

Investigation of Vegetable-Oil-Based Coupling Agents for Kenaf-Fiber-Reinforced Unsaturated Polyester Composites

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ABSTRACT: Kenaf fibers are modified with three novel coupling agents that consist of an isocyanate and acrylated epoxidized soybean oil. The untreated-kenaf-UPE (unsaturated polyester) composites and coupling-agent-treated-kenaf-UPE composites are obtained by a compression molding process. Modifications of kenaf fibers with coupling agents significantly increase mechanical properties, and enhance water resistance of the resulting kenaf-UPE composites. Characterization of coupling-agent-treated-fibers with Fourier transform infrared spectroscopy reveals that coupling agents are covalently bonded onto kenaf fibers. Improved interfacial adhesion between kenaf fibers and UPE resin is confirmed with scanning electron microscopy. The mechanisms on which the chemical treatments of kenaf fibers improve the mechanical properties and water resistance are discussed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Natural fibers have the potential for replacement of glass fiber for the production of natural-fiber-reinforced polymer composites (NFRPs) due to their advantages of being abundant, renewable, inexpensive, and readily available.^{1–4} NFRPs are one of the fastest growing sectors in the composites industry. They have the advantages of higher specific modulus, higher specific strength, lower density, and lower cost than glass-fiber-reinforced polymer composites that are currently used in the composite industry. They have many potential applications in automotive, aircraft, electrical, and appliance components as substitutes for traditional materials.^{5–8}

Kenaf fibers are one of the natural fibers that are gaining popularity as reinforcing materials for kenaf-polymer composites. Kenaf is an herbaceous annual plant. It grows quickly, and can rise up to 4–5 m high and 25–35 mm in diameter in a growing period of 90–150 days.^{9–11}

Unsaturated polyester (UPE) is one of the most commonly used thermosetting resins for fiber reinforced composites. Its widespread application is due to its many favorable characteristics, including low cost, ease of cure at room temperature, ease of molding, a good balance of mechanical, electrical, and chemical properties, and a wide experience base in developing technologies and design parameters.^{12–15} In general, these advantages render UPE to be the first choice of the resin for many composite products.

Kenaf-UPE composites have some drawbacks that have to be improved before their wide spread applications. First, hydrophilic kenaf fibers are incompatible with hydrophobic UPE matrix. This incompatibility results in poor interfacial adhesion. Consequently, the strength of the fibers is not fully utilized for reinforcing the UPE matrix.^{16,17} The kenaf-UPE composites still have a fairly high water-uptake. The water-uptake may result in swelling, generation of voids and deformation of the composites, which typically lead to strength loss and dimensional instability of the composites.^{18,19} The chemical or physical treatment of fibers is currently an area of research receiving significant attention. Electron beam irradiation of kenaf fibers improved the mechanical properties of the kenaf-UPE composites, but did not reduce the water-uptake.²⁰ The modification of kenaf fibers with alkali successfully enhanced the flexural strength and flexural modulus of the kenaf-UPE composites. However, the treatments also did not reduce the water-uptake.²¹ Chemical modifications of kenaf fibers with silane coupling agents improved the mechanical properties of the kenaf-UPE composites, but the water-uptake of the resulting kenaf-UPE composites were not determined.²² Surface coating and edge sealing reduced the water-uptake of the composites. This treatment, however, has shown no evidence of enhancing the flexural strength and flexural modulus.²³ The treatment of kenaf fibers with a combination of 1, 6-diisocyanato-hexane and 2-hydroxyethyl acrylate, and with N-methylol acrylamide significantly

improved the mechanical properties and significantly reduced the water-uptake of the resulting kenaf-UPE composites.^{24,25} However, all those coupling agents are derived from petrochemicals, and are not renewable and not sustainable in the long run. More importantly, the mechanical properties and water resistance of the kenaf-UPE composites are still inferior to those of glass fiber-reinforced UPE composites. There is a need for further improvements on the mechanical properties and water resistance of the kenaf-UPE composites. Acrylated epoxidized soybean oil (AESO) is commercially produced from the reaction of epoxidized soybean oils with acrylic acid. AESO is commonly used as a plasticizer, a crosslinking agent, a stabilizer, and a prepolymer.^{26,27} However, little has been published on whether AESO can serve as an effective coupling agent for kenaf-UPE composites. In this study, combinations of partly renewable AESO and isocyanates were investigated as coupling agents for the kenaf-UPE composites.

EXPERIMENTAL

Materials and Apparatus

Kenaf fibers were obtained from Wilhelm G. Clasen services (Dhaka, Bangladesh). Aropol 7030 (a mixture of about 60% unsaturated polyester and 40% styrene) and LP-4016 [poly(vinyl acetate)] were obtained from Ashland Chemical (Columbus, OH). Zinc stearate was purchased from Acros Organics (Morris Plains, NJ). Styrene, *tert*-butyl peroxybenzoate (TBPB), AESO (average $M_n = 1200$), 1, 6-diisocyanatohexane (DIH) (98%), and 4, 4'-methylenediphenyl diisocyanate (MDI) (98%) were purchased from Sigma-Aldrich (St. Louis, MO). Polymeric methylene diphenyl diisocyanate (PMDI) was obtained from Huntsman Polyurethanes (West Deptford, NJ). Anhydrous ethyl acetate was purchased from EMD Chemicals (Gibbstown, NJ). Differential scanning calorimetric (DSC) graphs were obtained from a TA DSC 2092 (TA Instruments, New Castle, DE). The hot-pressing was performed on an automatic Benchtop Carver press (Carver, Wabash, IN). Flexural properties were obtained from a Sintech machine (MTS Systems, Enumclaw, WA). Scanning electronic microscope (SEM) graphs were obtained by a FEI Quanta 600 SEM (Hillsboro, OR). Fourier transform infrared (FTIR) spectra were obtained with a Nexus 470 spectrometer (Thermo Nicolet, Madison, WI), using a KBr pellet method.

