

Preparation and Characterization of Chemically Modified Jute–Coir Hybrid Fiber Reinforced Epoxy Novolac Composites

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ABSTRACT: In this study, the effects of fiber surface modification and hybrid fiber composition on the properties of the composites is presented. Jute fibers are cellulose rich (>65%) modified by alkali treatment, while the lignin rich (>40%) coconut coir fibers consist in creating quinones by oxidation with sodium chlorite in the lignin portions of fiber and react them with furfuryl alcohol (FA) to create a coating around the fiber more compatible with the epoxy resins used to prepare polymer composites. The maximum improvement on the properties was achieved for the hybrid composite containing the jute–coir content of 50 : 50. The tensile and flexural strength are recorded as 25 and 63 MPa at modified coir fiber content of 50 vol %, respectively, which are 78% and 61% higher than those obtained for unmodified fiber reinforced composites, i.e., tensile and flex-

ural strength are 14 and 39 MPa, respectively. The reinforcement of the modified fiber was significantly enhanced the thermal stability of the composites. SEM features correlated satisfactorily with the mechanical properties of modified fiber reinforced hybrid composites. SEM analysis and water absorption measurements have confirmed the FA-grafting and shown a better compatibility at the interface between chemically modified fiber bundles and epoxy novolac resin. Hailwood–Horrobin model was used to predict the moisture sorption behavior of the hybrid composite systems. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 3038–3049, 2012

Key words: composites; biofibers; mechanical and thermal properties; structure–property relations; dynamic mechanical Analysis

INTRODUCTION

Natural fibers such as jute, coir, hemp, sisal, bagasse, etc., are available in abundance and inexpensive compared to other man-made synthetic fibers. These natural fibers are used as a suitable reinforcing material to satisfy the environment, and they are now rapidly emerging as a potential alternative for traditional glass and organic fibers (carbon fiber and aramid fibers) in engineering composites during the last decades.^{1–3} The natural fibers are used as reinforcements for composite materials because of its various advantages such as low cost, low densities, low energy consumption, etc., over conventional fibers.^{4,5} In addition, they are renewable as well as biodegradable, and indeed wide varieties of fibers are locally available.⁶ Natural fibers have a few disadvantages when used as reinforcements such as lower impact strength, higher moisture absorption that brings dimensional changes thus leading to microcracking and poor thermal stability.^{7,8}

Among the different lignocellulosic natural fibers, jute fibers (*Chorchorous capsularis*) are a well-known

reinforcing material in the fabrication of different types of polymer-based composites, mainly due to cost effectiveness, high mechanical strength, modulus, etc. However, it is also has some crucial disadvantages such as high coarseness, high stiffness, low extensibility, wash shrinkage, ready susceptibility to microbial attack, poor abrasion resistance, etc.^{9,10} The coir (*Cocos nucifera*) is also an important lignocellulosic fiber obtained from coconut trees, which grow extensively in tropical countries. Coir fibers have many advantages like low density, high lignin content, and high strain to failure up to approximately 40%, hardwearing quality, durability. However, the main drawback of these natural fiber/polymer composites is the inherent incompatibility between hydrophilic lignocellulosic fibers and hydrophobic polymeric matrices.^{11,12} The resulting composites present low mechanical properties due to lack of adhesion between the fibers and the resin at the interface. This problem is minimized when phenolic matrices are used, as in this study, due to polar hydroxyl groups in their structure. To produce composites with good mechanical and thermomechanical properties, it is necessary to promote improvements in the interface area, for example by increasing the adhesion between the fiber and the polymer matrix through a chemical modification of the fiber surface and/or by decreasing the thickness

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of the fiber bundles. Many reports are available on improvement of properties of the natural fiber reinforced polymer composites through chemical modifications of the fibers.^{13–16} In this study, we have a new way of chemical treatment of the fiber surfaces involving selective modification of the lignin moiety of the fiber through surface oxidation with ClO_2 , followed by chemical reaction with furfuryl alcohol.

