The effect of alkalization on the mechanical and water absorption properties of non-woven kenaf fiber/unsaturated-polyester composites produced by resin-transfer molding (RTM)

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Abstract
In the present study, mechanical and water absorption properties of non-woven kenaf fiber/unsaturated-polyester composites manufactured by resin transfer molding (RTM) were studied. Non-woven kenaf fiber mat with an aerial density of 1350 g/m² were treated with 6% NaOH solution for 3 hours. The influence of fiber treatment was investigated with dynamic contact angle, flexural, fracture toughness and scanning electron microscopy (SEM), measurements. A general trend was observed whereby alkalized kenaf fiber composites gave superior mechanical properties compared with untreated kenaf fiber composites. The immersion into water induced a drastic loss of mechanical properties of the composites albeit better retention of properties have been observed in the case of alkalized composites. The fracture surfaces were inspected by SEM which confirmed the quality of the interface.

1. Introduction

The use of natural fibers nowadays has gained much interest and moved into higher levels of applications and potential fields such as buildings, automotive and furniture industries. Most studies on natural fibers have focussed on fibers either in short and twisted forms and depending on the types of polymer matrices, the composites are being produced using techniques such as hand lay-up, injection and compression mouldings. Limited studies appear to be reported on the usage of natural fiber in non-woven form. From processing point of view, there are very limited publications reported on preparation of natural fiber composites using resin transfer molding (RTM) [1]. Recent studies on the use of kenaf fiber (*Hibiscus cannabinus L*) suggest that these fibers have the potential to be used as the reinforcing fibers in both thermoplastics and thermosetting polymers [2]. Kenaf fiber (KF) in the form of nonwoven mat ensures that the fiber are arranged homogenously within the RTM molded composites and exhibit better mechanical properties compared to composites produced using randomly arranged fiber [3]. The nonwoven mat is mechanically bonded by needle punching process which is responsible to consolidate the fiber by means of fiber interlocking, giving the nonwoven a firm three dimensional mat system.

The high polar characteristics of natural fibers render them less compatible with weakly polar or nonpolar polymers [4]. Alkalization is proven to be effective in increasing the adhesion between cellulosic fiber and polymeric matrix thereby enhancing the mechanical properties of composites [5]. This treatment improves fiber surface adhesive characteristic by removing hemicellulose and wax on fiber surface, and increase surface contact between defibrillation fibers and matrix [6]. In this research focus was given in investigating the effect of fiber treatment on the mechanical properties of the composites in both ambient and humid environments. Water absorption behavior was of particular interest since in service composites are frequently exposed to an environment in which the temperature and humidity vary in a prescribed manner. The influence of fiber treatment was investigated with dynamic contact angle, mechanical properties and scanning electron microscopy (SEM) measurements.

2. Experimental methods

2.1. Materials

KF non-woven mat was prepared using DILO nonwoven line. The areal density of the mat used is 1350 g/m^2 with stitching density of 50 cm^{-2}. Unsaturated polyester resin Reversol P9565 obtained from Synthomer Sdn. Bhd. was used as matrix. This polyester was cured with 1% methyl ethyl ketone peroxide from Merck as catalyst and 1% wt cobalt napthalene from Sigma Aldrich as accelerator. Table 1 shows typical properties of Reversol P9565

Viscosity (Cp)	Density (g/cm^3)	Volume shrinkage (%)	Gel time at 25^{o}C (Min)	Tensile strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
200 - 300	1.2	8.7	12-15	63.9 - 72	3.40 – 3.59	2.5 - 3.1

Table 1. Properties of unsaturated polyester (Reversol P9565)

2.2 Composite manufacturing

Alkalization was carried out by immersing nonwoven KF mats for 3 h in 6% NaOH solution [5]. After treatment, KF mats were rinsed with 1% acetic acid solution to neutralize excess sodium hydroxide. The KF mats were then thoroughly rinsed with water and were dried at room temperature. Composite laminates were prepared using RTM Innovator Megaject 3250 (Plastech). The ratio of hardener to unsaturated polyester was 1:100. Prior to molding, KF mats were re-dried at 60^{o}C for 3 h before were introduced into the mold cavity [7]. Resin was injected into the mold with an injection pressure of 1.3 bar and composite laminates were allowed to cure at room temperature for 12 h. All composite samples were prepared with KF content of 30 vol. %. Untreated and alkali treated nonwoven KF composites were referred as UKUPC and AKUPC respectively, while unsaturated polyester neat resin was denoted as UPR.

