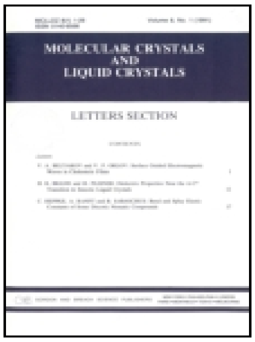

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Effects of Alkali Treatment on the Properties of Kenaf Fiber-Unsaturated Polyester Composites Prepared by Resin Transfer Molding

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Composites of untreated and 6% sodium hydroxide (NaOH) treated kenaf fiber mat and unsaturated polyester resin matrix were manufactured via a resin transfer molding (RTM) technique. The treated fibers were characterized with SEM and XRD. Contact angle measurements of the fibers were performed using a tensiometer. Alkali treated fiber-unsaturated polyester composites showed superior flexural properties than the composites with untreated fibers. The water absorption pattern of these composites was found to follow Fickian behavior. The tendency of the composites to absorb water decreased when alkali treated fiber mats were used.

Keywords Kenaf fiber; polyester; alkali treatment; crystallinity; tensile properties; flexural properties

Introduction

Natural fibers have been considered as reinforcements in many polymer matrix composites. In addition to being biodegradable, other advantages of such fibers are: low cost, low specific gravity, renewability, abundance, and high specific strength and stiffness. Currently, a wide variety of natural fibers such as sisal [1], hemp [2], jute [3, 4] and kenaf [5] fibers have been used in the production of thermoplastic and thermoset-based composites. There are, however, some major restrictions for the successful use of natural fibers in these composites. Among them are high susceptibility to moisture absorption and inherent incompatibility of natural fibers with many non-polar polymeric matrices both of which may result in composites with undesirable mechanical properties [2, 4]. Absorption of water by natural fiber can be minimized by modifying the basic chemistry of the fibers with chemicals such as NaOH via alkalization. Alkalization or alkali treatment leads to removal of non-structural materials such as wax and oils from the fiber surface [6] and partial removal of the fiber cell wall polymers, i.e. hemicelluloses and lignin [7, 8]. Such modifications resulted in some changes to the fiber surface morphology as well as chemistry and also the fiber strength

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*Address correspondence to Razaina Mat Taib, School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia. Tel.: 604-5996123; Fax: 604-5941011. E-mail: razaina@usm.my, dody_ariawan_uns@yahoo.com, zarifin@usm.my and stiffness. This eventually may impart some positive improvements on the mechanical properties of natural fiber-polymer composites.

Natural fiber-thermoset composites can be prepared via wet hand lay-up, press-molding, pultrusion, vacuum infusion molding and resin transfer molding techniques. The latter technique is an industrially important process, used to produce composites of various shapes, sizes and degrees of complexity. Studies reported on natural fiber-thermoset composites prepared by this technique are very limited [9].

In this research, composites were prepared from unsaturated polyester and non-woven kenaf fiber mat fiber via a RTM technique. The fiber mat was treated with NaOH solution prior to composite fabrication. The effects of treatment times on the flexural properties and water absorption behavior of these composites were determined and compared.

Experimental

Materials

The polymer matrix used was unsaturated polyester (Reversol P9565) obtained from Synthomer Sdn. Bhd. The initiating system comprised of methyl ethyl ketone peroxide (MEKP, 1.0 wt%) together with cobalt nafthenate (1 wt%). Kenaf fibers were supplied by Kenaf Fiber Industries Sdn. Bhd. Non-woven kenaf fiber mats were prepared using a carding machine followed by needle punching.

Fiber Treatment

Kenaf fiber mats were immersed in 6% solution of NaOH for 1, 2, 3, 4 and 5 hours at room temperature, then neutralized in dilute solution of glacial acetic acid. Finally the fiber mat was rinsed with deionized water and dried at room temperature for 24 h.

Resin Transfer Molding

The RTM machine used was the Innovator Megaject 3250 (8000) equipped with 2 reciprocating pumps. The pumps were filled with hardener and unsaturated polyester resin at a ratio of 1:100. The pump pressure was set at 0.13 MPa while the mold pressure guard was set at 0.06 MPa. Unsaturated polyester resin and hardener mixer was injected into the mold cavity at a constant flow rate. Kenaf fiber mat was placed in the mold cavity prior to filling. After injection was completed, the composite part was cured in the mold. The composite part was post-cured at 80°C (for 6 h) and at 130°C (for 2 h) to ensure a maximum conversion of styrene (the curing agent). Composites parts with fiber volume fraction of 30 wt% were produced via this technique.