Preparation of Kenaf Fiber Mats

Kenaf fibers (100 g, 2 inches in length) with a moisture content of 10% were fed into a LOUET drum carder for tearing apart fiber bundles and forming unidirectional oriented kenaf fiber mats through a carding, layering and needle-punching process. The resulting fiber mats were cut by a paper cutter into 5 mats, with each mat having the dimension of 200 mm × 200 mm × 10 mm. The fiber mats were stacked horizontally in an aluminum tray and oven-dried at 103°C for at least 20 h before use.

Preparation of UPE Resin

Aropol 7030 resin (62.2 parts) and LP-4016 (28.6 parts) were mixed together to form a solution. Styrene (4.8 parts) and zinc stearate (4.4 parts) were added to the solution and the resulting mixture was mechanically stirred at room temperature for 2 h to form a UPE resin.

Treatment of Kenaf Fiber Mats with Combinations of AESO and an Isocyanate

Treatment of Kenaf Fiber Mats with Combinations of AESO and DIH. The AESO (5.560 g, 4.64 mmol) and DIH [0.780 g dry weight, 4.64 mmol, 9.28 mmol isocyanate functional group (NCO)] were dissolved in anhydrous ethyl acetate (80 mL). The mixture was magnetically stirred at room temperature for 10 min and was then sprayed onto five oven-dried kenaf fiber mats (78 g). More specifically, the resulting solution (about 16 mL) was evenly sprayed onto both faces of each oven-dried kenaf fiber mat (about 15.6 g) by a spray bottle. The resulting five AESO-DIH-treated fiber mats were stacked horizontally in an aluminum tray and oven-dried at 80°C for 3 h. The resulting fiber mats were designated as DIH-1, meaning that the treated fibers contained 1 wt % DIH based on the dry weight of kenaf fiber mats. The molar ratio of NCO/AESO was 2 : 1 (the number average molecular weight of 1200 was used for calculating moles of AESO).

This same procedure was used for preparation of AESO-DIH-treated kenaf fibers that contained 3, 5, and 7 wt % of DIH with the molar ratio of NCO/AESO being 6 : 1, 10 : 1, and 14 : 1, respectively. The resulting AESO-DIH-treated kenaf fibers were designated as DIH-3, DIH-5, and DIH-7, respectively. The usage of AESO was maintained at 5.560 g for the 78 g of dry kenaf mats for all AESO-DIH-treated kenaf fibers. After the oven-drying, the AESO-DIH-treated fiber mats were immediately used for making kenaf-UPE composite boards.

Treatment of Kenaf Fiber Mats with Combinations of AESO and MDI, and Combinations of AESO and PMDI. The same procedure as described previously for treatment of kenaf fiber mats with combinations of AESO and DIH was used for treatment of fiber mats with combinations of AESO and MDI, and combinations of AESO and PMDI. The isocyanate usage, AESO usage, and molar ratios of NCO/AESO are specified in Table I.

Hot-Press Procedure for Preparation of Kenaf-UPE Composites

UPE resin (78 g) and TBPB (1.2 g) were mixed by spatula for 1 min and the resulting UPE-TBPB mixture (15.8 g) was uniformly poured onto an oven-dried kenaf fiber mat that had been placed into a stainless steel mold with the dimension of 200 mm × 200 mm × 3 mm. The second mat was stacked above the first mat in a way that the length of kenaf fibers was oriented in the same direction, and the resulting UPE-TBPB mixture (15.8 g) was then uniformly poured onto the second mat. This process was repeated until a stack of five mats was made. The mold was placed onto the lower platen of an automatic Benchtop Carver press, and pressed at 3.24 MPa for 10 min at room temperature allowing for thorough penetration of UPE resin into fibers. The mold was pressed at 4.24 MPa while the temperature of platens was raised to 160 °C. The hot press was maintained with a pressure of 4.24 MPa at 160 °C for 20 min. After that, the heating of the hot-press was turned off and two plywood boards were put at the top and bottom of the mold, respectively, to insulate the heat. The mold was pressed at 4.24 MPa for 100 min and then removed from the hot press and cooled at ambient environment. The resulting composites

Table I. Treatment of Kenaf Fiber Mats with Combinations of AESO and Isocyanates

	Isocyanate weight (dry) (g)	AESO weight (g)	Molar ratio of NCO/AESO
DIH-1	0.78	5.560	2 : 1
DIH-3	2.34	5.560	6 : 1
DIH-5	3.90	5.560	10 : 1
DIH-7	5.46	5.560	14 : 1
MDI-1	0.78	3.740	2 : 1
MDI-3	2.34	3.740	6 : 1
MDI-5	3.90	3.740	10 : 1
MDI-7	5.46	3.740	14 : 1
PMDI-1	0.78	3.477	2 : 1
PMDI-3	2.34	3.477	6 : 1
PMDI-5	3.90	3.477	10 : 1
PMDI-7	5.46	3.477	14 : 1

had a fiber loading of 50 wt%. The kenaf fiber mats without any treatment were used for making untreated-kenaf-UPE composites as control.

Determination of Flexural Properties of the Kenaf-UPE Composites

For the flexural test, each specimen had a rectangular dimension of 70 mm × 14 mm × 3 mm. The longitudinal direction of the test specimen was parallel to the longitudinal direction of the fibers. The three-point flexural test was performed on a Sintech testing machine in accordance with ASTM D 790-03, with a 50 mm span, crosshead moving downward at a speed of 5 mm/min. The flexural strength and flexural modulus were obtained from the test.