2.3 Fiber characterization

The crystallinity index (CrI) values of KF before and after treatments were performed on a D8 Diffractometer (Bruker-AXS) with copper radiation. The Cu K_α (λ = 1.5406 Å) was operated at 40 kW and 40 mA. CrI of untreated and treated fibers was calculated using equation reported elsewhere [8]. The wetting behavior of the fibers was characterized using a dynamic contact angle measuring instrument DCAT 21 (Dataphysics). All measurements were performed in 50% distilled water and 50% ethylene glycol. The water/material contact angles and polar and disperse components of surface energy for KF were calculated using Washburn equation [9] and Owens–Wendt–Rabel– Kaelble (OWRK) equations, respectively [10]. Micrographs of untreated and alkali treated fiber and composites were observed using a scanning electron microscope (SEM) Model Carl Zeiss Leo Supra 50 VP**.** Prior to the examination, the specimens were sputter-coated with gold.

2.4 Mechanical property measurements

Tensile properties of single kenaf fibers were evaluated in accordance to ASTM C 1557 standard test method using miniature tensile model Lex810 Dia-stron with a load cell of 300 gr. All mechanical tests i.e. flexural, fracture toughness and interlaminar shear strength (ILSS) of composites laminates were determined on universal testing machine model Instron 5960 at room temperature with 5 kN load cell according to ASTM D-790, ASTM D-5045 and ASTM D-2344, respectively. Dynamic Mechanical Analysis (DMA) was done using Mettler Toledo Model 861 under three-point bending configuration according to ASTM D5023-7 in a temperature range of 30-180 ^{o}C. The storage modulus (E') and tangent delta (tan δ) of the composites were measured at a frequency of 1Hz.

2.5 Water absorption tests

Water absorption study was performed in accordance to ASTM D 570-98. The percentage of water uptake at different time of immersion, diffusion coefficient (D) and maximum water uptake (M_m) were investigated using equations reported elsewhere [11]. After all samples achieved saturation, flexural and fracture toughness tests were carried out on the wet and re-dried samples to determine the residual properties of the composites.

3. Results and Discussion

3.1 Characterization of kenaf fibers

Crystallinity index (CrI) and tensile properties of untreated and alkali treated KF are depicted in Table 2. The CrI value, tensile strength and modulus of KF were found to increase upon alkalization. This is attributed to the removal of amorphous hemicellulose and lignin from the fiber and the rearrangement of cellulose chain into more compact manner which lead to an increase in its packing density [9]. Closer packing rearrangement of cellulose chains causes improvement in fiber strength and its mechanical properties [8].

Surface morphology of untreated and alkali treated KF as examined using SEM is shown in Figure 1. The presence of wax, oil and surface impurities on untreated KF can be observed covering the untreated fiber surface. On the contrary, modification of fiber by alkalization has effectively removed these impurities resulted in cleaner fiber surface. In addition, the surface of treated KF was found to be fragmented with groove-like structures due to the removal of cementing materials i.e. hemicellulose and lignin from the interfibrillar region [9]. Such structures favour better interfacial adhesion by increasing the specific contact area between fiber and matrix, promote friction between them, thus higher mechanical properties of the resultant composites can be expected.

Property	CrI	Tensile strength (MPa)	Elastic Modulus (GPa)
Untreated fiber	55.73 ± 0.83	251.4 ± 49.29	13.38 ± 5.36
Alkali treated fiber	60.39 ± 0.72	384.7 ± 67.77	29.40 ± 8.17

Table 2. The crystallinity index and the average tensile properties of untreated and alkali treated KF

