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Effects of Different Extraction Solvents on the Extractive Removal and Properties of Oil Palm Empty-Fruit Bunch Cellulosic Nanofibers

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Abstract

In this study, the effect of different extraction solvents on the isolation and properties of cellulosic nanofibers (CNFs) were investigated. The unextracted and different solvent-extracted CNFs formed horn-like features and irregularly aggregated nanofibers after oven drying. Scanning electron microscopy at 10000× magnification revealed the smooth external surfaces of all extracted CNFs; this finding is attributed to the limited deposition of amorphous lignocellulosic components on the fibers. All resultant CNF solutions revealed aggregation, with a particle size distribution and zeta average of 21.39–513.00 nm and 162.26–342.13 nm, respectively. Extraction with different solvents and chemical treatment yielded CNF solutions with good transparency. Increases in crystallinity indices were generated by extractive removal and enhanced the delignification and bleaching processes. The atomic crystal size of untreated and different solvent-treated CNFs varied with the type of native cellulose. A dramatic decrease in organic (i.e., C, N, and O) and inorganic (i.e., Na, K, and Si) elements was observed following extractive removal and cellulose purification.

Keywords: empty-fruit bunch fibers, extractives removal, solvent extraction, cellulose nanofibers

Introduction

Oil palm empty-fruit bunch (OPEFB) is an abundant biopolymer characterized with abundant resources, renewability, and biodegradability. This biopolymer consists of spikelets (70%–80%) and stalks (20%–30%). OPEFB comprises several chemical components, including 62.64% hollocellulose, 21.64% lignin, and 1.29% extractives. The biopolymer shows great potential use as a source of nanofibers, which may be used as reinforcing agents in nanocomposites.

Several types of nanostructured fibers, such as lignocellulosic nanofibers, nanofibrillated cellulose, cellulosic nanofibers (CNFs), cellulosic nanocrystals, microcrystalline cellulose, and bacterial nanocellulose, could be derived from lignocellulosic sources. CNFs are very common nanocelluloses isolated via chemical treatment-assisted mechanical disintegration. The chemicals utilized most often for isolation include sodium hydroxide, ammonium sulfite, aqueous ammonia, acetic acid, hydrogen peroxide, oxygen, potassium hydroxide, calcium hydroxide, nitrogen oxides, and ozone [1, 2]. These chemicals promote delignification and bleaching to remove amorphous materials (e.g., lignin and

hemicellulose) encrusted in the cellulose and, in some cases, to prevent crystalline structural damage.

Besides chemical treatment, retting and extraction of fresh or dry OPEFB fibers could be performed to remove impurities, such as sand, soil, stone, resin, waxes, and oil. Retting, a controlled degradation process, is used to produce homogenous and clean fibers and allows the fibers to be separated from their core [3]. Water, dew, and enzyme retting are conducted by submerging the fibers in water for 3–14 days [2, 4]. Immersion of wet or dry fibers in water could promote the removal of gummy substances surrounding these fibers via the action of microorganisms [5].

Extractives are chemical impurities found in lignocellulosic sources; these substances usually comprise resin, waxes, and oil residues. The presence of extractives can inhibit the pulping process, as well as acetic acid and levoglucosan production [6, 7]. Water and organic solvents, such as ethanol, benzene, acetone, toluene, ether, and hexane, can be employed for extractive removal. Hot-water can recover condensed tannins and water-soluble low-molecular weight carbohydrates [8] and remove hemicellulose [9, 10]. Alcohol is used for wax determination [11], pectic

extraction [12], and phenolic-compound extraction [13], while acetone is useful for oil and phenolic extraction [14, 15]. These solvents may be combined for extractive removal and isolation. For instance, the combinations of ethanol/acetone [16, 17], ethanol/toluene [18], ethanol/benzene [19, 20], and ethanol/chloroform [21], usually at a ratio of 1:2, have been used for extractive removal and isolation. CNFs can be obtained via a number of mechanical disintegration methods, including ultrasonication, homogenization, grinding, and milling, after extractive removal and cellulose purification.

The research described above generally indicates that extractive removal with different solvents is highly beneficial for extracting nanocellulose from cellulose. To date, however, studies on the utilization and influences of different solvents on CNFs have not been reported. In the present work, changes in the morphology, nanostructure, elemental components, and cellulosic crystallinity of CNFs extracted with different solvents were analyzed via scanning electron microscopy (SEM), particle size analysis (PSA), energy-dispersive X-ray spectroscopy (EDX), UV-Vis spectroscopy, and X-ray diffractometry (XRD).

Materials and Methods

Materials. OPEFB fibers were obtained from PT Perkebunan Kelapa Sawit VIII, Bogor, West Java, Indonesia. The chemicals used included 99.9% ethanol 99.5% benzene, 30% hydrogen peroxide, 98% formic acid, and sodium hydroxide pellets. These reagents were purchased from an Indonesian chemical shop, which were supplied from Merck KgaA, 64271 Darmstadt, Germany.

