

PROPERTIES OF NANOCELLULOSE
OBTAINED FROM SUGAR PALM (*ARENGA PINNATA*) FIBER BY ACID
HYDROLYSIS IN COMBINATION WITH HIGH-PRESSURE
HOMOGENIZATION

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Nanocellulose was isolated from sugar palm (*Arenga pinnata*) fiber, using a combined treatment of acid hydrolysis and high-pressure homogenization. Sugar palm fibers (SPF) were initially pretreated with an acid solution to dissolve cellulose. Then, the aqueous solution of cellulose fibers (0.2% w/v) was passed through a high-pressure homogenizer at 20 MPa during 15 cycles to provide sugar palm (SP) nanocellulose. The morphology and structure of SP nanocellulose was characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and CP/MAS ¹³C-NMR spectroscopy. The results showed that the acid hydrolysis of SP fiber, combined with high-pressure homogenization, produced nanocellulose with increased crystallinity, but it did not change the chemical structure of cellulose.

Keywords: nanocellulose, sugar palm fiber, physico-chemical treatment, properties

INTRODUCTION

Nanocellulose has received substantial attention in the last decade due to its promising characteristics, such as high active surface area and low cost.^{1,2} With its excellent properties, nanocellulose is applied for various utilization, such as for polymer composites reinforcement,³ drug delivery,⁴ conductive paper,⁵ transparent films⁶ and filter paper for virus removal.⁷

The properties of nanocellulose are highly dependent on the isolation techniques applied and on the raw materials. To obtain nanocellulose, chemical treatment is effective for delignification and hemicellulose solubilization.⁸ Much research effort has been done to isolate nanocellulose. Hydrolysis has been carried out to extract nanocellulose from wood flour,⁹ sugarcane bagasse,¹⁰ sisal fiber,¹¹ and naturally white and colored cotton.¹² Also, physical or mechanical treatment to isolate nanocellulose from wood, rice straw,¹³ potato,¹³ jute,¹⁴ sugarcane bagasse¹⁵ and wood dissolving pulp¹⁶ has been performed.

Moreover, the combination of chemical and mechanical treatment methods has been also investigated for obtaining nanocellulose from such sources as sugar beet pulp,¹⁷ hemp,¹⁸ water hyacinth fiber,¹⁹ kenaf,²⁰ flax,²¹ banana racis,²² balsa tree,²³ barks of *Helicteres isora* plant,²⁴ wheat straw and soybean hull,²⁵ corncorb,²⁶ and pineapple leaf fiber.²⁷

Sugar palm fiber is also considered as a potential source of nanocellulose. Nanocrystalline cellulose from sugar palm fiber was successfully isolated through delignification and mercerization treatments using 60 wt% concentrated sulphuric acid.²⁸ Other nanocrystalline celluloses were obtained from sugar palm fiber by treating it with sodium hypochloride, bleaching with sodium hydroxide and hydrolyzing with acid. The obtained nanocrystalline cellulose was further applied for manufacturing bionanocomposites.²⁹ Moreover, nanofibrillated cellulose of sugar palm was obtained by several chemical pretreatment

steps, such as pulping, bleaching, mercerization, finally followed by high-pressurized homogenization.³⁰

In contrast to previous works, this study aimed to obtain nanocellulose from sugar palm fiber by simple acid hydrolysis, directly combined with high-pressure homogenization. The structural and physical-chemical properties of the nanocellulose were evaluated by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and CP/MAS ¹³C-NMR spectroscopy.

EXPERIMENTAL

Materials

SPF was obtained from a private plantation in Ciburial, Dago Pakar, Bandung, West Java. The raw sugar palm fibers were cut to 2-3 cm length, washed thoroughly with running water to remove dirt, and air-dried. The fibers were ground to pass a 100 mesh sieve.

Treatment of cellulose fibers

The dried SP powder was extracted with toluene-ethanol (2:1, v/v) in a Soxhlet apparatus to remove the extractives (TAPPI standard T 204 cm-97), then filtered, washed with ethanol and oven dried (50 °C for 24 h).

