepared cellulose nanocrystals by the ionic liquid method. Wang *et al.* (2014) successfully prepared nanocellulose-II fibers by mechanical fibrillation treatment with cellulose I purified pulps pretreated in 17.5 wt% NaOH. Shankar and Rhim (2016) proposed a facile approach to prepare the nanocellulose from micro-crystalline cellulose using NaOH/urea dissolution combined with ultrasonication.

Acid hydrolysis is the most commonly used method to prepare nanocellulose. The major drawback of this method is the use of highly concentrated acid (Man *et al.* 2011). Highly concentrated acid has a highly corrosive effect on the reaction container; in addition, the acid waste liquid is difficult to recycle, causing serious pollution to the environment. It is also difficult to control the degree of cellulose hydrolysis, which makes the yield of nanocellulose fibers usually lower than 50%. Moreover, TEMPO oxidation treatment is toxic, and the enzymatic approaches are also expensive and time-consuming. Thus, there is need to develop a facile approach for preparing nanocellulose fibers.

Recently, an aqueous solution mixture (with a weight ratio of NaOH:urea:H₂O of 7:12:81), precooled to -12 °C, was used to “dissolve” cellulose (Cai and Zhang 2005). In this system, temperature is the key factor in dissolving cellulose. Based on this theory, a method was introduced for the preparation of nanocellulose fibers (Adsul *et al.* 2012). First, the fibers were swelled in a NaOH/urea pretreatment solution; following the isolation of the pretreated fibers by high-pressure homogenization, the nanocellulose fibers were obtained. Compared with conventional pretreatment reagent, such as concentrated sulfuric acid, ionic liquid, and TEMPO, NaOH/urea pretreatment has the advantages of low cost

and relatively low toxicity. The possible swelling mechanism of the aqueous mixture is that sodium hydroxide hydrates destroy the intermolecular and intramolecular hydrogen bonds in cellulose, whereas the amino groups of urea easily form hydrogen bonds with hydroxyl groups in cellulose. The synergistic action of NaOH and urea prevents binding between cellulose molecules and finally weakens the binding force of cellulose molecules (Cai and Zhang 2005; Yan and Gao 2008). Compared with single NaOH solution, the presence of urea could further enhance the effect of pretreatment due to its synergy with NaOH and lead to better swelling of the cellulose (Wang *et al.* 2016).

In this study, the aim of the pretreatment was simply to make cellulose fully swelled, instead of resulting in a complete dissolution. Therefore, the reaction conditions were changed compared to dissolution values mentioned in the previous paragraph. The temperature to liquid ratio was increased. Chemical pretreatments were used to swell the fibers prior to the mechanical treatment in order to make fibers fibrillated easily. The bleached oil palm fibers were used as raw materials, pretreated in the NaOH/urea/H₂O mixture liquid, and then isolated by high-pressure homogenization to obtain the nanocellulose fibers. The morphology, crystal structure, functional groups, and thermal properties of the nanocellulose fibers prepared by the comparatively eco-friendly method were explored.

EXPERIMENTAL

Materials and Chemicals

The bleached oil palm trunk pulp (95% cellulose content) was supplied by Ecopalm SDN BHD (Kuala Lumpur, Malaysia). Reagent grade urea and NaOH were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China).

Chemical Pretreatment

Bleached fiber (BF) powder (1 g, over dried) was dispersed into a 20 mL pretreatment solution in a beaker and stirred mechanically 5 min for even mixing. The mixed liquid was frozen at -7 °C for 2 hours. In the pretreatment solution, the weight ratio of NaOH:urea:H₂O was 7:12:81 (Cai *et al.* 2007). After freezing, the mixed liquid was centrifuged at 5000 rpm for 10 min several times to remove the supernatant. The residue was vacuum filtrated and rinsed with deionized water until the pH reached 7. Subsequently, the precipitate (0.5 wt.%) was re-dispersed in deionized water by ultrasonication. The pretreated cellulose fibers were coded as PCF.

Preparation of Nanocellulose

Suspensions of PCF (0.5 wt.%) were homogenized at 1000 bar for 60 min to obtain nanocellulose fibers. The homogenized transparent suspensions were stored at 4 °C and used for subsequent characterization. Nanocellulose fibers pretreated by NaOH/urea/H₂O and homogenization were coded as NCF.