Extractive removal. The OPEFB fibers were shredded with a sharp machete to form individual, short vascular bundles. The bundles were wet-retted with the assistance of a detergent and naturally dried for 7 days under sunlight. Wet retting removes sand, stones, soils, waxes, and oils attached to the external surfaces of the fibers. The fibers were then dry-disk milled for 27 min at 10 min intervals at room temperature to obtain a 200-mesh pulverized fiber sample; the fibers in this sample are referred to as microfibrils.

The remnants of wax, oil, low-molecular weight carbohydrates, and other extractives in the microfibrils were pretreated by hot-water, ethanol, and ethanol/benzene extraction. An untreated microfibril sample was prepared for comparison. Extraction was conducted in a Soxhlet extractor equipped with a 500 mL Schott Soxhlet apparatus set (Duran Group GmbH, Germany) with (300 mL) or ethanol/benzene (100 mL: 200 mL) solution. Extraction was carried out by precisely weighing 20 g of air-dried OPEFB microfibrils and then wrapping the fibers around a thimble. Each thimble was

placed inside the extractor containing 300 mL of each solvent. Extraction was conducted for 8 h at a refluxing rate of 8 cycles per hour. Hot-water extraction was performed by immersing 20 g of air-dried OPEFB microfibrils in 300 mL of distilled water. Extraction was performed for 8 h at 100 °C in a water bath (WNB Memmert, Germany). Non-extracted OPEFB microfibrils were prepared as a control.

Cellulose purification. Cellulose purification was conducted according to the methods of Jahan *et al.* [22] and Nazir *et al.* [23]. In brief, approximately 2 g of extracted and unextracted OPEFB microfibrils were delignified with a mixture of 100 mL of 5% sodium hydroxide and 100 mL of 5% hydrogen peroxide. The mixtures were autoclaved (ES-315; Tomy Kogyo Co. Ltd., Japan) at 121 °C under a pressure of 1.5 bar for 1 h for autohydrolysis. Turbid microfibrils were flushed several times with deionized water to obtain clean microfibrils. The clean microfibrils of each sample were immersed in a mixture of 10% hydrogen peroxide and 20% formic acid at a ratio of 1:1 and then heated in a bath (WSB-30, South Korea) at 85 °C for 2 h with shaking at 75 rpm. The turbid microfibril suspensions were rinsed several times with deionized water. The OPEFB microfibrils were re-immersed in a mixture of 5% hydrogen peroxide and 5% sodium hydroxide and then electrically heated in a shaking waterbath at 60 °C and 90 rpm for 90 min. Purified cellulose was finally obtained by washing with deionized water.

Nanocellulose production. Clean cellulose microfibrils (1wt%) were centrifugated (Cole-Parmer 17250-10 fixed-speed centrifuge, USA) for 15 min at 3400 rpm to obtain CNFs. The centrifugated microfibrils was ultrasonicated (ultrasonic processor; Cole-Parmer Instrument, USA) for 25 min in an ice-water bath an amplitude of 40%, power of 130 W, and frequency of 20 kHz. Oven-dried CNFs were obtained by drying in a vacuum oven (Mettler SFE 600 Heißluftsterilisator, Germany). The supernate and oven-dried CNFs were then characterized using the designated instruments.

Characterization. The morphological, physical, and chemical properties of the CNFs were analyzed by SEM, PSA, UV-Vis spectroscopy, XRD, and EDX. The external surface of all oven-dried CNFs was examined by SEM (JEOL JSM6510LV, Japan) at 10 kV after coating with gold by using an autofine coater (JEOL JFC 1600). PSA (VASCO Flex™, France) was conducted to investigate the distribution of the nanosized fibers. The instrument was installed with NanoQ software, and three methods (i.e., cumulant method, statistical method, and Pade-Laplace method) were employed for PSA testing but only cumulant method was harnessed for further analysis. Testing was conducted at pH 7.0 and 34 °C with a laser power of 100%. The optical properties of the CNFs were

identified by UV-Vis spectrophotometry (USB4000 Miniature Fiber Optic Spectrometer, Ocean Optics Inc., USA) over the wavelength range of 200–850 nm. An XRD instrument (MAXima X XRD-7000; Shimadzu, Japan) was used to probe the crystallinity indices (CrIs) and atomic crystal sizes (ACS) of the CNFs; analysis was conducted at 2°/min within a diffraction pattern of $2\theta = 10^\circ$ to 40° . The CrIs and ACSs of the CNFs were determined via the following formulas:

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

$$\tau = K \lambda / \beta \cos \theta \quad (2)$$

where I_{002} is the crystalline cellulose intensity ($2\theta = 22.5^\circ$), I_{am} is the amorphous cellulose intensity ($2\theta = 18^\circ$), τ is the atomic crystal size (nm), K is the medium form factor, which depends on the crystal shape (0.94), λ is the X-ray radiation wavelength of the incident beam (1.5406 \AA), β is the full width at half maximum of the 002 reflection in radians, and θ is the peak position of the diffraction angle in radians. An EDX instrument (JEOL EDS, Tokyo, Japan) equipped with a beryllium-drifted silicon detector was used to investigate changes in the elemental composition of the CNFs after extraction with different solvents, and the EDX analysis was conducted using a ZAF method standardless quantitative analysis.