Fiber Testing

The treated fiber was observed in a FESEM model Supra 35 VP to characterize the fiber surface morphology. Crystallinity index, *Crl*, of the fiber was determined using an X-ray diffractometer type D8 Bruker. The equatorial diffraction patterns (2θ) were recorded from 10 to 35° using Cu-Kα radiation at 40 KV and 40 mA. The crystallinity index, *Crl,* was calculated by using the following equation [10].

$$Crl = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \tag{1}$$

where I_{002} is the counter reading at peak intensity at a 2θ angle close to 22° representing the crystalline region and I_{am} is the counter reading at a 2θ angle of around 18° representing the amorphous region in the natural fibers. Contact angle measurements were performed using a Dataphysics tensiometer DCAT 21. The capillary rise technique was used and the wetting liquids were deionized water and ethylene glycol. The Washburn equation was used to determine contact angles.

Flexural Testing

Three-point bend tests were performed using an Instron model 5960 in according to ASTM D 790. Samples were tested at a crosshead speed of 2 mm/min. 5 samples for each composite were tested and their average was reported.

Water Absorption Study

Water absorption was conducted according to ASTM D 570. Samples of the composites were immersed in deionized water for 70 days. After removal from the water the samples were surface dried with a towel before measuring the weight. The weights of the samples were measured at regular intervals and the water uptake at any time (W_t) was calculated according to the following equation:

$$W_t(\%) = \frac{W_1 - W_2}{W_2} \times 100 \tag{2}$$

where W_1 and W_2 are the weight after the exposure time t and the dry weight, respectively.

Results and Discussion

Fiber Properties

Scanning Electron Microscopy. Observations of the treated fiber surface (Fig. 1(B)) revealed that the alkali treatment had resulted in the removal of cementing materials, hemicelluloses and lignin, from the interfibrillar regions and impurities such as oils and wax from the fiber surface. Very similar observations have been reported by other researchers

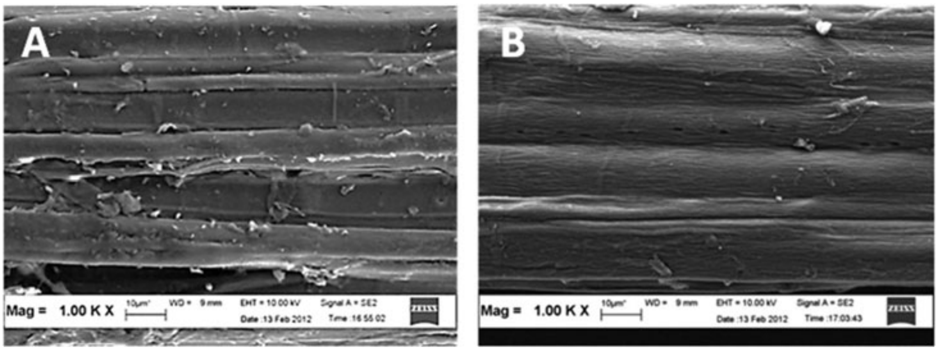

Figure 1. SEM micrographs of surfaces of (A) untreated and (B) 6% alkali treated kenaf fiber (treatment time = 5 hours).

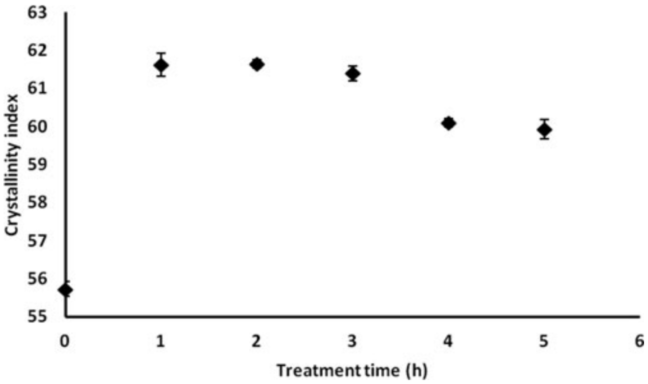

Figure 2. Crystallinity index of untreated and alkali treated kenaf fiber.

for grass fibers [8]. The exposed interfibrillar regions increased the specific surface area [11] of the fiber comes in contact with the polymer matrix during composite fabrication. Removal of impurities resulted in a cleaner and smoother fiber surface of the treated fiber.

X-Ray Diffraction. The crystallinity index of the kenaf fibers improved with alkali treatment (Fig. 2). The maximum improvement was observed after 2 h of treatment (+11%). Beyond that the crystallinity index of the treated fiber reduced but the values were higher than that of the untreated fiber. Changes in crystallinity through alkali treatment for natural fibers have been reported by many researchers [7, 10]. The improved crystallinity of natural fibers after the treatment can be attributed to the removal of cementing materials, which probably leads to better packing of cellulose chains [7] and thickening of the fiber cell wall [10]. Removal of these materials releases the initial strain between the cellulose chains. This allows the formation of new hydrogen-bonds leading to a closer packing of cellulose chains. At longer treatment times, i.e. longer than 2 h, excess extraction of hemicelluloses and lignin might have occurred and resulted in a slight disturbance of cellulose chain arrangement or alignment leading to a decrease in the cystallinity index of the alkali treated fiber [10].