Water-Uptake of the Kenaf-UPE Composites

Method 1: Soaking the Composite Specimens in Distilled Water at Room Temperature. Each specimen had a dimension of 80 mm × 25 mm × 3 mm. All specimens were weighed and then soaked in water at room temperature in accordance with ASTM D 5229 M-04. At a predetermined time, the specimens were removed from water, wiped with tissue paper, weighed and then put back to water for continued soaking. The water-uptake was obtained from the weight gain divided by dry weight of the specimen.

Method 2: Soaking the Composite Specimens in Boiling Water. Each specimen was cut into a dimension of 80 mm × 25 mm × 3 mm. All specimens were weighed and then soaked in boiling water for 4 h. The specimens were then removed from water, wiped with tissue paper, and weighed. The water-uptake was obtained from the weight gain divided by dry weight of the specimen.

Characterization of Fractured Kenaf-UPE Composites with SEM

Specimens after the flexural test were cut to small pieces for SEM imaging, the cross area of fractured surface having a

dimension of 5 mm × 3 mm. The fractured surfaces of the specimens were coated with an Au-Pd film in the coater for 50 s before testing. The SEM images were obtained at an accelerating voltage of 10.0 kV.

Characterization of Untreated and Coupling-Agent-Treated Kenaf Fibers with FTIR

The AESO (0.56 g) and DIH (0.24 g) were dissolved in anhydrous ethyl acetate (8 mL). The solution was magnetically stirred at room temperature for 10 min. Oven-dried kenaf fibers (8 g) were immersed into the resulting AESO-DIH solution for 5 min, and the fibers with the solution were oven-dried all together at 80°C for 3 h for forming AESO-DIH-treated kenaf fibers. The AESO (0.37 g) and MDI (0.24 g) were dissolved in anhydrous ethyl acetate (8 mL). The AESO (0.35 g) and PMDI (0.39 g) were dissolved in another anhydrous ethyl acetate (8 mL). The same procedure as described previously for making AESO-DIH-treated kenaf fibers was used for preparation of AESO-MDI- and AESO-PMDI-treated kenaf fibers.

Untreated kenaf fibers and each of coupling-agent-treated kenaf fibers (3 g) were wrapped with filter paper and then extracted with ethyl acetate in a Soxhlet extractor for 48 h, respectively. The extracted fibers were oven-dried at 80°C for 3 h and then cut into small pieces for FTIR characterization. FTIR spectra were recorded using a KBr pellet method and the number of scans for each sample was 64. The kenaf/KBr weight ratio was the same for all kenaf fibers.

Statistical Analysis

Data from flexural tests and water-uptake tests were analyzed with two sample *t*-test method for comparing whether the average difference between two groups is really significant or if it is due to random chance using *R* statistical software (Boston, MA). All *P*-values were based on a 95% confidence interval.

RESULTS AND DISCUSSION

The effect of AESO-DIH treatment on the flexural properties of kenaf-UPE composites is shown in Table II. Compared with the control, i.e., at 0% DIH, the AESO-DIH treatment at 1 wt % DIH, i.e., DIH-1, did not increase the flexural strength or flexural modulus of the composites. The treatment at 3 wt % DIH (i.e., DIH-3) significantly increased the flexural strength ($P = 0.001$), but did not significantly increase the flexural modulus ($P = 0.296$). AESO-DIH treatments of kenaf fibers at 5 wt % DIH (i.e., DIH-5) significantly improved both the flexural strength ($P = 0.002$) and flexural modulus ($P = 0.018$) by 28 and 10% over the control, respectively. However, the flexural strength and flexural modulus sharply decreased when the DIH usage was further raised from 5 wt % (i.e., DIH-5) to 7 wt % (i.e., DIH-7). Results from Table II demonstrated that the kenaf-UPE composites at 5 wt % DIH had the highest flexural strength and flexural modulus.

The effects of AESO-MDI as a coupling agent on the flexural properties of the composites are shown in Table II. The AESO-MDI treatment at 1 wt % MDI (i.e., MDI-1) did not significantly improve the flexural strength or flexural modulus of the composites over the control. The treatment at 3 wt % MDI (i.e., MDI-3) significantly increased the flexural strength ($P =$

Table II. Results of Flexural Properties and Water-Uptake for the Coupling-Agents-Treated Kenaf-UPE Composites

	Flexural strength (MPa)	Flexural modulus (GPa)	Flatten-out water-uptake at room temperature (%)	Water-uptake in boiling water (%)
Control	121 ± 5.1 ^a	11.5 ± 0.3	33.3 ± 2.5	35.7 ± 1.8
DIH-1	125 ± 2.9	11.4 ± 0.3	22.1 ± 0.7	15.3 ± 2.7
DIH-3	155 ± 3.6	12.1 ± 0.4	20.4 ± 0.4	17.7 ± 2.2
DIH-5	153 ± 4.3	12.7 ± 0.2	21.5 ± 0.7	12.3 ± 0.7
DIH-7	140 ± 2.2	10.8 ± 0.3	19.4 ± 0.6	8.4 ± 0.7
MDI-1	127 ± 5.0	11.9 ± 0.2	25.1 ± 0.1	22.0 ± 4.4
MDI-3	158 ± 5.5	13.0 ± 0.5	22.3 ± 1.0	20.8 ± 4.3
MDI-5	156 ± 5.6	11.6 ± 0.5	25.5 ± 0.4	16.1 ± 2.6
MDI-7	128 ± 5.4	11.0 ± 0.4	26.0 ± 0.3	15.5 ± 2.4
PMDI-1	124 ± 5.4	11.7 ± 0.3	22.5 ± 0.9	18.6 ± 1.7
PMDI-3	137 ± 4.4	11.4 ± 0.3	20.8 ± 1.3	14.3 ± 1.7
PMDI-5	152 ± 1.4	12.5 ± 0.4	21.4 ± 0.7	13.8 ± 1.5
PMDI-7	139 ± 2.9	11.2 ± 0.3	23.0 ± 0.8	19.4 ± 1.7

^aFor all the values in the Table A ± B, A is the mean of five replicates and B is a standard error of the mean.