Characterization

Fourier transform infrared spectroscopy (FTIR)

The chemical bond and group of lignocellulosic materials were characterized by FTIR. Each sample suspension was filtered to a membrane and dried in ambient conditions.

FTIR spectra were recorded using a Perkin Elmer Spectrum 2000 (Bruker, Germany), in the wave number range of 4000 cm^{-1} to 400 cm^{-1} at a 4 cm^{-1} resolution for 64 scans.

Microscopy analysis

The morphology of the bleached fibers, pretreated fibers, and nanocellulose fibers was observed by SEM (JEOL JSM-5600 LV, Tokyo, Japan), operating at 10 kV) and transmission electron microscopy (TEM; H-7650, Hitachi, Tokyo, Japan). A drop of the 10 μL diluted NCF suspension (0.01 wt.%) was deposited onto carbon-coated TEM grids, and after 3 min, 15 μL of (1% w/w) phosphotungstic acid was added. The dried sample was observed at an accelerating voltage of 80 kV.

X-ray diffraction (XRD)

The crystalline structure of the fibers was determined by wide-angle XRD analysis from 5° F/C to 40° F/C (2θ) using a Bruker D8-advance (Bruker, Germany), at 40 kV and 40 mA with a scan speed of 3°/min. The crystallinity index (CrI) was calculated as previously described equation (Segal *et al.* 1959),

$$\text{CrI}=(I_{002} - I_{\text{amorph}})/I_{002}\times 100\% \quad (1)$$

where I_{002} is the maximum of the diffraction intensity (the 002 plane), and I_{amorph} is the minimum diffraction intensity(between 101 and 002 peaks).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a TGA Q500 (TA Instruments, New Castle, DE, USA). Thermograms were acquired in a temperature range from 25 °C to 600 °C at a heating rate of 10 °C/min, with nitrogen as purge gas at a flow rate of 25 mL/min.

RESULTS AND DISCUSSION

FTIR Analysis

The structural changes in chemical composition were analyzed by FTIR spectroscopy. Figure 1 shows the spectra of the BF, PCF, and NCF. Interestingly, there was no obvious difference in the spectra of these three samples. This result indicates that no chemical reaction occurred and that no new substance was produced during the pretreatment or mechanical refining process. The final product was cellulose itself and not a derivative of cellulose (Zhou *et al.* 2004; Cai and Zhang 2005; Wang *et al.* 2016). While the cellulose fibers pretreated by 64 wt% sulfuric acid or TEMPO oxidation, the partial primary hydroxyl group will undergo esterification and oxidized to carboxyl hydroxyl groups ,respectively (Wang *et al.* 2007; Isogai *et al.* 2011).

For the BF, the broad bands in the 3600 to 3000 cm^{-1} region were hydrogen-bond O-H stretching vibrations, and the peak at 2902 cm^{-1} corresponded to -CH stretching vibrations. The peak at 1643 cm^{-1} was the O-H bending of adsorbed water. The peak at 1430 cm^{-1} corresponded to -CH₂ bending vibration that it is a typical of the “crystallinity band” in cellulose. The peak at 893 cm^{-1} is considered the “amorphous band”. Compared with BF, the intensity of the band at 1430 cm^{-1} crystallinity was reduced in NCF, indicating that the crystallinity of NCF decreased (Shankar and Rhim 2016). In contrast, the intensity

of vibrational peak at 893 cm^{-1} increased compared with BF, suggesting that NCF lost crystallinity. This result confirmed the XRD result showing that decreased crystallinity in NCF.

