

CHARACTERISTICS OF NANOFIBERS EXTRACTED FROM KENAF CORE

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Cellulose nanofibers were isolated from kenaf core fibers by employing chemo-mechanical treatments. The morphologies and sizes of the fibers were explored with environmental scanning electron microscopy (ESEM) and transmission electron microscopy (TEM). The results of chemical analysis showed that the cellulose contents of the bleached pulp fibers and nanofibers increased from 46% to 92% and to 94%, respectively. Most of the produced nanofibers had diameters in the range of 20 to 25 nm, whereas kenaf nanofibers ranged in diameter diameters from 10 to 75 nm. Fourier transform infrared spectroscopy (FTIR) analysis revealed the removal of lignin and the majority of the hemicelluloses from the kenaf core fibers. The thermogravimetric analysis (TGA), which was carried out to evaluate the thermal properties of the fibers, demonstrated that the thermal stabilities of these fibers were increased by the chemo-mechanical treatments. The results of X-ray analysis confirmed that chemical and mechanical treatments can improve the crystallinity of fibers.

Keywords: Kenaf core; Nanofiber; Chemical characterization; Structural characterization; Microstructure

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INTRODUCTION

In recent years, kenaf has been listed by the Malaysian government on the national agenda as a commercial, industrial crop. In light of this, it has been adopted as an alternative source of raw material by the biocomposite industries in Malaysia. The kenaf plant consists of two separate parts known as bast and core. The bast fibers have been found to possess attractive mechanical properties that enable their use as alternatives to glass fibers as reinforcing elements in polymer composites (Liu et al. 2007; Zampaloni et al. 2007). However in some cases the core fibers are equally commonly used.

Kenaf core is used as source of pulp and cellulose derivatives, especially for papermaking, absorption material, cosmetics, medicine, industrial chemicals, and other bio-polymers (Juhaida 2008). Paper from kenaf core fibers has demonstrated high tensile and burst strength compared to hardwood pulps (Sabharwal 1994). Moreover, kenaf core fibers have lengths in the range of 0.5 to 0.6 mm and are accordingly more homogeneous than the hardwood fibers (Bowyer 1999). On the other hand, the relatively high

hemicelluloses (30%) and cellulose (45%) contents of these fibers have made kenaf core a suitable bio-chemical source of cellulose derivatives such as cellulose nanofibers.

Cellulose nanofibers have been drawing world attention since the last decade. They are derived from cellulose fibrils, which themselves are composed of nano-sized microfibrils having high structural strength and stiffness (Wang and Sain 2007). A number of research efforts have been conducted to extract cellulose microfibrils from various natural sources such as wood, wheat straw, soy hulls, hemp, sisal, and bacteria and to evaluate their potential use as reinforcements in composite manufacturing (Nakagaito and Yano 2005; Alemdar and Sain 2008; Hubbe et al. 2008). Nanofibers from bacteria have been found to have widths between 9.7 to 12 nm (Brown and Laborie 2007), whereas the diameters of wheat straw and soy hull nanofibers are within a range of 30 to 40 nm and 20 to 120 nm, respectively (Alemdar and Sain 2007). Moreover radiata pine wood nanofiber widths have been reported as 15nm, sisal nanofiber as 30.9 ± 12.5 nm, and bleached hemp nanofiber as 54 nm (Abe et al. 2007; Moran et al. 2008; Wang et al. 2007). However, according to Oksman and Sain (2006), since this is a new field there are still some disadvantages concomitant to the techniques employed in extracting cellulose nanofibers that should be considered. Examples on these include the separation processing techniques, fiber isolation process, and strong hydrogen bonding. These disadvantages were reported to be associated with low yield cellulose nanofibers production that is not practical in large scale production, and in the entanglement and dispersion of fiber fibers.

The main goal of this study was to evaluate extraction of cellulose nanofibers from kenaf core using chemical and mechanical processes. This paper concentrates on the pulping process using sodium hydroxide-anthraquinone (NaOH-AQ) chemical treatment. The NaOH-AQ treatment was found to reduce the rate of degradation and to cause less damage to the cellulose chains (Helmy and Abd El Motagali 1993). The TEM and ESEM methods were used to characterize the morphology of the fibers produced. The chemical composition of the fibers was determined using TAPPI standards. Thermogravimetric (TGA), Fourier transform infrared (FTIR) and X-ray analyses were also used to characterize the fibers produced.