0.002) and flexural modulus ($P = 0.047$) by 31% and 13% over the control, respectively. Increasing the MDI usage from 3 to 5 wt % (i.e., from MDI-3 to MDI-5) in the AESO-MDI treatments did not significantly change the flexural strength ($P = 0.796$) or the flexural modulus ($P = 0.103$) of the composites. The flexural strength and flexural modulus dramatically decreased when the MDI usage was further raised from 5 to 7 wt % (i.e., from MDI-5 to MDI-7). Thus, 3 wt % MDI usages, i.e., MDI-3 was optimum for the treatment of kenaf fibers in terms of enhancing the flexural properties.

The effects of kenaf fiber treatment with AESO-PMDI on the flexural properties of the composites are shown in Table II. When compared with the control, the AESO-PMDI treatments at 1 wt% PMDI (i.e., PMDI-1) and 3 wt% PMDI (i.e., PMDI-3) did not significantly increase the flexural strength or flexural modulus of the composites. The 5 wt% PMDI (i.e., PMDI-5) increased the flexural strength ($P = 0.0005$) by 28%, but did not improve the flexural modulus ($P = 0.123$) over the control. Increasing the PMDI usage from 5 wt% to 7 wt%, i.e., from PMDI-5 to PMDI-7 significantly decreased the flexural strength and flexural modulus. Results from Table II demonstrated that PMDI-5, i.e., the kenaf-UPE composites at 5 wt % PMDI usage had the highest flexural strength.

DIH-5, MDI-3, and PMDI-5 were the optimum, respectively, in terms of improving the flexural properties of the kenaf-UPE composites. The two-sample *t*-test analysis revealed that flexural strengths and flexural modulus for DIH-5, MDI-3, and PMDI-5 were not significantly different from each other.

The water-uptake of the AESO-DIH-treated-kenaf-UPE composites at room temperature is shown in Figure 1. All the water-uptake increased with increase in the soaking time below 20 days at each pre-determined soaking time and then flattened

out when the soaking time was above 20 days. The AESO-DIH treatment at 1 wt% DIH (i.e., DIH-1) significantly lowered the water-uptake of the composites at each pre-determined soaking time when compared to the control. The two-sample *t*-test revealed that the water-uptake after 20 days of soaking was not significantly different for DIH-3 and DIH-5 at each predetermined soaking time. The water-uptake after 20 days of soaking between DIH-1 and DIH-7 was significantly different, while the

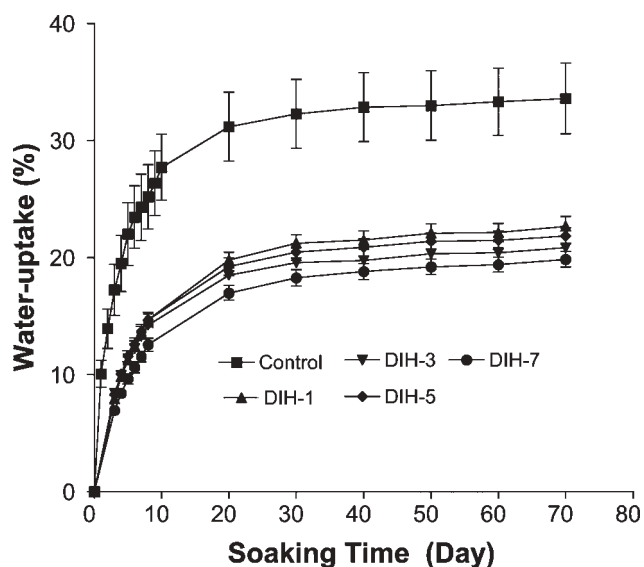


Figure 1. Effect of AESO-DIH treatments of kenaf fibers on the water-uptake of the composites in water at room temperature. (Data are the mean of five replicates and the error bars represent a standard error of the mean.)

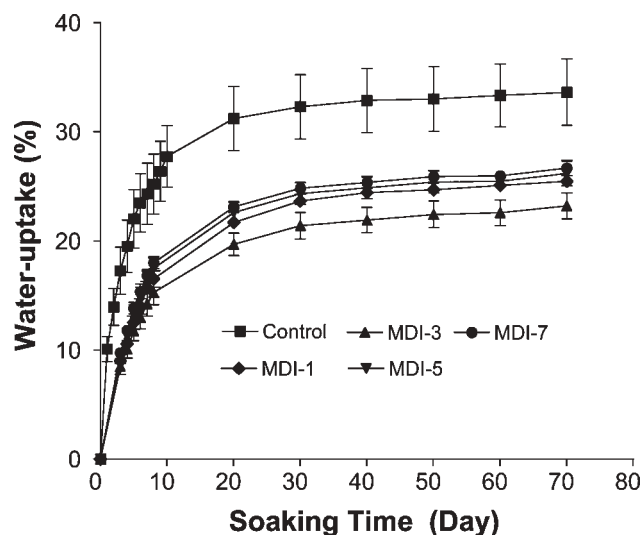


Figure 2. Effect of AESO-MDI treatments of kenaf fibers on the water-uptake of the composites in water at room temperature. (Data are the mean of five replicates and the error bars represent a standard error of the mean.)

water-uptakes between DIH-1 and DIH-3, DIH-1 and DIH-5, and DIH-3 and DIH-5 were not significantly different at each predetermined soaking time.

