

Effect of Fiber Surface Treatment on the Properties of Biocomposites from Nonwoven Industrial Hemp Fiber Mats and Unsaturated Polyester Resin

Geeta Mehta,¹ Lawrence T. Drzal,¹ Amar K. Mohanty,² Manjusri Misra¹

¹Department of Chemical Engineering and Material Science, Composite Materials and Structures Center, 2100 Engineering Building, Michigan State University, East Lansing, Michigan 48824

²School of Packaging, 130 Packaging Building, Michigan State University, East Lansing, Michigan 48824

Received 19 July 2004; accepted 14 April 2005

Published online in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/app.22620

ABSTRACT: Biocomposites were made with nonwoven hemp mats and unsaturated polyester resin (UPE). The hemp fiber volume fraction was optimized by mechanical testing. The effect of four surface treatments of industrial hemp fibers on mechanical and thermal properties of biocomposites was studied. The treatments done were alkali treatment, silane treatment, UPE (matrix) treatment, and acrylonitrile treatment. Bending strength, modulus of elasticity, tensile strength, tensile modulus, impact strength, storage modulus, loss modulus, and $\tan \delta$ were evaluated and compared for all composites. The mechanical as well as

thermal properties of the biocomposites improved after surface treatments. The properties of the above biocomposites were also compared with E-glass-mat composite. To achieve balance in properties, a hybrid composite of industrial hemp and glass fibers was made. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1055–1068, 2006

Key words: biocomposites; natural fiber; biofiber; nonwoven hemp mat; unsaturated polyester resin; thermoset resin

INTRODUCTION

Increasing environmental consciousness and demands of legislative authorities are leading to the scrutiny of manufacture, use, and removal of traditional composite structures, usually made of glass, carbon, or aramid fibers reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics, by governmental and other agencies. The most important disadvantage of such composite materials is the problem of removal at the end of lifetime, as the components are closely interconnected, relatively stable, and therefore difficult to separate and recycle.¹ In modern production environment, there is a great demand for every material to be recyclable or degradable.

Natural fibers like industrial hemp, flax, kenaf, coir, and henequen have the potential to be used as glass fiber replacements in certain composite applications. The biofibers derived from annually renewable resources, and used as reinforcing fibers in both thermoplastic and thermoset matrix composites, provide environmental benefits with respect to ultimate disposability and raw material utilization.^{1–3} Advantages

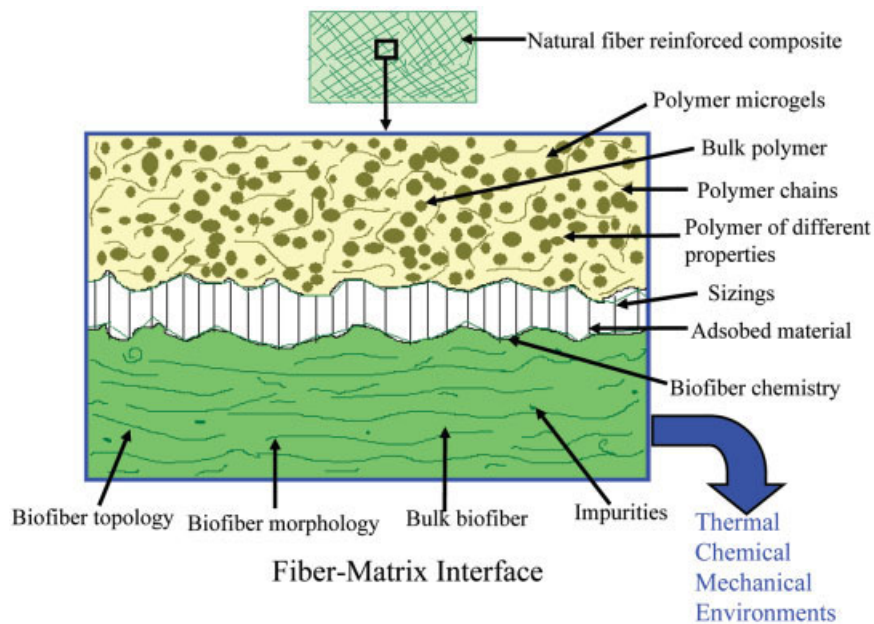
of biofibers over traditional reinforcing materials such as glass fibers, talc, and mica are low cost, low density, high toughness, acceptable specific strength and modulus, reduced tool wear, reduced dermal and respiratory irritation, good thermal properties, ease of separation, enhanced energy recovery, and biodegradability. The main drawback of biofibers is their hydrophilic nature, which lowers their compatibility with hydrophobic polymeric matrixes during composite fabrication.^{1,2}

To get a good reinforcing effect using these plastics, it is necessary to increase the adhesion between fibers and matrix by using surface treatments. Thermoset composites are more desirable than thermoplastics, because of their superior mechanical properties. The matrix resins in the thermoset biocomposites are nonbiodegradable. However, they maintain a balance between economics and the environment.^{4–8}

Due to the hydrophilic nature of the natural fibers, their compatibility with relatively hydrophobic polymeric matrixes is reduced. Therefore, biocomposites have water absorption characteristics that reduce their utility in many applications. For useful composites, fiber-matrix adhesion has to be optimized for ensuring good mechanical properties. The surface chemical modifications of natural fibers like dewaxing, alkali treatment, cyanoethylation, vinyl grafting, and treatment with various coupling agents are some means to improve fiber-matrix adhesion of the resulting bio-

Correspondence to: M. Misra (misraman@egr.msu.edu).

Contract grant sponsor: NSF-PATH; contract grant number: 0122108.



Scheme 1 Schematic representation of the fiber–matrix interface and various factors affecting the fiber–matrix adhesion. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composites (as shown in Scheme 1).^{2,3,9–15} Surface modification also results in enhancement of the aspect ratio, improves the wettability of the fibers, and forms a strong interface between polar natural fiber and nonpolar matrix.

Surface treatments relying on water-based systems are of interest as they incur low costs.

The objective of this research is to investigate the properties and processing of unwoven, biofiber-reinforced, unsaturated polyester resin composites. Although there have been many studies on natural fiber thermoset composites, only a few mention the use of nonwoven fiber mats as reinforcement in biocomposites.^{16–19} The biggest advantage of panels made from this type of biocomposite is their low cost, combined with their ecological and technological advantages. If composite panels with acceptable properties can be developed, they can be used for making housing panels for the future. In this paper, low cost methods were used to try to improve the properties of industrial hemp fiber composites.

EXPERIMENTAL

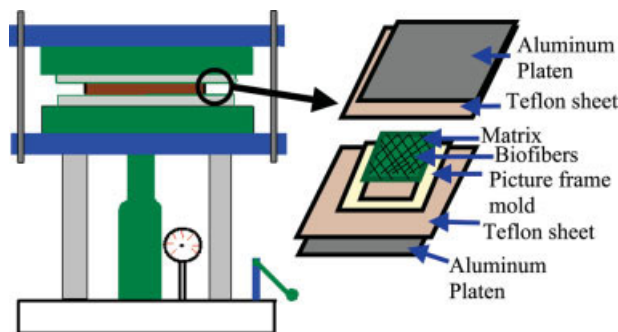
Materials

The natural fiber used in this work, nonwoven industrial hemp fiber mat (will henceforth be called hemp fiber through out the paper), (density 274 g/m³) containing 90% randomly oriented hemp fibers (1–2-in. long, randomly distributed in three dimensions) and 10% poly(ethylene terephthalate) (PET) as binder was kindly provided by FlaxCraft Inc. (Cresskill, NJ). The

E-glass fiber nonwoven mat (UPE compatible glass fibers, 3–4-in. long in a random array) was received from Kemlite Co. Inc. (Joliet, IL). The polymer matrix, ortho unsaturated polyester resin (UPE), containing approximately 30% styrene by weight, was also obtained from Kemlite Inc. The initiator used was methyl ethyl ketone peroxide (MEKP). The promoter used to aid the curing of the UPE was cobalt naphthenate (CoNap). Both MEKP and CoNap were bought from Aldrich. Sodium hydroxide pellets were procured from J. T. Baker. Acrylonitrile (99%) was provided by Aldrich. γ -methacryloxypropyltrimethoxy silane (γ -MPS, SIM6487.4) was obtained from Gelest Inc. Tullytown, PA. Ethanol and acetone were purchased from J.T. Baker. Glacial acetic acid and dicumyl peroxide (DCP) were procured from Sigma Aldrich. All materials were used as such without further purification.