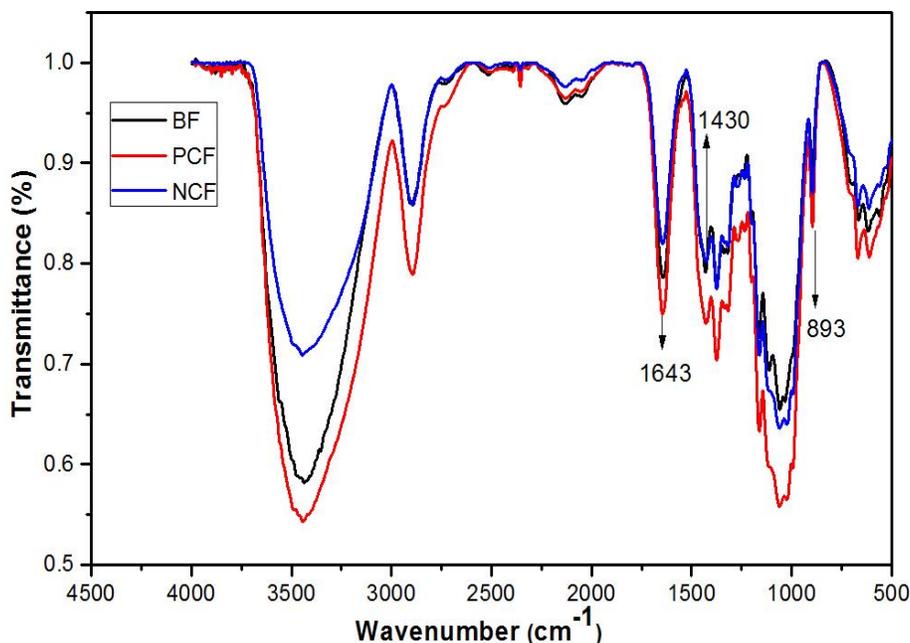


Fig. 1. FTIR spectra of the BF, PCF, and NCF

Morphology Analysis of the Pretreated Fibers and Nanocellulose Fibers

The surface morphological changes between the original fibers and the pretreated fibers are shown in Fig. 2. The bleached fibers were relatively flat and straight. In addition to having the structure of the original fiber lines, the surface had no obvious gully. In the pretreated fibers, the surfaces were distorted and wrinkled. The fine fibrillation disappeared, and a deep gully appeared along the longitudinal direction of the fibers. The structures of the fibers were hierarchical, cracked, and incompact, and the surface area was increased, indicating that the pretreatment destroyed the cellulose molecules and intramolecular hydrogen bonds. Thus, the cellulose molecules chain was opened, forming a loose special structure.

Figure 2c shows that after homogenization, the pretreated fibers disintegrated into nanocellulose fibers. The NCF were approximately 10 nm to 100 nm in diameter, while the length varied from hundreds of nanometers to several micrometers. The ratio of length to diameter in NCF was relatively large, and the size distribution was not uniform compared with the method of sulfuric acid hydrolysis (Fahma *et al.* 2010). Figure 2d is a TEM image of cellulose nanoparticles, which were the supernatant liquid of NCF separated by centrifugation. Their size was smaller than NCF. This difference may be due to the slight dissolution of cellulose in the pretreatment process by NaOH/urea/ H_2O .