Nanocellulose production

Cellulose fibers were hydrolyzed with a 60 wt% sulphuric acid (H₂SO₄) solution, at 45 °C, for 30 min under continuous agitation. Hydrolysis was quenched by adding water, and then centrifuging. The resulted residue was suspended in water, followed by centrifugation. The process was repeated until constant pH was reached. A 0.2% w/w suspension of cellulose was homogenized using a laboratory disintegrator (Phycotron, Japan), with a rotational speed of 1550 rpm for 30 seconds. The disintegrated cellulose was then homogenized using a high-pressure homogenizer (Sugino, HJP 25001) at 20 MPA for 15 cycles. The resulted nanocellulose was kept at room temperature.

Characterization

Morphology observation

The morphology of SP cellulose after acid hydrolysis treatment was observed with a Miniscope1235, operated at accelerating voltage of 15 kV. SP nanocellulose was also observed by a JEOL JEM 1200EX transmission electron microscope, operated at accelerating voltage of 80 kV.

Particle size measurement

The nanocellulose suspension of 5% (w/v) was diluted in water at a ratio of 1:50 and ultrasonicated for 30 min. The particle size was then measured using a

particle size analyzer (Photal Otsuka Electronics ELS-Z).

X-ray diffraction (XRD) analysis

The crystalline part of the samples was determined by XRD measurement on an XR diffractometer, with Ni-filtered CuK α radiation at 45 kV and 40 mA. Samples were scanned at 2 θ ranges varying from 5 to 40° at a speed of 3 °/min.

Fourier transform infrared (FTIR) analysis

Suspensions of nanocellulose were casted on Petri dishes, then oven-dried at 50 °C, for 2 h. Nanocellulose was prepared using the KBr pellet method. FTIR spectra were recorded using a Thermo Scientific Nicolet 155 FTIR spectrometer.

Solid-state CP/MAS ¹³C-NMR

Solid-state ¹³C-NMR spectra, with cross polarization/magic angle spinning (CP/MAS), were recorded on a 600 MHz NMR spectrometer (150.95 MHz for ¹³C, Advance III, Bruker BioSpin GmbH, Rheinstetten, Germany) at room temperature.

RESULTS AND DISCUSSION

Morphology evaluation

Figure 1 shows the microscopic image of SP cellulose, whereas Figure 2 shows the TEM image of SP nanocellulose. Figure 1 shows long and thick fibers, with the diameter ranging around 2-10 μ m, while the longest fiber was up to, or even more than, 200 μ m. Meanwhile, the effect of high-pressure homogenization after acid hydrolysis of SP cellulose is shown in Figure 2. From the TEM image, it is clearly visible that the morphological structure of the SP cellulose changed drastically after the treatment. Long and thin fiber, either single or in bundles, can be clearly seen. Although some of the fibers are aggregated, individual fibers had the diameter in the range of 50-100 nm. The existence of fiber bundles revealed by TEM is probably due to the incomplete removal of hemicellulose during the acid hydrolysis treatment, as also indicated by a previous study.²² However, current results suggest that the sugar palm fiber could be altered to its nano-dimension by the combination of acid hydrolysis and high-pressure homogenization.

Particle size analysis

The effect of high-pressure homogenization after acid hydrolysis on the particle size of SP fiber is shown in Figure 3. It shows that the particle size of SP cellulose obtained by hydrolysis treatment is in the range of 1000-4500 nm (Fig. 3A),

whereas the particle size of SP nanocellulose (Fig. 3B) is in the range of 45-92 nm. This result is in agreement with the findings regarding microcrystalline cellulose derived from Norway spruce (*Picea abies*) by sulfuric acid hydrolysis, followed by ultrasonic treatment,³¹ whose size