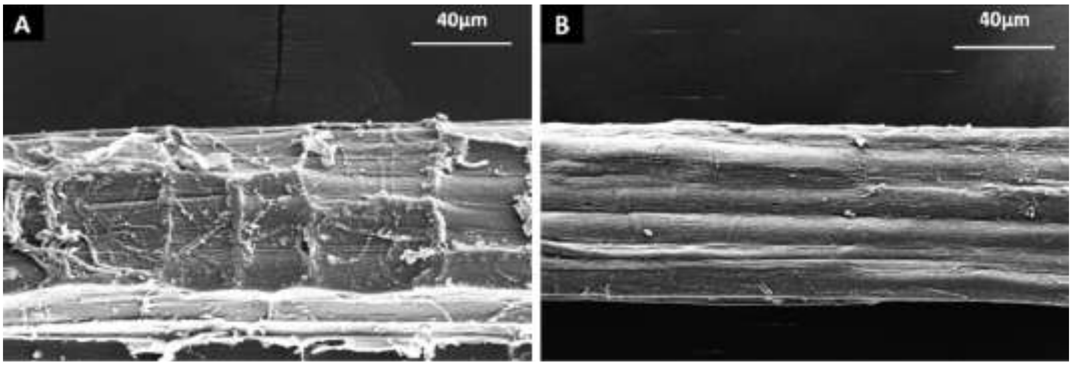

Figure. 1. SEM micrographs of longitudinal views of (a) untreated KF and (b) Alkali treated KF

According to Young-Dupree equation (Eq 1) [10], the increase of surface energy of fiber will enhance the work of adhesion. In other words, fibers can be wetted by the matrix if the surface energy of the fiber is higher than the matrix.

$$W_a = \gamma_1(1 + cos\theta) = \gamma_1 + \gamma_2 - \gamma_{12} \quad (1)$$

Where W_a is the work of adhesion, γ_1 is the surface energy of fluid, γ_2 is the surface energy of solid, γ_{12} is the interfacial surface energy and θ is the contact angle. Based on Table 3, alkalization increases the surface energy of KF, suggesting that alkali treated KF may exhibit better wettability towards UPR during molding. A good wettability is expected to improve the fiber-matrix interfacial adhesion thus mechanical properties of the composites.

Material	Contact angle in distilled water (^{o})	Contact angle in 50% ethylene glycol (^{o})	Dispersion (mN/m)	Polarity (mN/m)	Surface energy (mN/m)
Untreated KF	87.24 ± 0.01	75.25 ± 0.01	3.01	51.3	54.31
Alkali treated KF	82.62 ± 0.03	68.99 ± 0.03	4.81	63.51	68.31
Uncured UPR	-	-	-	-	33.11

Table 3. Contact angle, dipersion energy, polarity energy and surface energy of untreated and treated KF, and uncured UPR

3.2. Mechanical Properties of Composites

Table 4 shows mechanical properties of the composites and neat resin. An improvement of ILSS value by 32% is observed for AKUPC compared to UKUPC. Similar trend was observed for flexural properties of the composites. These findings are in agreement with the work done by Seki et al. [12]. AKUPC recorded higher flexural strength and modulus by 12% and l3%, respectively compared to UKUPC. This may be attributed to better fiber-matrix adhesion which improved stress distribution and stress transfer mechanism between KF and UPR. Alkalization improves the crystallinity of cellulose, making KF relatively stiffer and positively contributes towards higher flexural properties [13]. Figure 2 illustrates SEM showing the quality of adhesion between the untreated and treated KF with UPR. For AKUPC, some matrix patches are found to be attached to the fiber surfaces, as indicated by arrows shown in Figure 2(b).

	ILSS (MPa)	Flexural strength (MPa)	Flexural modulus (GPa)	K_c (MPa.m$^{1/2}$)
UPR	-	70.76±1.96	3.55±0.03	0.85±0.10
UKUPC	5.93±0.61	52.51±2.90	4.91±0.07	3.01±0.15
AKUPC	7.83±0.57	58.98±1.64	5.57±0.07	2.75±0.13

Table 4. Flexural, fracture properties, inter laminar shear strength properties of neat resin and its composites