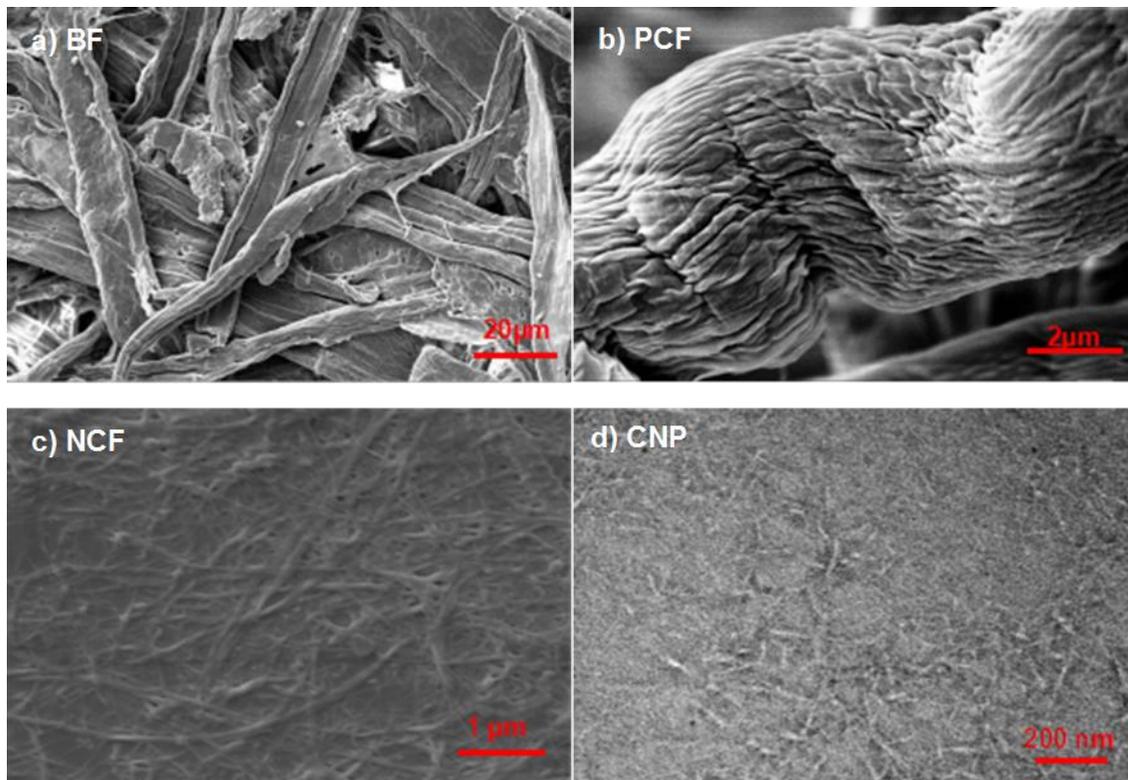


Fig. 2. SEM of (a) bleached fibers, (b) pretreated cellulose fibers, and (c) cellulose nanofibers after homogenization. (d) TEM of cellulose nanoparticles (CNP)

Figure 3 shows that the transparency of the nanocellulose fibers solution decreased after chemical pretreatment and high-pressure homogenization. The size of cellulose reached the nano level, and the nanocellulose fibers existed stably in the presence of gel in the aqueous solution. Images of the bleached fibers in the aqueous solution show an obvious stratification: the upper layer is water, and the lower layer is the fiber. Figure 3b shows that the nanocellulose fibers were dispersed in water to form a stable colloid.



Fig. 3. Aqueous solutions of (a) bleached fibers (BF) and (b) cellulose nanofibers (NCF)

Degree of Crystallinity

The BF, PCF, and NCF were characterized by XRD to check the crystallinity, and the X-ray diffractograms are shown in Fig. 4. Each diffractogram exhibited two diffraction peaks at $2\theta = 22.42^\circ$ and from 15° to 17° , indicating that BF, PCF, and NCF were present as cellulose I but not cellulose II (Nishiyama *et al.* 2002). These results indicated that the pretreatment and homogenization did not affect the crystalline structure of cellulose, and this conclusion was consistent with the FTIR analysis.

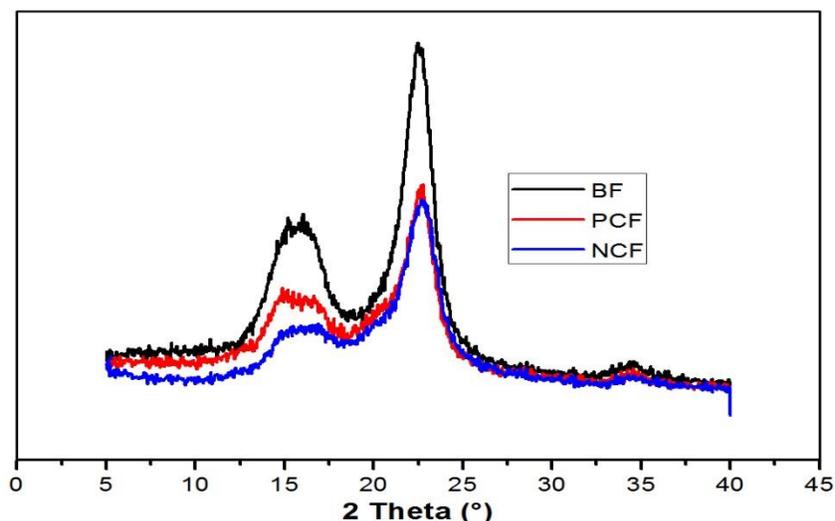


Fig. 4. XRD curves of the BF, PCF, and NCF

The crystallinity index (CrI) of BF, PCF, and NCF was 69.33%, 64.07%, and 59.35%, respectively. The CrI of PCF and NCF was lower than that of BF. This phenomenon may be due to the destruction of the intermolecular and the intramolecular hydrogen bonding in the crystalline region during the pretreatment (Jin *et al.* 2007). In the next mechanical treatment, due to the strong shear effect, the crystalline region of cellulose was further destroyed (Zhang *et al.* 2007), so that the final crystallinity of the NCF was further reduced. However, there was little difference in crystallinity between the three samples. The pretreated cellulose did not show the cellulose II structure, which is somewhat different from previous results (Li *et al.* 2014; Shankar and Rhim 2016). This result may be caused by different pretreatment conditions, including the key factors of temperature, liquid ratio, and others.

