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EFFECT OF CHEMICAL AND HEAT TREATMENT ON THE TENSILE STRENGTH, CRYSTALINITY AND SURFACE MORPHOLOGY OF KENAF FIBRES

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Abstract

This paper studies the effects of chemical and thermal treatments on the tensile strength, crystallinity and surface morphology of kenaf (*Hibiscus Cannabicus L.*) fibres. Raw kenaf fibres (KF) were chemically treated with 3%, 6% and 9% w/w alkali solutions of sodium bicarbonate ($NaHCO_3$) at different immersion time (24 h, 72 h, and 120 h), at room temperature. Next, the fibres were thermally treated at 70°C for 24 h. Fibre tensile tests were performed to evaluate the effects of these surface treatments on the tensile strength of KF. Changes in progressive crystallinity and surface morphology of untreated and treated KF were characterized through X-ray diffraction (XRD) and scanning electron microscope (SEM). The tensile strength of the fibre increased up to 382.3 MPa for optimum treatment (concentration of mild 6% $NaHCO_3$ and 72 h immersion time), a 26% increase compared to untreated fibre. Results also show that the optimum treatments improved the crystallinity of KF and provide favourable surface morphology for better fibre-matrix bonding in composite. Thermal and chemical treatments of $NaHCO_3$ have improved the strength, crystallinity and surface morphology of KF.

Keywords: Chemical and thermal treatment, Crystallinity, Kenaf fibres, Mechanical properties, Surface morphology.

1. Introduction

The automotive, marine, and construction industries are establishing plant fibres (PF) as alternative materials in composites as replacement to synthetic fibres. PF are sustainable, renewable and have received well acceptance among these industries [1]. Amongst all PF, kenaf has become an attraction worldwide. The Malaysian government, as an example, fully supports the use of kenaf fibres (KF) as component in food packaging, automotive, construction materials, absorbent, and furniture industries. Apart from economic considerations, the application of PF for commercial purposes also are boosted by the benefits provided in terms of the satisfactory physical and mechanical properties of the fibres compared to synthetic. However, some unfavourable characteristics of PF, such as sustaining high polarity, poor resistance to moisture absorption, hydrophilic, and require low processing temperature have hindered the choice of PF as reinforcement in composites. Thus, surface treatments using physical (thermal) and chemical modifications have been investigated to improve these properties. As chemical treatment with alkaline solution may reduce the density and strength of the PF, hence combination with physical treatment are encouraging and had shown significant increase in the tensile strength and surface roughness due to thermal effect.

Table 1. Effect of chemical and thermal treatments on tensile strength of PF.

Fibres	Treatment		Strength		Ref.
	Chemical	Thermal	Tensile (MPa)	Increase/ Decrease (%)	
Kenaf	Untreated	Untreated	289	-	[2]
	NaOH soaking for 24h	Oven dried			
	5%	at 220°C	355	+22.8	
	10%	(10h)	261	-9.7	
	15%		213	-7.4	
Kenaf	Untreated	Untreated	16.8	-	[3]
	NaOH soaking for 24h	Oven dried			
	3%	at 80°C	17.5	+4.2	
	6%	(10h)	17.6	+4.8	
	9%		16.8	-	
Sisal	Untreated	Untreated	406.9	-	[4]
	NaOH soaking for 1h	Oven dried			
	2%	at 60°C	411.2	+1.1	
	5%	(72h)	455.3	+11.9	
	10%		495.6	+21.8	
	15%		522.4	+28.4	
	20%		487.2	+19.7	
Sisal	Untreated	Untreated	312.5	-	[5]
	$NaHCO_3$ 10%	Oven dried			
	soaking for 24h	at 40°C	745.2	+138.5	
	120h	(4h)	930.9	+197.9	
	240h		911.2	+191.6	

Table 1 shows the effects of thermal and chemical treatments using sodium hydroxide (NaOH) and sodium bicarbonate ($NaHCO_3$) on some PF. Obviously, soaking the fibre with $NaHCO_3$ for 120 h and exposure to low heat treatment at 40°C for 24 h had improved the tensile strength of sisal fibre up to almost 200% compared to NaOH. The effects of alkaline treatment on fibre has enhance the surface coarseness and interfacial bonding. The accountable effect was relate to the increased amount of cellulose exposed on PF surfaces that generate compatibility between the fibre-matrix in composite [6]. The removals of natural and artificial impurities from the fibre surface with alkali treatment also enhance the fibre-matrix adhesion in composite due to changes in cellulose crystalline structure [7].

