

REGULAR ARTICLE

Cellulose nanowhiskers from sugar palm fibers

Farah Fahma^{1*}, Naruhito Hori², Shinichiro Iwamoto³, Tadahisa Iwata², Akio Takemura^{2*}

¹Department of Agroindustrial Technology, Faculty of Agricultural Engineering and Technology, Bogor Agricultural University, Bogor, Indonesia,

²Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan, ³National Institute of Advanced Industrial Science and Technology (AIST), Hiroshima, Japan

ABSTRACT

In this study, cellulose nanowhiskers from sugar palm fibers were isolated by sulfuric acid hydrolysis. The dimension of neutralized and un-neutralized obtained nanowhiskers was similar of each other. Two films from cellulose nanowhiskers suspension (without and with neutralization) were produced using a vacuum filtration technique. Comparing with native cellulose, the decomposition of nanowhiskers started at lower temperature. Meanwhile after neutralization of its acid sulfate groups the decomposition of nanowhiskers shifted to higher temperature to be close to native cellulose. This work indicated that the neutralization of acid sulfate groups improved the mechanical properties of cellulose nanowhiskers film while morphology, thermal stability, degree of crystallinity and chemical composition of cellulose nanowhiskers obtained could be maintained.

Keywords: Sugar palm fiber; Nanofibers; Nanowhisiker; Sulfate group

INTRODUCTION

Much attention on the development of eco-friendly products has encouraged many researchers to exploit the resources of cellulose, such as woods and agricultural biomass. The cellulose nanofibers which are produced from those resources have generated a great interest as nanometer-sized fillers. This is due to their sustainability, abundant availability, and some related characteristics such as lower density compared to inorganic fillers, no abrasion of the processing equipment, good thermal properties and biodegradability (Sain and Bhatnagar, 2008; Deepa et al., 2011).

Many researchers have studied on the isolation of nano-sized fibers from various agricultural biomasses, such as cassava baggase (Teixeira et al., 2009), soybean stock (Wang and Sain, 2007), rice straw and potato tuber (Abe and Yano, 2009; Zimmermann et al., 2010), banana fibers (Gañán et al., 2004; Cherian et al., 2008), sugarcane baggase (Bhattacharya et al., 2008), wheat straw and soy hulls (Alemdar and Sain, 2008), coconut husk (Rosa et al., 2010; Fahma et al., 2011), oil palm empty-fruit-bunch (Fahma

et al., 2010) and a bio-residue from wood bioethanol production (Oksman et al., 2011). The use a variety of biomass as raw material will lead to increase the supply of cellulose material that can be used for nanocomposite materials.

Sulfuric acid hydrolysis is a well-known chemical method to obtain the stable suspension of cellulose nanowhiskers because the negative sulfate groups are introduced into the outer surface of cellulose during the hydrolysis process. This method significantly decreases the thermal stability of cellulose nanowhiskers. This drawback can be recovered by partly neutralizing the sulfuric acid groups with strong bases such as sodium hydroxide to increase its thermal stability (Wang et al., 2007a; Rosa et al.; 2010). Garcia de Rodriguez et al. (2006), Rosa et al. (2010), and Fahma et al. (2011) prepared cellulose nanowhiskers from coconut husk by 64-65 wt.% sulfuric acid hydrolysis at 45-65°C. They investigated delignification process as pre-treatment hydrolysis and characterized the nanowhiskers. Elazzouzi-Hafraoui et al. (2008) specifically analyzed the shape and size distribution of nanowhiskers obtained by 65 wt.% sulfuric acid hydrolysis from cotton, avicel and tunicate. Meanwhile Beck-Candanedo et al. (2005)

*Corresponding authors:

Farah Fahma, Department of Agroindustrial Technology, Faculty of Agricultural Engineering and Technology, Bogor Agricultural University, Bogor, Indonesia. E-mail: farah_fahma@yahoo.com.

