

ELEMENTARY KENAF FIBRE EXTRACTION

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ABSTRACT

Elementary kenaf fibres were separated by the HNO₃ treatment and the H₂O₂/CH₃COOH treatment. It was found that the HNO₃ treatment caused fibre fragmentation causing a decrease in the fibre length and an increase in the fibre defect density. However, the H₂O₂/CH₃COOH treatment was not strong as the HNO₃ treatment and this had much less effect on the fibre length and the fibre defects. The fibres had an average length of 0.2 mm and 2.3 mm and an aspect ratio of 15 and 179 for the HNO₃ treated fibres and the H₂O₂/CH₃COOH treated fibres, respectively. The defect density of the HNO₃ treated fibres and the H₂O₂/CH₃COOH treated fibres was 21 and 14 defects/mm, respectively. Both the treatments removed lignin, pectin and waxes. They also increased cellulose crystallinity in the fibres, especially for the HNO₃ treatment. However, these treatments resulted in some oxidation of cellulose to occur.

KEYWORDS

Kenaf, elementary fibres, fibre extraction, fibre separation, fibre isolation.

INTRODUCTION

Natural fibres, particularly bast fibres, have been used as the reinforcement in polymer-matrix composites in recent years. These fibres have been developed to improve mechanical properties of the composites. Most methods found are to modify fibre surfaces. An another method found is to increase fibre aspect ratios by isolating natural fibres and this method is also more potential than the fibre surface modification conducted for enhancing mechanical properties of composites, especially strength (Hughes, 2012).

The objectives of this study were to develop an appropriate process for breaking down the kenaf fibre bundles into elementary fibres. Two chemical treatment methods used were nitric acid and a mixture of hydrogen peroxide and acetic acid. The fibres were physically characterized to determine their diameter, length and aspect ratio, and examine the defects present in the fibres. In addition, the fibres were characterised chemically using Fourier transform infrared spectroscopy (FTIR) while the level of cellulose crystallinity was determined by X-ray diffraction (XRD) and solid state ¹³C nuclear magnetic resonance (NMR). NMR was also used for determining the degree of oxidation of cellulose in the fibres.

METHODOLOGY

Materials

Untreated kenaf fibres (UKF) were obtained by the Malaysian Agriculture Research and Development Institute (MARDI). Holocellulose, cellulose, hemicellulose, lignin, pentosan and ash which are the chemical composition of the UKF are 91%, 61%, 30%, 11%, 17% and 0.65%, respectively. The moisture content, alkali solubility and hot water solubility of the UKF are 10%, 19% and 1.2%, respectively (Zakaria, 2014). 70% Nitric acid (HNO₃), 30% hydrogen peroxide (H₂O₂) and glacial acetic acid (CH₃COOH) were supplied by Ajax Finechem. Alpha-cellulose was supplied by Sigma-Aldrich.

Isolation of Elementary Fibres

The fibre bundles were treated using two types of the chemical treatments, these being the nitric acid treatment and the hydrogen peroxide and acetic acid treatment. The nitric acid treatment was carried out using 60% HNO₃ in a 20:1 liquid to fibre ratio at 80 ± 2°C for 30 minutes. The treatment was continued in the same solution at room temperature for a minimum of 5 weeks as the yield from this process was low. The hydrogen

peroxide/acetic acid treatment was carried out using a 50:50 mixture of 20% hydrogen peroxide and glacial acetic acid, in a 75:1 liquor to fibre ratio, at $98 \pm 2^\circ\text{C}$ for 7 hours. Both of the treated fibre types were then filtered, washed with water, until the pH of the solution was approximately 7. These fibres were subsequently frozen and then freeze dried using a Lyovac GT 2 freeze drier. The treated fibres are referred to hereafter as KFTN for the nitric acid treated fibres and KFTHA for the hydrogen peroxide/acetic acid treated fibres.

