Hemp-Fiber-Reinforced Unsaturated Polyester Composites: Optimization of Processing and Improvement of Interfacial Adhesion

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ABSTRACT: The processing variables for making hemp-fiber-reinforced unsaturated polyester (UPE) composites were optimized through orthogonal experiments. It was found that the usage of initiator, methyl ethyl ketone peroxide, had the most significant effect on the tensile strength of the composites. The treatment of hemp fibers with a combination of 1,6-diisocyanatohexane (DIH) and 2-hydroxyethyl acrylate (HEA) significantly increased tensile strength, flexural modulus of rupture, and flexural modulus of elasticity, and water resistance of the resulting hemp-UPE composites. FTIR spectra revealed that DIH and HEA were covalently bonded to hemp fibers. Scanning electron microscopy graphs of the fractured hemp-UPE composites demonstrated that treatment of hemp fibers with a combination of DIH and HEA greatly improved the interfacial adhesion between hemp fibers and UPE. The mechanism of improving the interfacial adhesion is proposed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 862–868, 2011

Key words: hemp fiber; unsaturated polyester; modification; 1,6-diisocyanatohexane; 2-hydroxylethyl acrylate

INTRODUCTION

The use of natural plant fibers as reinforcing fillers in fiber-polymer composites has drawn much interest in recent years.[1–4] Natural plant fibers as reinforcing fillers have several advantages over inorganic fillers such as glass fibers; they are abundant, readily available, renewable, inexpensive, biodegradable, of low density, and of high specific strength. Hemp fibers are one of the most attractive natural plant fibers for fiber-reinforced composites because of their exceptional specific stiffness.[5]

Unsaturated polyester (UPE) is one of the most commonly used polymer matrices for glass-fiber-reinforced composites. These composites are widely used in marine structures, automobiles, home construction, sports goods, and furniture. Several studies have been done on the replacement of glass fibers with hemp fibers for reinforcing UPE.[6–12] One of the major obstacles to wide use of fibers as reinforcing fillers is the relatively low strength and high water absorption of the hemp-UPE composites.[13] This is a result of the fact that the hydrophilic hemp fibers are not compatible with the hydrophobic UPE and tend to absorb water.

The modification of hemp fibers with methacrylic anhydride was shown to significantly improve interfacial adhesion in hemp-UPE composites.[6] The modification of hemp fibers with acrylonitrile and dicumyl peroxide was also shown to increase the tensile strength and tensile modulus of the resulting hemp-UPE composites.[7] Effects of alkali treatment, silane treatment, UPE treatment, and acrylonitrile treatment of hemp fibers on the mechanical and thermal properties of the hemp-UPE composites were investigated.[8] A separate study showed that the treatments of hemp fibers with a sizing agent (alkylketene dimer, rosin acid, or styrene-(maleic anhydride) copolymer), alkali, or a silane agent (3-aminopropyltriethoxysilane) did not substantially increase the resistance to water absorption.[9] A novel method of treating hemp fibers with a fungus was investigated for the improvement of the strength and water resistance.[11] In each of these studies, the hemp-UPE composites are observed to have lower strength and higher water absorption than

glass-fiber-UPE composites. More study on chemical treatment of hemp fibers is needed for further improvement of the strength and water resistance of the hemp-UPE composites. In this study, we investigated a new and simple method of modifying hemp fibers.

EXPERIMENTAL

Materials and apparatus

UPE and methyl ethyl ketone peroxide (MEKP) were obtained from AOC (Collierville, TN). Hemp fibers were provided by Hempline Incorporated (Delaware, ON, Canada). The 1,6-diisocyanatohexane (DIH) was purchased from Sigma-Aldrich (Milwaukee, WI). Anhydrous ethyl acetate was purchased from EMD Chemicals Incorporated (Gibbstown, NJ) and 2-hydroxyethyl acrylate (HEA) was purchased from TCI America (Portland, OR). Scanning electron microscope (SEM) images were obtained by a FEI Quanta 600 SEM (Hillsboro, OR). Fourier Transform Infrared (FT-IR) spectra were obtained on a Nexus 470 FT-IR spectrometer (Thermo Nicolet, Madison, WI). The hot-pressing was performed on an automatic Benchtop Carver press (Carver, Wabash, IN). Strength properties were evaluated with a Sintech machine (MTS Systems, Enumclaw, WA).