Surface Free Energy. The specific (SP) and London (L) dispersive components of the surface free energy of the untreated and alkali treated kenaf fiber were determined by measuring the contact angles of two test liquids with their known specific and London dispersive components and analyzing the results in accordance with the method proposed by Owens and Wendt [12] and Kaelble [13] using the geometric mean

$$\gamma_L\left(1+\cos\theta\right)=2\left(\gamma_L^L\gamma_S^L\right)^{\frac{1}{2}}+2\left(\gamma_L^{SP}\gamma_S^{SP}\right)^{\frac{1}{2}} \tag{3}$$

where the subscripts L and S represent the liquid and solid states, respectively. Using the two wetting liquids the specific and London dispersive components of the fibers were calculated by the following equations

$$\gamma_S^{SP}=\frac{1}{4}\left[\frac{\left(1+\cos\theta_2\right)\gamma_2\left(\gamma_1^L\right)^{\frac{1}{2}}-\left(1+\cos\theta_1\right)\gamma_1\left(\gamma_2^L\right)^{\frac{1}{2}}}{\left(\gamma_1^L\gamma_2^{SP}\right)^{\frac{1}{2}}-\left(\gamma_2^L\gamma_1^{SP}\right)^{\frac{1}{2}}}\right]^2 \tag{4}$$

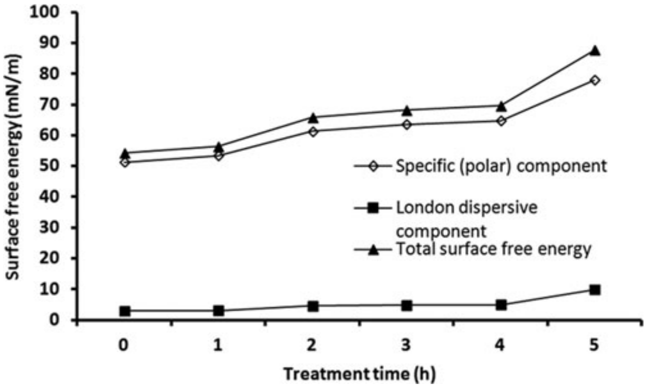

Figure 3. Surface free energies of untreated and alkali treated kenaf fiber.

$$\gamma_S^L = \frac{1}{4}\left[\frac{(1+\cos\theta_1)\,\gamma_1\left(\gamma_2^L\right)^{\frac{1}{2}} - (1+\cos\theta_2)\,\gamma_2\left(\gamma_1^L\right)^{\frac{1}{2}}}{\left(\gamma_1^L\gamma_2^{SP}\right)^{\frac{1}{2}} - \left(\gamma_2^L\gamma_1^{SP}\right)^{\frac{1}{2}}}\right]^2 \tag{5}$$

where the subscripts 1 and 2 in this study represent water and ethylene glycol, respectively.

The results of the surface free energies or surface tensions of the alkali treated kenaf fibers calculated from equations (4) and (5) are shown in Fig. 3. The total surface free energy of the alkali treated kenaf fibers increased, while the London dispersive component remained nearly constant with increasing treatment time. This surface free energy increase can be attributed to the increase in polarity due to the increased cellulose content on the fiber surface, resulting from the removal of impurities as well as cementing materials, hemicelluloses and lignin from the fiber surface following the alkali treatment.

Flexural Properties

Figure 4 shows the flexural modulus and flexural strength of kenaf fiber-unsaturated polyester composites. The flexural strength of the alkali treated kenaf fiber composites was greater than that of the untreated composite (Fig. 4(A)). Such positive improvement was observed when the kenaf fiber mat was treated with alkali for more than 1 h. The highest improvement in the property (+12%) was observed when the fiber mat was alkali treated for 3 h. The increased in the property can be attributed to the enhanced interfacial adhesion between the resin matrix and the kenaf fiber. Alkali treatment may result in fiber fibrillation due to the removal of cementing materials, hemicelluloses and lignin, between the macrofibrils [8]. The exposed interfibrillar regions increased the effective fiber surface area available for wetting by the unsaturated polyester resin during the composite fabrication [11]. In addition, such fiber surface morphology may improve fiber-matrix adhesion by introducing sites of mechanical interlocking [3]. Another factor that can be considered is improved fiber strength due to the increase in cellulose crystallinity following the alkali treatment [10]. Beyond 3 h of alkali treatment the flexural strength of the composites started to decrease but the values were higher than the untreated composite. This observation can be attributed to the decrease in the cellulose crystallinity of the kenaf fiber after prolonged alkali treatment [14].