Akio Takemura, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan, E-mail: akiot@mail.ecc.u-tokyo.ac.jp

Received: 22 February 2016;

Revised: 17 May 2016;

Accepted: 19 May 2016;

Published Online: 03 June 2016

examined the effect of reaction time and acid-to-pulp ratio on properties of nanocrystals and suspension prepared by 64 wt.% sulfuric acid hydrolysis from wood. Martinez-Sanz *et al.* (2011) examined the various factors (such as sulfuric acid hydrolysis time, neutralization and dialysis) on the properties of the nanoparticles obtained.

Preparing only-cellulose films have attracted much attention of some researchers. This is because cellulose nano-sized fibers have a high surface area that can form a highly dense hydrogen bonding network. Spence *et al.* (2010) reported that film of microfibrillated celluloses (MFCs) from softwood prepared by high pressure homogenization have $6,670 \pm 650$ MPa of elastic modulus and 105.3 ± 19.4 MPa of tensile strength. Meanwhile, from hardwood MFC film showed $6,310 \pm 630$ MPa of elastic modulus and 91.7 ± 25.2 MPa of tensile strength. Henriksson *et al.* (2008) also reported that the elastic modulus and tensile strength of MFC-based films prepared by a combination of enzymatic and mechanical method from softwood dissolving pulp were found in the range between 10.4 and 13.7 GPa and 129 - 214 MPa, respectively.

The objective of this study is to investigate the effect of acid sulfate group on the morphology and properties of cellulose nanowhiskers from sugar palm fibers. Dictionary – In this study, the cellulose fibers from sugar palm fibers were hydrolyzed by sulfuric acid solution to obtain cellulose nanowhiskers. We neutralized cellulose nanowhiskers obtained with a small amount of sodium hydroxide to obtain neutralized-nanowhiskers. We also prepared cellulose nanowhiskers films by using filtration technique. The morphology and mechanical properties of neutralized-nanowhiskers film was compared with un-neutralized nanowhiskers film. So far, there has been no published study to our knowledge on the isolation of cellulose nanowhiskers from sugar palm fibers. Besides that, from this study, information of mechanical properties of cellulose nanowhiskers films could be obtained.

MATERIALS AND METHODS

Materials

Sugar palm fibers were used for obtaining nanofibers. Sulfuric acid (95%) and other chemicals such as sodium hydroxide, ethanol, benzene, sodium chlorite, acetic acid, and potassium hydroxide were supplied by WAKO Pure Chemical Industries Ltd.

Cellulose nanowhiskers suspension

Cellulose fibers were prepared as described in our previous work (Fahma *et al.*, 2010, 2011). The cellulose fibers (20 g) were hydrolyzed in sulfuric acid solution (64 wt.%)

under strong agitation at 45°C for 90 min. The hydrolysis reaction was stopped by adding cold water. The diluted suspension was washed until the pH of the suspension reached 5 by successive centrifugations at 11,000 rpm for 10 min. Dialysis was carried out for 3 days until the pH became constant. Subsequently, the suspension was sonicated for 20 min to disperse nanowhiskers in water using an ultrasonic homogenizer at 19.5 kHz and 300 W output power (26 mm probe tip diameter, US-300T, Nissei, Japan), then stored in a refrigerator. Neutralized-nanowhiskers as coded as “SPNF-neutralized” were prepared by adding 0.25 M sodium hydroxide (NaOH) solution for several drops of pipette until the suspension was neutrality. In order to separate the salt which might be formed, the suspension was centrifuged again for two times. Un-neutralized nanowhiskers were coded as “SPNF”.

Cellulose nanowhiskers films

Cellulose nanowhiskers films were prepared as described in previous report (Iwamoto *et al.*, 2007). The cellulose nanofiber suspension (124 g) was vacuum filtered using polytetrafluoroethylene membrane (0.1 μ m mesh), producing a thin mat around 60 μ m of thickness. The films were oven-dried at 55°C for 72 h and further dried at 105°C for 2 h.

Characterization atomic force microscopy (AFM)

The morphology of nanowhiskers was observed by using an AFM scanning probe system comprising SPA-300 and SN-3800 units and an SI-AF-01 cantilever (SII Nanotechnology Inc., Japan). AFM images were processed in Spis32 software. In order to prepare a sample, a droplet of diluted nanowhiskers suspension (0.001 wt % of fiber content) was placed onto freshly cleaved mica and dried at room temperature.