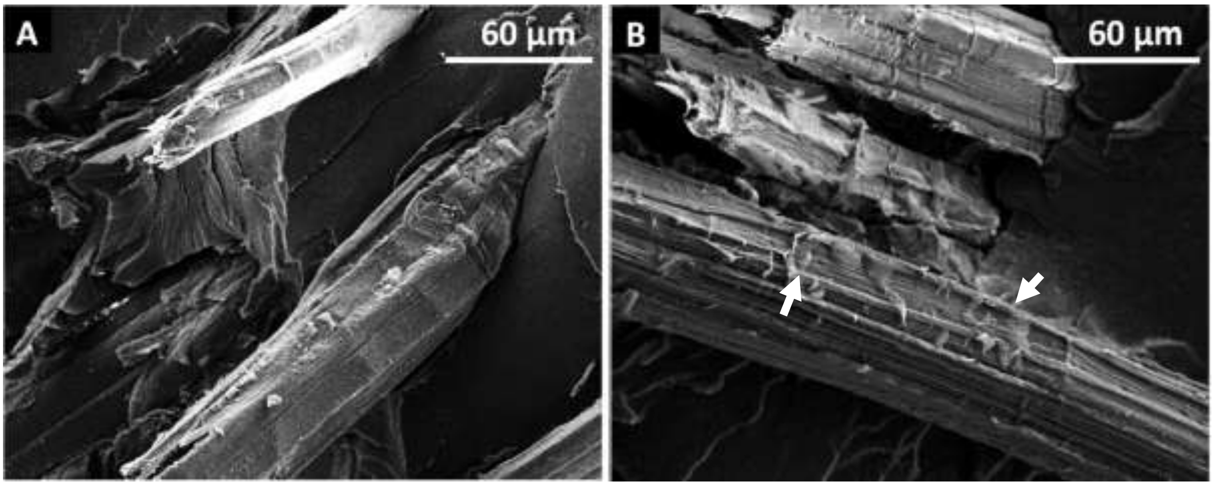

Figure 2. SEM micrographs of flexural fracture surface of: (a) UKUPC (b) AKUPC

As depicted in Table 4, incorporation of nonwoven imparts better fracture toughness, K_c, to polymer matrix. A significant increase in K_c values recorded for both UKUPC and AKUPC. However, AKUPC shows lower K_c than UKUPC suggesting that alkali treated fibers impaired the toughness of composites. The improved fiber-matrix adhesion in AKUPC inhibits the development of energy absorption mechanisms i.e. through fiber de-bonding and fiber pull-out consequently reducing the work of fracture for composites [14]

3.3. Dynamic mechanical analysis of composites

Figure 3 illustrates the temperature dependence of dynamic storage modulus (E') and tan (δ) of the neat resin and composites. The E' values of all samples decline in the transition region ranging from 70-100^{o}C. It can be seen that incorporation of KF in UPR has resulted in dramatic increase in E' of both UKUPC and AKUPC and the stiffening effect of KF is particularly obvious in the transition region. Prior to transition region, AKUPC exhibits higher E' values than UKUPC. As indicated earlier, this could be attributed to a greater fiber-matrix interfacial adhesion [13, 14]. It is interesting to note that, the effect of alkalization diminishes once the composites approach the transition region. This is obviously relates to the softening effect of the UPR. As expected, the presence of stiff KF has reduced the intensities of tan (δ) of UPR without significantly affecting its T_g. T_g of UPR, UKUPC and AKUPC obtained from the tan (δ) values were in the range of 81-85^{o}C.

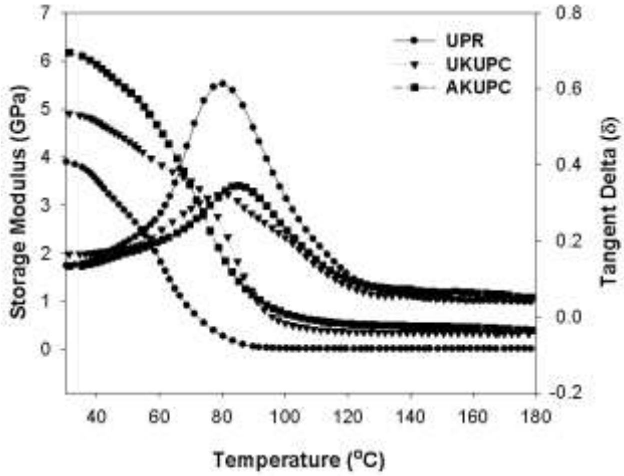

Figure 3. Dynamic storage modulus and tan δ of UPR, UKUPC and AKUPC.