Based on results in Table 1, this study is conducted to determine the optimum concentration of $NaHCO_3$, temperature and immersion time on the tensile strength of KF. The changes in the surface morphology and crystallinity are also observed to study their link with the changes in tensile strength. The result is useful for consideration of the best treatment of KF for usage as reinforcement in composite.

2. Material and Methods

2.1. Kenaf fibres

KF are supplied by Kenaf and Tobacco Industrial Board, Malaysia. After 1-3 days being harvested, kenaf plants undergo water retting process for about 14 days to separate the skin from their stalks. After that, the fibres were cleaned with tap water and dried under hot sun.

2.2. Density measurement

The density of KF is determined using Archimedes method following ASTM D3800-99 [8] standard and using acetone as an immersion fluid. The specimens were place in vacuum desiccators' for 5 minutes to remove unwanted air from between the fibre cells. Then, the bundle specimens of a minimum weight of 0.5 g were soaked into acetone for 1 minute and the reading was recorded.

2.3. Fibre surface treatment

Raw KF were cut into short length to provide uniformity for alkaline penetration, cleaned with tap water and dried under hot sun for 24 h. Later, KF were treated with different concentrations of 3%, 6% and 9% weight of weight (w/w) of $NaHCO_3$ for different immersion time (24 h, 72 h, and 120 h). The treated KF are identified with the codes as in Table 2. After the treatment, KF were thoroughly washed with running water to remove absorbed alkali from the surface. Then, KF were allowed to dry at room temperature for 24 h. KF were exposed to thermal treatment at 70°C±5°C in oven for 24 h to release lignin and increase the crystallinity index (CrI) before undergo related test.

Table 2. Fibres series for treatment.

Percentage of alkalization	Soaking Period in $NaHCO_3$		
	24 h	72 h	120 h
Untreated	-	-	-
3%	K24-3%	K72-3%	K120-3%
6%	K24-6%	K72-6%	K120-6%
9%	K24-9%	K72-9%	K120-9%

2.4. Fibre tensile test

Ten samples for each condition were prepared to determine the average fibres strengths according to ASTM C1557-14 [9] using Universal Testing Machine by Zwick-Roell model Z005, equipped with a load cell of 1 kN. The strain rate was set equal to 1.5 mm/min and gage length of 10 mm. The tests were carried out in a laboratory ambient temperature of 23±5°C with relative humidity of 70±5%.

2.5. Crystalline structure measurement

Crystallinity measurements were carried out on ground KF powder using XRD, Bruker D8 Advance, 40 kV power and 40 mA X-ray diffractometer with Cu Kα radiation (k = 1.5406 Å). The KF's crystalline fraction was obtained through the amorphous peak areas under the diffraction X-ray plot. The percentage of crystallinity (%Cr) was obtain from XRD data analysis. This analysis was carried out to ascertain the effect of heat treatment on the tensile properties of the treated fibres.

2.6. Morphology analysis

Scanning Electron Microscopy (SEM) is an important tool for observing the surface morphology of untreated and treated KF. SEM analysis was conducted to analyse the surface morphology of treated fibres with different concentration of $NaHCO_3$. Untreated and treated KF were observed with a Zeiss Evo MA 10 (UK) VPSEM. The samples were covered with a thin layer of gold using a sputter coater and operated at 10 kV using the secondary electron mode with images collected digitally. Structural and diameter changes during the fibre modification are identified through microscopy analysis on fibre surface morphology.

3. Results and Discussion

3.1. Density and diameter measurements of alkali-treated kenaf fibres

The KF average densities and diameters are shown in Table 3. The density and diameter of treated fibre was found to vary between 1.23-1.29 g/cm^3 and 55.71-75.38 μm, respectively with the decline of 5% after a period of treatment were increase. The decrease was correlated with the increasing concentration of $NaHCO_3$. The result indicates that modification of fibres has affecting the fibre surface significantly. Further, alkalization process also has been found to reduce the fibre diameter about 20% by partially remove the hemicellulose, lignin, pectin, and waxy substances of fibres [10]. According to Mwaikambo and Ansell [11], it is due to peel off effect of the surface impurities, resulted in the decrease of the surface volume and density of the fibre. Despite the reduction in diameter and density, we will see that the tensile strength is enhanced and later justified by morphological analysis and XRD results. The recorded density and diameter of KF treated with $NaHCO_3$ is higher than the average data using NaOH recorded by Mahjoub et al. (2014)[12]. Thus, it can be conclude that $NaHCO_3$ can be used for surface treatment and enhanced mechanical properties of fibre.

Table 3. Effect of $NaHCO_3$ and NaOH on the density and diameter of KF.