EXPERIMENTAL

Raw materials

Raw kenaf (*Hibiscus cannabinus*) core fibers were provided by the Institute of Tropical Forestry and Forest Products, Malaysia (INTROP). Sodium hydroxide (99%) used for the production of NaOH-AQ pulp was obtained from Merck Bhd., Malaysia. Sodium chlorite, acetic acid, and hydrogen peroxide used in bleaching were also obtained from the aforementioned company. On the other hand, the anthraquinone (98%) was purchased from System Bhd., Malaysia.

Pulping procedure

Kenaf core purification was performed by using sodium hydroxide and by subsequent bleaching. Details on the purification and bleaching processes are found elsewhere (Jonoobi et al. 2009).

Mechanical treatments

Kenaf bleached pulp was ground using a mechanical grinder to produce fine powder. Afterward, the fibers were immersed in distilled water to prepare a diluted suspension of 0.3% concentration. The fibers were distributed in the water using a mechanical blender apparatus (Ihon-Rigoku-SP ¼ Japan) for 15 min. Subsequently, the suspension was passed through a homogenizer (APV-1000) 40 times, and the pressure was set and held constant at 500 bars (Jonoobi et al. 2010).

Characterization

Microscopic techniques (TEM)

A Philips XL30 ESEM was used to study the effects of treatments on the fiber morphology. The intensification of velocity voltage was set up to 20 kV. All samples were sputter-coated with gold to avoid charging. The configuration and sizes of the nanofibers were analyzed using a Hitachi electron microscope (Model H-7100). A drop of the diluted kenaf nanofiber suspension was deposited on the carbon-coated grid and dried at room temperature. An image analyzer program, XL Docu, measured the fiber diameters manually. Altogether, one hundred and fifty fibers of each studied material were measured, and the results were reported as the mean values of the data for each set of measurements.

Chemical analysis

The chemical composition of the kenaf core fibers was analyzed before and after treatment. Cellulose, hemicellulose, and lignin were extracted for 8 hours using Soxhlet extraction with alcohol-acetone. The cellulose content of the fibers was assessed according to TAPPI test method 203 om-93, while the percentages of hemicellulose and lignin were determined following Wise and Murphy (1946) method and TAPPI standard 222 om-88, respectively.

Fourier transform infrared (FTIR) spectroscopy

To determine the changes in functional groups caused by treatments, Fourier transform infrared (FTIR) spectroscopy was performed using Perkin-Elmer spectrometer 100 (USA). Before the analysis, a 100-mg mass of the fibers was pulverized and mixed with potassium bromide (KBr). The resultant suspensions were pressed into crystal clear pellets and examined in the transmittance mode within the range of 4000-500 cm⁻¹.

X-ray diffraction

An X-ray diffractometer (Philips PW 3040/60 Xⁱpert Pro) with CuK α radiation (wavelength of 1.5405 Å) and step-scan mode (2 θ range: 5-50°) was employed for performing the arrangement and phase analysis for the samples. Phase recognition of the samples was achieved by use of the Xⁱpert Highscore software with support of the ICDD-PDF-2 database. The crystalline index of cellulose, C_{Ir}, was estimated by means of the Segal empirical method (1959),

$$C_{Ir} (\%) = [(I_{200} - I_{am}) / I_{200}] \times 100 \quad (1)$$

where I_{200} is the peak intensity corresponding to cellulose I, and I_{am} is the peak intensity of the amorphous fraction.

Thermogravimetric analysis (TGA)

After each treatment, thermogravimetric examination was carried out to investigate the thermal decomposition of kenaf fibers. Thermal stability data were obtained via a TGA/SDTA 851 (Mettler Toledo) thermogravimetric analyzer under linear temperature conditions. The temperature range was 25 °C to 500 °C with a heating rate of 10 °C/min in a nitrogenous atmosphere.