Thermal Stability Analysis

The thermal stability of the BF, PCF, and NCF, are shown in Fig. 5. TG curves show the weight loss of the BF, PCF, and NCF when they were heated. The DTG is the differential curve of TG, showing the rate of weight loss during heating.

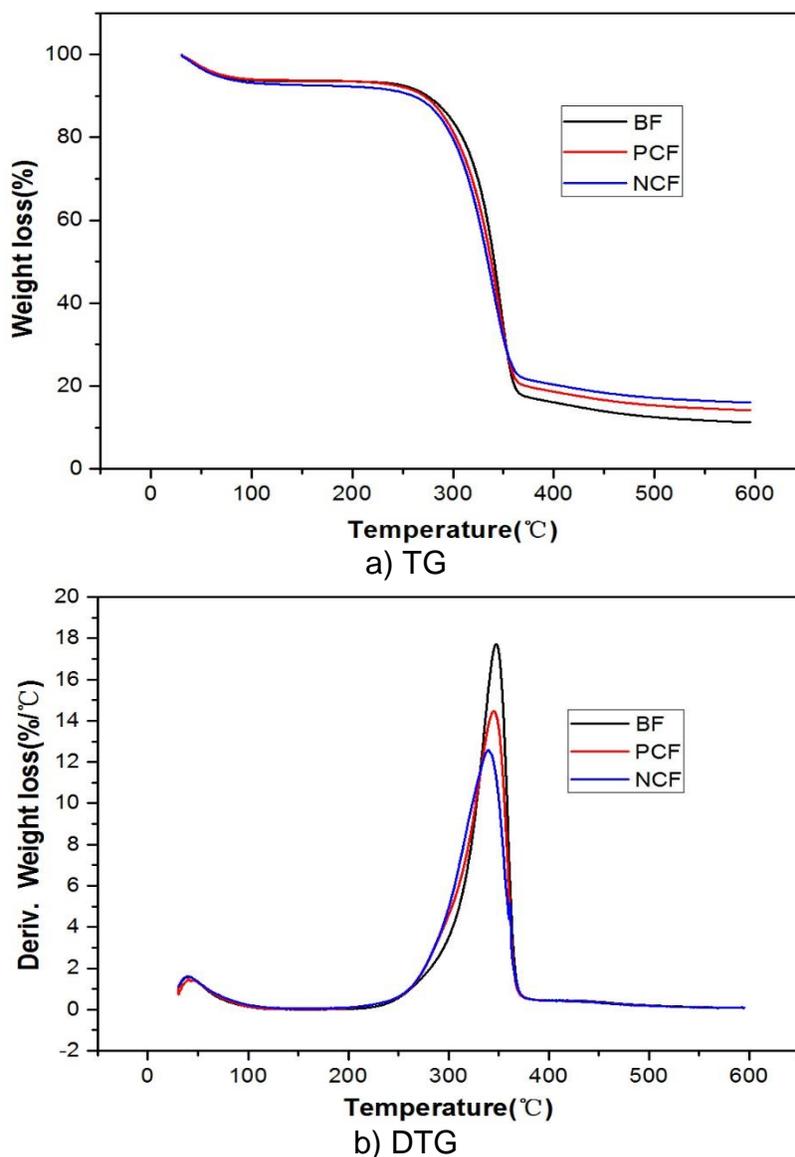


Fig. 5. TG and DTG curves of the BF, PCF, and NCF

An initial weight loss of about 6% was observed from BF, PCF, and NCF at the temperature range of 30 °C to 105 °C, due to the absorbed water. The degradation behavior of the three samples reflected some differences. The BF and PCF started to degrade at 240 °C and 230 °C, respectively. The NCF started degrading at 223 °C, with about 20% weight loss. According to the DTG peak, the maximum degradation temperatures of BF, PCF, and NCF were 350 °C, 342 °C, and 338 °C, respectively. Due to the NaOH/urea penetration into the crystalline region during pretreatment, the binding force between cellulose molecules was weakened, and the cellulose microfibrils were more likely to be stripped. In addition, the strong mechanical shearing force destroyed the crystalline area of the cellulose, which further led to the poor thermal stability of NCF compared with that of BF.