Treatments of kenaf fibers with AESO-MDI significantly lowered the water-uptake at all MDI usage levels (Figure 2). The water-uptake increased with increase in the soaking time below 30 days at each soaking time and then flattened out when the soaking time was above 30 days. The composites with 1 wt% MDI (i.e., MDI-1) had a significantly lower water-uptake than the control. Increasing the MDI usage from 1 wt% to 3 wt% (i.e., from MDI-1 to MDI-3) significantly decreased the water-uptake. However, further increase in the MDI usage from 3 wt% to 5 wt% (i.e., from MDI-3 to MDI-5) increased the water-uptake. The composites with 5 wt% MDI had the water-uptake comparable to those with 7 wt% MDI at all soaking times. The results from Figure 2 indicated that 3 wt% MDI was optimum for the treatment of kenaf fibers in terms of reducing the water-uptake. The flatten-out water-uptake of MDI-3 was about 22%, significantly lower than that of the control which was 33%.

Treatments of kenaf fibers with AESO-PMDI significantly decreased the water-uptake at all PMDI levels (Figure 3). All water-uptake increased with the soaking time below 30 days at each pre-determined soaking time and then flattened out above 30 days. 1 wt% PMDI (i.e., PMDI-1) significantly lowered the water-uptake over the control. Increasing the PMDI usage to 3 wt% (i.e., PMDI-3) further decreased the water-uptake. However, increasing the PMDI usage to 5 wt% (i.e., PMDI-5) and 7 wt% (i.e., PMDI-7) enhanced the water-uptake over PMDI-3. The results from Figure 3 indicated that 3 wt% usage of PMDI was optimum for the treatment of kenaf fibers regarding the water-uptake. The flatten-out water-uptake of PMDI-3 was about 21%, significantly lower than that of the control which was 33%.

DIH-7, MDI-3, and PMDI-3 were the optimum treatments, respectively, in terms of reducing the water-uptake of the kenaf-UPE composites at room temperature when the water-uptake flattened out. DIH-7 significantly lowered water-uptake as compared to MDI-3 ($P = 0.027$), and MDI-3 had no statistical difference in terms of lowering water-uptake as compared with PMDI-3 ($P = 0.192$). Effects of these treatments on reduction of the water-uptake were $DIH-7 > PMDI-3 \approx MDI-3$.

The boiling water test is an accelerated aging test for the composites. This test can potentially be used for predicting the water-uptake of the composites when they are used in a hot and wet environment such as an exterior wet environment under direct sunlight. For AESO-DIH treated-kenaf-UPE composites, DIH-1 significantly lowered the water-uptake over the control in boiling water (Table II). DIH-3 did not further change the water-uptake over DIH-1. Increasing DIH usage to 5 wt % (i.e., DIH-5) and 7 wt % (i.e., DIH-7) further decreased the water-uptake over DIH-1. DIH-7 decreased the water-uptake by 76% over the control.

MDI-1 significantly lowered the water-uptake over the control in boiling water (Table II). Increasing the MDI usage from 1 wt % (i.e., MDI-1) to 3 wt % (i.e., MDI-3) did not significantly enhance the water resistance. MDI-5 decreased the water-uptake by 58% over the control. MDI-7 had the water-uptake comparable to that of MDI-5.

PMDI-1 significantly lowered the water-uptake over the control in boiling water (Table II). PMDI-3 lowered the water-uptake by 60% over the control. PMDI-5 did not significantly decrease the water-uptake over PMDI-3. PMDI-7 had an increased water-uptake over PMDI-5.

DIH-7, MDI-5, and PMDI-3 were the optimum treatments, respectively, in terms of reducing the water-uptake of the kenaf-

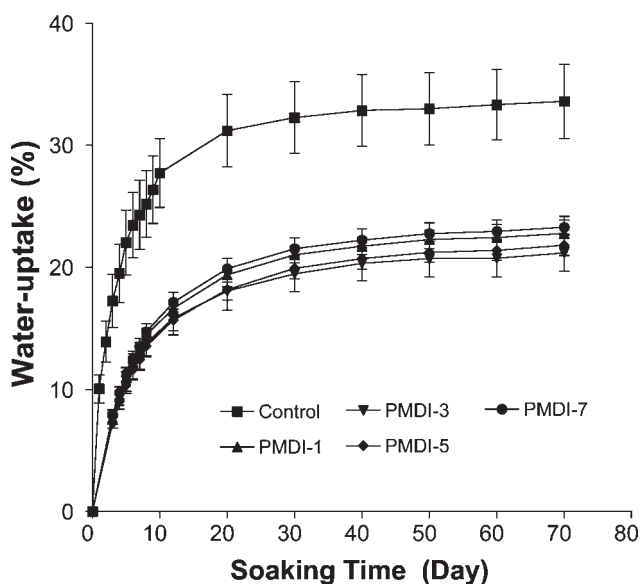


Figure 3. Effect of AESO-PMDI treatments of kenaf fibers on the water-uptake of the composites in water at room temperature. (Data are the mean of five replicates and the error bars represent a standard error of the mean.)