Differential scanning calorimetry analysis

Differential Scanning Calorimetry (DSC) graphs were obtained from a TA DSC 2092 (TA Instruments, New Castle, DE) with argon as a purge gas. Argon flow was adjusted to a rate of 40 mL min^{-1}. The calorimeter was calibrated against indium (m. p. 156.6°C, $\Delta H = 28.45$ J g^{-1}) at 10°C min^{-1}. Neat UP (5–15 mg) and the mixture of UPE and hemp fibers (5–15 mg) were weighed in hermetic aluminum pans with lids. An empty aluminum pan with a lid was used as a reference. The thermograms were recorded from 25 to 300°C at a heating rate of 10°C min^{-1}. The Universal Analysis V3.3B software, supplied by TA Instruments, Inc. (TA Instruments, New Castle, DE) was used to plot and analyze the thermal data. The DSC spectra were normalized to represent 1 g of a sample.

Experimental design for optimal processing parameters

Orthogonal experiments of four variables (hot-press temperature, the hemp fiber content, hot-press time, and the usage of MEKP) with three levels for each variable were conducted to determine the optimum processing parameters for hemp-UPE composites. The tensile strength of composites was used as the criterion for the process optimization. Variances of the orthogonal experiments were analyzed to determine the effects of different variables on the tensile strength of the composites.

The chemical modification of hemp fibers

Hemp fibers were shortened to about 1.3 cm in length with a paper cutter and oven-dried for 12 h at 103°C. DIH (0.78 g, 4.64 mmol) and HEA (0.54 g, 4.64 mmol) were dissolved in anhydrous ethyl acetate (70 mL). The resulting solution was evenly sprayed onto the oven-dried hemp fibers (78 g). The resulting DIH-HEA-coated fibers were then dried in an oven at 50°C for 5 h and were designated as DIH-1, meaning that the treated fibers contained 1 wt % of DIH based on the oven-dried hemp fibers. Using the same procedure, DIH-HEA solutions containing 2, 3, 4, and 5 wt % of DIH on oven-dried hemp fibers were used to treat hemp fibers to correspondingly generate DIH-2, DIH-3, DIH-4, and DIH-5. The DIH/HEA molar ratio was kept at 1 : 1.

The preparation of a UPE mixture

The following is an example procedure for making a UPE mixture containing 3% of MEKP based on UPE. UPE (78 g) and MEKP (2.34 g) were mixed by spatula for 1 min to generate a UPE mixture that was immediately poured onto a hemp fiber mat. The specific amount of MEKP was listed in each figure legend.

The preparation of UPE-hemp composites

Untreated hemp fibers, DIH-1, DIH-2, DIH-3, DIH-4, or DIH-5 were formed into a 20 cm × 20 cm mat with a uniform thickness by hand. The fiber mat was put in a stainless steel mold with dimension of 20 cm × 20 cm × 0.3 cm and the UPE mixture with a predetermined weight was uniformly poured onto the fiber mat by hand. The mold was put onto the lower platen of an automatic benchtop Carver press that was preheated to 110°C. The press was closed slowly, allowing the UPE mixture to flow and form a mold shape. The press pressure was maintained at 3.24 MPa for 10 min and then raised from 3.24 to 4.32 MPa while the platen temperature was raised to a preset final temperature (150, 170, or 190°C). Hot pressing at the final temperature continued for a given duration (20, 30, or 40 min according to the experimental design). When the hot-pressing was finished, the press was opened and the mold was removed from the hot press and cooled to room temperature. The hemp-UPE board was removed from the mold.

Evaluation of mechanical properties of hemp-UPE composites

Dumbbell specimens were prepared for the evaluation of tensile strength. The hemp-UPE composite

board was first cut into rectangular specimens (100 mm × 15 mm × 3.0 mm) that were further cut to a dumbbell shape with the gripping length of 10.0 mm and the width of 11.0 mm in the center section. Rectangular specimens with the dimension of 60 mm × 15 mm × 3.0 mm were prepared for the evaluation of the flexural modulus of rupture (MOR) and the flexural modulus of elasticity (MOE).

The tensile test and the bending test of the hemp-UPE composites were performed with a Sintech machine in accordance with ASTM D 3039-06 and ASTM D 790-03, respectively.