Hybridization with more than one type of fibers used in single matrix leads to the development of hybrid fiber reinforced composites. In principle, several different types of fiber could be incorporated into a hybrid system but in practice it is likely that a combination of only two types of fibers would be most useful.¹⁷ Carbon and glass fibers are often used in the same polymeric resin matrix to form hybrid composites. Carbon fiber provides strong, stiff, and low density reinforcement but it is relatively expensive and brittle, while glass fiber is relatively cheap and has better fracture property but its strength and stiffness are relatively low. By hybridization, it is possible to design the material to better suit various requirements. At the same time, material costs could be substantially reduced by careful selection of reinforcing fibers. By combining the two fibers with the same matrix, it is possible to achieve a balance between the properties of all natural fibers or synthetic fibers reinforced plastics. A review of the literature on carbon fiber and glass fiber hybrid reinforced plastics indicated that incorporation of both fibers into a single matrix leads to positive hybrid effect on flexural properties, but negative hybrid effect on tensile properties.^{18,19} Paiva et al.²⁰ used plain weave hybrid ramie-cotton fabrics as reinforcement in a polyester matrix and showed the high potential of ramie fiber and weak contribution of cotton fiber as reinforcement in lignocellulosic fiber composites. Jacob et al.²¹ and Idicula et al.²² studied the mechanical properties and cure characteristics of sisal and oil palm hybrid fiber reinforced natural rubber composites. John et al.²³ have studied the effects of chemical modification of fiber surface in sisal-oil palm reinforced rubber green composite and found improved mechanical properties for the modified hybrid fibers reinforcement. Idicula et al.²⁴ have found positive hybrid effect of banana-sisal fibers on the tensile and flexural properties of the hybrid fibers reinforced polyester composites. It can be seen that the studies on hybrid effects of two different natural fibers on the properties of short jute-coir fiber reinforced epoxy novolac hybrid composites have not been addressed so far.

In this study, we have studied the effect of jute-coir hybrid fibers reinforcement on the properties of epoxy novolac-based (EPN) composites. The jute fibers (short fiber and fabrics) were alkali treated before their reinforcement. The coir fibers were

TABLE I
Physical Properties of Jute and Coir Fiber

Physical properties	Jute fiber	Coir fiber
Density (gm/cc)	1.45 ± 0.1	1.3 ± 0.1
Cellulose content (%)	65 ± 2	33.28 ± 1.21
Hemicelluloses content (%)	20 ± 2	2.67 ± 1.44
Lignin content (%)	12 ± 2	46.84 ± 0.8
Microfibrillar angle (°)	8.1	39 ± 5
Diameter (μm)	54 ± 6	200 ± 10
Tensile Strength (MPa)	473	144.6
Young's Modulus (MPa)	19,500	3101.2
Elongation at break (%)	1.17 ± 0.2	32.3 ± 0.2
Aspect ratio (L/D)	365 ± 10	100 ± 5

chemically modified through milder chemical process involving oxidative treatment with ClO_2 solution and consequent surface grafting with furfuryl alcohol. The properties of the modified fibers reinforced EPN composites were compared with those obtained for unmodified fibers reinforced composites. The optimization of fiber composition for the hybrid composites was also investigated. The mechanical, thermal, and water absorption properties of the unmodified and modified fiber composites were correlated.