RESULTS AND DISCUSSION

Chemical Composition

Cellulose, hemicellulose and lignin are lignocellulosic fiber constituents of the kenaf core. Table 1 shows the chemical composition of kenaf core before and after chemo-mechanical treatments. The cellulose content of bleached pulp fibers increased, while both the hemicellulose and lignin contents decreased after the treatments. The cellulose content of pulp fibers increased from 46% to 92%, whereas the hemicellulose and lignin contents decreased from 33% to 4% and from 20% to 0.7%, respectively. These changes can be attributed to the effects of NaOH as well as to those of other chemicals employed in the pulping and bleaching steps. The hemicellulose and lignin, which are the cementing materials in the plant cell wall, form a matrix surrounding the cellulose microfibrils. In order to efficiently isolate cellulose microfibrils, the removal of lignin and hemicellulose is essential.

Table 1. Chemical Compositions of the Kenaf Core Fibers after Each Stage of Treatment

Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Ash (%)
Fibers	46.0 ± 0.5	33.0 ± 2.0	20.0 ± 1.0	2.20 ± 0.5	3.0 ± 0.4
Bleached pulp	92.0 ± 1.0	4.00 ± 1.0	0.70 ± 0.6	1.50 ± 0.2	0.5 ± 0.5
Nanofibers	94.0 ± 0.5	3.50 ± 0.7	0.50 ± 0.5	0.80 ± 0.5	0.5 ± 0.1

Morphology of the fibers

The morphological structure of kenaf core fiber can be examined by means of transmission electron microscopy. The results portrayed in Fig. 1 illustrate that the surfaces of the fibers were covered by impurities such as hemicellulose, lignin, pectin, and waxy substances. However, surfaces of the bleached pulp fibers were found to be smoother than those of the untreated ones. Furthermore, the results (Fig. 1a) indicated that the diameters of fibers (1a) were higher than those of the bleached pulp fibers (Fig. 1b). This can be explained by the fact that bundles of individual fibers had been linked together by lignin. Figure 1b shows that a significant reduction in the diameters of the fibers took place after chemical treatment, as fiber bundles disintegrated into individual fibers by effect of the pulping and bleaching processes.