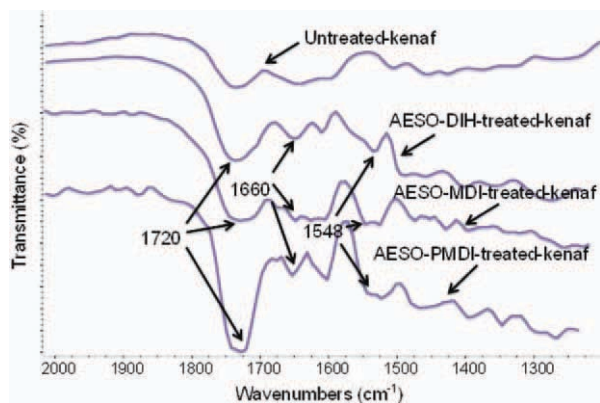


Figure 4. FTIR spectra of untreated and coupling agent treated kenaf fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

UPE composites in boiling water. DIH-7 significantly lowered water-uptake as compared to MDI-5 ($P = 0.040$) and PMDI-3 ($P = 0.013$), and MDI-5 had no statistical difference in terms of lowering water-uptake as compared to PMDI-3 ($P = 0.192$). Effects of these optimum treatments on reduction of the water-uptake were $\text{DIH-7} > \text{PMDI-3} \approx \text{MDI-5}$.

DIH, MDI, PMDI, and AESO dissolved well in ethyl acetate. Therefore, the residual DIH, MDI, PMDI, and AESO, if there was any, should be completely removed after the extraction with ethyl acetate. A separate experiment demonstrated that the reaction products of AESO-DIH, AESO-MDI, and AESO-PMDI that were prepared in anhydrous ethyl acetate at 80 °C for 3 h were soluble in ethyl acetate. Thus ethyl acetate could also remove the reaction products of AESO-DIH, AESO-MDI, and AESO-PMDI that were not covalently bonded onto fibers. The extracted fibers were characterized with FTIR spectroscopy (Figure 4). AESO-DIH-treated kenaf fibers, AESO-MDI-treated kenaf fibers, and AESO-PMDI-treated kenaf fibers showed strong peaks of urethane functional groups at 1660 cm^{-1} and ester groups from AESO at 1720 cm^{-1} (C=O stretching) and peaks of N-H bending vibration at 1548 cm^{-1} (Figure 4). However, untreated kenaf fibers only had a weak peak at 1660 cm^{-1} and 1720 cm^{-1} , and did not have the peak of N-H bending vibration. The FTIR spectra thus implied that all three coupling agents had formed covalent linkages with kenaf fibers.

The fiber pull-out and voids were clearly observed on the surface of the untreated kenaf-UPE composites [Figure 5(a)], showing poor interfacial adhesion between fibers and the UPE matrix. AESO-DIH-treated kenaf-UPE composites had less fiber pull-out and smaller voids over the untreated kenaf-UPE composites [Figure 5(b)]. AESO-MDI-treated kenaf-UPE composites had extensive fiber breaks and no fiber pull-out when compared to the untreated kenaf-UPE composites [Figure 5(c)]. AESO-PMDI-treated kenaf-UPE composites had no fiber pull-out and had smaller and less gaps between the kenaf fibers and the UPE resins over the untreated kenaf-UPE composites [Figure 5(d)]. Comparisons of Figure 5(a) with 5(b), Figure 5(a) with 5(c), and Figure 5(a) with 5(d) revealed that the treatment of kenaf fibers with AESO-DIH, AESO-MDI, and AESO-PMDI signifi-

cantly increased the adhesion between the fibers and UPE resin. The improved adhesion enhanced effective stress transfer from the UPE matrix to the fibers, thus increasing the flexural strength and flexural modulus of the coupling agent treated-kenaf-UPE composites shown in Table II. The enhanced adhesion also reduced hydrophilicity of the fibers and minimized the gap between kenaf fiber and UPE matrix, thus improving the wetting and penetration of UPE resins on fibers. The better penetrated UPE resins would form better mechanical interlocks with the fibers during curing, thus resulting in improved water resistance.

AESO contains multiple hydroxyl and acrylate groups (Figure 6). DIH, MDI, and PMDI contain multiple isocyanate groups that can form covalent bonds with hydroxyl groups on kenaf fibers and AESO. The possible reactions in the treatment of kenaf fibers with the AESO-MDI are proposed in Figure 7. Ideally, two isocyanate groups of MDI react with a hydroxyl group of AESO and a hydroxyl group on kenaf fiber surfaces, thus imparting the acrylate functional group onto kenaf fibers. The C=C bond of the acrylate functional group can react with unsaturated C=C groups in the UPE resin and styrene through a free-radical polymerization reaction during the hot-pressing. The FTIR spectra indeed verified that AESO was covalently bonded onto kenaf fibers. It is possible that both isocyanate groups of a MDI molecule react with two hydroxyl groups on the fiber surface or two hydroxyl groups of AESO. The treatment of kenaf fibers with AESO-DIH and AESO-PMDI is expected to undergo reactions similar to those shown in Figure 7. Therefore combinations of AESO with an isocyanate, such as AESO-DIH, AESO-MDI, and AESO-PMDI were able to form covalent linkages between kenaf fibers and the UPE resin, thus improving the interfacial adhesion between kenaf fibers and the UPE matrix. The improved interfacial adhesion could improve the stress transfer from the UPE matrix to kenaf fibers, thus enhancing the flexural strength and flexural modulus.

The kenaf-UPE composites with 1 wt % DIH, MDI, or PMDI usage did not show statistically significant increase in flexural properties probably due to the insufficient amount of coupling agents. When the amount of coupling agents was raised, the possibility of forming the covalent linkages between kenaf fibers and the UPE resin increased, thereby increasing the flexural strength or flexural modulus of the resulting kenaf-UPE composites. This explanation is consistent with the fact that the flexural properties of composites with DIH-5, MDI-3, and PMDI-5 were better than those with DIH-1, MDI-1, and PMDI-1, respectively. The covalent linkages between kenaf fibers and a coupling agent were limited by the amount of hydroxyl groups available on the AESO. The 5 wt% DIH (DIH-5), 3 wt% MDI (MDI-3), and 5 wt% PMDI (PMDI-5) were presumably enough to react with most of the hydroxyl groups on the AESO. Thus, raising the DIH, MDI, or PMDI usage to 7 wt% did not further increase the flexural strength or flexural modulus. Excess coupling agents might accumulate on fiber surfaces and formed a weak layer of polymeric materials that may weaken the interfacial adhesion between kenaf fibers and the UPE matrix, which might explain that increasing the usage of coupling agents to 7 wt % decreased the flexural strength and flexural modulus.