Processing

The hemp mats were cut into small uniform rectangles (8 in. \times 6 in.) and were dried in vacuum oven at the temperature of 80°C and -102 kPa for 5 h. UPE resin was mixed with 1.0 wt % of MEKP and 0.03 wt % of CoNap and was degassed in a vacuum oven without heating the solution. The dried fiber was then coated on both sides with the UPE formulation. The coated clothes were placed one over the other and sandwiched between two aluminum platens lined with two teflon easy release cloths on each of them. These two plates were then placed between two platens of



Scheme 2 Schematic representation of the compression molding process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Tetrahedron Press and cured at a pressure of about 80 psi for 2 h at 100°C, followed by post curing for 2 h at 150°C (compression molding process shown in Scheme 2).

The amount of fiber (volume %) was changed in each biocomposite to have different ratios of fiber and resin in the composites. The fiber content was optimized by making three composites of different fiber content, and then measuring their properties, and finally, choosing the best among them. In this study, composites with 20, 30, and 40 vol % fiber content were used for optimization.

The following surface treatments were done: alkali treatment, γ -MPS treatment, acrylonitrile treatment, and UPE-MEKP treatment.

Alkali treatment

Five percent solution of sodium hydroxide was made using pellets of NaOH in deionized (DI) water using a magnetic stirrer. The fiber mats were completely immersed in this solution for 1 h at room temperature. Then the fiber mats were washed with tap water until all foam and adhered alkali was removed from their surface. The fiber mats were then neutralized in tap water with 2% glacial acetic acid, and tested for neutralization using pH paper to maintain a pH of 6. This solution was then drained and the fibers were washed with DI water and then kept for drying under the hood. After 24 h of room drying, they were vacuum dried at standard conditions.

Silane treatment

One percent γ -MPS solution was made in 99% DI water and ethanol (1:1), maintaining the pH of the solution at 4, using 2% glacial acetic acid. The solution was continuously stirred in a closed lid plastic container and kept under the hood to complete hydrolysis, for 2 h. The fiber mats were soaked in this solution, under the hood, for 1 h. The solution was then drained

from the fiber mats, and they were dried under the hood for 12 h. On the following day, they were cured in an air oven, for 5 h. The fibers were then vacuum dried at standard conditions.

Acrylonitrile treatment

Dried hemp fiber mats were soaked in a premixed solution containing 3.0% acrylonitrile, 0.5% DCP, and 96.5% ethanol for 15 min. The excess solution was drained off from surface of the hemp mats and they were dried overnight under the hood. They were vacuum dried the next morning at standard conditions.

UPE-MEKP treatment

Five percent solution of UPE and MEKP (99:1) was made in 95% acetone. Dried hemp fiber mats were soaked in the UPE-MEKP solution for 15 min. The excess solution was drained off from their surface and they were dried overnight under the hood. The treated mats were vacuum dried the next morning at standard conditions.

These surface-treated fiber mats were then used for fabricating biocomposites with same optimized fiber content in each of them. The fabrication of the composite was done in the same way as for untreated hemp mat-UPE composites. The resulting composite was cut in desired shapes for various tests.

For making the control, degassed UPE solution was poured over degassed silicone molds²⁰ and cured in a conventional oven at same curing conditions. For comparison, a composite with E-glass mats and UPE was made in the same way, by compression molding. A hybrid composite composed of two mats of hemp sandwiched between two mats of E-glass at top and bottom was also made.

The volume fraction of fiber (v_f) in the composite was calculated from the equation:

$$v_f = (m_f / \rho_f) / V$$

where m_f is the weight of the fibers in the composites of volume V , and ρ_f is the density of the fiber.

Analysis

The biocomposites and UPE control samples were used for tensile, flexural, and notched Izod impact test complying with ASTM D638, ASTM D790, and ASTM D256 protocols respectively. A United Calibration Corp. SFM-20 was used for tensile and flexural testing. The impact test was carried out using Testing Machines Inc. 43-OA-01. Dynamical mechanical analyzer (TA DMA 2890) was used for measuring the storage modulus, loss modulus, and $\tan \delta$. For DMA, rectangular bars, 50 mm \times 12 mm \times 3 mm were placed on

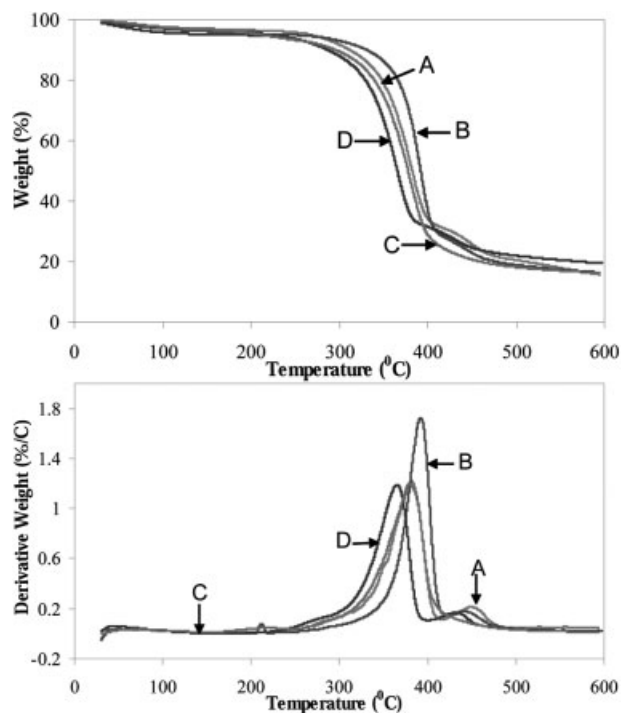


Figure 1 (a) TGA of surface-treated hemp fibers: A, untreated hemp fiber; B, alkali-treated hemp fiber; C, UPE-MEKP-treated hemp fiber; D, acrylonitrile-treated hemp fiber. (b) Derivative thermogravimetric analysis (DTGA) of surface-treated hemp fibers: A, untreated hemp fiber; B, alkali-treated hemp fiber; C, UPE-MEKP-treated hemp fiber; D, acrylonitrile-treated hemp fiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the three point bending fixture in the furnace and heated at 4°C/min from room temperature to 150°C. The viscoelastic properties are characterized by the storage modulus G' (the elastic component of the modulus), the loss modulus G'' (the viscous component of the modulus), and $\tan \delta = G''/G'$ (the tangent of the phase shift between stress and strain), which are functions of the deformation rate and temperature.

Hi-Res TGA 2950 TA model was used for finding variation of sample weight and derivative weight with temperature. The finely chopped fibers were kept in

an aluminum pan, which goes inside the furnace. The furnace was programmed to a temperature ramp from 25 to 600°C, at the rate of 20°C/min. TA 2920 Modulated DSC was used for finding the variation of heat with temperature. A reference aluminum pan and a sample pan were kept inside the DSC furnace, which was programmed to go from -60 to 200°C at 10°C/min.

The fibers and impact-fractured surfaces of composites were investigated using environmental scanning electron microscopy (ESEM). The ESEM used for this work was manufactured by Electroscan Corp. (Model no. 2020). It was equipped with a lanthium hexaboride filament. In the ESEM, water vapor acted as the imaging gas. The samples to be examined were placed in a sample holder located in the sample chamber. The imaging pressure (chamber pressure) was set between 2 and 3 Torr. The working distance between the detector and the sample was set between 8 and 10 mm. The accelerating voltage was set to 20 kV. Failure surfaces were coated with 20-Å-thick layer of gold to obtain a better contrast under the microscope. The sample was focused at different points in its area, and micrograph pictures were taken at different magnifications. X-ray photoelectron spectroscopy (XPS, Physical Electronics 5400 ESCA) was used for studying the elemental composition of untreated and surface-treated hemp fibers.