Water uptake of hemp-UPE composites

The water uptake of hemp-UPE composites was measured by soaking the composite specimens in distilled water at room temperature in accordance with ASTM D 5229M-04. The composite boards were cut into bars with 7.62-cm long and 2.54-cm wide. All specimens were conditioned in an oven at 50°C for 3 h, cooled at ambient environment for 10 min, weighed and then soaked in water. At a predetermined time, the specimens were removed from water, wiped with tissue paper, weighed to measure the weight gain, and then put back in water for continued soaking. The water uptake percentage was determined as the weight gain divided by the dry weight of the specimen.

Analysis of interfacial adhesion of composites

The fractured surfaces of the specimens from the tensile test were examined with a SEM at an accelerating voltage of 5.0 kV. Specimens were coated with an Au-Pd film (8–10 nm) before testing.

The following hemp fiber samples were extracted with chloroform and characterized with FT-IR: (1) hemp fibers without any treatment, (2) hemp fibers treated with a DIH-HEA solution in anhydrous ethyl acetate containing 3 wt % DIH, (3) hemp fibers treated with 3 wt % DIH in anhydrous ethyl acetate. The samples (5 g) were first wrapped with filter paper and then extracted with chloroform in a modified Soxhlet extractor for 24 h. The thimble holder of the Soxhlet extractor was wrapped with a heating tape and heated to maintain the temperature of the solution in the holder at 70°C. The extracted fibers were dried at 103°C for 24 h and then cut into small pieces for characterization with FT-IR.

Statistical analysis

Strength data were analyzed with a standard two-tailed t tests using S-plus statistical software (version 8.0, Insightful Corp, Seattle, WA). All comparisons were based on a 95% confidence interval.
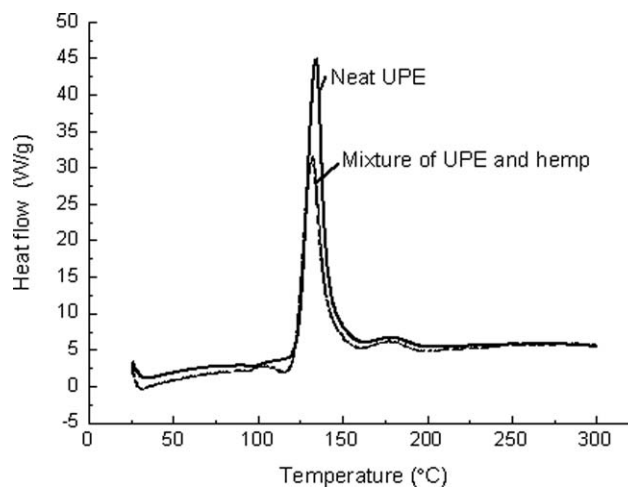
Figure 1 DSC curves of neat UPE and a mixture of UPE and hemp fibers.

RESULTS AND DISCUSSION

DSC curves of UPE and a hemp-UPE mixture are shown in Figure 1. Neat UPE had an exothermal peak at 134.3°C. The peak started at 114°C and ended at 160°C. The exothermal peak of the hemp-UPE mixture shifted to 132.2°C, slightly lower than that of neat UPE. These results indicated that the curing of the UPE began at 114°C. Given enough time, a temperature of above 132°C should be able to completely cure the UPE. Therefore, 150, 170, and 190°C were selected as temperature variables in the subsequent optimization study.

The experimental design and results of orthogonal experiments are shown in Table I. When the hemp fiber content was above 50 wt %, the amount of the UPE resins was not sufficient to form a uniform mixture of hemp fibers and the UPE resins, thus resulting in hemp-UPE composite boards with inconsistent properties. The tensile strength of the hemp-UPE boards significantly decreased when the fiber content was below 30 wt % (data not shown). Therefore, 30, 40, and 50 wt % were selected as variables of the fiber content. Our preliminary experiments revealed that the UPE used in this study was completely cured at 160°C for about 30 min. The curing times of 20, 30, and 40 min were thus selected as variables of the curing time. The usage of MEKP initiator required for the full cure of the UPE resins may vary with the composition and sources of the UPE resins and is typically in the range of 1–3 wt %.[8,12] Therefore, three usages of MEKP (1, 2, and 3 wt %) were selected for the optimization study. Results from the orthogonal experiments revealed that the optimum combination of process variables was as follows: A_1, B_3, C_2 and D_3, that is, 150°C press temperature, 50 wt % hemp fibers, 30-min hot-press time, and 3 wt % MEKP (Table I). An