Table 1. Degradation Temperature of BF, PCF, and NCF

Samples	Onset temperature (°C)	Max temperature (°C)
BF	240	350
PCF	230	342
NCF	223	338

CONCLUSIONS

1. Nanocellulose fibers were successfully prepared by pretreating bleached fibers in a NaOH/urea/H₂O mixture and then defibrillating the pretreated cellulose fibers *via* homogenization. This facile preparation method has superiority on account of its low cost and less environmental pollution. Making cellulose fully swelled by NaOH/urea aqueous solution to prepare nanocellulose fibers may be a significant finding.
2. There was no obvious difference in the FTIR spectra of the three samples. This result indicates that no chemical reaction occurred in the pretreatment process or the mechanical refining process, and the final product was not a derivative of cellulose.
3. XRD analysis revealed that the crystallinity of PCF and NCF were decreased, and their crystal structure was in the form of cellulose I.
4. The obtained NCF were approximately 10 nm to 100 nm in diameter, while the length varied from hundreds of nanometers to several micrometers. The onset thermal degradation of NCF is 223 °C, and the maximum degradation temperature is 338 °C from the thermal stability analysis.
5. The PCF surface was damaged by NaOH/urea aqueous solution, and presented both a distorted structure and a coarser surface. Under pretreatment, the cellulose molecules chain was opened and formed a loose special structure.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (31470608) and the fundamental Research Funds for the Central Universities (201522117).

REFERENCES CITED

- Abraham, E., Deepa, B., Pothan, L. A., Jacob, M., Thomas, S., Cvelbar, U., and Anandjiwala, R. (2011). "Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach," *Carbohydrate Polymers* 86, 1468-1475.
DOI: 10.1016/j.carbpol.2011.06.034
- Abe, K., Iwamoto, S., and Yano, H. (2007). "Obtaining cellulose nanofibers with a uniform width of 15nm from wood," *Biomacromolecules* 8(10), 3276-3278.
DOI: 10.1021/bm700624p
- Adsul, M., Soni, S. K., Bhargava, S. K., and Bansal, V. (2012). "Facile approach for the

- dispersion of regenerated cellulose in aqueous system in the form of nanoparticles,” *Biomacromolecules* 13(9), 2890-2895. DOI: 10.1021/bm3009022
- Cai, J., and Zhang, L. (2005). “Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions,” *Macromolecular Bioscience* 5(6), 539-48. DOI: 10.1002/mabi.200400222
- Cai, J., Zhang, L., Zhou, J., Qi, H., Chen, H., Kondo, T., Chen, X., and Chu, B. (2007). “Multifilament fibers based on dissolution of cellulose in NaOH/urea aqueous solution: Structure and properties,” *Advanced Materials* 19(6), 821-825. DOI: 10.1002/adma.200601521
- Chen, W., Li, Q., Wang, Y., Yi, X., Zeng, J., Yu, H., Liu, Y., and Li, J. (2014). “Comparative study of aerogels obtained from differently prepared nanocellulose fibers,” *ChemSusChem* 7(1), 154-161. DOI: 10.1002/cssc.201300950
- 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 & Manufacturing* 40(2), 218-224. DOI: 10.1061/j.compositesa.2008.11.009
- Ching, Y. C., and Ng, T. S. (2014). “Effect of preparation conditions on cellulose from oil palm empty fruit bunch fiber,” *BioResources* 9(4), 6373-6385. DOI: 10.15376/biores.9.4.6373-6385
- Fahma, F., Iwamoto, S., Hori, N., Iwata, T., and Takemura, A. (2010). “Isolation, preparation, and characterization of nanofibers from oil palm empty-fruit-bunch (OPEFB),” *Cellulose* 17(5), 977-985. DOI: 10.1007/s10570-010-9436-4
- Fatah, I. Y., Khalil, H. P. S., Hossain, M. S., Aziz, A. A., Davoudpour, Y., Dungani, R., and Bhat, A. (2014). “Exploration of a chemo-mechanical technique for the isolation of nanofibrillated cellulosic fiber from oil palm empty fruit bunch as a reinforcing agent in composites materials,” *Polymers* 6(10), 2611-2624. DOI: 10.3390/polym6102611
- Fernandes, A. N., Thomas, L. H., Altaner, C. M., Callow, P., Forsyth, V. T., Apperley, D. C., Kennedy, C. J., and Jarvis, M. C. (2011). “Nanostructure of cellulose microfibrils in spruce wood,” *Proceedings of the National Academy of Sciences* 108(47), E1195-E1203. DOI: 10.1073/pnas.1108942108
- Haafiz, M. M., Hassan, A., Zakaria, Z., and Inuwa, I. M. (2014). “Isolation and characterization of cellulose nanowhiskers from oil palm biomass microcrystalline cellulose,” *Carbohydrate Polymers* 103, 119-125. DOI: 10.1016/j.carbpol.2013.11.055
- Hideno, A., Abe, K., and Yano, H. (2014). “Preparation using pectinase and characterization of nanofibers from orange peel waste in juice factories,” *Journal of Food Science* 79(6), N1218-N1224. DOI: 10.1111/1750-3841.12471
- Isogai, A., Saito, T., and Fukuzumi, H. (2011). “TEMPO-oxidized cellulose nanofibers,” *Nanoscale* 3(1), 71-85. DOI: 10.1039/C0NR00583E
- Iwamoto, S., Nakagaito, A. N., and Yano, H. (2007). “Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites,” *Applied Physics A: Materials Science & Processing* 89(2), 461-466. DOI: 10.1007/s00339-007-4175-6
- Jonoobi, M., Khazaeian, A., Tahir, P. M., Azry, S. S., and Oksman, K. (2011). “Characteristics of cellulose nanofibers isolated from rubberwood and empty fruit bunches of oil palm using chemo-mechanical process,” *Cellulose* 18(4), 1085-1095. DOI: 10.1007/s10570-011-9546-7