EXPERIMENTAL

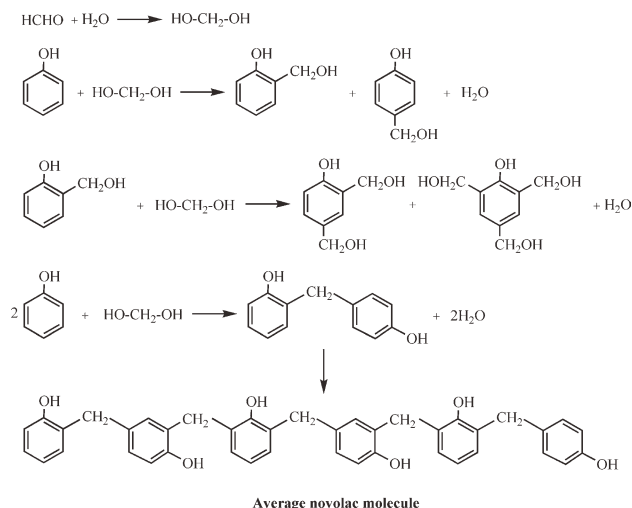
Materials

The coir fiber (diameter = 200–240 μm; density = 1.2–1.4 g/cm³, and microfibril angle = 30–39°) was obtained from Central Coir Research Institute, Coir Board, Kerala, India. Jute fiber (Grade – W2, *Chorchorus capsularis*) was obtained from Fort-Gloster Jute Mill, Howrah, India. The physical properties of jute and coir fibers are given in Table I. Reagent grade sodium chlorite, furfuryl alcohol, acetic acid, acetone, and toluene were obtained from E. Merck, India. Phenol and formaldehyde (37% w/w) were obtained from E. Merck, India, and used as received. Epichlorohydrin and sodium hydroxide were procured from S.D. Fine Chemicals, India. The hardener, di-ethylene-triamine (DETA), was obtained from E. Merck, India.

Methods

Synthesis of epoxy novolac resin

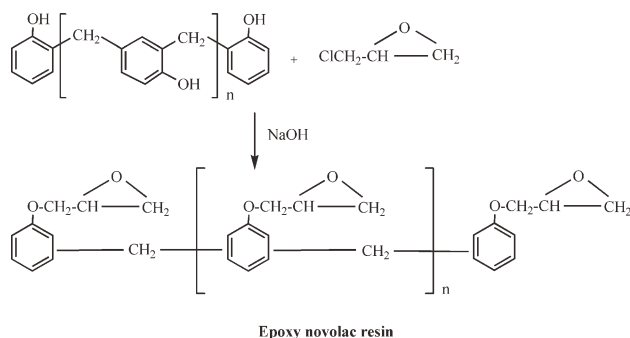
Step 1: Synthesis of novolac resin. Novolac resins were prepared by reacting phenol with formaldehyde in a specific molar ratio (phenol/formaldehyde = 1 : 0.8) with oxalic acid as catalyst (in proportion of 1.5% w/w of phenol)²⁵. The constituents were mixed in a four-necked round bottom flask by stirring them for 2 h at 100°C. After reaction, the whole viscous mass was taken in a separating funnel and



Scheme 1 Chemical reactions involved in the synthesis of novolac resin.

extracted with toluene (1 : 1 v/v). Finally, the brown viscous liquid of novolac resin is obtained. The chemical reaction involved in the preparation of novolac resin has shown in Scheme 1.

Step II: Epoxidation of novolac resin.. A precalculated quantity of novolac resin ($MW_{avg} = 624$) was taken in a conical flask fitted with a reflux condenser in an inert atmosphere. Calculated quantity of epichlorohydrin was added to it and slowly heating with continuous stirring for 2 h. The 40 wt % of sodium hydroxide was added to the aforementioned solution over a period of 6 h at 100°C. After the addition of total amount of NaOH, the temperature of mixture was kept at 100°C for 1 h and then cooled down to room temperature. After completion of reaction, the yellowish viscous mass was taken in a separating funnel and extracted with toluene (1 : 1 v/v). The epoxy novolac (EPN) resin was isolated by evaporating the toluene. Finally, the resin was washed with distilled water and dried. The chemical reaction involved during epoxidation of novolac resin is given in Scheme 2.



Scheme 2 Chemical reactions involved in the epoxidation of novolac resin.

The epoxy equivalent was calculated by means of hydrochlorination method by titration the residual acid, which remained after reaction between known quantity of resin and hydrochloric acid in the pyridine medium, by 40% aqueous sodium hydroxide. The epoxy equivalent was found to be 191 gm-equivalent/mole. The typical properties of the synthesized epoxy novolac (EPN) resin are given in Table II.