TABLE I
Orthogonal Experiments for Optimal Processing Parameters of Composites

Experiment no.	Factor A (hot-press temperature, °C)	Factor B (hemp fiber content, wt %)	Factor C (hot-press time, min)	Factor D (usage of MEKP, wt % of UPE)	Tensile strength (MPa)
1	A_1 (150°C)	B_1 (30%)	C_1 (20 min)	D_1 (1%)	8.4
2	A_1	B_2 (40%)	C_2 (30 min)	D_2 (2%)	30.3
3	A_1	B_3 (50%)	C_3 (40 min)	D_3 (3%)	33.9
4	A_2 (170°C)	B_1	C_2	D_3	29.8
5	A_2	B_2	C_3	D_1	9.2
6	A_2	B_3	C_1	D_2	25.6
7	A_3 (190°C)	B_1	C_3	D_2	19.2
8	A_3	B_2	C_1	D_3	25.2
9	A_3	B_3	C_2	D_1	19.4
Mean 1	24.200	19.133	19.733	12.333	
Mean 2	21.533	21.567	26.500	25.033	
Mean 3	21.267	26.300	20.767	29.633	
Maximum difference	2.933	7.167	6.767	17.300	

independent experiment indeed verified that the hemp-UPE composite boards made under the optimum combination of process variables had the tensile strength of 34.62 MPa, the highest among all combinations of process variables investigated.

Analysis of variances for the orthogonal experiments showed that the MEKP usage had the most significant effect among all variables investigated on the tensile strength of hemp-UPE composites. Therefore, the effect of the MEKP usage on the tensile strength was further investigated (Fig. 2). The tensile strength did not significantly increase when the MEKP usage was increased from 3 to 4 wt %, but markedly increased when the MEKP usage was raised from 4 to 5 wt % (Fig. 2). The tensile strength did not significantly change when the MEKP usage was raised from 5 to 10 wt %. The optimum MEKP usage observed was higher than usage levels reported in the literature.[8,12] It is possible that the UPE resins used in this study contained a higher amount of impurities that terminated the free radicals generated from MEKP than those used in other studies.[8,12] Another possibility is that such a high usage was indeed the optimum usage for maximizing the tensile strength of the hemp-composites because this was the first systematic optimization study for the process variables of making hemp-UPE composites published so far.

The average tensile strength at 6 wt % MEKP was higher than that at 5 wt % MEKP. Therefore, the following variables were used for the investigation of interfacial adhesion between hemp fibers and UPE: 150°C hot-press temperature, 50 wt % hemp fibers, 30-min hot-press time, and 6 wt % MEKP.

Hemp fibers are hydrophilic and UPE resins are hydrophobic. Hemp fibers and UPE resins are not compatible with each other, thus failing to transfer stress from the UPE matrix to the reinforcing hemp fibers in hemp-UPE composites. In this study, a combination of DIH an HEA was used as a novel system for surface modification of hemp fibers. The possible reactions during the fiber modification and formation of the hemp-UPE composites are shown in Figure 3.