Results and Discussion

Morphological properties. The external surface of oven-dried CNFs is shown in Figure 1. Extractive removal led to noticeable changes in the appearance of the external surfaces of the CNFs compared with that of the control. Control sample had more unsmooth external surfaces and the fibers were bundled into sheets. Delignification and bleaching also contributed to the changes in the external surfaces of the oven-dried CNFs. Oven-dried CNFs demonstrated irreversible self-assembly to form agglomerates or aggregates, as observed by SEM at magnifications of $500\times$ (Figure 1a–d) and $10000\times$ (Figure 1e–h). This phenomenon is referred to as hornification and occurs during oven- or freeze-drying. Hornification can enhance the hydrophobicity of CNFs via the evaporation of free water; bound water evaporates at temperatures above 100°C . Both free and bound water deposited in CNFs can play a role as a plasticizing agent for hornified nanocellulose, which have a greater affinity to hydroxyl groups. The tendency of CNFs to agglomerate is

magnified by decreases in particle size [24], which induces the exposure of reactive hydroxyl groups ($-\text{OH}$ groups), and van der Waals forces. Besides crystalline regions, amorphous regions in the CNFs also contribute to hornification via the formation of hydrogen bonds among the fibers. Agglomeration could bring about the deterioration of the mechanical properties of nanocomposites [24, 25].

Removal of wax, oil, resin, and low-weight molecular carbohydrates (e.g., hemicellulose and pectin) could lead to CNFs with smooth, irregular, and even external surfaces (Figure 1e–1h). After extractive removal and cellulose purification, the amounts of hemicellulose, lignin, and extractives encrusted on the external surfaces of the extracted CNFs remarkably decreased compared with those on the unextracted fibers. Unextracted CNFs feature large amounts of cementing agents, such as hemicellulose, a low-molecular weight carbohydrate, lignin, and extractives, in their fibers, resulting in folding and uneven and rough external surfaces. Hot-water, ethanol, and ethanol/benzene extraction could be utilized as a solvent pretreatment for cellulose purification; extraction could remove some inhibiting agents, such as low-molecular weight carbohydrates, resin, waxes, and oil residue. The removal of these extractives is similar to that observed in previous studies [9, 10, 13, 20, 23].

Particle size distribution. Table 1 and Figure 2 show the PSA results of CNFs extracted with different solvents. The results of the cumulant method indicated that the particle size distribution ranges of the CNFs were as follows: 21.39–85.14 nm (no extraction), 112.23–513.00 nm (hot-water extraction), 141.29–234.49 nm (ethanol extraction), and 67.63–489.91 nm (ethanol/benzene extraction). TEM analysis (data not shown) supported the aforementioned findings and revealed that the CNFs measured less than 100 nm in size. However, TEM also revealed CNF aggregation, which creates microsized or microstructured CNFs. In contrast to the results of TEM, the data obtained by PSA revealed a remarkable difference in nanomaterial size, especially in terms of particle size distribution by number or numbers of particles counted of each size (Figure 2a–2d). Differences between the PSA or dynamic light scattering measurements and TEM findings may be attributed to the function and means of testing. PSA is functioned to investigate hydrodynamic diameter of particles in suspension whereas TEM is harnessed to analyse particle boundaries (shape, size, and size distribution).