Surface modification of jute fiber, jute fabric, and coir fibers

Alkali treatment of jute fiber and fabric.. Jute fabrics were cut into 100 × 100 cm² dimensions, and jute fiber was cut into short fiber with 1 cm length. Both short fibers and fabrics were initially washed with distilled water to remove dirt, mud, and other water-soluble impurities. The washed jute fiber and fabrics were then immersed in 5% NaOH solution for 2 h at 50°C. The jute was taken out from the NaOH solution, and neutralized with dilute acetic acid, and finally washed with distilled water. The jute fiber and fabrics were then dried at room temperature (25°C) for 48 h, followed drying at 70°C for 5 h using air-oven.

Removal of surface impurities of coir fiber.. To remove the low-molecular weight substances such as waxes, terpenes, and other natural impurities from the fiber surface, the fibers were Soxhlet-extracted with cyclohexane-ethanol (1 : 1 v/v) for a period of 48 h and then with water for 24 h. The fibers were dried in air oven at 60°C until constant weight. The removal of wax was tested through gravimetric method.

Surface oxidation of coir fiber.. The dewaxed fibers (2 g) were oxidized with an aqueous chlorine dioxide (ClO₂) solution (18 mL, 1.88 mmol), which was prepared by reactions between sodium chlorite and acetic acid in aqueous medium as shown in eq. (1). After oxidation reaction, the yellow-red colored fibers were washed with DI-water until neutrality.

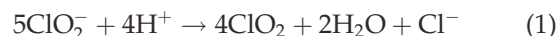


TABLE II
Typical Properties of the Synthesized EPN Resin

Properties	Evaluation
Appearance	A clear pale yellow liquid
Specific gravity at 25 °C (gm/cc)	1.119
Epoxy equivalent number	191
Gel point in minutes	26
Solid content (%)	84
Tensile strength (MPa)	7.4
Tensile modulus (MPa)	176
Impact strength (kJ/m ²)	1.2

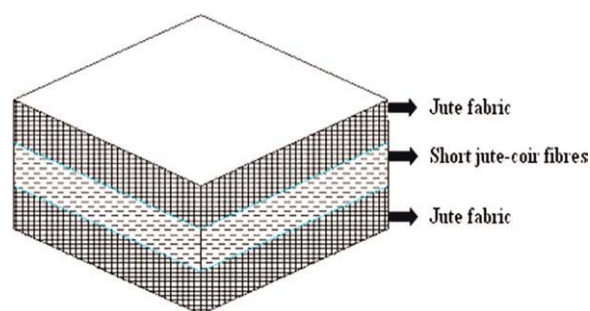


Figure 1 Schematic representation of layering pattern of fibers in the hybrid composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

Furfuryl alcohol grafting on oxidized fiber. The oxidized coir fibers (2 g) impregnated with furfuryl alcohol (FA) (11.35 g) was heated at 100°C for 4 h in presence of N₂ flow. The excess of FA was removed by soxhlet extraction using ethanol for 15 h. Then, the fibers were dried at 50°C for 24 h. The weight gains due to reaction were determined based on unmodified and grafted fiber weight, using following eq. (2).

WPG

$$= \frac{\text{Dry weight grafted CF} - \text{Dry weight unmodified CF}}{\text{Dry weight unmodified CF}} \quad (2)$$

Fabrication of EPN-based jute-coir hybrid composites

The hand lay-up method followed by compression molding was adopted for composite fabrication. For this composite fabrication, jute fiber were considered as bidirectional fabrics acting as reinforcement, and short jute and coir hybrid fibers were considered as filler materials because of smaller sizes. Both unmodified and modified jute and coir fibers were used in the composite fabrication. In the composites, the mixture of short jute and coir fibers were distributed in between the two jute fabric layers (skin layers) having uniform dimension (100 × 100 mm²). Jute fabrics with short jute and coir fibers were impregnated in EPN resin. For each formulated composite, the volume ratio of matrix to fiber is 70 : 30. The EPN-based hybrid composites were prepared at different ratio of relative volume fraction of the two short fibers (jute : coir = 100 : 0, 80 : 20, 65 : 35, 50 : 50, 35 : 65, and 0 : 100), keeping the total volume fraction of fiber in the composite constant. The schematic diagram of the layer pattern of fibers in hybrid composites is presented in Figure 1.