DIH and HEA were first dissolved in anhydrous ethyl acetate and the resulting solution was sprayed onto hemp fibers. The hydroxyl group of HEA might begin to react with the isocyanate (—NCO) group of DIH once they were both dissolved in ethyl acetate. However the reaction was expected to be incomplete because the solution was prepared at room temperature and was sprayed onto hemp fibers shortly after its preparation. The molar ratio between DIH and HEA was kept at 1 : 1 throughout
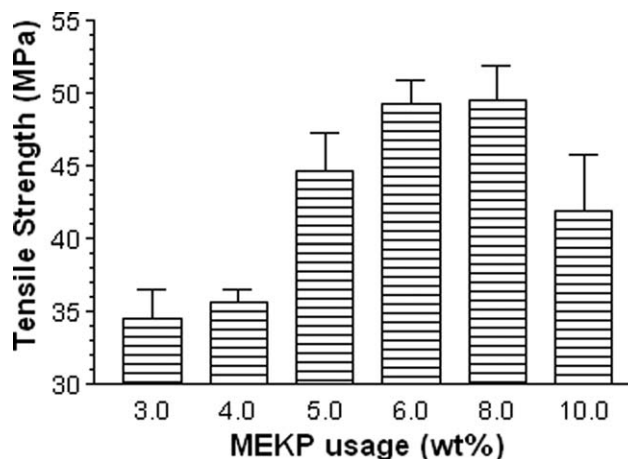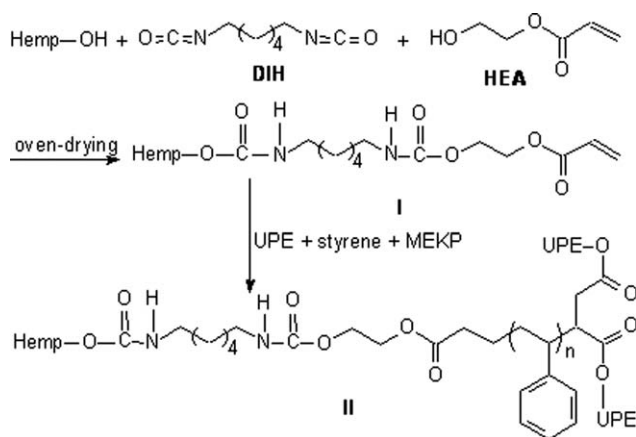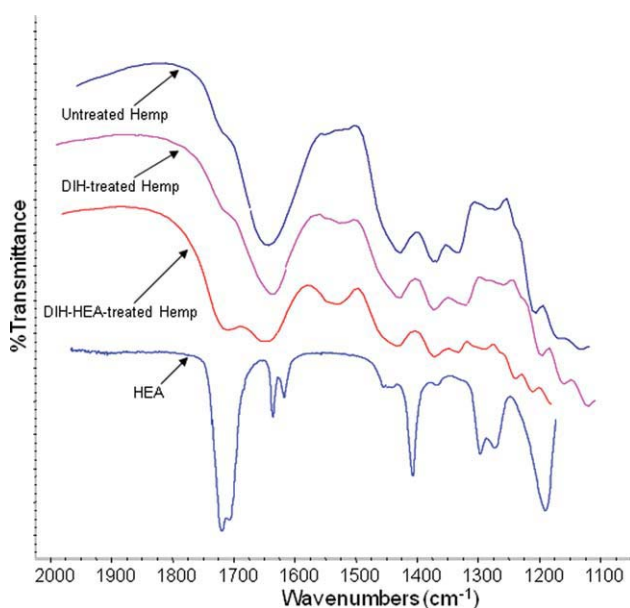

Figure 2 Effect of the MEKP usage on the tensile strength of the hemp-UPE composites. Data are the means of five replicates and the error bar represents one standard error of the mean.
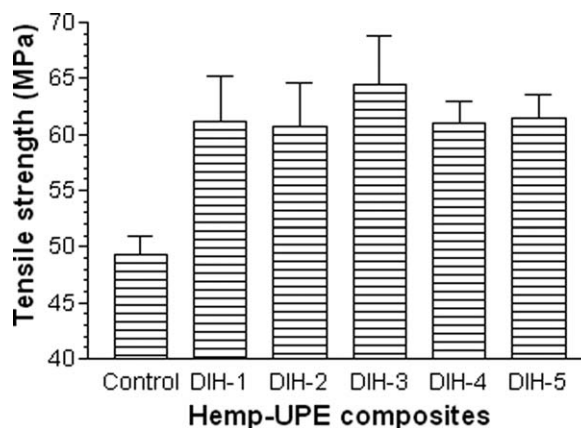
Figure 3 Proposed reactions in the DIH-HEA-treated hemp-UPE composites.

Figure 5 Effect of chemical treatments of hemp fibers on the tensile strength of hemp-UPE composites.

this study. There were certainly excess isocyanate groups in the DIH-HEA solution for their reactions with hydroxyl groups of hemp fibers. The Structure **I** shown in Figure 3 is a representative structure. It was possible that both isocyanate groups of DIH reacted with either two HEA or two hydroxyl groups of hemp fibers. However, FTIR spectra of DIH-HEA-treated hemp fibers demonstrated that the Structure **I** certainly existed (Fig. 4). The conjugated C=C in the Structure **I** was expected to form covalent linkages with the UPE resins via the styrene unit (Fig. 3) during free radical polymerization curing of the UPE resin/styrene system. The Structure **II** is only a representative structure (Fig. 3). The

conjugated C=C in the Structure **I** might be directly linked to the UPE backbone without the styrene unit in between.