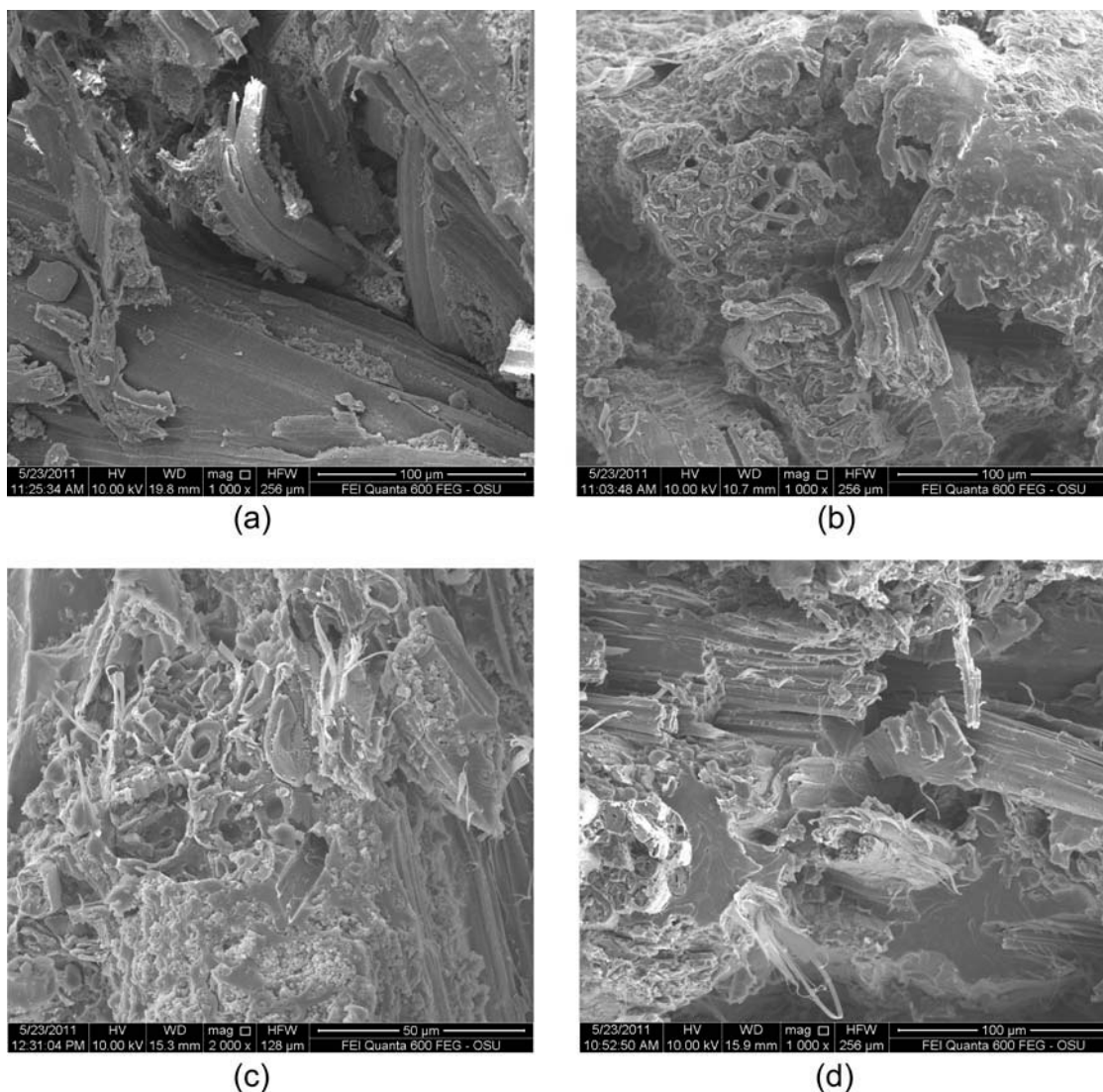


Figure 5. SEM images of flexural-fractured surfaces of kenaf-UPE composites. (a) (untreated kenaf)-UPE composites, (b) (AESO-DIH-treated kenaf)-UPE composites, (c) (AESO-MDI-treated kenaf)-UPE composites, (d) (AESO-PMDI-treated kenaf)-UPE composites.

The greater water-uptake for the control was attributed to the hydrophilicity of the kenaf fibers. Treatment of kenaf fibers by all three coupling agents made the fibers more hydrophobic and improved interfacial adhesion between the fibers and UPE resin, thus reducing the water-uptake. Results indicated that all three coupling agents were efficient in terms of reducing the water-uptake of the resulting kenaf-UPE composites that were either soaked in water at room temperature or in boiling water.