As cellulose is the main component in the fibres, α -cellulose (AC) was treated using the nitric acid and hydrogen peroxide/acetic acid treatments as explained above to study the effect of the treatments in the absence of the other components in the fibres. The nitric acid treated α -cellulose and the hydrogen peroxide/acetic acid treated α -cellulose are referred to hereafter as ACTN and ACTHA, respectively.

In addition, the untreated fibres were hand-cut to a length of approximately 2 mm and then manually separated. These chopped technical fibres were prepared for the purpose of comparison. These fibres are referred to hereafter as UKF.

Scanning Electron Microscopy (SEM)

The treated fibres were imaged using a Hitachi S3400-X scanning electron microscope. The fibre specimens were first sputter coated with gold using an Emitech K550x gold sputter. The SEM was operated in high vacuum at an accelerating voltage of 10 kV.

Fibre Length, Diameter and Aspect Ratios

The untreated and treated fibres were sprinkled onto glass slides and then examined using a Nikon Eclipse ME600 optical microscope. The length and diameter were then measured for 500 UKF, 500 KFTN and 50 KFTHA fibres using UTHSCSA ImageTool program. Subsequently, the aspect ratio was determined for each type of the fibres using the average values of these two parameters.

Defects in Elementary Fibres

The defects present in the KFTN and KFTHA fibres were assessed using a Hitachi S3400-X scanning electron microscope as described in the previous SEM section, but with an accelerating voltage of 15 kV. Ten fibres were examined in each case.

Fourier Transforms Infrared (FTIR) Spectroscopy

The kenaf fibres and α -cellulose in the untreated and treated conditions were analysed using FTIR spectroscopy. The analyses were carried out using a Perkin Elmer Spotlight 400 FTIR microscope in the range of $4,000\text{--}650\text{ cm}^{-1}$, with a resolution of 4 cm^{-1} .

Cellulose Crystallinity

The level of crystallinity (crystallinity index) in the cellulose was determined for both the fibres and α -cellulose in both the untreated and treated conditions using a Philips X'pert Multipurpose XRD System. The specimens were scanned from 8° to 55° at 2θ . A step size of 0.026° , a voltage of 45 kV and a current of 40 mA were used. Time per step was 51 seconds and revolution time was 4 seconds. Percentage crystallinity indexes were calculated using Segal's equation and multiplying by 100 (Sayeba et al., 2010). The Segal's equation is then given by

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

where I_{002} denotes the maximum intensity of the 002 peak at about $2\theta = 22.0\text{--}22.5^\circ$ and I_{am} is the lowest intensity corresponding to 2θ value near $18.0\text{--}18.5^\circ$ (Segal et al., 1959; Wang et al., 2010).

The crystallinity index of cellulose was also determined for the same materials using a Bruker Avance III 300 Solid State NMR. The crystalline and amorphous peaks at 89 ppm and 84 ppm, respectively, in the C4 region (from 80 ppm to 93 ppm) were used for determining the crystallinity index of the cellulose (Park et al., 2010).

Degree of Oxidation

The degree of oxidation of cellulose in the treated kenaf fibres and treated α -cellulose was determined from NMR spectra by integrating the peak at 174 ppm (C6') corresponding to the carboxyl groups (Lasseuguette, 2008).

RESULTS AND DISCUSSION

Isolation of Elementary Fibres

Both of the HNO_3 and $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ treatments were successful in isolating the elementary fibres. Both of the KFTN and KFTHA fibres had almost the same appearance (Figure 1). However, the KFTHA fibres had much longer length than the KFTN fibres. The KFTHA fibres had narrow tapered ends while the KFTN fibres had square ends.

The yield for the KFTN and KFTHA processes was 36% and 58%, respectively. However, these are slightly higher than the yields of 34% and 48% obtained by Mazumder et al. (2000) using similar treatments also on kenaf fibres.