Sulfate group content analysis

The sulfate content of nanowhiskers was determined by polyelectrolyte titration. NaCl solution (0.01 M, 5 mL) was mixed with the nanowhiskers suspension (45 g, about 0.4wt.% of solid content). The 0.01 M NaOH solution was added to the suspension with continuous stirring (Wang *et al.*, 2007b) and the change in conductivity was recorded.

X-ray diffraction analysis

In order to make a pellet for X-ray diffraction analysis, 200 mg of the freeze-dried sample was pressed at 5 MPa for 30 s. The crystallinity of the cellulose fiber and its nanowhiskers was determined by wide-angle X-ray diffraction (WAXD) analysis from 5 to 35° (2 θ) using a Rigaku RINT 2000 at 20 kV and 2 mA. The degree of crystallinity was calculated from diffraction profiles as the ratio of the area under the crystalline diffraction peaks to

the total area under the curve (Wang et al., 2007b). The d-spacing and crystallite sizes of cellulose I structures were calculated using the Bragg's equation and full widths at half heights of the diffraction peaks by Scherrer's equation, respectively (Kim et al., 2010).

Bragg's equation:

$$n\lambda = 2d\sin\theta$$

Scherrer's equation:

$$L = \frac{0.9\lambda}{H\cos\theta}$$

where L is the crystallite size perpendicular to the plane; λ is the X-ray wavelength; H is the full-width at half maximum in radians; and θ is the Bragg angle.

Three peaks of X-ray profiles ($1\bar{1}0$, 110 , and 200) were separated by peak fitting using software PeakFit v4.12, even though two peaks ($1\bar{1}0$ and 110) seem overlapping due to low crystallinity.

Mechanical test

Tensile strength and Young's modulus of cellulose nanowhiskers film were measured using Shimadzu EZ Test instrument equipped with a 500 N load cell for sample 10 mm in length, 3 mm in width, and 60 mm in thickness at a crosshead speed of 10 mm/min. Three measurements were carried out to characterize each film.

Thermogravimetric analysis (TGA)

TGA was performed using a Thermo Plus TG 8120 instrument. Thermograms were acquired from room temperature to 500°C using a heating rate of 10 K min⁻¹ under a flow of nitrogen (110 mL min⁻¹).

Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy analyses

In order to prepare a FTIR sample, suspension of nanowhiskers (5 g, 0.4 wt.% of fibers content) was cast in a Petri dish followed by drying overnight at 50°C, then at 70°C for 2 h before analysis (Fahma et al., 2010, 2011). Meanwhile cellulose fiber sample for FTIR analysis was prepared using KBr pellet. FTIR spectra were recorded using a Nicolet MAGNA-IR 860 spectrometer in absorbance mode with resolution 4 cm⁻¹; 64 scans were accumulated for each sample.

Raman spectra were recorded using NXR FT-Raman module (ThermoScientific, USA) and 1000 scans were accumulated for each sample. The pellet sample was prepared as same as preparation for X-ray diffraction analysis.

RESULTS AND DISCUSSION

Morphology of cellulose nanowhiskers and their films

The average thickness of nanowhiskers without and with neutralization was not significantly different, 2.3 ± 0.9 and 2.4 ± 0.8 nm, respectively (Fig. 1). This might be due to a little of NaOH added resulting no change of nanowhiskers morphology. The AFM images confirmed that the nanowhiskers suspensions contained mostly of individual fibrils indicating the treatments of cellulose fibers preparation and the sulfuric acid hydrolysis were effective to obtain nanowhiskers. This agreed with our previous works (Fahma et al., 2010, 2011). The salt of sodium chlorite (NaCl) which might be formed could not be detected in the image of neutralized-nanowhiskers. This means that the centrifugation after adding the NaOH for neutralization was effective to remove the salt. The nanowhiskers film with neutralization showed white film while nanowhiskers film without neutralization showed brown film (Fig. 2). This was due to sulfate group content inside the film. The acid sulfate group content of SPNF sample was 44.80 mmol kg⁻¹, while the content of acid sulfate group of SPNF-neutralized was not detectable. In our previous work, we reported that for 90 min of hydrolysis time (same as with this present study) the sulfate group content of cellulose nanowhiskers from oil palm empty-fruit-bunches (OPEFBs) was 48.85 mmol kg⁻¹ (Fahma et al., 2010). Because those values are very close