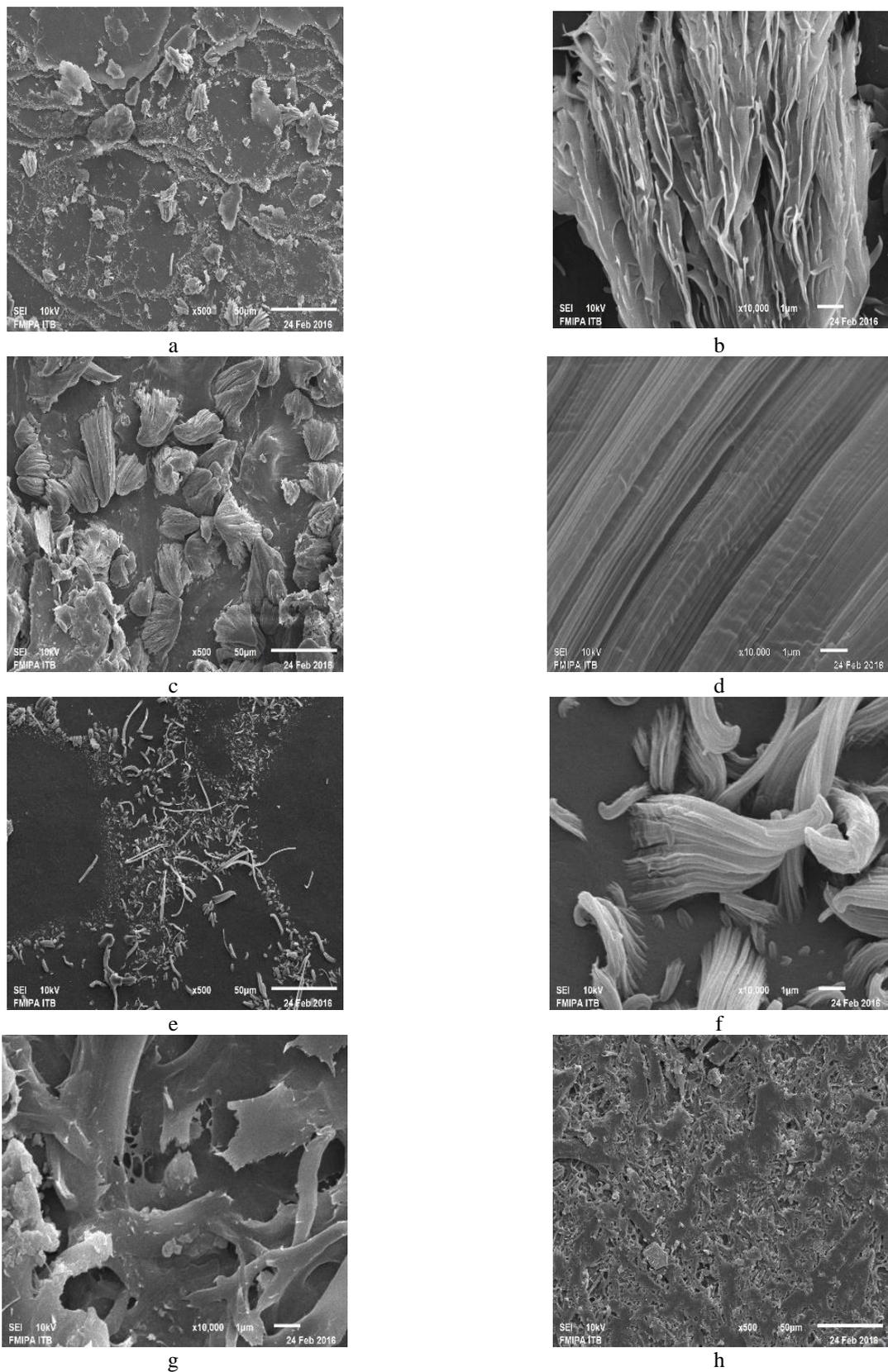
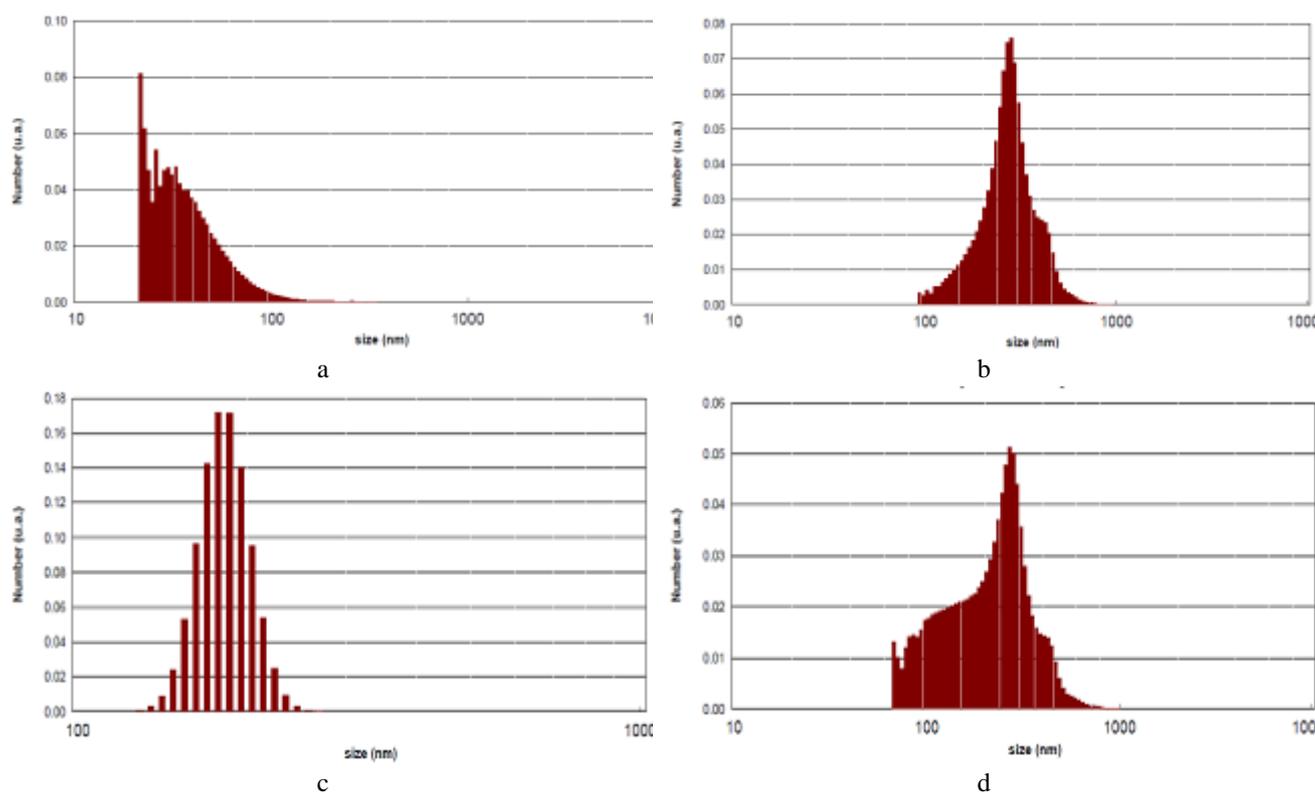