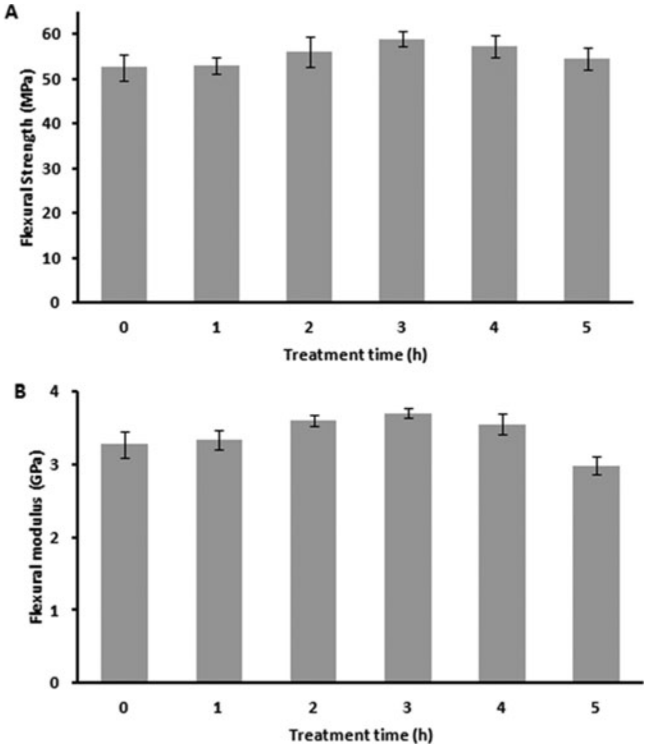

Figure 4. (A) Flexural strength and (B) flexural modulus untreated and alkali treated kenaf fiber composites.

The flexural modulus of the alkali treated kenaf fiber mat composites also exhibited similar trends. After 5 h of alkali treatment, however, the flexural modulus of the composite decreased (−9%) to a value much lower than that of the untreated composite. Prolonged immersion in alkali solution might have resulted in an excessive extraction of the cementing materials that could have loosened the bound structure of the macrofibrils [14] and damaged the fiber cell walls. This eventually may decrease the fiber stiffness to some extent and resulted in a decrease in the flexural properties of the composites.

Water Uptake

Figure 5 shows the water uptake curves for untreated and alkali treated kenaf fiber mat composites. The uptake of water by the composites was due to the hydrophilic character of the kenaf fiber. Both water uptake curves show similar patterns, i.e. a linear increase in water uptake followed by gradual increase and finally a plateau suggesting that the water absorption behavior of these composites follows the Fickian behavior. The alkali treated kenaf fiber mat composite absorbed less water overall than the untreated composite. This is probably due to the removal of hygroscopic hemicelluloses to some extent from the fiber cell walls due to the alkali treatment. Another factor is better wetting out of the unsaturated polyester resin onto the fiber surface which reduces the relative number of interfacial voids through which water may ingress into the composite samples.

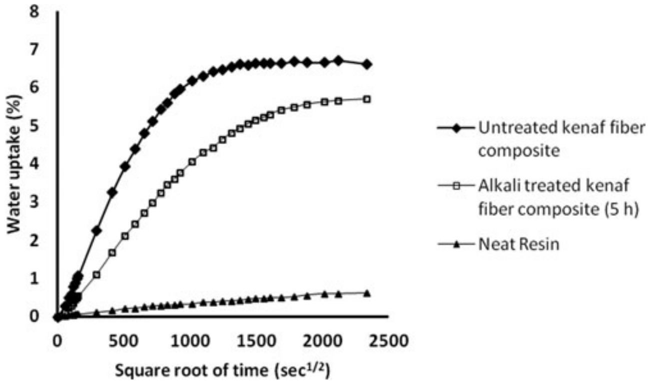

Figure 5. Water uptake curves for untreated and alkali treated kenaf fiber composites (the fiber mat was alkali treated for 5 h).

Conclusions

1. The morphology and structure of the kenaf fibers changed after the alkali treatment. SEM micrographs revealed that the fiber surface became cleaner and smoother after the treatment. The interfibrillar regions were also clearly observed. The crystallinity index as well as surface free energies of the fibers increased following the alkali treatment.
2. Composites with alkali treated kenaf fiber mat showed better both flexural strength and modulus compared to composites with untreated kenaf fiber mat. Maximum improvement in the flexural properties was observed when the kenaf fiber mat was alkali treated for 3 h.
3. Prolonged alkali treatment resulted in a decrease of the flexural properties of the composites due to the negative impact of the treatment on the fiber properties.
4. Composites with alkali treated kenaf fiber mat showed better resistance to water uptake than composites with untreated kenaf fiber mat due to improved fiber wetting by the matrix resin as well as the removal of hygroscopic hemicelluloses from the fiber surface.

Funding

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