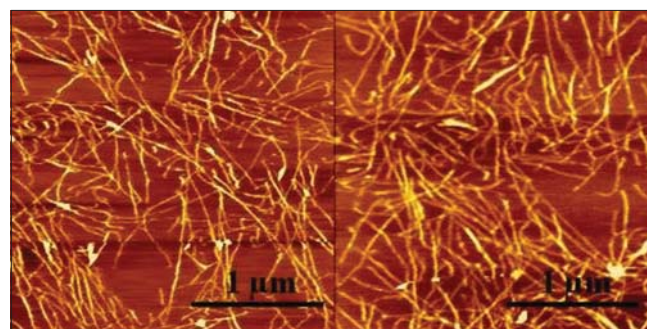


Fig 1. AFM images of un-neutralized (left) and neutralized (right) cellulose nanowhiskers from sugar palm fibers.

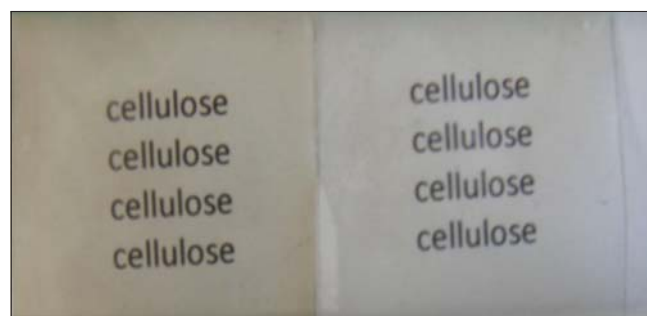


Fig 2. Films made from un-neutralized (left) and neutralized (right) cellulose nanowhiskers from sugar palm fibers.

each other, we suppose that the acid sulfate group content was strongly influenced by acid hydrolysis time.

Crystallinity of cellulose nanowhiskers

The X-ray analyses were used to evaluate the crystalline structure of all samples. Fig. 3 showed that native cellulose fiber, nanowhiskers without and with neutralization had the same typical cellulose I crystal structure. From Fig. 3, it was clearly observed that the X-ray diffraction patterns of nanowhiskers without and with neutralization were similar. This indicated that by adding several drops of NaOH until neutral pH into cellulose nanowhiskers the crystalline structure of cellulose I had been maintained.

The degree of crystallinity and crystallite size of cellulose decreased after sulfuric acid hydrolysis (Table 1). A decrease of degree of crystallinity is probably because the drastic conditions of sulfuric acid hydrolysis cause not only destroyed amorphous regions but also crystalline regions. Meanwhile the phenomena of crystallite size reduction after acid hydrolysis were supposed due to shrinking the crystallite size to be smaller by acid hydrolysis.

Mechanical Properties of cellulose nanowhiskers films

Tensile test was carried out to evaluate the effect of acid sulfate groups on the mechanical properties of the cellulose nanowhiskers obtained. The mean values of the mechanical properties of the nanowhiskers films without and with neutralization were summarized in Table 1.

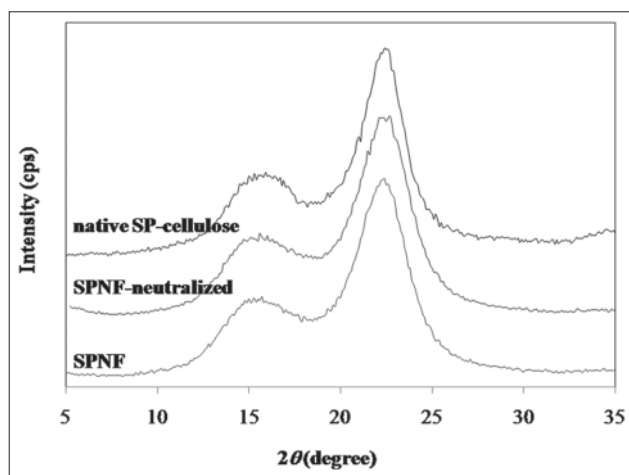


Fig 3. WAXD curves of native cellulose and its nanowhiskers from sugar palm fibers.