Figure 1. Micrographs (Different SEM Magnifications) of the External Surfaces of CNFs Extracted with Different Solvents: (a and e) No Extraction, (b and f) Hot-water Extraction, (c and g) Ethanol Extraction, and (d and h) Ethanol/Benzene Extraction

Table1. Particle Size Distribution of CNFs Extracted with Different Solvents

Solvent Extraction Pretreatment	Particle Size by Number (nm)	Z Average (nm)	D Mean Intensity (nm)	D Mean Volume (nm)	D Mean Number (nm)	PDI
No extraction	21.39–85.14	162.26	210.90	197.85	39.22	0.39
Hot-water extraction	112.23–513.00	342.13	368.48	389.00	562.49	0.13
Ethanol extraction	141.29–234.49	185.66	186.59	189.20	183.08	0.01
Ethanol/benzene extraction	67.63–489.91	321.80	362.41	396.15	227.98	0.20

**Figure 2. Particle Size Analysis of CNFs Extracted with Different Solvents: (a) No Extraction, (b) Hot-water Extraction, (c) Ethanol Extraction, and (d) Ethanol/benzene Extraction**

The above data reveal that no extraction and solvent extraction can promote CNF isolation; in particular, solvent extraction enhances extractive removal, which is beneficial to the isolation process. However, CNFs extracted with different solvents generally showed higher particle size distribution compared with those that had not been extracted. These findings may be attributed to several reasons: 1) Less deposited amorphous part in CNFs which still had reactive hydroxyl groups had greater affinity with other hydroxyl groups of amorphous CNFs domain, thereby allowing the CNFs to create aggregates due to strong hydrogen bonding among amorphous domain of individual CNFs, and 2) Extractive removal assists in delignification and bleaching by inducing the exposure of higher surface charges in the amorphous regions of

cellulose/CNFs, resulting in strong electrostatic repulsion, which aggregates the nanofibers.

The use of ethanol and ethanol/benzene is also beneficial for solvent exchange that can hamper aggregations and create good dispersion of CNFs, while CNFs are used for film nanocomposite production. These solvents have low hydrophilicity and are able to alter a strong hydrophilic nature of CNFs to acquire less hydrophobic properties via replacing reactive functional groups or charges in CNFs surfaces with polar and non-polar organic solvents. Besides solvent exchange, mechanical disintegration, such as by ultrasonication and homogenization, and surfactants, such as fatty acids, may also be utilized to prevent aggregation and promote surface modification, respectively [26–28].

Optical properties. The UV and visible light properties of the CNFs are tabulated in Table 2. In the UV light wavelength of 183 nm, the transmittance of the CNFs extracted with hot-water, ethanol, and ethanol/benzene noticeably decreased compared with that of the control. In the visible wavelength range of 400–800 nm, the unextracted and hot-water-extracted CNFs showed the highest opacity among the CNF samples (Figure 3). The transmittance values of the unextracted and hot-water-, ethanol-, and ethanol/benzene-extracted CNFs at 600 nm were 0.78%, 19.87%, 59.66%, and 92.02%, respectively. The high opacity of unextracted CNFs is due to the presence of extractives, which could inhibit delignification and bleaching. Good transparency was obtained when the CNFs were extracted with solvents. These CNFs also exhibited good dispersion and homogeneity in distilled water without aggregation, inducing much visible light scattering and absorption from CNFs' inter-nanoparticles. These findings reveal that nanosized structures may also be responsible for the high transparency and low opacity of CNFs. The presence of lignin, extractives, and aggregated CNFs can play a role as a UV blocking agent, leading to the low transparency of CNFs suspension.