RESULTS AND DISCUSSION

Analysis of surface-treated hemp fibers

The surface-treated fibers were characterized with TGA, DSC, and XPS.

Thermogravimetric analysis (TGA)

Thermogravimetric curves for untreated and surface-treated hemp fibers are shown in Figures 1(a) and 1(b). Table I summarizes the maximum decomposition temperatures for untreated and surface-treated hemp fibers. Up to 200°C, there was less than 5% loss in weight of untreated as well as surface-treated hemp

TABLE I
Thermogravimetric Results for Surface-Treated Hemp Fibers

	Temperature (°C)			Max. degradation temperature (°C)
	10% Weight loss	20% Weight loss	30% Weight loss	
A	311	348	363	381
B	332	366	378	395
C	295	339	357	383
D	288	329	346	369

A, untreated hemp fiber; B, alkali-treated hemp fiber; C, UPE-MEKP-treated hemp fiber; D, acrylonitrile-treated hemp fiber.

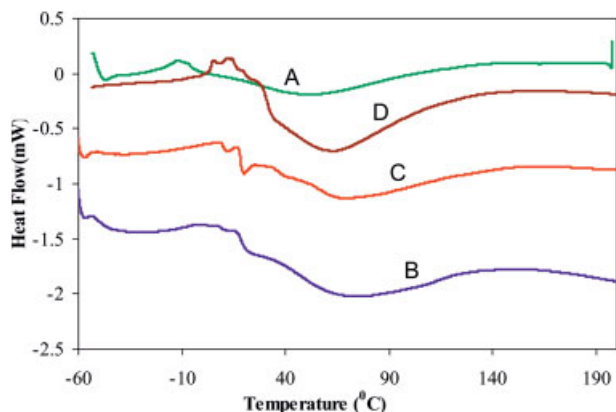


Figure 2 DSC of surface-treated hemp fibers: A, untreated hemp fiber; B, alkali-treated hemp fiber; C, UPE-MEKP-treated hemp fiber; D, acrylonitrile-treated hemp fiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

fibers. After the alkali treatment, the temperature at the maximum rate of decomposition of hemp fiber increased, indicating that the alkali treatment leads to an enhancement in the thermal stability of the hemp fiber, as has been noted by other researchers.^{21,22} Weight loss of 10% occurred between 288 and 332 °C for the untreated and surface-treated fibers, while a weight loss of 20% occurred in the range of 329–366 °C, and weight loss of 30% was observed in range of 346–378 °C for untreated and surface-treated hemp fibers.

Differential scanning calorimetry (DSC)

The DSC curves for untreated and surface-treated fibers expressed in terms of heat flow are shown in Figure 2. The melting point of cellulose has been reported to be near 300 °C.²³ However, a controversy surrounds the glass transition temperature (T_g) of cellulose, which has been reported between -30 and 160 °C.²⁴ The T_g for lignin has been reported between 135 and 172 °C.^{25,26} It is observed from Figure 2 that the crest associated with weight loss due to evaporation of water was found in all fiber samples, and ranged from 10 to 130 °C in hemp fibers, depending

TABLE III
Elemental Ratios of Surface-Treated Hemp Fibers
(from XPS Analysis)

	C/O	C/N	C/Si	C/Ca
A	2.94	27.24	95.52	137.77
B	3.48	33.07	—	131.68
C	4.94	103.17	25.46	134.64
D	4.25	81.81	—	—
E	2.61	23.94	—	183.97

A, untreated hemp fiber; B, alkali-treated hemp fiber; C, silane-treated hemp fiber; D, UPE-MEKP-treated hemp fiber; E, acrylonitrile-treated hemp fiber.

upon the degree of hydrogen bonding interaction.²⁷ Furthermore, this transition shifted towards the right after surface treatment of the hemp fiber. It was also observed that fibers had less amount of moisture percentage because they had been predried before any kind of treatment. This ensured that the inherent moisture of the fibers, which is 12–14% of the total fiber weight, was not able to interact with the surface treatments in any way. Therefore, the chemicals of the surface treatments had an opportunity to react with the actual fiber surface and fiber constituents. This would lead to a direct link between the chemicals used and the fiber constituents such as cellulose and hemicellulose. The T_g for lignin and cellulose were not observed by this particular method in DSC. Two exothermic peaks were observed by some researchers from 300 to 500 °C for untreated and surface-treated natural fibers, indicating the thermal stability of the fibers as a function of the treatment.²⁸ However, we were not able to see such peaks in our DSC thermograms as our experiments were conducted only up to 300 °C.

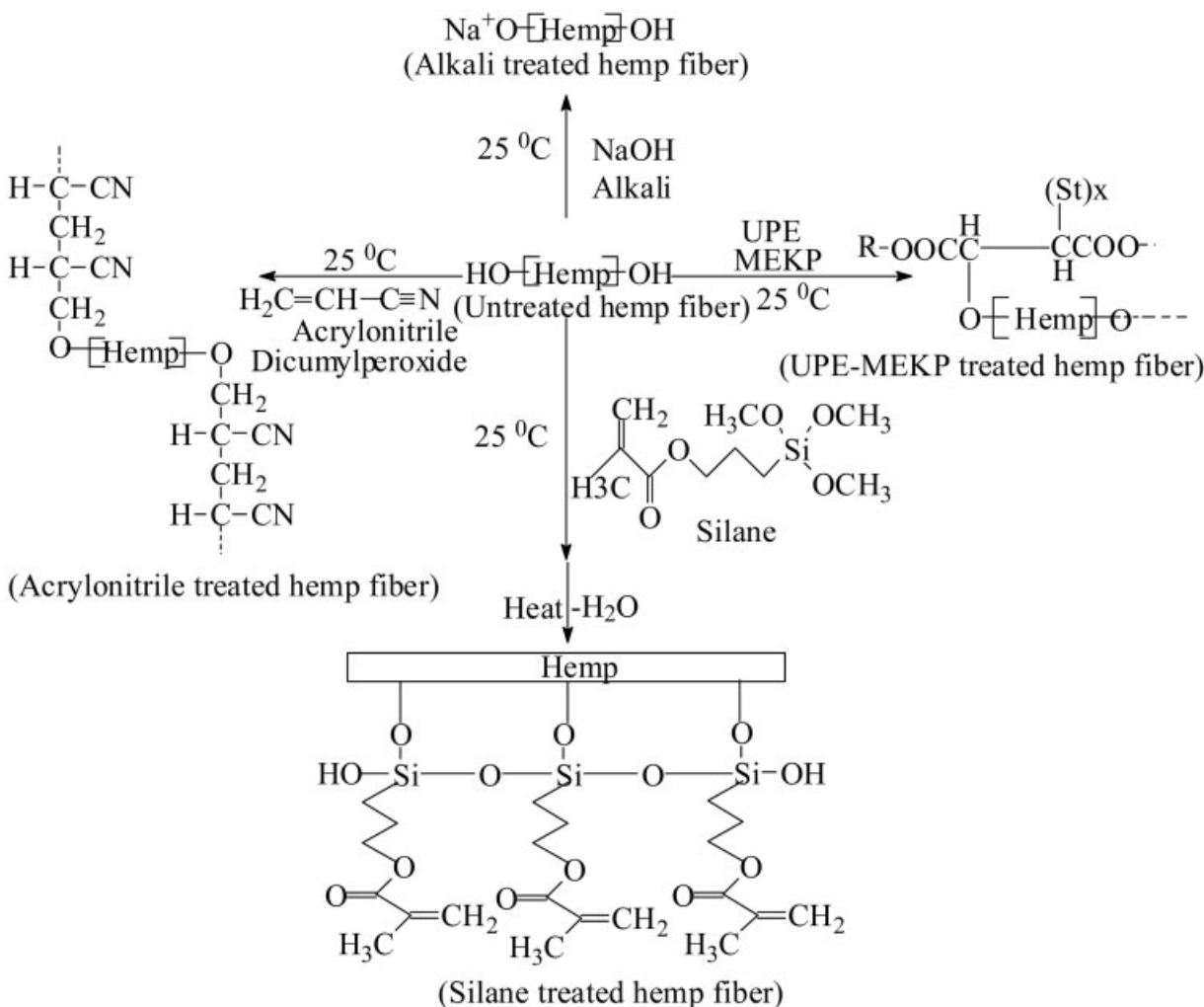
X-ray photon spectroscopy (XPS)