The tensile strength and Young's modulus of nanowhiskers film with neutralization were around 98 MPa and 5 GPa, respectively. These values were almost twice larger than that of nanowhiskers film without neutralization. The improvement on the mechanical properties of the films was related to the elimination of the sulfate group content from cellulose nanowhiskers. The charged sulfate groups result in stable suspension of cellulose nanowhiskers due to electrostatic repulsion. The elimination of surface charge leads to the formation of strongly bound nanofibrils, and thus a good interaction between nanofibrils-nanofibrils is obtained.

As comparison the tensile strength and modulus of cellulose nanofibers film from wood, rice straw and potato tuber prepared by mechanical method were around 210 - 230 MPa and 11 GPa, respectively, with the degree of crystallinity around 76 - 80% (Abe and Yano, 2010). The values of their mechanical properties are higher than that of our result (Table 1). This may be due to the difference of the degree of crystallinity caused by different nanofibers-isolation method. In crystalline regions, cellulose chains are tightly packed together in crystallites, which are stabilized by a strong and very complex intra- and inter-molecular hydrogen-bond network. This is the reason why the degree of crystallinity of cellulose nanofibers obtained is one of key factors determining the mechanical properties (Abe and Yano, 2009; Habibi et al., 2010).

Thermal analysis

Thermogravimetric analysis was performed to observe the effect of neutralization on the thermal stability of cellulose nanowhiskers obtained. Fig. 4 showed the TG and DTG curves of native cellulose from sugar palm fibers and its nanowhiskers obtained without and with acid sulfate groups content.

From Fig. 4, SPNF sample with acid sulfate group content 44.80 mmol kg⁻¹ showed that its degradation occurred within a wider temperature range and started to degrade at about 150°C, earlier than the native cellulose and the nanowhiskers with neutralization. The DTG curves showed that the SPNF sample had two main separated pyrolysis process. First process occurred at around 150 - 280°C and the second one occurred at around 300 - 500°C. The first process might be corresponding to the primary pyrolysis of nanocrystals catalyzed by acid hydrolysis and the second one might be relating to the slow charring process of the solid residue which has not been attacked by sulfuric acid (Wang et al., 2007a; Martinez-Sanz et al., 2011). Meanwhile the thermal

Tabel 1: Crystallinity of cellulose nanowhiskers from sugar palm fibers and their mechanical properties films

	Acid sulfate content (mmol kg ⁻¹)	Crystallinity (%)	Crystal size (nm)	Tensile Strength (MPa)	Young's Modulus (GPa)
SP-cellulose	-	57.84	3.12	-	-
SPNF	44.80	54.56	2.57	52.28±1.83	3.67±0.46
SPNF-neutralized	nd	54.97	2.63	98.12±2.40	5.19±1.22