From the present study, it is concluded that the $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ treatment is better than the HNO_3 treatment in terms of both yield and treatment time. Moreover, this treatment is milder than the HNO_3 treatment and is less likely to degrade the cellulose in the fibres (Zhao et al., 2010).

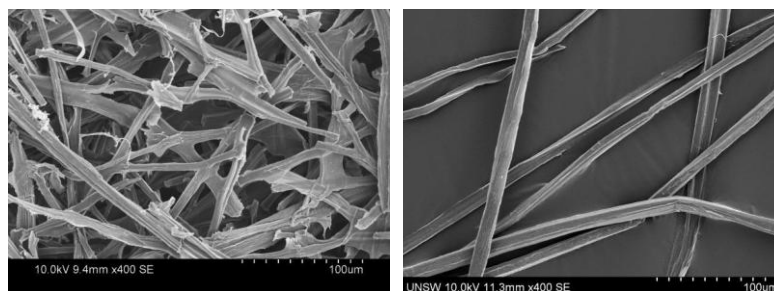


Figure 1 SEM micrographs of KFTN (left) and KFTHA (right).

Aspect Ratios of Elementary Fibres

The mean length of the UKF, KFTN and KFTHA fibres was 730 μm (standard deviation 51%), 180 μm (standard deviation 53%), and 2312 μm (standard deviation 27%), respectively. The mean diameter was 97 μm (standard deviation 47%), 11.7 μm (standard deviation 26%), and 13.0 μm (standard deviation 23%) for the UKF, KFTN and KFTHA fibres, respectively. The aspect ratio of the UKF, KFTN and KFTHA fibres was 7.5, 15.3 and 179, respectively.

The average diameter of the treated fibres is within the range of 10-20 μm considered to be indicative of elementary fibres (Van den Oever et al., 2000) and this provides quantitative evidence that the treatments had been successful in converting the fibre bundles to elementary fibres. However, there was a very substantial difference in the fibre lengths, with the elementary fibres obtained from the $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ treatment being an order of magnitude longer (average length of 2.3 mm) than that obtained from the HNO_3 treatment (average length of 0.18 mm). Accordingly, the aspect ratios also differed by an order of magnitude (179 compared with 15 for the two different types of treatment, respectively).

Calamari et al. (1999) also treated kenaf fibres with hydrogen peroxide/acetic acid, but in this case they used an alkali pretreatment. They obtained a fibre length of 2,450 μm and an aspect ratio of 204, again in good agreement with the results of the present study.

As noted above, the much shorter length of the HNO_3 treated fibres (KFTN) is considered to be due to fibre breakage resulting from acid attack at fibre defects. This occurs because the defects are chemically more active (Hughes, 2012).

Defect Density of Elementary Kenaf Fibres

The HNO₃ treated fibres (KFTN) and H₂O₂/CH₃COOH treated fibres (KFTHA) had fibre defects, such as kinks, micro-compressions, pits, nodes, dislocations and initial breaks. These are similar to the defects observed by Fan (2010) in elementary hemp fibres.

The average defect density was significantly higher for the KFTN fibres than for the KFTHA fibres with the values being 21 (standard deviation of 9) and 14 (standard deviation of 4) defects/mm, respectively. This is attributed to the higher level of hydrolysis produced by the stronger acid (Bailaret et al., 1989).

FTIR Spectra

The assignments of peak positions of FTIR spectra of the kenaf fibres and α -cellulose in untreated and treated conditions are shown in Table 1.

The FTIR spectrum of the untreated fibres (UKF) was similar to that for the untreated α -cellulose (AC), except for the absence of the 1716 cm⁻¹, 1593 cm⁻¹, 1500 cm⁻¹, and 1238 cm⁻¹ peaks. The peaks in the spectrum of the untreated fibres at 3329 cm⁻¹, 2900 cm⁻¹ and 1102 cm⁻¹ are seen not only in cellulose, but also in hemicellulose and lignin. The spectrum of the untreated fibres also contained the same absorption peaks as the spectrum for a kenaf stem published previously by Öztürk et al. (2010).