XPS survey scans were taken for untreated as well as surface-treated hemp fibers. These scans revealed the presence of carbon, oxygen, nitrogen, calcium, and silicon in the hemp fibers. Table II and III show the elemental composition and elemental ratios of the hemp fibers, respectively. It is observed that after an

TABLE II
Elemental Composition of Surface-Treated Hemp Fibers (from XPS Analysis)

	C 1s [0.314]	N 1s [0.499]	O 1s [0.733]	Si 2p [0.368]	Ca 2p [1.927]
A	71.64	2.63	24.39	0.75	0.52
B	73.74	2.23	21.21	0.36	0.56
C	79.44	0.77	16.09	3.12	0.59
D	80.17	0.98	18.85	—	—
E	69.91	2.92	26.79	—	0.38

A, untreated hemp fiber; B, alkali-treated hemp fiber; C, silane-treated hemp fiber; D, UPE-MEKP-treated hemp fiber; E, acrylonitrile-treated hemp fiber.



Scheme 3 Proposed reaction for surface treatment of hemp fibers.

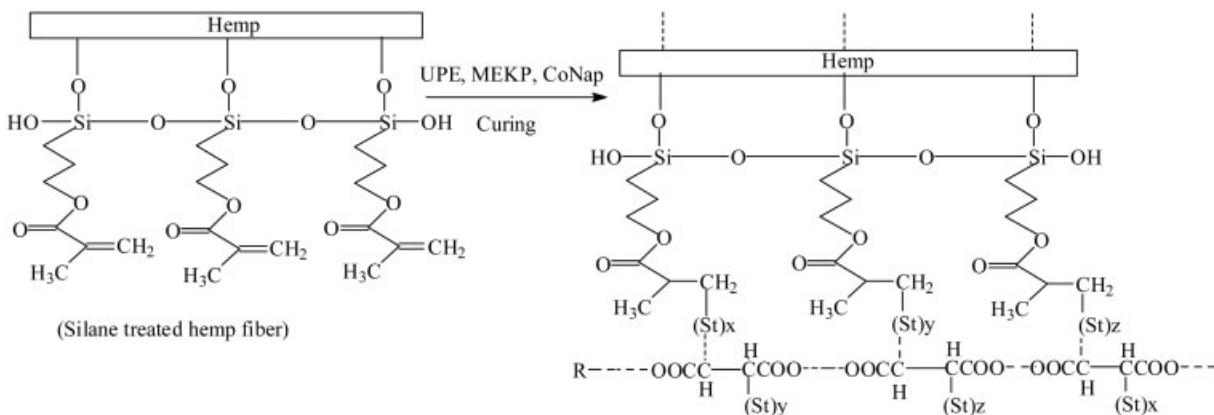
hour-long treatment with alkali solution the carbon content increases, while oxygen and nitrogen contents decrease. After silane treatment, there is a marked increase in silicon as well as carbon contents, and a decrease in oxygen and nitrogen contents. Again, after treatment with the matrix, there is an increase in carbon content, while a decrease in oxygen and nitrogen contents. However, with acrylonitrile treatment, there is a decrease in carbon content and an increase in nitrogen and oxygen contents.

It is well known that natural fibers consist of cellulose, hemicellulose and lignin.¹ Hemicellulose consists of a mixture of different sugars and other substituents that are soluble in water or bases. Lignin is similar to a highly unsaturated or aromatic polymer in structure and has low oxygen-to-carbon ratio, and is partially soluble in water.^{1,29} Because of the alkali treatment, a part of hemicellulose and lignin might have dissolved and washed away, leading to a decrease in oxygen content. The increase in carbon and silicon content after silane

treatment might be due to the attachment of bulky alkyl group and silicon to the hemp fiber as a result of this treatment. The large increase in carbon content of UPE-treated hemp fiber can again be due to the large oligomer molecule of UPE reacting with hydroxyl groups of the fiber. Meanwhile, the increase in nitrogen content after treatment with acrylonitrile might be due to grafting of acrylonitrile monomer to the fiber surface.

Reaction schemes

The schematic diagram of reactions that might result because of surface treatment of fibers is shown in Scheme 3. Scheme 4 and 5 show the reactions that might take place after the surface-treated fibers react with UPE matrix, during curing, and produce three-dimensional networked structures. Conclusive proofs for these reactions will be discussed in future publications.



Scheme 4 Proposed reaction for curing of surface-treated hemp fibers and UPE.

Optimization of fiber volume fraction

The fiber volume fraction was optimized by making biocomposites with nonwoven hemp mat fiber volume fractions of 20, 30, and 40%, and testing the mechanical properties of the resulting biocomposites. It should be noted that with 40 vol % fraction of hemp fibers, a consolidated biocomposite with a complete wet-out could not be manufactured. Figure 3 shows the result from flexural test of fiber volume fraction optimization study. The biocomposite with 30 vol % hemp fibers had higher bending strength and modulus of elasticity as compared with composite with 20 vol % hemp fibers as well as UPE control. The bending strength of 30 vol % hemp fiber composite was 16% higher than that of UPE control, and 9% higher than that of 20 vol % hemp fiber composite. Its modulus of elasticity was 150% higher than that of the neat resin, and 45% higher than that of 20 vol % hemp fiber composite. Similar results were obtained from tensile strength, tensile modulus, and impact strength (data not shown). Therefore, it was decided that 30 vol % of hemp fibers were optimum for a biocomposite made of hemp mats and UPE resin.

Tensile properties

Figure 4 shows the comparison of tensile properties of various composites. The tensile properties of biocomposites with surface-treated hemp fibers were higher than that of untreated hemp mat composite as well as that of neat resin. The tensile strength and modulus of untreated hemp fibers-based biocomposite was 45 and 325% higher than that of neat resin, respectively. Comparing surface-treated fiber-based composites, the tensile strength of alkali-treated fiber-based biocomposite was 34% higher than that of untreated hemp fiber-based composite, while that of silane-treated fiber-based biocomposite was 48% higher than that of untreated hemp composite. UPE-MEKP-treated hemp