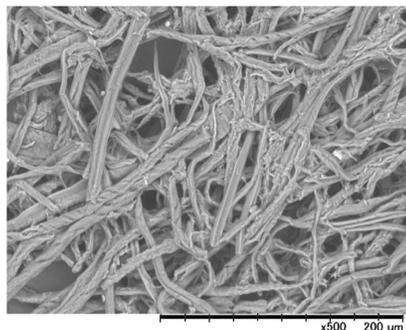


Figure 1: Microscopic image of SP cellulose

was around 5-80 nm. The results of the present study also show similarity with those achieved by other authors with regard to nanocellulose from sisal fiber, with a size of 30.9 nm,³² and from wheat straw soy hulls, with a size of 10-80 nm.³³

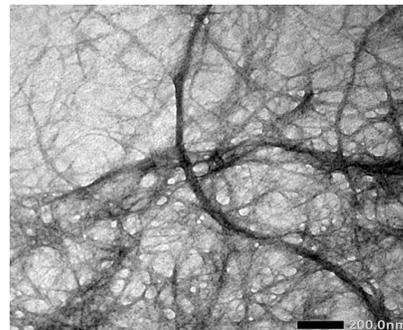


Figure 2: TEM image of SP nanocellulose

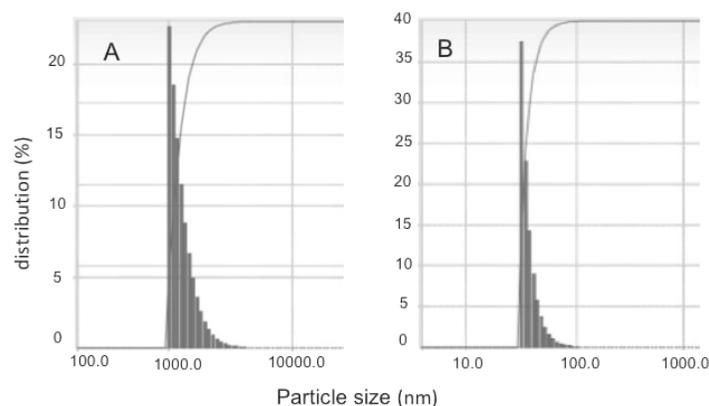


Figure 3: Particle size of SP cellulose (A) and SP nanocellulose (B)

Sugar palm fiber was also used in a previous study to obtain crystalline nanocellulose with a much lower size, of 3-18.19 nm. The significant difference in the size of nanocellulose is probably explained by the different pretreatment, as the holocellulose was first converted to α -cellulose, as well as by the higher pressure applied, of 50 MPa.³⁰

X-ray diffraction (XRD) analysis

X-ray diffraction spectra of SP cellulose are shown in Figure 4. The figure clearly reveals that a broad peak arises at 22° for SP cellulose (A), indicating that the crystalline region represents the main structure. The subsequent treatment of

SP cellulose by high-pressure homogenization allowed the formation of cellulose I, since the doublet intensity in the main peak was not found.^{31,32} The diffraction peak at 22° became sharper (B), revealing a rise in crystallinity. Intensive homogenization possibly realigned the cellulose structure and allowed the amorphous region of cellulose to split off the glycosidic bonds, ultimately liberating individual crystallites. The increase in the crystallite size was due to the increasing free motion after acid hydrolytic cleavage.³³ Similar results have been achieved earlier for cellulose whiskers extracted from mulberry.³⁴

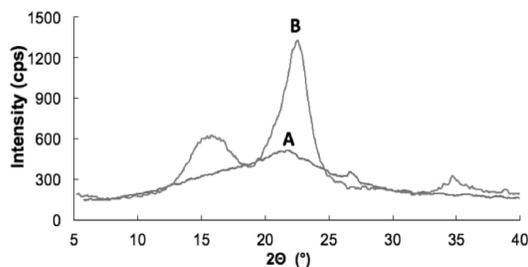


Figure 4: X-ray diffraction pattern of SP cellulose (A) and SP nanocellulose (B)