- Jin, H., Zha, C., and Gu, L. (2007). "Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution," *Carbohydrate Research* 342(6), 851-858. DOI:10.1016/j.carres.2006.12.023
- Khalil, H. A., Davoudpour, Y., Islam, M. N., Mustapha, A., Sudesh, K., Dungani, R., and Jawaid, M. (2014). "Production and modification of nanofibrillated cellulose using various mechanical processes: A review," *Carbohydrate Polymers* 99, 649-665. DOI: 10.1016/j.carbpol.2013.08.069
- Klemm, D., Heublein, B., Fink, H. P., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angewandte Chemie International Edition* 44(22), 3358-3393. DOI: 10.1002/anie.200460587
- Lima, M. M. D. S., and Borsali, R. (2004). "Rodlike cellulose microcrystals: Structure, properties, and applications," *Macromolecular Rapid Communications* 25(7), 771-787. DOI:10.1002/marc.200300268
- Li, W., Wang, R., and Liu, S. (2011). "Nanocrystalline cellulose prepared from softwood kraft pulp via ultrasonic-assisted acid hydrolysis," *BioResources* 6(4), 4271-4281. DOI: 10.15376/biores.6.4.4271-4281
- Li, Y., Zhu, H., Xu, M., Zhuang, Z., Xu, M., and Dai, H. (2014). "High yield preparation method of thermally stable cellulose nanofibers," *BioResources* 9(2), 1986-1997. DOI: 10.15376/biores.9.2.1986-1997
- Malainine, M. E., Mahrouz, M., and Dufresne, A. (2005). "Thermoplastic nanocomposites based on cellulose microfibrils from *Opuntia ficus-indica* parenchyma cell," *Composites Science & Technology* 65(10), 1520-1526. DOI: 10.1016/j.compscitech.2005.01.003
- Man, Z., Muhammad, N., and Sarwono, A. (2011). "Preparation of cellulose nanocrystals using an ionic liquid," *Journal of Polymers and the Environment* 19(3), 726-731. DOI: 10.1007/s10924-011-0323-3
- Metreveli, G., Wågberg, L., Emmoth, E., Belák, S., Strømme, M., and Mihranyan, A. (2014). "A size-exclusion nanocellulose filter paper for virus removal," *Advanced Healthcare Materials* 3(10), 1546-1550. DOI:10.1002/adhm.201300641
- Montanari, S., Roumani, M., Laurent Heux, A., and Vignon, M. R. (2011). "Topochemistry of carboxylated cellulose nanocrystals resulting from tempo-mediated oxidation," *Macromolecules* 38(5), 1665-1671. DOI: 10.1021/ma048396c
- Nickerson, R. F., and Habrle, J. A. (1947). "Cellulose intercrystalline structure," *Industrial & Engineering Chemistry* 39(11), 1507-1512. DOI: 10.1021/ie50455a024
- Nishiyama, Y. (2009). "Structure and properties of the cellulose microfibril," *Journal of Wood Science* 55(4), 241-249. DOI: 10.1007/s10086-009-1029-1
- Nishiyama, Y., Sugiyama, J., Chanzy, H., and Langan, P. (2002). "Crystal structure and hydrogen bonding system in cellulose I(alpha) from synchrotron x-ray and neutron fiber diffraction," *Journal of the American Chemical Society* 124(31), 9074-9082. DOI: 10.1021/ja0257319
- Segal, L. C., Creely, J., Martin, A. E. J., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the x-ray diffractometer," *Textile Research Journal* 29(10), 786-794. DOI: 10.1177/004051755902901003
- Shankar, S., and Rhim, J. W. (2016). "Preparation of nanocellulose from microcrystalline cellulose: The effect on the performance and properties of agar-based composite films," *Carbohydr. Polym.* 135, 18-26. DOI: 10.1016/j.carbpol.2015.08.082