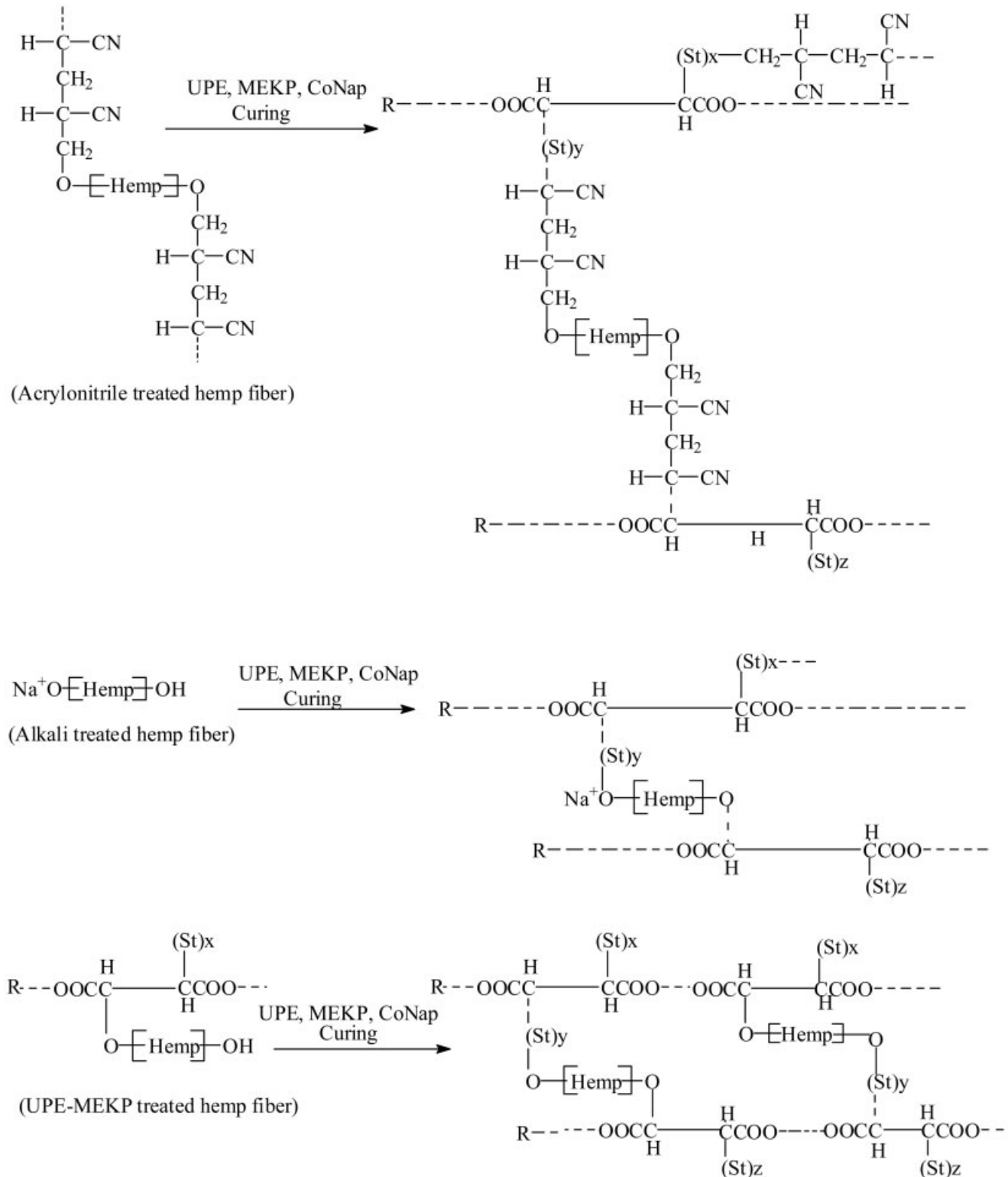
fiber-based biocomposite has tensile strength of 57% higher than that of untreated hemp composite, and for acrylonitrile-treated fibers it was 80% higher than that of untreated hemp fiber-based composite. In terms of tensile modulus, silane-treated fiber had enhancement of 6% as compared with that of untreated hemp, while UPE-MEKP-treated fibers had an enhancement of 4%, and acrylonitrile-treated fibers had a 25% enhancement compared with that of untreated hemp.

The tensile strength of E-glass-UPE composite was 130% higher, and the tensile modulus was 70% higher as compared with that of untreated hemp mat biocomposite at same volume %. The hybrid E-glass-hemp mat-UPE composite had an increment of 76% in tensile strength, and 34% in tensile modulus compared with that of untreated hemp mat-based biocomposite. The E-glass-UPE composite had 23% higher tensile strength as compared with that of hybrid composite of E-glass and hemp mats. On comparing specific tensile strength (tensile strength divided by density of composite) and specific tensile modulus (tensile modulus divided by density of composite) of all composites, it was found that the biocomposites and glass composites were in the same range.

This increase in tensile strength and modulus of the chemically-treated hemp fibers-based biocomposites may be an outcome of the improved adhesion between the fiber and the matrix. This improved adhesion might have enhanced the interfacial bonding and thus made it easier for the stress to be effectively transferred from the matrix to the fiber (as depicted in reaction Schemes 3, 4, and 5).²⁻⁴

Flexural properties

Flexural strength is a combination of the tensile and compressive strengths, which directly varies with the interlaminar shear strength. In flexural testing, various mechanisms such as tension, compression, shearing



Scheme 5 Proposed reaction for curing of surface-treated hemp fibers and UPE.

etc. take place simultaneously. In a three point flexural test, the failure occurs due to bending and shear failure. The bending strength and modulus of elasticity of different composites are compared in Figure 5.

The flexural properties of biocomposites with surface-treated hemp fibers were higher than that of un-

treated hemp mat composite; also, the flexural properties of all composites were higher than that of neat resin. Comparing surface-treated fiber-based composites, the modulus of elasticity as well as bending strength of alkali-treated, silane-treated, and UPE-MEKP-treated hemp fiber-based biocomposites lie in

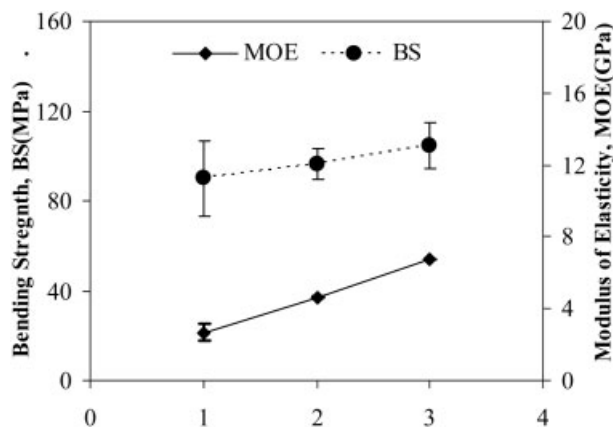


Figure 3 Optimization of fiber volume fraction by evaluation of mechanical properties: A, UPE control; B, untreated hemp mat (20% vol)-UPE; C, untreated hemp mat (30% vol)-UPE.

the same range. However as discussed earlier,³⁰ the modulus of elasticity and bending strength of acrylonitrile-treated fibers-based composites were 7% and 35% higher than those of untreated hemp fiber biocomposite respectively. As compared with UPE control, the surface-treated fiber-based biocomposites had a 10–16% enhancement in bending strength, and 140–225% increment in modulus of elasticity.

The bending strength of E-glass-UPE composite was 144% higher, and the modulus of elasticity was 56% higher as compared with that of untreated hemp mat biocomposite. The hybrid E-glass-hemp mat-UPE composite had a bending strength 83% higher, and modulus of elasticity 66% higher than that of untreated hemp mat-based biocomposite. The E-glass-UPE composite had 25% higher bending strength as

compared with that of hybrid composite of E-glass and hemp mats, but its modulus was 7% lower than that of hybrid composite. On comparing specific bending strength and specific modulus of elasticity of all composites, it was found that the biocomposites and glass composites were in the same range.

The increment in the flexural properties of biocomposites after surface treatment of the hemp fibers can be attributed to the modifications in the molecular level of the fibers due to chemical bonding between fiber components and the treatment reagents. Such linkage might have lead to better interfacial bondage, better adhesion, and effective stress transfer (as depicted in reaction Schemes 3, 4, and 5).^{2–4}

Impact strength

Impact strength is the ability of a material to resist the fracture under stress applied at high speed. The impact properties of the composite are directly related to its overall toughness. The fibers play a very important role in the impact resistance of the composite as they interact with the crack formation in the matrix and act as stress transferring medium. It is a common observation that with any surface treatment, the flexural and tensile properties of the composite increase, but the impact strength (shown in Fig. 6) will decrease.