The contents of remnant extractives influenced the transparency of hot-water-extracted CNFs. The extractive remnants of CNFs extracted with hot-water could

remove hemicellulose, pectin, and condensed tannins, whereas non-polar extractive compounds (resin, turpentine, fatty acid, and so forth) were still extant. CNFs treated by ethanol and ethanol/benzene extraction were translucent and well dispersed (i.e., no flocs) in deionized water, thereby demonstrating low light scattering. The particle size and size distribution of the fibers could control their transparency in a suspension [29]. From the aforementioned explanation and Table 2, CNFs pretreated with ethanol and ethanol/benzene had low UV transmission and higher transmittance in visible light so that it will be potential as a reinforcing agent for food packaging.

Crystallinity and cellulose polymorphs. The XRD patterns shown in Figure 4 reveal that the CrIs of unextracted and hot-water-, ethanol-, and ethanol/benzene-extracted CNFs were 57.18%, 47.27%, 63.57%, and 69.52%, respectively. CNFs extracted with ethanol and ethanol/benzene showed the highest CrIs because these samples were subjected to three consecutive chemical treatments, namely, extractive removal, delignification, and bleaching. These can be indicated with the sharp and narrow peaks with higher peak intensity over hot-water and non-extraction pretreated CNFs. Extractive removal could help prepare the CNFs for further isolation by delignification and bleaching.

Table 2. UV and Visible Light Wavelengths of the CNFs

Solvent Extraction Pretreatment	183 nm	500 nm	600 nm	700 nm	800 nm
No extraction	89.39	0.57	0.78	1.27	2.23
Hot-water extraction	39.83	15.24	19.87	23.90	27.48
Ethanol extraction	18.96	53.03	59.66	65.20	69.97
Ethanol/benzene extraction	12.84	89.42	92.02	94.59	97.49

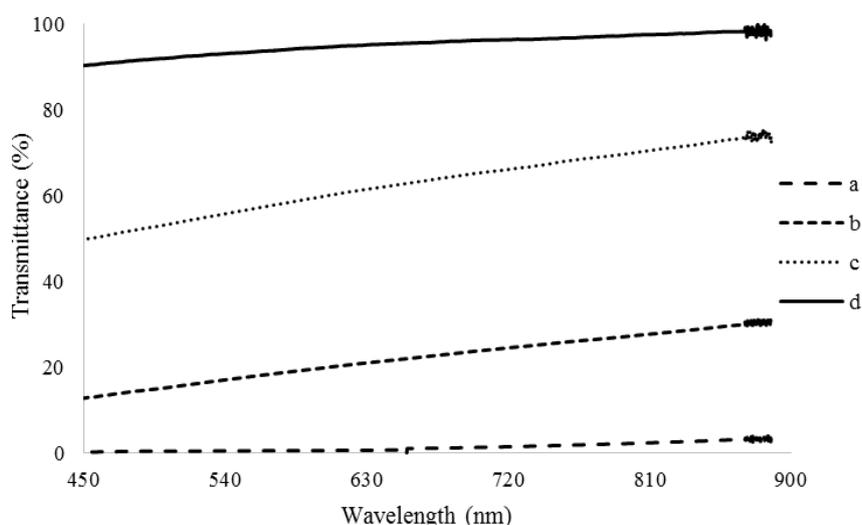


Figure 3. Visible Light Analysis of CNFs at Wavelengths of 500, 600, 700, and 800 nm: (a) No Extraction, (b) Hot-water Extraction, (c) Ethanol Extraction, and (d) Ethanol/benzene Extraction