Fibres reference code	Average density (g/cm^3)	Average diameter (μm)	Fibres reference code	Average density (g/cm^3)	Average diameter (μm)
	$NaHCO_3$			NaOH	
Untreated	1.39	75.38	Untreated	1.202	66.2
K24-3%	1.29	69.27	3 h-5%	-	65.1
K24- 6%	1.28	67.39	3 h-7%	-	64.3
K24- 9%	1.27	63.76	3 h-10%	damage	damage
K72-3%	1.28	68.13	3 h-15%	damage	damage
K72- 6%	1.27	66.22			
K72- 9%	1.26	63.92	24 h-5%	-	63.9
K120-3%	1.25	60.47	24 h-7%	-	55.0
K120- 6%	1.24	57.69	24 h-10%	damage	damage
K120- 9%	1.23	55.71	24 h-15%	damage	damage
Sources	Current			[12]	

3.2. Fibre tensile analysis

Figure 1 shows the average tensile strength of treated KF with 3% $NaHCO_3$ (for 24 h, and 72 h, and 120 h) is higher compared to the untreated. When the $NaHCO_3$ concentration is increased up to 6%, the tensile strength of KF shows further increment except for fibre with immersion period of 120 h. However, at $NaHCO_3$ concentration of 9%, the tensile strength decreased. But, the decrease still higher compared to the untreated except for KF immersed for 120 h, which exhibit lower tensile strength.

These results indicate that KF still yield tensile strength but in low rates although the density and fibres diameter decrease. Overall, KF treated with 6% $NaHCO_3$ and immerse for 72 h show the highest average unit break among all by 382.3 MPa. From the results, it can be concluded that 3% $NaHCO_3$ concentration were not enough to expose the surface layer of the treated KF. Treatment with over 6% concentration of $NaHCO_3$ has been identified in eliminating the hemicellulose in fibres. Hence, the decreasing in hemicellulose has affected the mechanical properties and stiffness of KF by way of hemicellulose act as binder to strengthen the bonds between individual fibres. However, with exposure to heat treatment at 70°C for 24 h, the strength properties is enhanced regardless in any immersion period and it shows that the output from Table 1 is realistic with this findings.

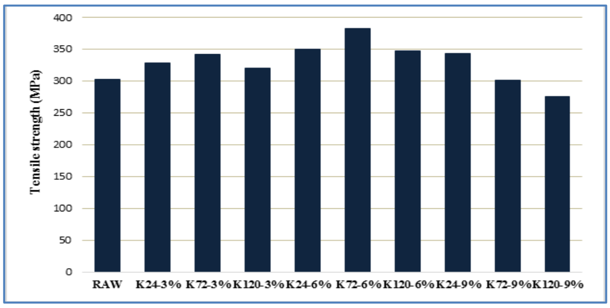


Fig. 1. Effect of $NaHCO_3$ on tensile strength of KF.

3.3. Crystallinity index

The effect of thermal treatment on tensile properties of KF was performed by XRD analyses for untreated and treated KF with 6% concentration of $NaHCO_3$. From the observation in Fig. 2, the spectrum of the K120-6% treated KF showed growth of similar spectra of untreated fibres. However, the peak of K72-6% became slightly sharper than the others due to effect of alkalization. Consequently, the cellulose crystallinity content had accelerated by eliminating hemicellulose, pectin, and lignin and it was parallel with discussion in the literature. While, the %Cr of untreated KF, K24-6%, K72-6%, and K120-6% are 51.3%, 58.9%, 60.2% and 54.8% respectively. After surface modification, it is obvious that the crystallinity phase of treated KF was increased significantly compared with untreated KF. While a decreased of %Cr shown in K120-6% due to longer time exposed to heat condition and the absorption of $NaHCO_3$ on the surface of KF. From the result, it can be conclude that CrI and %Cr of treated KF increase under heat treatment, but longer heating period will decreased the CrI. Moreover, it is related with removal of lignin with amorphous constituents from the fibre, resulting in stress relaxation and closer packing of the fibres. Thus, output from this research indicate that tensile strength of natural fibres have strong relationship with the crystallinity content in fibres.