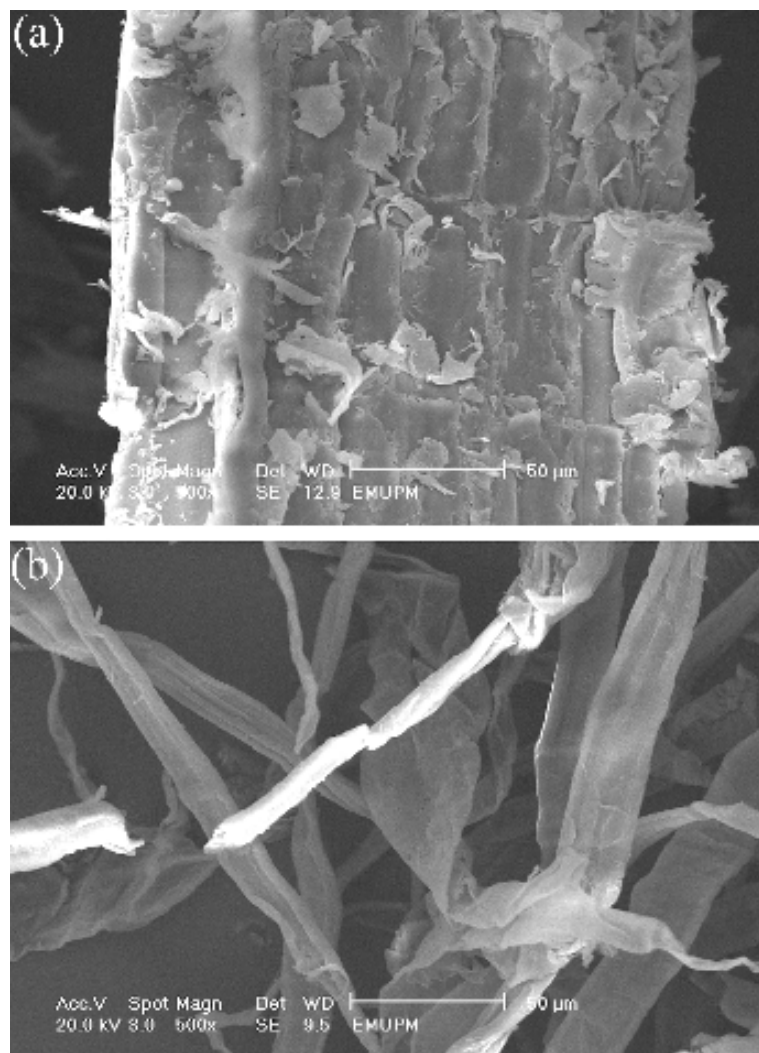


Fig. 1. ESEM micrographs of (a) fibers, (b) bleached pulp fibers

Figure 2 shows TEM images of the fibers after 40 passes through the high pressure homogenizer and indicates that the bleached pulp fibers were completely separated to the nanosize level, i.e., to diameters less than 100 nm. Diameters of the kenaf core fibers decreased after the mechanical treatment. Around 65% of the nanofibers had diameters in the range of 20-25 nm and lengths amounting to several thousands of nanometers. However, the maximum diameter of the nanofibers measured was 75 nm. The isolated nanofibers in the current study were finer if compared to isolated fibers from wood and hemp, while the diameter of nanofibers was similar to the isolated nanofibers from kenaf stem (Seydibeyoglu and Oksman 2008; Wang et al. 2007; Jonoobi et al. 2010).

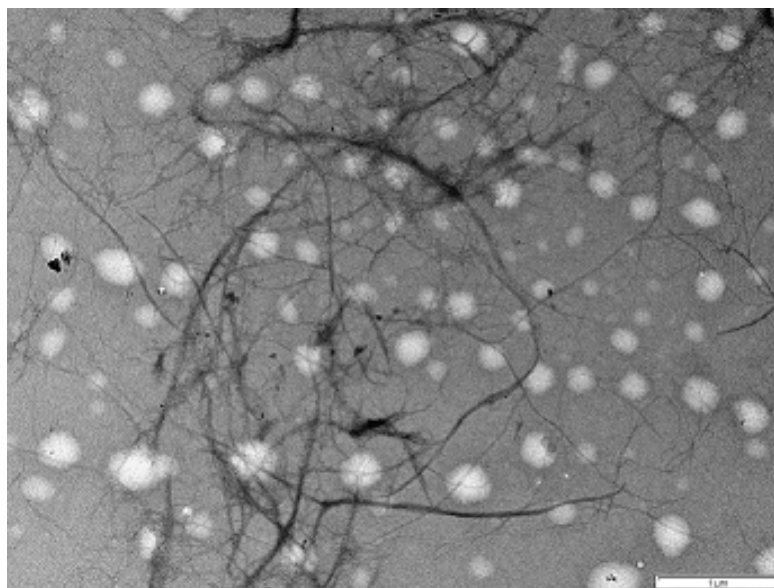


Fig. 2. Transmission electron micrographs of kenaf core nanofibers

FTIR analysis

FTIR analysis was used with the aim of revealing the composition of the lignocellulosic fibers after the treatments. The IR spectra of the untreated and treated fibers are shown in Fig. 3. Spectra had a broad band around 3400 cm^{-1} that matches the free OH groups on cellulose molecules and those OH groups corresponding to intra- and inter-molecular hydrogen bonds. Moreover, the spectra of all samples showed the characteristic C–H stretching absorption around $2900\text{--}2800\text{ cm}^{-1}$ (Khalil et al. 2001). The absorption peak at 1734 cm^{-1} in the spectra of the fibers is associated with C=O stretching of the acetyl group in the hemicelluloses (Sgriccia et al. 2008). The peak can also be attributed to the p-coumeric acids of lignin and/or hemicelluloses (Alemdar and Sain 2007). This peak disappeared completely from the spectra of the bleached pulp as well as from those of the nanofibers, thus suggesting the removal of lignin and most of the hemicellulose during the chemical treatments. Likewise, the absorption peak at 1600 cm^{-1} disappeared, indicating that lignin removal took place as a result of the chemical treatment (Wang et al. 2009).