The spectrum from the HNO₃ treated fibres (KFTN) contained the same peaks as the α -cellulose treated with HNO₃ (ACTN), except for the addition a peak at 1716 cm⁻¹, which is attributed to the presence of some oxidized cellulose.

The spectrum from the H₂O₂/CH₃COOH treated fibres (KFTHA) contained the same peaks as the H₂O₂/CH₃COOH treated α -cellulose (ACTHA).

Table 1 Assignments of peak positions of FTIR bands of kenaf fibres and α -cellulose in untreated and treated conditions

Peak Position (cm ⁻¹)	Assignment	Source
3,329	O-H stretching vibrations in cellulose, hemicellulose and lignin	Moran et al. (2008)
2,900	C-H stretching vibrations in cellulose, hemicellulose and lignin	Moran et al. (2008)
1,716	C=O stretching vibrations of ketone and carbonyl groups in hemicellulose, pectin and waxes	Dai & Fan (2010), Li & Pickering (2008), Moran et al. (2008)
	C=O stretching vibrations of carboxylic groups in oxidised cellulose and/or those of acetyl groups due to mixtures of H ₂ O ₂ and CH ₃ COOH	Luz et al. (2008), Silverstein et al. (2005)
1,635	O-H bending vibrations due to moisture absorption	Han et al. (2007), Moran et al. (2008)
1,593	C=C aromatic in-plane vibrations combined with C=O stretching vibrations in lignin	Garside & Wyeth (2003), Kubo & Kadla (2005)
	-NO ₂ asymmetrical stretching vibrations	Samal & Ray (1997)
1,500	C=C aromatic in-plane vibrations in lignin	Kubo & Kadla (2005)
1,420	-CH ₂ and OCH in-plane bending vibrations in cellulose	Dai & Fan (2010)
1,360	C-H bending vibrations in cellulose	Dai & Fan (2010)
1,313	-CH ₂ wagging vibrations in cellulose	Dai & Fan (2010)
1,280	-NO ₂ symmetrical stretching vibrations	Edge et al. (1990), Silverstein et al. (2005)
1,238	C-O stretching vibrations of acetyl groups in lignin	Sgriccia et al. (2008)
	C-O stretching vibrations of acetyl groups due to mixtures of H ₂ O ₂ and CH ₃ COOH	Tserki et al. (2005)

1,170-1,082	Pyranose ring skeletal in cellulose	Dai & Fan (2010)
1,102	C-OH group frequency in cellulose, hemicellulose and lignin	Dai & Fan (2010)
893	COC, CCO and CCH deformation and stretching vibrations in cellulose	Dai & Fan (2010)

Crystallinity of Cellulose

The crystallinity indexes of the cellulose in the untreated and treated α -cellulose and fibres examined using XRD and NMR are shown in Figure 2.

The crystallinity indexes examined using XRD range from 75% to 97%. The values are generally lower for α -cellulose than for the fibres. They are also lower for the untreated than for the treated materials. The crystallinity index for the untreated α -cellulose was 75% compared with 83% for the untreated fibres. The HNO_3 treatment substantially increased the crystallinity index with values of 97% and 96% being obtained for the ACTN and KFTN materials, respectively. The $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ treatment also increased the level of crystallinity, but to a lesser extent, especially in the α -cellulose. Park et al. (2010) determined the crystallinity index of α -cellulose and obtained a value of 78% which is in good agreement with the value of 75% obtained in the present study.