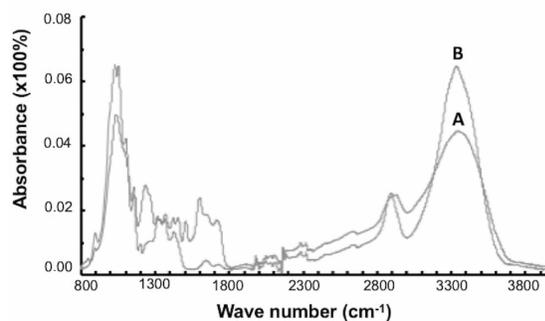
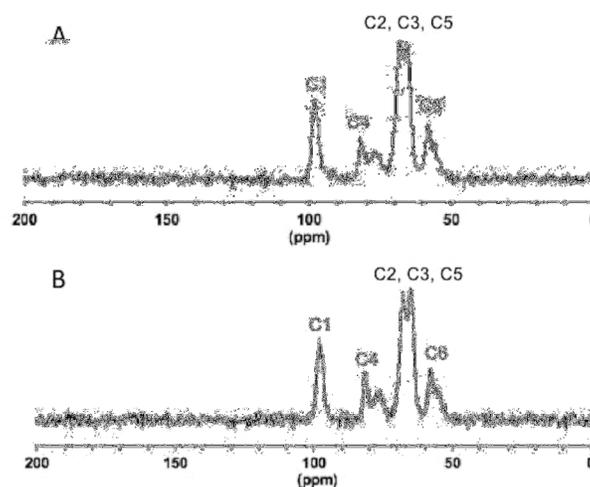


Figure 5: FTIR spectra of SP cellulose (A) and SP nanocellulose (B)

Figure 6: CP/MAS ^{13}C -NMR of SP cellulose (A) and SP nanocellulose (B)

FTIR analysis

FTIR is a suitable technique for evaluating the chemical structure and its evolution as a result of any kind of chemical or physical treatments. FTIR spectra of SP cellulose are presented in Figure 5. The slight increase of the absorbance at 898 cm^{-1} is attributed to the typical structure of cellulose.³⁴ The strong absorbance at 1040 cm^{-1} corresponds to the stretching vibration of C–H in cellulose,³³ whereas the band at 1230 cm^{-1} is related to the vibration of COH bending at C6.³⁵ The prominent peaks at 2890 and 3360 are attributed to C–H symmetrical stretching and OH stretching, respectively. The peak observed at 3360 cm^{-1} is associated with the stretching vibration of OH in cellulose.³⁴ From the analysis of the spectra, it may be concluded that high-pressure homogenization changed the intensity of the prominent absorption peaks, but it did not alter the cellulose structure.

Solid-state ^{13}C -NMR

Solid-state CP/MAS ^{13}C -NMR evaluation is a valuable method to investigate the morphology of cellulose. The ^{13}C -NMR spectra of SP cellulose and SP nanocellulose are presented in Figure 6 A and B, respectively. The peak correlated with C2, C3 and C5 appears at 60–72 ppm, while the chemical shift for C6 is at 58 ppm. It was observed that C4, attributed to the crystalline region, became sharper after the treatment by homogenization, thus demonstrating increasing crystallinity. This result is in accordance with the findings of the XRD analysis. Moreover, the appearance of a thin shoulder at the C6 peak is defined as belonging to the amorphous region and the disordered component of cellulose. This result is similar with those reported in a previous work, in which birch pulp, cotton linter and *Cladophora sp.* were used.³⁶ From SP nanocellulose, it was noticed that the peak became sharper and the

shoulder reduced faintly, suggesting the occurrence of cellulose degradation. This finding is similar to that reported by other authors regarding cellulose microfibers obtained from bagasse by the hydrolysis method.³⁷

CONCLUSION

Sugar palm fiber was treated by acid hydrolysis, followed by high-pressure homogenization, to obtain cellulose and nanocellulose, respectively. Based on the characterization, it was concluded that the acid hydrolysis of SP fiber, combined with high-pressure homogenization, changed the dimension of cellulose, to produce nanocellulose with increased crystallinity, but it did not alter the chemical structure of cellulose.

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