The peaks observed in the spectra of the fibers around 1239 cm^{-1} is due to the C–O stretching of the aryl group in lignin (Troedec et al. 2008). Disappearance of this peak from the spectra of the bleached pulp fibers as well as from those of the nanofibers could be explained by to removal of lignin by the chemical treatments. In addition, the vibration peak detected in the region $1340\text{--}1330\text{ cm}^{-1}$ in all samples has been related to, and explained by, the bending vibration of the C–H and C–O bonds in the polysaccharides aromatic rings (Nacos et al. 2006; Troedec et al. 2008). Besides, the absorbance peaks observed in the spectra of the bleached pulp fibers and the nanofibers in the region $1650\text{--}1640\text{ cm}^{-1}$ are attributed to the adsorbed water (Troedec et al. 2008).

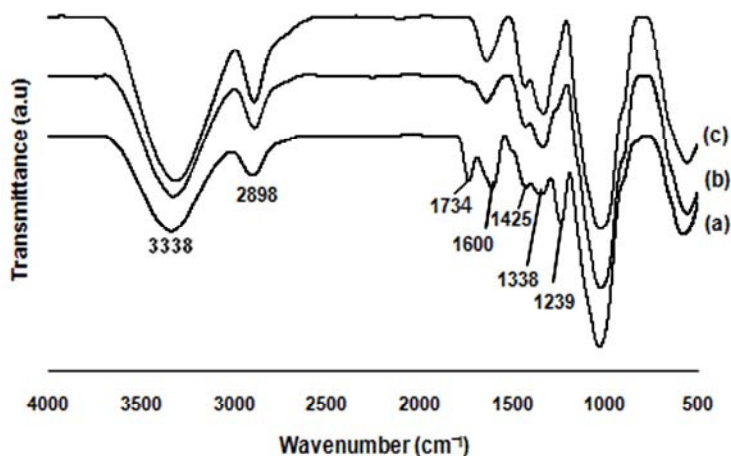


Fig. 3. Infrared spectra of (a) fibers, (b) bleached pulp fibers, (c) nanofibers

X-ray diffraction

X-ray diffractograms and crystallinity indices of the fibers, bleached pulp fibers, and nanofibers are shown in Fig. 4 and Table 2, respectively. Crystallinity is frequently expressed as the ratio of the diffraction portion from a crystalline part of a sample to the total diffraction from the very sample (Alemдар and Sain 2007). Crystallinity patterns characteristic of native cellulose (cellulose I) were exhibited by all of the samples. However, in contrast with the fibers, there were no crystalline transformations in the structures of the treated samples, which displayed their major peak intensities at 2θ values close to 22.5° .

Table 2. Crystallinity of Kenaf Core Fibers Before and After Chemo-Mechanical Treatments

Material	Crystallinity (%)
Fibers	41 ± 2
Bleached pulp	53 ± 1
Nanofibers	62 ± 2

The X-ray crystallinity indices of the fibers, bleached pulp fibers, and nanofibers were calculated according to Segal et al. (1959) and found to be equal to 41, 53, and 62%, respectively. Moreover, the crystallinity data were confirmed by the results in Table 1. The degree of crystallinity of cellulose was found to be higher in the bleached pulp fibers and nanofibers samples than in the fibers. Alemдар and Sain (2007) argued that there should be an increase in crystallinity index following chemical treatments. Furthermore, the results revealed an increase in crystallinity after homogenization using the high pressure homogenizer.

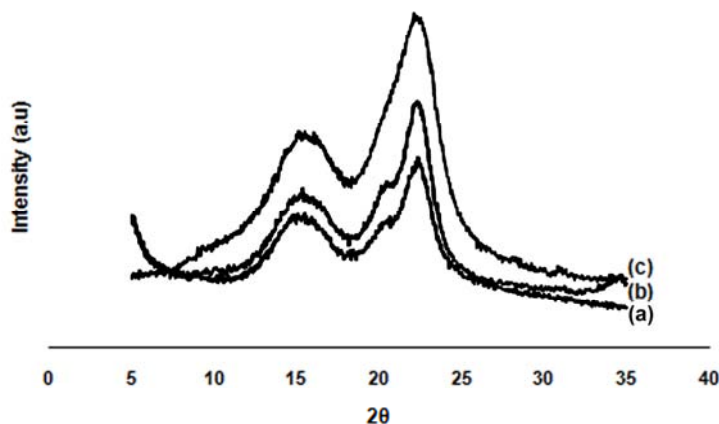


Fig.4. X-ray diffraction patterns of (a) fibers, (b) bleached pulp fibers, and (c) nanofibers