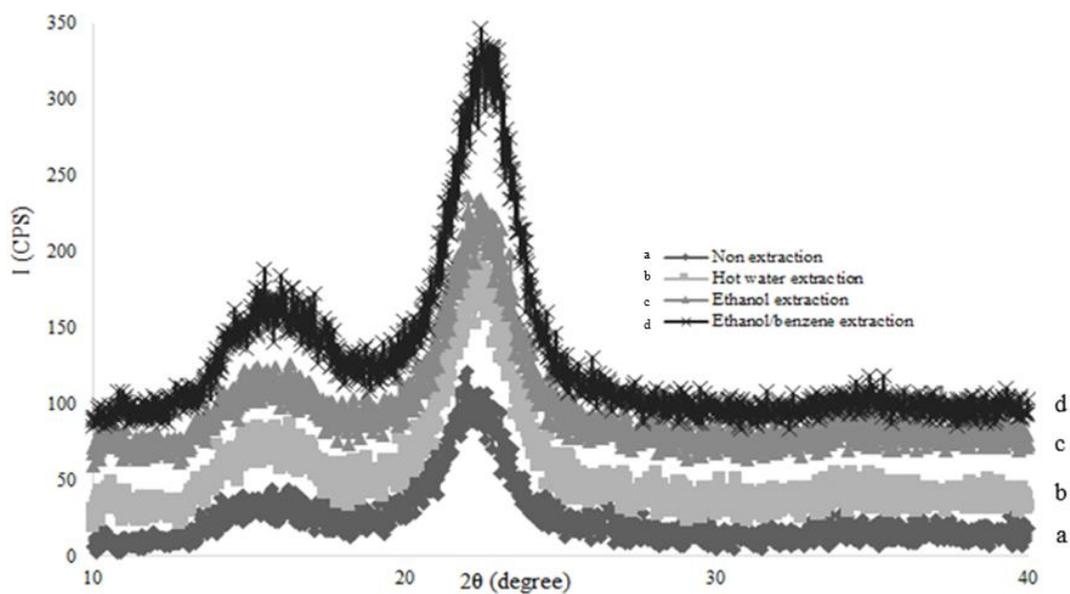


Figure 4. X-ray Diffraction Spectra of CNFs Extracted with Different Solvents: (a) No Extraction, (b) Hot-water Extraction, (c) Ethanol Extraction, and (d) Ethanol/benzene Extraction

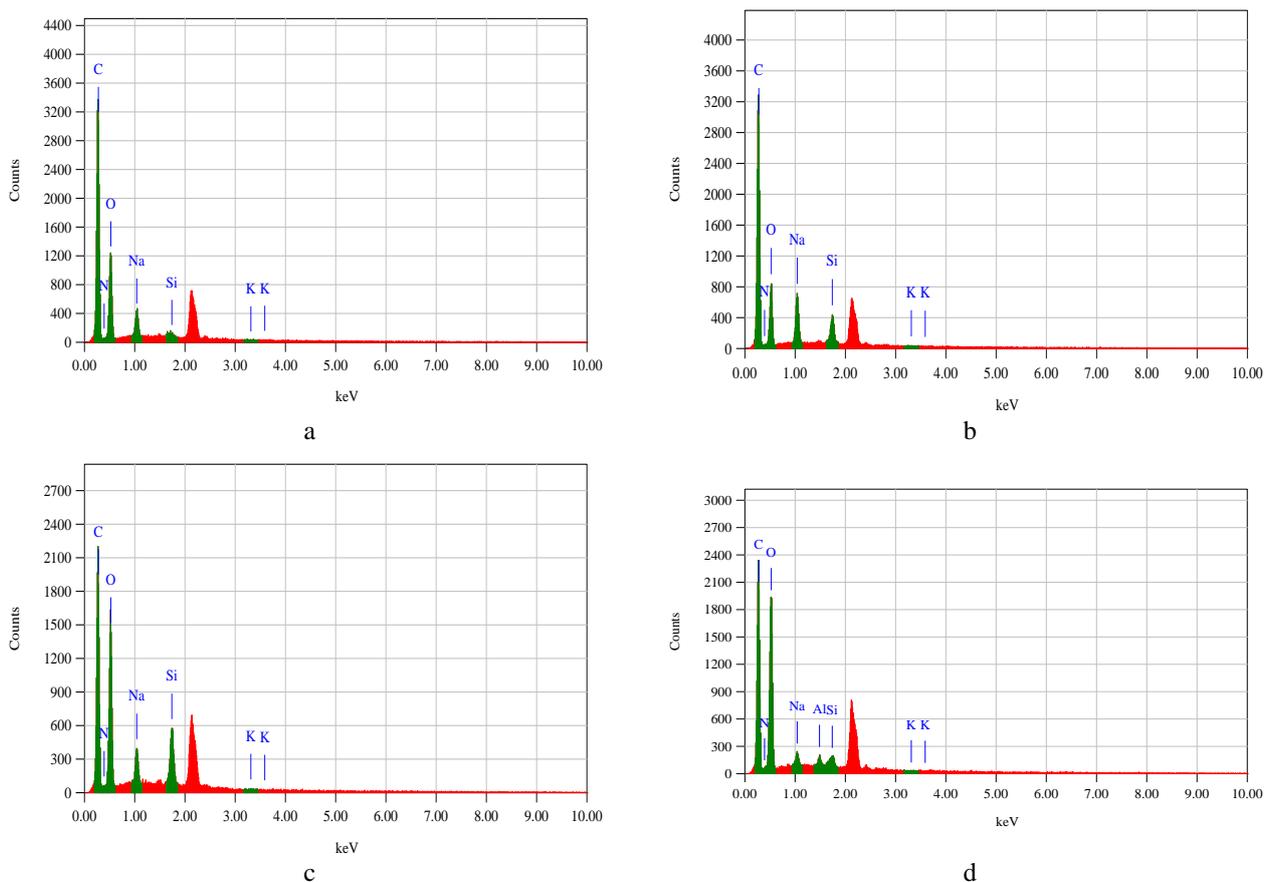


Figure 5. Elemental Composition Analysis of CNFs Extracted with Different Solvents: (a) No Extraction, (b) Hot-Water Extraction, (c) Ethanol Extraction, and (d) Ethanol/benzene Extraction