The impact strength of all composites were higher than that of neat resin. The impact strength of biocomposites with surface-treated hemp fibers was higher than that of untreated hemp mat composite. As compared with neat resin, there was an increment of 82% in impact strength of untreated hemp fiber-based composites, 49% for alkali-treated fibers, 94% for silane-

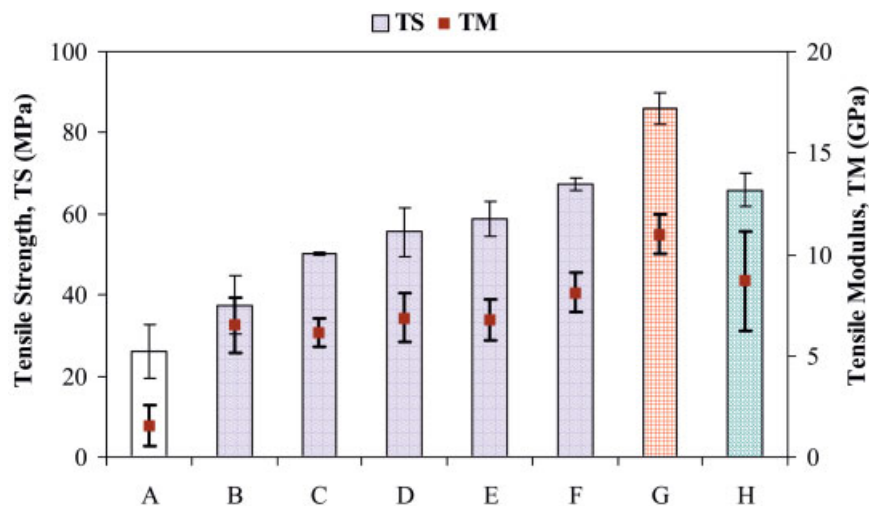


Figure 4 Comparison of tensile properties of surface-treated composites: A, UPE control; B, untreated hemp mat (30% vol)-UPE; C, alkali-treated hemp mat (30% vol)-UPE; D, silane-treated hemp mat (30% vol)-UPE; E, UPE-MEKP-treated hemp mat (30% vol)-UPE; F, acrylonitrile-treated hemp mat (30% vol)-UPE; G, E-glass mat-UPE; H, E-glass mat-hemp mat-UPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

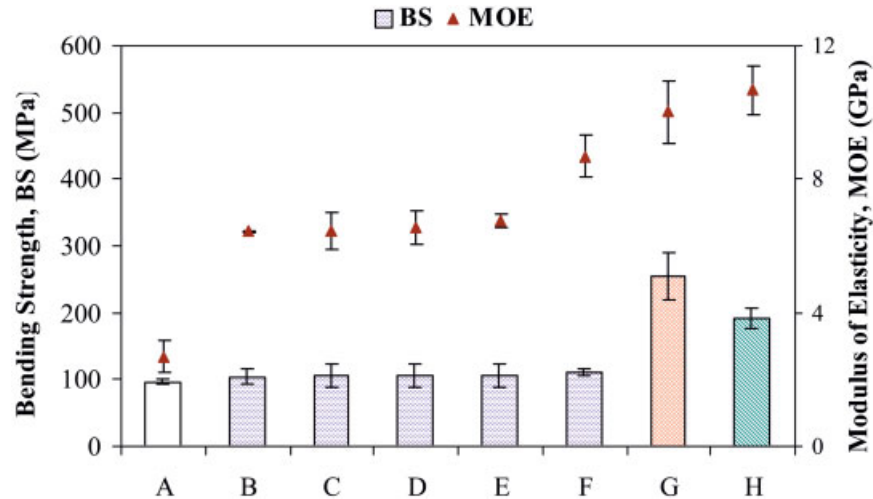


Figure 5 Comparison of flexural properties of surface-treated composites: A, UPE control; B, untreated hemp mat (30% vol)-UPE; C, alkali-treated hemp mat (30% vol)-UPE; D, silane-treated hemp mat (30% vol)-UPE; E, UPE-MEKP-treated hemp mat (30% vol)-UPE; F, acrylonitrile-treated hemp mat (30% vol)-UPE; G, E-glass mat-UPE; H, E-glass mat-hemp mat-UPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

treated fibers, 120% for UPE-MEKP-treated fibers, and 180% for acrylonitrile-treated hemp fiber-based biocomposites. On comparing the impact strength of untreated and surface-treated biocomposites, it was found that the impact strength of silane-treated fibers was 7% more than that of untreated fibers, while that of UPE-MEKP-treated fibers was 21% more than that of untreated fibers, and that of acrylonitrile-treated fibers was 54% more than that of untreated fibers.

The impact strength of E-glass-UPE composite was 16.3 times higher than that of neat resin and 8.5 times higher than that of untreated hemp fiber-based biocomposite. The

hybrid E-glass-hemp mat-UPE composite had impact strength 16.5 times higher than that of neat resin and 8.6 times higher than that of untreated hemp fiber-based biocomposite. The impact strength of hybrid composite of E-glass mats and hemp mats was almost same as that of E-glass-UPE composite (within error bars).

Dynamic mechanical analysis

Dynamic mechanical methods expose the specimen to periodic stresses. The polymer is subjected continuously to forced oscillations, and the applied stress is

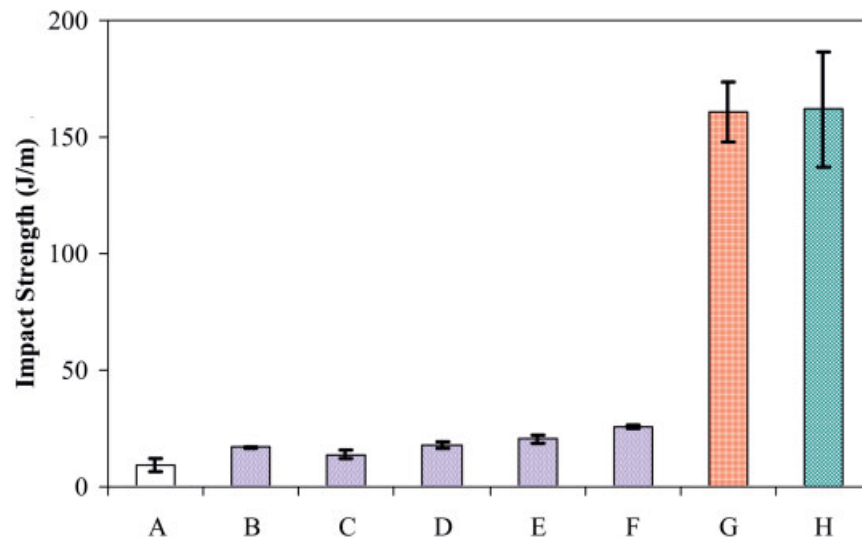


Figure 6 Impact strength of surface-treated composites: A, UPE control; B, untreated hemp mat (30% vol)-UPE; C, alkali-treated hemp mat (30% vol)-UPE; D, silane-treated hemp mat (30% vol)-UPE; E, UPE-MEKP-treated hemp mat (30% vol)-UPE; F, acrylonitrile-treated hemp mat (30% vol)-UPE; G, E-glass mat-UPE; H, E-glass mat-hemp mat-UPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

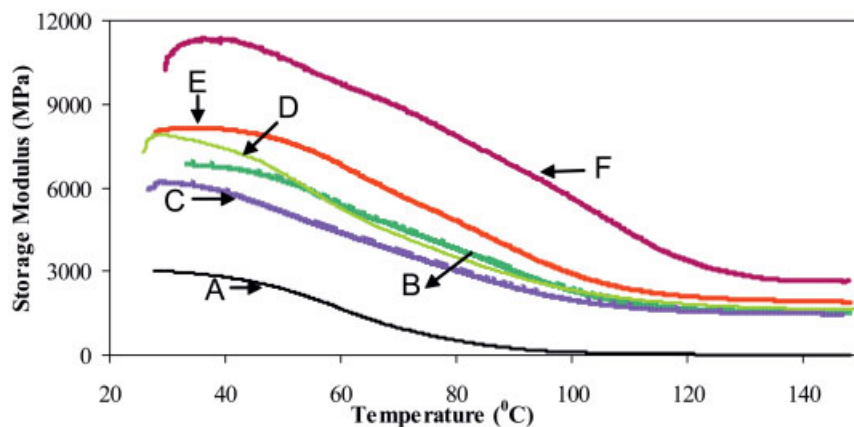


Figure 7 Typical storage modulus curves of surface-treated composites: A, UPE control; B, untreated hemp mat (30% vol)-UPE; C, alkali-treated hemp mat (30% vol)-UPE; D, UPE-MEKP-treated hemp mat (30% vol)-UPE; E, acrylonitrile-treated hemp mat (30% vol)-UPE; F, E-glass mat-UPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

sinusoidal with a frequency. The deformation of ideal-elastic bodies follows the stress instantaneously but that of viscoelastic polymer experiences a delay. The stress vector is assumed to be a sum of two components: one component is in phase with the deformation; the other is not. Each of these two components possesses a modulus. The real modulus (shear storage modulus) G' measures the stiffness and shape stability of the specimen, whereas the imaginary modulus (shear loss modulus) G'' describes the loss of usable mechanical energy by dissipation as heat. The maximum of $\tan \delta$ as a function of temperature is generally identified as the glass transition temperature $T_{g'}$, which is dependent on the deformation rate. The damping properties of the material are related to energy absorption.