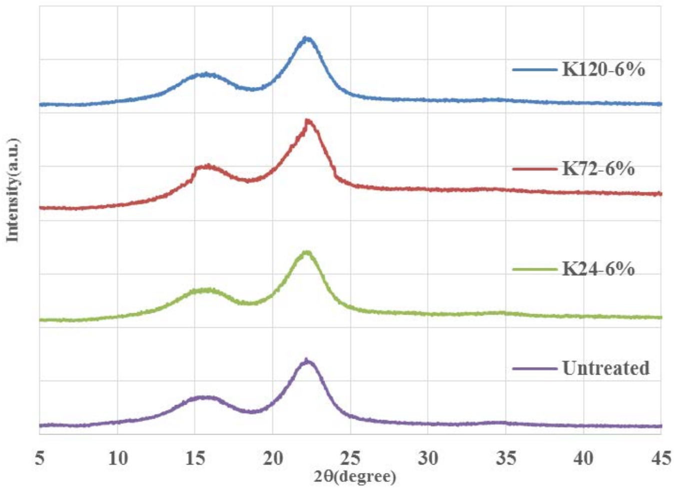
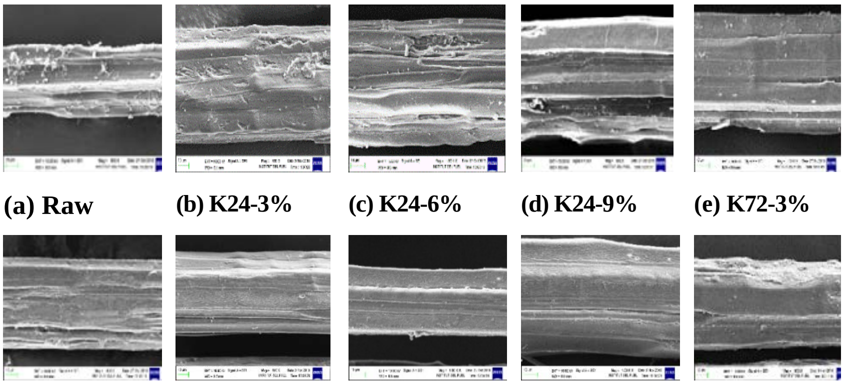


Fig. 2. XRD diffractograms of raw and alkali treated KF bundles.

3.4. Surface morphology of kenaf fibres

Surface morphology of untreated and treated KF is shown in Fig. 3. Figure 3(a) shows the SEM micrograph of untreated KF and observation shows the surface roughens with impurities. The appearance of hemicellulose, lignin, and wax is observed and the content of these compositions relate to the mechanical strength and stiffness to the fibre. After alkalization and heat treatment for 24 h, the fibres soaked in 3-9% $NaHCO_3$ concentration shows similar roughen surface. The impurities still remain on the fibre surface in Fig. 3(b) but the amount is reduced and the fibre in Figs. 3(c) and (d) is having cavities due to high concentration of $NaHCO_3$. Small particles can be seen sticking onto the fibres surface. It signifies that 24 h treatment with 3-9% $NaHCO_3$ was not the adequate percentage and period for effectively removing the impurities from the surfaces.

The SEM micrograph in Figs. 3(e) to (g) of KF treated for 72 h with $NaHCO_3$ shows the fibre surface slightly roughen and there is no cavities spotted with almost all impurities have been eliminates. While SEM micrograph of fibre surface immersed for 120 h with 3-9 % $NaHCO_3$ in Figs. 3(h) to (j) display no impurities and the surface was relatively smooth. However, density, diameter and tensile strength of fibres soaked for 120 h is relatively decreased which disclose the effect of fibre mineralization and degradation. The effectiveness of the alkali treatment which confirmed by SEM analysis indicate that longer immersion time has negative effect on the surface conditions. The use of $NaHCO_3$ with influent of time can eliminate impurities and enhance the tensile strength. Nonetheless, if used more than 6% concentration with soaking period over 72 h can accelerate stress weakness zones on the fibres and reduce the mechanical properties.



(a) Raw **(b) K24-3%** **(c) K24-6%** **(d) K24-9%** **(e) K72-3%**

(f) K72-6% **(g) K72-9%** **(h) K120-3%** **(i) K120-6%** **(j) K120-9%**

Fig. 3. SEM micrograph of raw and treated fibres.

4. Conclusions

KF are treated chemically with $NaHCO_3$ solution of different concentrations and immersion period and exposed to physical treatment (oven dried at 70°C±5°C for 24 h). The results shows that alkalization with thermal treatment have a great impact on tensile strength of KF. However, alkali concentration percentage was not the most significant factor that influences the KF tensile strength during fibres surface modification. Duration of immersion (from 72 h to 120 h) is found signify in further reduction of KF tensile strength. It is suggested that 6% mild $NaHCO_3$ and 72 h immersion period along with thermal treatment (70°C±5°C for 24 h) is the most effective combination for KF treatment. Higher fibre tensile strength has been proven by increment of tensile strength up to 382.3 MPa. SEM micrograph also showing high CrI in treated KF and further confirmed the observation. Thus, alkali treated KF shows better potential as reinforcement in composite with improved tensile strength that modified the fibres structure and generate high CrI. It also suggest that $NaHCO_3$ can be used as an alternative solution beside NaOH for alkalization treatment.

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