- Spence, K. L., Venditti, R. A., Rojas, O. J., Habibi, Y., and Pawlak, J. J. (2011). "A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods," *Cellulose* 18(4), 1097-1111. DOI: 10.1007/s10570-011-9533-z
- Tang, L. R., Huang, B., Ou, W., Chen, X. R., and Chen, Y. D. (2011). "Manufacture of cellulose nanocrystals by cation exchange resin-catalyzed hydrolysis of cellulose," *Bioresource Technology* 102(23), 10973-10977. DOI: 10.1016/j.biortech.2011.09.070
- Tibolla, H., Pelissari, F. M., and Menegalli, F. C. (2014). "Cellulose nanofibers produced from banana peel by chemical and enzymatic treatment," *LWT-Food Science and Technology* 59(2), 1311-1318. DOI: 10.1016/j.lwt.2014.04.011
- Wang, H., Li, D., Yano, H., and Abe, K. (2014). "Preparation of tough cellulose II nanofibers with high thermal stability from wood," *Cellulose* 21(3), 1505-1515. DOI: 10.1007/s10570-014-0222-6
- Wang, N., Ding, E., and Cheng, R. (2007). "Thermal degradation behaviors of spherical cellulose nanocrystals with sulfate groups," *Polymer* 48(12), 3486-3493. DOI: 10.1016/j.polymer.2007.03.062
- Wang, J., Li, Y., Wang, Z., Li, Y., and Liu, N. (2016). "Influence of pretreatment on properties of cotton fiber in aqueous naoh/urea solution," *Cellulose* 23(3), 1-11. DOI: 10.1007/s10570-016-0938-6
- Wanrosli, W. D., Rohaizu, R., and Ghazali, A. (2011). "Synthesis and characterization of cellulose phosphate from oil palm empty fruit bunches microcrystalline cellulose," *Carbohydrate Polymers* 84(1), 262-267. DOI: 10.1016/j.carbpol.2010.11.032
- Yan, L., and Gao, Z. (2008). "Dissolving of cellulose in PEG/NaOH aqueous solution," *Cellulose* 15(6), 789-796. DOI: 10.1007/s10570-008-9233-5
- Zhang, W., Liang, M., and Lu, C. (2007). "Morphological and structural development of hardwood cellulose during mechanochemical pretreatment in solid state through pan-milling," *Cellulose* 14(5), 447-456. DOI: 10.1007/s10570-007-9135-y
- Zhou, J., Zhang, L., Deng, Q., and Wu, X. (2004). "Synthesis and characterization of cellulose derivatives prepared in NaOH/urea aqueous solutions," *Journal of Polymer Science Part A: Polymer Chemistry* 42(23), 5911-5920. DOI: 10.1002/pola.20431
- Zhu, H., Fang, Z., Preston, C., Li, Y., and Hu, L. (2014). "Transparent paper: Fabrications, properties, and device applications," *Energy & Environmental Science* 7(1), 269-287. DOI: 10.1039/C3EE43024C

Article submitted: April 13, 2017; Peer review completed: June 10, 2017; Revised version received and accepted: June 21, 2017; Published: July 3, 2017.
DOI: 10.15376/biores.12.3.5826-5837