A separate experiment demonstrated that the reaction products of DIH and HEA that were prepared in anhydrous ethyl acetate at 50°C for 3 h were soluble in chloroform. DIH and HEA are also both completely soluble in chloroform. The fiber samples were thoroughly extracted with chloroform before they were used for obtaining FTIR spectra. Therefore, any residual DIH and HEA, and any reaction products between DIH and HEA that were not covalently bonded onto hemp fibers should have been removed by the chloroform extraction.

The FTIR spectra of HEA and hemp fibers with and without chemical treatments are shown in Figure 4. HEA had a strong ester carbonyl peak at 1700–1720 cm^{-1}. Untreated hemp and DIH-treated hemp had a very weak peak at 1700–1720 cm^{-1}, whereas DIH-HEA-treated hemp had a strong peak at 1700–1720 cm^{-1}, which implied that DIH-HEA was covalently bonded to hemp fibers.

Figure 4 FT-IR spectra of HEA and chloroform-extracted hemp fibers with or without chemical treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
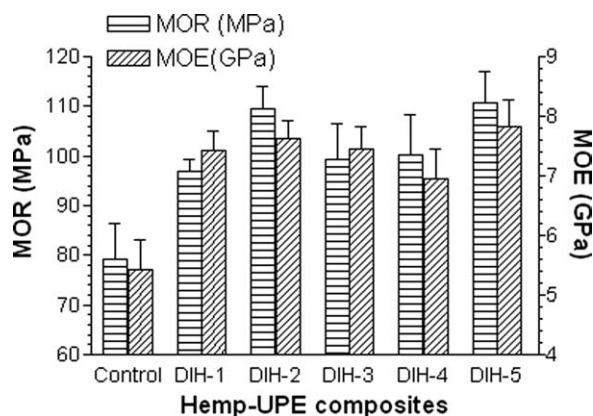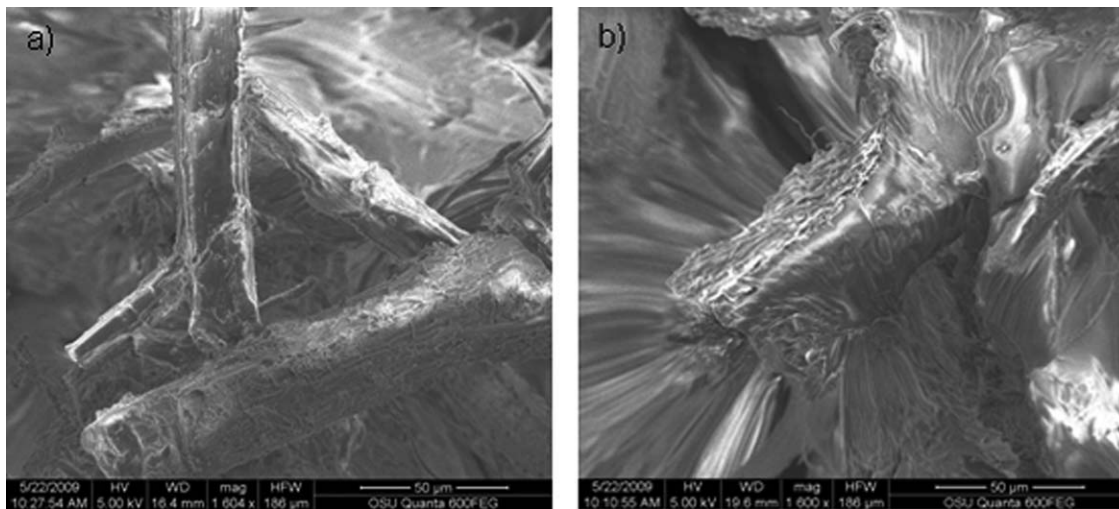

Figure 6 Effect of chemical treatments of hemp fibers on the MOR and MOE of hemp-UPE composites.

Figure 7 SEM images of tensile-fractured surfaces of hemp-UPE composites. (a) the control, i.e., without the chemical treatment of hemp fibers, (b) DIH-3.