No transformation of native cellulose or cellulose I to other cellulose polymorphs was observed, as confirmed by the similarity of diffraction peaks at 2θ of approximately 15° , 16° , 22° , 26° , and 34° . These peaks are similar to those reported in previous studies [30, 31]. The increase in intensity of peaks at 15° , 16° , and 22° after extractive removal could be attributed to increases in CrIs, and the broadening of these peaks may indicate structural changes in the CNFs. The decrease in peak intensity at 18° may be due to a reduction in the amorphous region of the CNFs.

After analyzing with JCPDS ICDD Software 1997, those CNFs appertained to native cellulose ($C_6H_{12}O_6$)_x CAS No. 9004.34.6, featured with a highest peak at $2\theta = 22^\circ$ and highest relative intensity (I/I_1) at the peak. The ACS values of the unextracted and hot-water-, ethanol-, and ethanol/benzene-extracted CNFs were 1.28, 2.81, 2.10, and 1.11 nm, respectively. Variations in ACS may be attributed to differences in the solvent used for extraction and the effectiveness of these solvents in inhibiting agent removal.

Elemental composition analysis. All of the CNFs demonstrated different percentages of organic and inorganic elemental components (Figure 5). Nitrogen contents decreased after treatment with ethanol (29.54%) and ethanol/benzene (29.97%) compared with those obtained after no extraction (35.12%) and hot-water extraction (35.81%). The decrease in content of this element may be due to the ability of the solvents to extract protein, which is chemically linked with lignin. Amino acids linked with lignin can be removed via delignification with alkaline treatment followed by autohydrolysis. Compared with the raw OPEFB fibers, the solvent-extracted and chemically purified CNFs revealed dramatic decreases in C (36.01%–45.42%) and O (14.16%–32.26%), which is likely due to the removal of aliphatic compounds (e.g., fatty acid, wax, and resin acids), phenolic compounds (e.g., simple phenols and condensed tannins), and other cementing agents (e.g., hemicellulose, lignin, and pectin). By contrast, CNFs subjected to ethanol and ethanol/benzene extraction revealed higher O elements than unextracted and hot-water-extracted CNFs, thus indicating strong hydrophilic nature of cellulose. Decreases in inorganic elements (e.g., Na and K) were also observed in ethanol/benzene extraction treatment. The decrease in Si in control sample may be caused by dry-disk milling and autohydrolysis. However, after pretreated with ethanol and hot water, Si was increased indicating that these treatments exposed trace elemental Si deposited in CNFs. Changes in the elemental compositions of the CNFs may be attributed to the consecutive treatments (e.g., extraction, dry-disk milling, autohydrolysis, delignification, and bleaching) applied to the samples.

Conclusion

Extractive compounds can inhibit cellulose purification and CNF isolation, leading to noticeable changes in the morphological, physical, and chemical properties of CNFs. The oven-dried CNFs demonstrated irreversible self-aggregation, whereas the CNF suspensions showed reversible self-aggregation, which could be attributed to hydrogen bonding and van der Waals forces. The CNF aggregates in the suspensions had a particle size distribution in the range of 21.39–513.00 nm. At 600 nm, the transmittance of suspensions containing unextracted and hot-water-, ethanol-, and ethanol/benzene-extracted CNFs increased by approximately 0.78%, 19.87%, 59.66%, and 92.02%, respectively. This improvement in transmittance is due to the removal of inhibiting agents in the extractives and encrusting agents of lignin. The CrIs of the CNFs increased after solvent extraction by 47.27% (hot-water extraction), 63.57% (ethanol extraction), and 69.52% (ethanol/benzene extraction). Extractive removal enhanced the delignification process. Intense peaks at 15° , 16° , and 22° could be attributed to the increase in CrIs, and the broadening of these diffraction peaks indicated structural changes in the CNFs. All of the CNF samples demonstrated a similar cellulose polymorph, i.e., cellulose I, and different ACS values of 1.28 nm (no extraction), 2.81 nm (hot-water extraction), 2.10 nm (ethanol extraction), and 1.11 nm (ethanol/benzene extraction). A dramatic decrease in C (36.01%–45.42%), O (14.16%–32.26%), Na (0.51%–2.96%), K (0.00%–0.06%), and Si (0.08%–2.81%) was noted after extractive removal and cellulose purification.

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