nd: Not detected

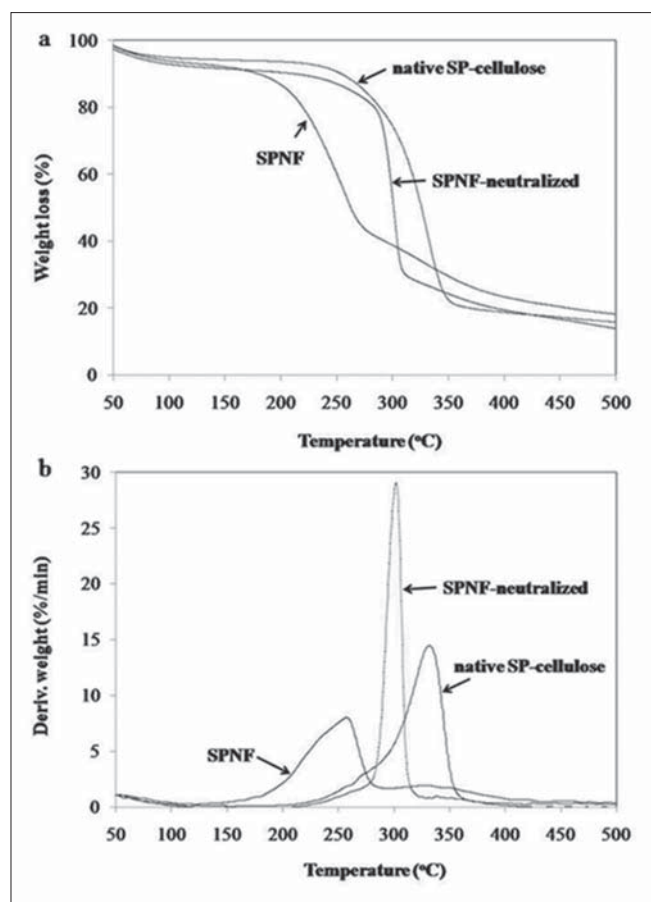


Fig 4. (a and b) TG and DTG curves of native cellulose and its nanowhiskers from sugar palm fibers.

decomposition of the nanowhiskers with neutralization (SPNF-neutralized) shifted to the higher temperature (at about 250°C, almost similar with native cellulose fiber) and occurred within a narrow temperature range. The degradation of SPNF-neutralized sample showed only one pyrolysis process as similar as the native cellulose (Fig. 4). It can be concluded that the acid sulfate groups in cellulose nanowhiskers obtained by sulfuric acid hydrolysis leads to a significant decrease in the thermal stability.

FTIR and Raman spectroscopy analyses

The FTIR and Raman spectroscopy analyses were carried out to observe polymorphic changes of the native cellulose due to sulfuric acid hydrolysis and its nanowhiskers due to neutralization. The FTIR spectra in Fig. 5a exhibited that every band was very similar for cellulose fiber, nanowhiskers without and with neutralization, indicating a close similarity on their chemical composition. All spectra exhibited the OH-stretching at around 3349 cm⁻¹. After sulfuric acid hydrolysis, that peak became narrower indicating hydrogen bonds were broken due to acid hydrolysis. Neutralization of acid sulfate groups did not affected the peak to bring back as like as before hydrolysis. This is evidence that acid sulfate groups occurred only on the surface of cellulose.

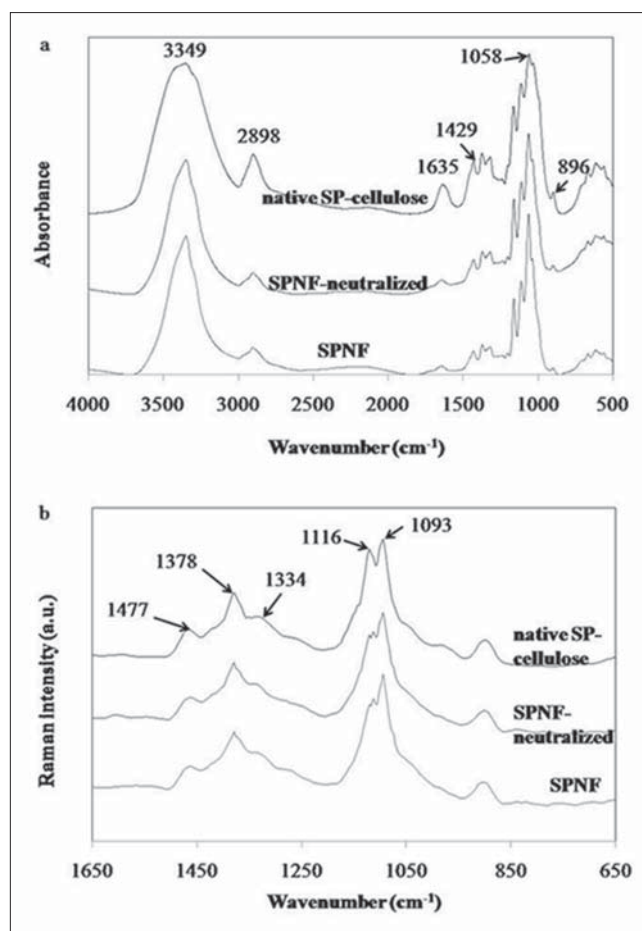


Fig 5. (a and b) FTIR and Raman spectra of native cellulose and its cellulose nanowhiskers from sugar palm fibers.