Effect of the fiber treatment with DIH-HEA on the tensile strength of hemp-UPE composites is shown in Figure 5. DIH-1 had much higher tensile strength than the control. DIH-1, DIH-2, DIH-3, DIH-4, and DIH-5 had comparable tensile strengths. In other words, the tensile strength did not significantly change when the usage of DIH-HEA increased.

The MOR of DIH-1 was much higher than that of the control (Fig. 6). DIH-2 had a higher MOR than DIH-1, that is, the MOR significantly increased when the usage of DIH was increased from 1 to 2 wt %. DIH-2, DIH-3, DIH-4, and DIH-5 had comparable MOR. DIH-1 had a much higher MOE than the control (Fig. 6). DIH-1, DIH-2, DIH-3, DIH-4, and DIH-5 had comparable MOE, that is, the MOE did not significantly change when the usage of DIH was raised from 1 to 5 wt % (Fig. 6).

For the hemp-UPE composites without the chemical treatment of the fibers, individual fibers were observed on the fractured surface [Fig. 7(a)]. The fiber surfaces were fairly clean, which indicates poor interfacial adhesion between hemp fibers and the UPE matrix [Fig. 7(a)]. For the hemp-UPE composites with the DIH-HEA-treated fibers, the fibers were completely covered by the UPE matrix, which indicates superior interfacial adhesion between the fibers and the UPE matrix [Fig. 7(b)].

The water-uptake rate of all hemp-UPE composites increased along with increase in the soaking time when the soaking time was below 12 days and then flattened out when the soaking time was longer than 12 days (Fig. 8). The control had a much higher water-uptake rate than all DIH-HEA-treated hemp-UPE composites (DIH-1, DIH-2, DIH-3, DIH-4, and DIH-5) at each soaking time. There was a general trend that the water-uptake rate

decreased along with increase in the usage of DIH-HEA at each soak time, that is, the water-uptake rate had the follow order: DIH-1>DIH-2>DIH-3>DIH-4>DIH-5 (Fig. 8). Results from the Figure 8 revealed that the chemical treatment significantly reduced the water uptake rate of the resulting hemp-UPE composites. Some hydroxyl groups on the surfaces of hemp fibers reacted with the isocyanate groups of DIH, thus reducing the hydrophilicity of the fibers. The improved interfacial adhesion between the fibers and the UPE matrix also reduced the water penetration into the fibers, thus reducing the water uptake rate.
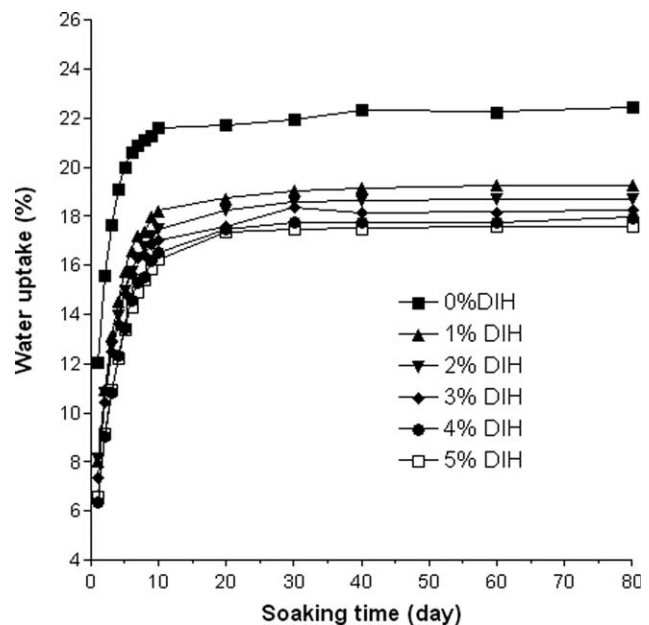
Figure 8 Water uptake rate of hemp-UPE composites.

CONCLUSIONS

The optimum processing variables for improving the tensile strength of the hemp-UPE composites were a hot-pressing temperature of 150°C, a hot-press time of 30 min, 50 wt % hemp fibers and 6 wt % usage of MEKP.

Treatment of hemp fibers with a combination of DIH and HEA significantly increased the tensile strength, MOR and MOE of the hemp-UPE composites and significantly improved water resistance of the composites as well.

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