Isocyanate groups from DIH, MDI, and PMDI reacted with the hydroxyl groups of the fibers, thus reducing the hydrophilicity

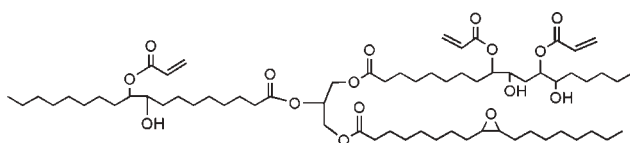


Figure 6. Chemical structure of acrylated epoxidized soybean oil (AESO).

of the fiber and blocking the water sorption sites. The free-radical polymerization of coupling agent-treated fibers with the UPE resin would form tight networks surrounding the fibers. The hydrophobic chains of AESO-DIH, AESO-MDI, and AESO-PMDI also prevented water from penetrating the kenaf fibers. These factors might account for the lower water-uptake of the coupling agent-treated-kenaf-UPE composites. The increased usage of an isocyanate from 1 wt% to 3 wt% or more contributed to decreased hydrophilicity and improved interfacial adhesion, which explains the ranking of the enhanced water resistance as DIH-3>DIH-1, MDI-3>MDI-1, and PMDI-3>PMDI-1. As discussed previously, excess coupling agent might not be covalently bonded onto kenaf fibers and might form weak layers between fibers and UPE. The kenaf fibers were not tightly wrapped by the UPE matrix, which allowed water to penetrate the fibers. This may explain why PMDI-7 had a higher water-uptake than PMDI-1, PMDI-3, and PMDI-5. It's not completely understood why AESO-DIH was more effective than AESO-

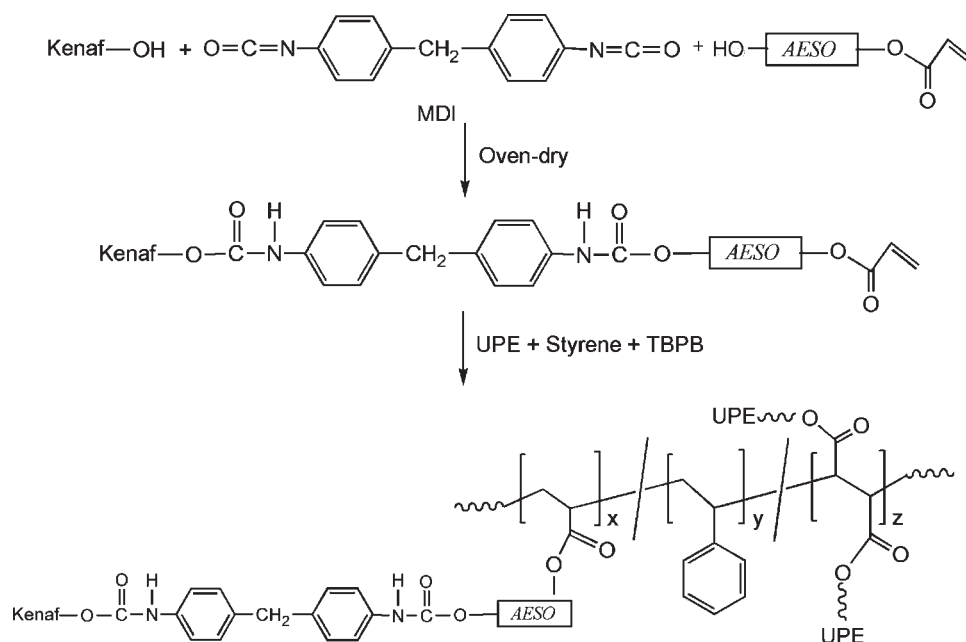


Figure 7. Proposed reactions in the formation of the AESO-MDI treated-kenaf-UPE composites (TBPB functions as a free radical initiator for the copolymerization).

MDI and AESO-PMDI in terms of improving the water resistance under corresponding optimum conditions.

AESO-DIH, AESO-MDI, and AESO-PMDI appeared to be more effective than DIH-HEA and NMA in terms of enhancing the flexural strength and water resistance.^{24,25} From our previous investigations of using the same kenaf fibers and the same UPE resins as those used in this study, the highest flexural strengths of DIH-HEA-treated kenaf-UPE composites and NMA-treated kenaf-UPE composites were 118 MPa and 143 MPa, respectively,^{24,25} whereas the highest flexural strengths of the AESO-DIH-, AESO-MDI-, and AESO-PMDI-treated kenaf-UPE composites were 153, 158, and 152 MPa, respectively. However, NMA seemed to be most effective regarding increasing the flexural modulus of the composites, which was 14.3 GPa, higher than the flexural modulus of all other coupling agents treated kenaf-UPE composites.^{24,25} The flatten-out water-uptake of DIH-HEA-treated kenaf-UPE composites and NMA-treated kenaf-UPE composites in water at room temperature were 28% (DIH-1) and 26%,^{24,25} respectively, whereas the flatten-out water-uptake of AESO-DIH-, AESO-MDI-, and AESO-PMDI-treated kenaf-UPE composites were 19% (DIH-7), 22% (MDI-3), and 21% (PMDI-3), respectively. The water-uptake of NMA-treated kenaf-UPE composites in boiling water was 23% under the optimum conditions, and was significantly higher than those of AESO-DIH-, AESO-MDI-, and AESO-PMDI-treated kenaf-UPE composites, which were 8% (DIH-7), 16% (MDI-5), and 14% (PMDI-3), respectively.^{24,25}

CONCLUSIONS

Three novel coupling agents, AESO-DIH, AESO-MDI, and AESO-PMDI improved the compatibility and interfacial adhesion between kenaf fibers and UPE matrix. Treatments of kenaf

fibers with these coupling agents significantly increased the flexural properties and water resistance of the resulting kenaf-UPE composites. The usage of a coupling agent had significant impacts on the flexural properties and water resistance of the composites. DIH-5, MDI-3, and PMDI-5 resulted in the highest flexural strength and flexural modulus, respectively. DIH-7, MDI-3, and PMDI-3 resulted in the lowest water-uptake at room temperature soaking. DIH-7, MDI-5, and PMDI-3 resulted in the lowest water-uptake in boiling water, respectively. Under corresponding optimum conditions, there was no significant difference in terms of the effects of these three coupling agent treatments on improvement of the flexural properties. AESO-DIH was more effective than AESO-MDI and AESO-PMDI on improving the water resistance.

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