The crystallinity indexes for the untreated and treated α -cellulose and fibres examined using NMR are much lower than those obtained by XRD, ranging from 30-56% compared with 75-97%. However, the trends were generally similar. The untreated cellulose and fibres had the lowest crystallinity indexes (30% and 36%, respectively) while the HNO_3 treated samples had the highest crystallinity indexes (55% and 56%, respectively). The crystallinity indexes were intermediate for the $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ treatment (38% and 39%, respectively) but there was now no difference in the crystallinity levels in the α -cellulose and fibre samples. Park et al. (2010) used NMR to determine the crystallinity index of α -cellulose and obtained a value of 42%, which is in reasonable agreement with the value of 30% obtained in the present study. Focheret et al. (2001) determined the crystallinity index of cellulose extracted from kenaf using NMR, and obtained a value of 42%. This is again in reasonable agreement with the value of 36% obtained here.

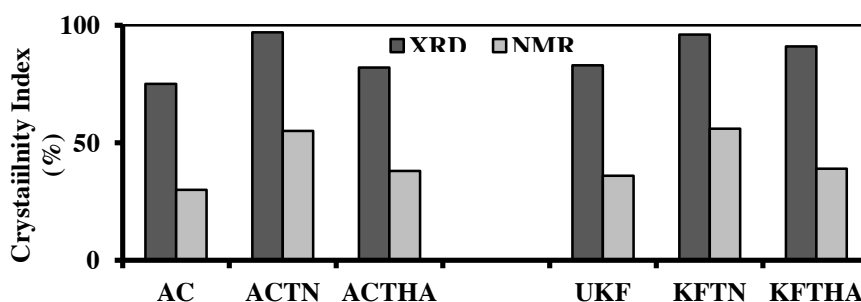


Figure 2 Crystallinity indexes of cellulose in the untreated and treated α -cellulose and fibres examined using XRD and NMR.

The increase in crystallinity as determined by XRD and NMR was 16% and 56%, respectively, for the HNO_3 treated fibres (KFTN), 10% and 8%, respectively, for the $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ treated fibres (KFTHA). The increase in crystallinity is attributed to oxidation of the cellulose (Abdel Moteleb & El Akabawy, 1999). In addition, oxidation would reduce the degree of polymerisation (DP) by constraining movement of cellulose molecules, which would lead to an increase in cellulose crystallinity, (Sandy et al., 2010).

Degree of Oxidation

The degree of oxidation of cellulose of the treated samples for the α -cellulose and fibres ranges from 4-15%. The results for the HNO_3 treatment (ACTN and KFTN) were 14.5% (standard deviation of 0.8%) and 7.4% (standard deviation of 0.4%) for the α -cellulose and fibres, respectively. Substantially lower values of 4.4% (standard deviation of 0.3%) and 6.9% (standard deviation of 0.3%), respectively, were obtained from the $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ treatment (ACTHA and KFTHA).

CONCLUSIONS

Elementary kenaf fibres were successfully isolated using HNO₃ and a mixture of H₂O₂ and CH₃COOH. The main findings are as follows:

- The H₂O₂/CH₃COOH treatment required a shorter treatment time and gave a 60% higher yield than the HNO₃ treatment.
- The average length and aspect ratio were 2.31 mm and 179, respectively, for the H₂O₂/CH₃COOH treated fibres (KFTHA) while those of the HNO₃ treated fibres (KFTN) were 0.18 mm and 15.3, respectively. The reduced length of the HNO₃ treated fibres is considered to be due to fibre breakage arising from chemical attack at defects in the fibres.
- The defect density in the HNO₃ treated fibres (KFTN) was double that found in the H₂O₂/CH₃COOH treated fibres (KFTHA). This is again considered to be due to chemical attack of the fibres during the harsher HNO₃ treatment.
- Both the treatments removed lignin, pectin and waxes, as would be expected in elementary fibreisolation. However, they caused some cellulose oxidation to happen.
- Both of the treatments increased the level of cellulose crystallinity in the fibres which is beneficial to their mechanical properties. The increase in crystallinity in the fibres was higher for using the HNO₃ treatment than the H₂O₂/CH₃COOH treatment.

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