The area below $\tan \delta$ is function of the absorption of the energy necessary to pass from glassy state to rubbery state.

The typical curves of storage modulus and $\tan \delta$ for neat resin and composites can be seen in Figures 7 and 8 respectively. The storage modulus decreased as a function of temperature, as is commonly observed for composites. At higher temperatures, all biocomposites plateau to the same value of modulus. The storage moduli of surface-treated hemp fibers-based biocomposites were higher than that of untreated hemp fiber-based biocomposite. A comparison of storage moduli of composites at 40°C was made in Figure 9. The storage modulus of biocomposites at 40°C was enhanced by 110–190% compared with neat resin. Glass mat-based composite had a storage modulus 307%

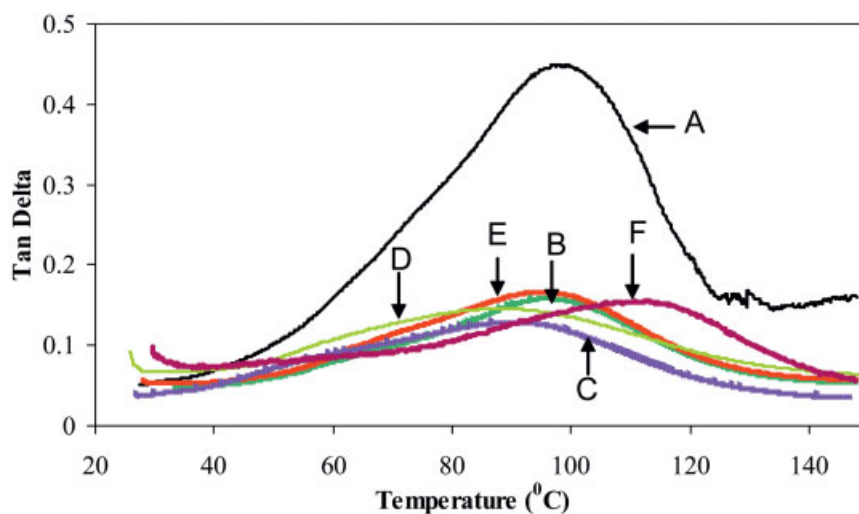


Figure 8 Typical $\tan \delta$ curves of surface-treated composites: A, UPE control; B, untreated hemp mat (30% vol)-UPE; C, alkali-treated hemp mat (30% vol)-UPE; D, UPE-MEKP-treated hemp mat (30% vol)-UPE; E, acrylonitrile-treated hemp mat (30% vol)-UPE; F, E-glass mat-UPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

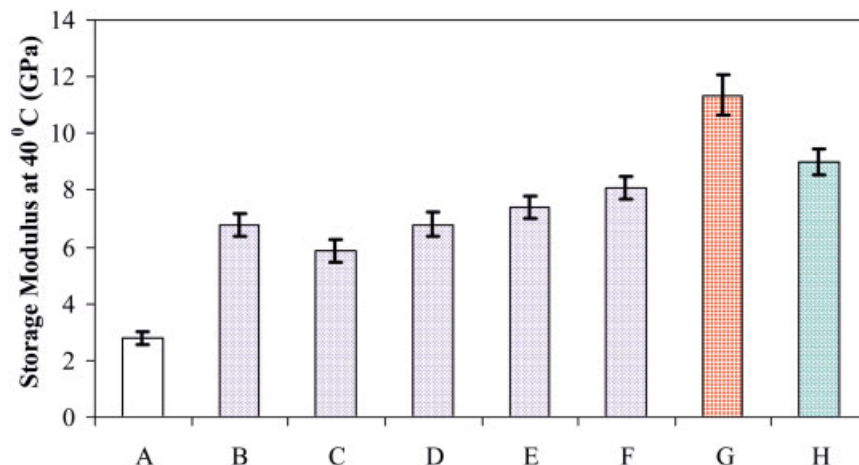


Figure 9 Storage modulus of surface-treated composites at 40°C: A, UPE control; B, untreated hemp mat (30% vol)–UPE; C, alkali-treated hemp mat (30% vol)–UPE; D, silane-treated hemp mat (30% vol)–UPE; E, UPE–MEKP-treated hemp mat (30% vol)–UPE; F, acrylonitrile-treated hemp mat (30% vol)–UPE; G, E-glass mat–UPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

higher than that of neat resin, 68% higher than that of untreated hemp fiber-based composite, and 26% higher than that of hemp mat–glass hybrid composite at 40°C.

The loss modulus of composites was higher than that of neat resin. This follows the trend found previously for natural fiber–thermoset composites, where the loss modulus increased after addition of fibers to the plastic.⁸

Over the entire range of temperature, $\tan \delta$ was highest for the neat resin because of huge reduction in the storage modulus values at higher temperatures. The lower values of $\tan \delta$ for the biocomposite made with surface-treated hemp fibers suggest that there is less damping in the chemically-treated hemp fiber-based composites. The $\tan \delta$ versus temperature plot for biocomposites as well as E-glass composite is similar. The $\tan \delta$ curve of all composites shifted towards right as compared with neat resin, but this shift was significant in case of glass-based composite. The T_g of the neat resin was 95°C. For biocomposites, the T_g increased about 2–5°C as compared with neat resin.

Morphology of fiber surface

The micrographs of untreated and surface-treated hemp fibers are shown in Figure 10. The distribution of the fibers in the hemp mat was random, and uneven. The micrographs in Figure 10 focus on single fiber surface. Fibrillation was observed in fibers after surface treatment. This could provide more anchorage for the matrix, and hence improve the strength of the composite. In general, the surface of chemically-treated fibers looked different from that of the untreated hemp fiber.

In the biocomposites, the fiber pull out was clearly observed (pictures not shown). Biocomposite with untreated hemp fibers showed poor interfacial bonding between the fiber and matrix, which resulted in relatively clean surface over the pulled out fibers due to greater extent of delamination. In case of untreated fiber-based biocomposites, shear failure results in high degree of pull out. The adhesion between the fiber and the matrix was enhanced in biocomposites with surface-treated fibers. The fibers were covered with matrix, and the fiber pull out was relatively smaller.

CONCLUSIONS

Renewable materials from sustainable sources are becoming increasingly used in a variety of applications. Polymer matrix composites reinforced with natural plant fibers are one such example. There is need for fundamental and applied research into products and processes based upon biomaterials and to transfer these technologies to industry. By placing natural fibers in unsaturated polyester resin matrix, novel low-cost biocomposites with desired properties can be made. Such biocomposites can provide many beneficial additions to the advanced global housing program.