The peaks at 2898 cm⁻¹ are assigned to the aliphatic saturated C-H stretching vibration in cellulose, hemicellulose and lignin. The peaks in the region 1429 cm⁻¹ are due to various lignin components and C-H deformation of cellulose and lignin. The peaks at 1058 and 896 cm⁻¹ are attributed to the C-O stretching and C-H rocking vibrations of cellulose, respectively (Fahma et al., 2010).

Three main peaks attributed to lignin and hemicelluloses are 1720, 1509, and 1267 cm⁻¹ which confirms C=O stretching of hemicelluloses and lignin, C=C aromatic skeletal vibration of lignin, and C-O stretching of hemicelluloses and lignin, respectively (Fahma et al., 2010). Fig. 5a showed that lignin and hemicelluloses were disappeared effectively as seen by the elimination of vibration at 1720, 1509, and 1267 cm⁻¹.

Fig. 5b showed Raman spectra of un-neutralized and neutralized cellulose nanowhiskers from sugar palm fibers. The bands at 1477, 1378 and 1334 cm⁻¹ are associated with CH₂ deformation vibrations. The 1334 cm⁻¹ can also be due to OH deformation vibrations. The bands observed at 1116 and 1093 cm⁻¹ are the stretching vibrations of the β-1,4-glycosidic ring linkages between the glucose units in

cellulose (Adebajo *et al.*, 2006). Comparing with the spectra of native cellulose, the peaks at 1116 cm^{-1} for SPNF and SPNF-neutralized decreased indicating that indeed some glycosidic ring linkages had already broken due to acid hydrolysis.

CONCLUSION

Cellulose nanowhiskers from OPEFBs were characterized on thermal stability, chemical compounds, and crystallinity using TGA, FTIR, and WAXD, respectively. The thermal stability of nanowhiskers increased due to neutralization with adding several drops of NaOH solution. FTIR spectra confirmed the similarity on the chemical composition of neutralized and un-neutralized cellulose nanowhiskers. Furthermore, WAXD analysis showed that the degree of crystallinity of cellulose decreased after sulfuric acid hydrolysis. Meanwhile, Neutralization did not change the degree of crystallinity of obtained cellulose nanowhiskers. The improvement of tensile strength and Young's modulus of nanowhiskers film due neutralization was related to the elimination of the sulfate group content from cellulose nanowhiskers. For further study on the effect of neutralization on the properties of films, it would be more interested to vary the amount of alkali (NaOH) to the cellulose nanowhisiker suspension.

Authors contributions

All the authors contributed equally to the writing of this paper. They were also involved in the overall work of experiments.