3.4 Water Absorption

Figure 4 shows water absorption curves of neat resins and its composites. All samples exhibited a typical Fickian behaviour i.e. an initial rapid water uptake followed by saturation at a later stage of absorption. As expected, the presence of hydrophilic KF in UPR has resulted in rapid diffusion of water into composites and both UKUPC and AKUPC recorded higher maximum water uptake, M_m as compared to UPR. Alkalization treatment of KF has reduced the maximum water uptake of AKUPC compared to UKUPC. This is attributed to the removal of hemicellulose and lignin during alkalization. Hemicellulose is considered to be mainly responsible for water uptake, given that it is more accessible than the crystalline regions of the cellulose [15]. In addition, improved wettability and better adhesion between KF and UPR in AKUPC contributes to lower diffusion coefficient value (D) as shown in Table 5.

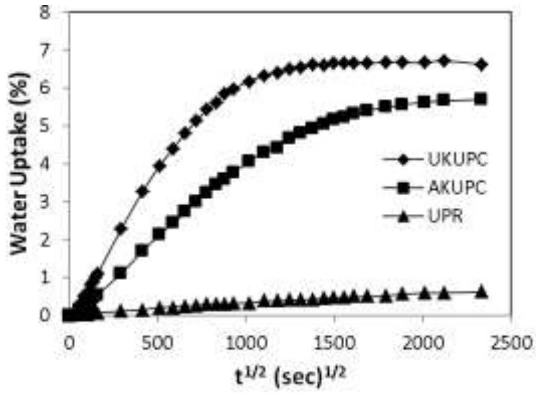

Figure 4. Water absorption behavior of UPR, UKUPC and AKUPC

Material	Maximum Water Uptake, M_m, (%)	Diffussion Coefficient, D, x 10^{-12} m^2/s
UPR	1.71	4.46
UKUPC	6.80	17.77
AKUPC	5.70	8.14

Tabel 5. The water absorption behavior of UPR, UKUPC and AKUPC

Table 6 shows the flexural properties and fracture toughness of neat resin and its composites in wet and re-dried states. Flexural strength and modulus values of composites decrease after immersion in water. The significant reduction in flexural strength of composites could be related to the effect of water on KF and damage at interfacial region. The water molecules act as plasticizers and destroy the rigidity of the cellulose structure [11, 16]. A good recovery of flexural properties upon redrying indicates that there was no permanent damage on KF and interfacial region incurred by water uptake. The slightly better retention of strength in AKUPC as compared to UKUPC may be attributed to the improved fiber- matrix adhesion which minimizes the adverse effect of water molecules at the interfacial region.

A similar trend could be observed in the case of toughness properties. Exposure to water has not affected the toughness of UPR. However, the effect is more profound in the case of UKUPC and AKUPC whereby the K_c values dropped by 24 % and 18%, respectively. A good recovery of toughness properties upon redrying provides a clear indication that the attack of water molecules at the constituent materials of the composites is of physical in nature.

Sample	Standard			Wet			Re-dried		
	Strength (MPa)	Modulus (GPa)	K_c (MPa.m$^{1/2}$)	Strength (MPa)	Modulus (GPa)	K_c (MPa.m$^{1/2}$)	Strength (MPa)	Modulus (GPa)	K_c (MPa.m$^{1/2}$)
UPR	70.76	3.55	0.82	59.16 (-16.39)	3.24 (-8.89)	0.84 (1.55)	65.07 [91.96]	3.44 [96.94]	0.82 [99.97]
UKUPC	52.51	4.91	2.97	35.14 (-33.08)	3.27 (-33.38)	2.26 (-24.01)	48.80 [92.93]	4.69 [95.56]	2.96 [99.29]
AKUPC	58.94	5.57	2.83	46.22 (-21.58)	3.57 (-35.88)	2.31 (-18.39)	58.12 [98.61]	5.18 [92.93]	2.47 [87.18]

( ) Percent change of wet sample toward control properties

[ ] Percent recovery of re-dried sample toward control properties

Table 6. Flexural and fracture toughness properties of UPR, UKUPC and AKUPC

4. Conclusions

The alkalization of KF not only improved the fiber tensile strength but also the quality of the fiber/matrix interface by increasing the fiber surface energy and removing impurities on fiber surface. This has led to the improvement of overall mechanical properties of the resulting composites. The water absorption was found to exhibit a Fickian behavior with alkali treated fiber composite exhibited lower water uptake and diffusivity. A good recovery of both flexural and fracture properties upon redrying provides a clear indication that the attack of water molecules on the composites is of physical in nature.

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