The adhesion between industrial hemp fibers and UPE matrix was increased by treatment of hemp fiber surface with alkali, silane, UPE (matrix), and acrylonitrile. The surface treatment of hemp mats also resulted in higher mechanical and thermal properties. Other modifications, which could bring about the same effects, are acetylation, bleaching, UV/plasma, microwave, and steam explosion. It is our future plan to optimize these treatments for natural fibers. The

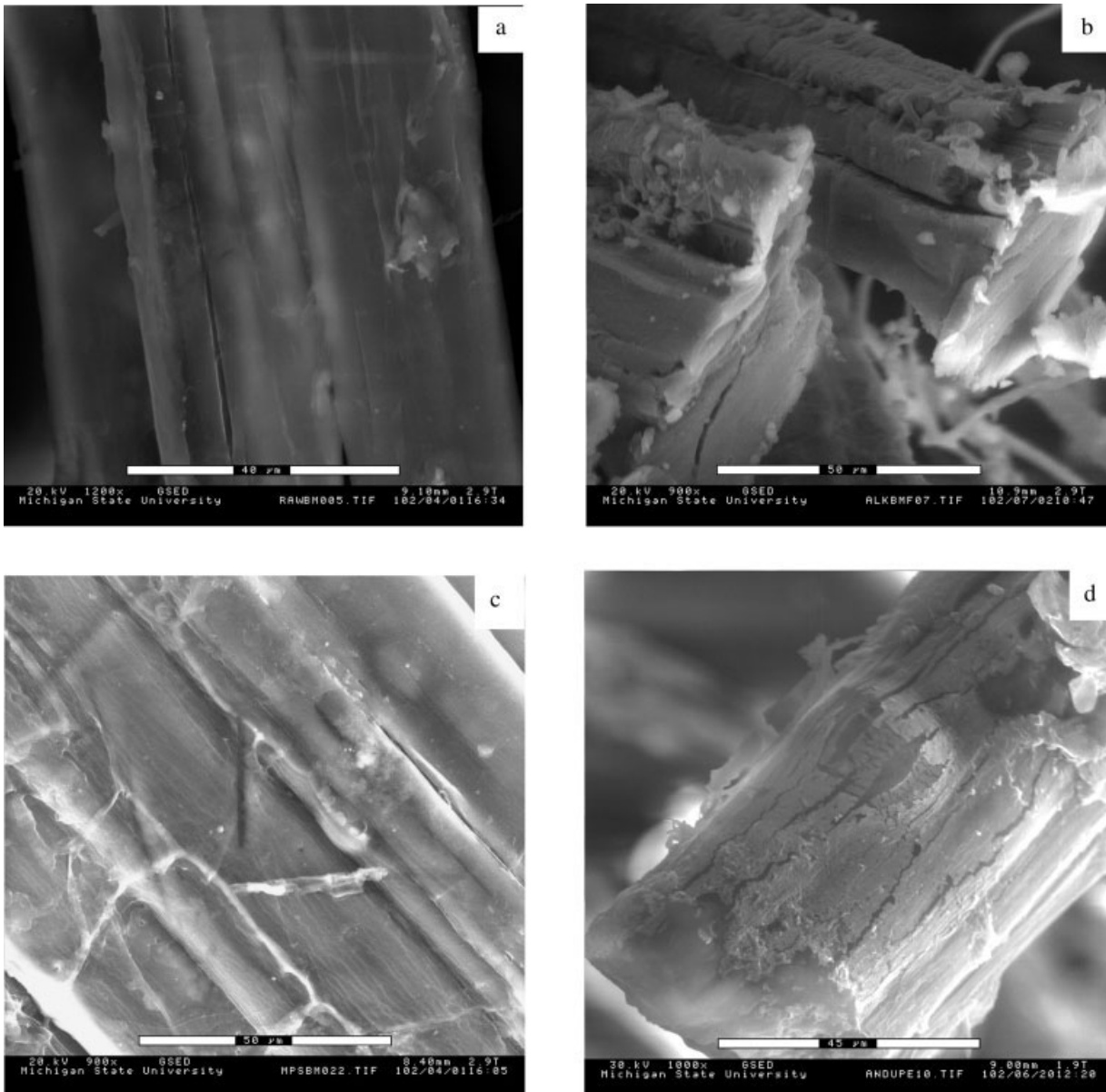


Figure 10 ESEM micrographs of surface-treated hemp mat fibers: (a) untreated hemp mat, magnification 1200 \times , scale bar 45 μm ; (b) alkali-treated hemp mat, magnification 900 \times , scale bar 50 μm ; (c) silane-treated hemp mat, magnification 900 \times , scale bar 50 μm ; (d) acrylonitrile-treated hemp mat, magnification 1000 \times , scale bar 45 μm .

gap between performance of glass-based composites and biocomposites was bridged by fabricating a hybrid composite comprising of glass and hemp fibers. In terms of specific modulus and strength, glass composites and biocomposites are in the same range.

Collaboration and samples from Kemlite Company Inc., Joliet, IL, and FlaxCraft Inc., Cresskill, NJ are highly appreciated.

References

- Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol Mater Eng* 2000, 276–277, 1.
- Mohanty, A. K.; Misra, M.; Drzal, L. T. *Compos Interface* 2001, 8, 313.
- Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
- Satyanarayana, K. G.; Sukumaran, K.; Kulkarni, A. G.; Pillai, S. G. K.; Rohatgi, P. K. *Composites* 1986, 17, 329.
- Varma, I. K.; Anantha Krishnan, S. R.; Krishnamoorthy, S. *Composites* 1989, 20, 383.
- Chand, N.; Verma, S.; Rohatgi, P. K. *Trop Sci* 1987, 27, 215.
- Hepworth, D. G.; Bruce, D. M.; Vincent, J. F. V.; Jeronimidis, G. *J Mater Sci* 2000, 35, 293.
- Rana, A. K.; Mitra, B. C.; Banerjee, A. N. *J Appl Polym Sci* 1999, 71, 531.
- Ray, D.; Sarkar, B. K.; Rana, A. K.; Bose, N. R. *Compos Appl Sci Manuf* 2001, 32, 119.
- Rout, J.; Tripathy, S. S.; Misra, M.; Mohanty, A. K.; Nayak, S. K. *J Appl Polym Sci* 2002, 84, 75.

11. Rout, J.; Tripathy, S. S.; Misra, M.; Mohanty, A. K.; Nayak, S. K. *Compos Sci Technol* 2001, 61, 1303.
12. Rout, J.; Misra, M.; Tripathy, S. S.; Nayak, S. K.; Mohanty, A. K. *Polym Compos* 2001, 22, 468.
13. Pavithran, C.; Mukherjee, P. S.; Brahmakumar, M. J. *Reinforc Plast Compos* 1991, 10, 91.
14. Gassan, J.; Bledzki, A. K. *Polym Compos* 1997, 18, 179.
15. Gassan, J.; Bledzki, A. K. *Compos Sci Technol* 1999, 59, 1303.
16. Zimmerman, J. M.; Lousure, N. S. *J Adv Mater* 1998, 30, 32.
17. Khot, S. N.; LaScala, J. J.; Can, E.; Morye, S. S.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S. H.; Wool, R. P. *J Appl Polym Sci* 2001, 82, 703.
18. Dweib, M. A.; Hu, B.; O'Donnell, A.; Shenton, H. W.; Wool, R. P. *Compos Struct* 2004, 63, 147.
19. O'Donnell, A.; Dweib, M. A.; Wool, R. P. *Compos Sci Technol* 2004, 64, 1135.
20. Belcher, L.; Drzal, L. T.; Misra, M.; Mohanty, A. K. *Polym Mater Sci Eng Am Chem Soc* 2002, 87, 256.
21. Mahato, D. N.; Mathur, B. K.; Bhattacharjee, S. *Ind J Fiber Text Res* 1995, 20, 202.
22. Varma, D. S.; Varma, M.; Varma, I. K. *Thermochim Acta* 1986, 108, 199.
23. Van Krevelan, D. W. *Properties of Polymers*; 3rd ed.; Elsevier: Amsterdam, 1990.
24. Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*; 3rd ed.; Wiley: New York, 1989.
25. Feldman, D.; Banu, D.; Khoury, M. *J Appl Polym Sci Part C* 1965, 11, 27.
26. Vazquez-Torres, H.; Canche-Escamilla, G.; Cruz-Ramos, C. A. *J Appl Polym Sci* 1992, 45, 633.
27. Goulart Silva, G.; De Souza, D. A.; Machado, J. C.; Hourston, D. J. *J Appl Polym Sci* 2000, 76, 1197.
28. Mwaikambo, L. Y.; Ansell, M. P. *Angew Makromol Chem* 1999, 272, 108.
29. Zafeiropoulos, N. E.; Vickers, P. E.; Baillie, C. A.; Watts, J. F. *J Mater Sci* 2003, 38, 3903.
30. Mehta, G.; Mohanty, A. K.; Misra, M.; Drzal, L. T. *J Mater Sci* 2004, 39, 2961.