REFERENCES

- Abe, K. and H. Yano. 2009. Comparison of the characteristics of cellulose microfibril aggregates of wood, rice straw and potato tuber. *Cellulose*. 16: 1017-1023.
- Adebajo, M. O., R. L. Frost, J. T. Klopogge and S. Kokot. 2006. Raman spectroscopic investigation of acetylation of raw cotton. *Spectrochim. Acta A*. 64: 448-453.
- Alemdar, A. and M. Sain. 2008. Isolation and characterization of nanofibers from agricultural residues-wheat straw and soy hulls. *Bioresour. Technol.* 99: 1664-1671.
- Beck-Candanedo, S., M. Roman and D. G. Gray. 2005. Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspension. *Biomacromol.* 6: 1048-1054.
- Bhattacharya, D., L. T. Germinario and W. T. Winter. 2008. Isolation, preparation and characterization of cellulose microfibrils obtained from baggase. *Carbohydr. Polym.* 73: 371-377.
- Cherian, B. M., L. A. Pothan, T. Nguyen-Chung, G. Mennig, M. Kottaisamy and S. Thomas. 2008. A novel method for the synthesis of cellulose nanofibril whiskers from banana fibers and characterization. *J. Agric. Food Chem.* 56: 5617-5627.
- Deepa, B., E. Abraham, B. M. Cherian, A. Bismarck, J. J. Blaker, L. A. Pothan, A. L. Leao, S. F. De Souza and M. Kottaisamy. 2011. Structure, morphology and thermal characteristics of banana nano fibers obtained by stem explosion. *Bioresour. Technol.* 102: 1988-1997.
- Elazzouzi-Hafraoui, S., Y. Nisuiyama, J. L. Putaux, L. Heux, F. Dubreuil and C. Rochas. 2008. The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose. *Biomacromol.* 9: 57-65.
- Fahma, F., S. Iwamoto, N. Hori, T. Iwata and A. Takemura. 2010. Isolation, preparation, and characterization of nanofibers from oil palm empty-fruit-bunch (OPEFB). *Cellulose*. 17: 977-985.
- Fahma, F., S. Iwamoto, N. Hori, T. Iwata and A. Takemura. 2011. Effect of pre-acid-hydrolysis treatment on morphology and properties of cellulose nanowhiskers from coconut husk. *Cellulose*. 18: 443-450.
- Gañán, P., J. Cruz, S. Garbizu, A. Arbelaiz and I. Mondragon. 2004. Stem and bunch banana fibers from cultivation wastes: Effect of treatments on physico-chemical behavior. *J. Appl. Polym. Sci.* 94: 1489-1495.
- Garcia de Rodriguez, N. L., W. Thielemans and A. Dufresne. 2006. Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose*. 13: 261-270.
- Habibi, Y., L. A. Lucia, O. J. Rojas. 2010. Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chem. Rev.* 110: 3479-3500.
- Henriksson, M., L. A. Berglund, P. Isaksson, T. Lindstrom and T. Nishino. 2008. Cellulose nanopaper structures of high toughness. *Biomacromol.* 9: 1579-1585.
- Iwamoto, S., A. N. Nakagaito and H. Yano. 2007. Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites. *Appl. Phys. A*. 89: 461-466.
- Kim, U. J., S. H. Eom and M. Wada. 2010. Thermal decomposition of native cellulose: Influence on crystallite size. *Polym. Degrad. Stab.* 95: 778-781.
- Martinez-Sanz, M., A. Lopez-Rubio and J. M. Lagaron. 2011. Optimization of the nanofabrication by acid hydrolysis of bacterial cellulose nanowhiskers. *Carbohydr. Polym.* 85: 228-236.
- Oksman, K., J. A. Etang, A. P. Mathew and M. Jonoobi. 2011. Cellulose nanowhiskers separated from a bio-residue from wood bioethanol production. *Biomass. Bioenergy*. 35: 146-152.
- Rosa, M. F., E. S. Medeiros, J. A. Malmonge, K. S. Gregorski, D. F. Wood, L. H. C. Mattoso, G. Glenn, W. J. Orts and S. H. Imam. 2010. Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydr. Polym.* 81: 83-92.
- Sain, M. and A. Bhatnagar. 2008. Manufacturing process of cellulose nanofibers from renewable feed stocks. US Patent 2008/0146701 A1.
- Spence, K. L., R. A. Venditti, Y. Habibi, O. J. Rojas and J. J. Pawlak. 2010. The effect of chemical composition on microfibrillar cellulose films from wood pilps: Mechanical processing and physical properties. *Bioresour. Technol.* 101: 5961-5968.
- Teixeira, E. M., D. Pasquini, A. A. S. Curvelo, C. E. Corradini, M. N. Belgacem and A. Dufresne. 2009. Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. *Carbohydr. Polym.* 78: 422-431.
- Wang, B. and M. Sain. 2007. Dispersion of soybean stock-based nanofiber in a plastic matrix. *Polym. Int.* 56: 538-546.
- Wang, N., E. Ding and R. Cheng. 2007a. Thermal degradation behaviors of spherical cellulose nanocrystals with sulfate groups. *Polymer*. 48: 3486-3493.
- Wang, B., M. Sain and K. Oksman. 2007b. Study of structural morphology of hemp fiber from the micro to the nanoscale. *Appl. Compos. Mater.* 14: 89-103.
- Zimmermann, T., N. Bordeanu and E. Strub. 2010. Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential. *Carbohydr. Polym.* 79: 1086-1093.