Thermal analysis

In order to investigate the effect of chemo-mechanical treatments on thermal decomposition of the fibers, a thermogravimetric analysis (TGA) of the study samples was carried out. The thermal behavior of lignocellulosic materials depends on their chemical composition, structure, and degree of crystallinity (Fisher et al. 2002). Figure 5 and Table 3 show the TGA results pertaining to kenaf core fibers. In the case of the fibers, the main decomposition steps (T_{max}) occurred at 300 °C while the main degradation (T_{max}) of the bleached pulp fibers and nanofibers occurred at 320 °C and 332 °C, respectively. The pulp and nanofibers had decomposition patterns similar to those of the fibers. The pulp exhibited a slight weight loss relative to the fibers, while the nanofibers showed a higher relative decrease in weight loss.

Table 3. Degradation Characteristics of Kenaf Core Fibers After Each Stage of Treatment

Material	Main degradation (°C)	Residue after 500 °C (%)
Fibers	300 ± 2	29 ± 0.5
Bleached pulp	320 ± 4	20 ± 1.0
Nanofibers	332 ± 1	17 ± 1.0

The fiber residues obtained after heating the fibers and the treated cellulosic fibers to 450 °C highlight the presence of carbonaceous materials in the fibers. As seen in Table 3, the amounts of fiber residues varied from one stage of treatment to another. The small amount of residues in the nanofibers obtained after chemo-mechanical treatment may be the result of removal of the non-cellulosic materials during these treatments.

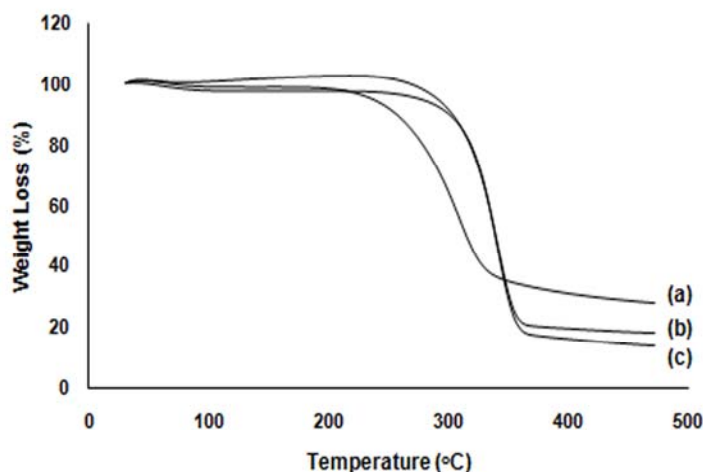


Fig. 5. TGA curves of (a) fibers, (b) bleached pulp fibers, (c) nanofibers.

CONCLUSIONS

1. Cellulose nanofibers were productively isolated from kenaf core fibers by means of chemo-mechanical treatments.
2. Nanofiber morphologies were examined in every stage based on ESEM. The TEM results showed that most of the nanofibers isolated from kenaf core fibers had diameters in the range of 20 to 25 nm. Chemical analysis of the fibers after each stage of treatment indicated increases in their cellulose contents and decreases in their lignin and hemicellulose contents relative to the corresponding contents before each respective treatment.
3. The results of the FTIR analysis confirmed that removal of lignin and hemicellulose is affected by chemical processes.
4. In comparison with the fibers, there was a slight increase in the weight loss of the pulp and a pronounced increase in that of the nanofibers. Moreover, we found that the nanofibers disintegrated at high temperatures.
5. Crystallinity results showed that the chemo-mechanical treatments did not change the crystalline structures of the bleached pulp fibers and nanofiber cellulose as compared to that of the fibers. Both the bleached pulp fibers and the isolated nanofibers demonstrated an increase in the diffraction. Furthermore, our results showed that the highest crystallinity was retained in the nanofibers.

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