The curing of epoxy novolac was done after mixing the EPN with diethylene triamine (DETA) hard-

ener (90 : 10 v/v) in acetone at 50°C. The prepreg was kept at room temperature for 24 h, and then it was cured by means of hydraulic press at 120°C under a pressure of 5 tones per unit area for 30 min of curing time. Before making the composite, the press machine was degassed completely to remove air-bubbles and to minimize voids and nicks in the composites. The postcuring of composite was done at 80°C in air-dried oven for 5 h. The unreinforced cured EPN samples were also prepared under same experimental curing process for comparative analysis with its composite materials.

Characterization of hybrid composites

Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) analysis of the precured matrix resin and hybrid composites was carried out in the DSC Q10 (TA Instruments) thermal analyzer under nitrogen atmosphere (50 mL/min). For each scan was performed at heating rate of 10°C/min from 20 to 400°C, by taking 8–10 mg of sample in an aluminum pan crimped with a pinhole.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of pure resin and formulated hybrid composites was performed in the DTG-60 (Schimadzu). Samples of approximately 10 mg were placed in appropriate pans and heated from 30 to 700°C at 10°C/min, under nitrogen atmosphere (30 mL/min).

Dynamic mechanical analysis

A dynamic mechanical thermal analyzer (DMA, Q 800, TA Instruments) was used for this analysis. Rectangular specimens having dimensions of 60 × 10 × 3 mm³ were used for the dynamic mechanical experiments. Three point-bending modes were used. The measurement was conducted in three point-bending mode at a frequency 10 Hz and temperature ramp rate of 5°C/min from 30°C to a maximum temperature of 200°C.

Mechanical properties

Dumbbell-shape tensile test specimens (width = 10 mm and thickness = 3 mm) were cut from composite sheets and cured EPN resin. Tensile testing was carried out in a universal tensile machine (UTM 3366, Instron) according to ASTM D 638 under ambient conditions. A crosshead speed of 5 mm/min was applied. The three-point flexural properties were determined by same tensile machine according to ASTM D 792. The test speed was maintained at

1.5 mm/min. Izod impact test was done on unnotched specimen ($70 \times 10 \times 3 \text{ mm}^3$) with an impact speed of 1 m/s and initials of 1.4 J according to ASTM D 256 using a standard Izod impact testing machine (model IT 1.4, Fuel instrument, India). For pure EPN and its composites, six measurements were executed with each sample.

The tensile properties of unmodified and chemically modified, both of these jute and coir fibers were determined using the same tensile machine at a strain rate of 1 mm/min and a gripping length of 50 mm at $23^\circ\text{C} \pm 1^\circ\text{C}$ and 58% relative humidity. The results of mechanical analysis are reported in Table I.

Scanning electron microscopy analysis

To study the morphological features of the fiber–matrix interface in the composite samples, the tensile test samples were fractured in liquid nitrogen after 15–20 min of freezing in liquid nitrogen. The fractured surfaces were sputtered with gold and analyzed by a scanning electron microscope (SEM) (JEOL-JSM 6390 LV).

Water absorption analysis

Water absorption analysis of the composite samples was carried out according to ASTM D 570-98 standard. Five specimens of each formulated composite were immersed in distilled water at two different temperatures, i.e. 25 and 50°C . The specimens were removed from the water after certain times, wiped with a cotton cloth, and weighed in a high precision balance and then immersed again in the water. The water content was calculated from the weight difference.

The moisture sorption analyses for different hybrid composites were performed. The preweighed dried composite samples were placed inside the digital humidity chamber at 25°C . The samples were weighed periodically until the percentage of sample mass, changed between two successive measurements, was less than 1%. Equilibrium moisture content was determined by using the equation, $W_q - W_o/W_o$, where W_o and W_q are weight of the sample at the initial and equilibrated state, respectively.

RESULTS AND DISCUSSION

Improvement of mechanical properties of hybrid composites by fiber surface modification

In this study, different surface modification techniques were adopted to modify the fiber–matrix interface in EPN/jute–coir fiber composites. The most conventional chemical treatment for surface modifi-

cation of jute fiber is mercerization (alkali treatment). A new coir fiber modification was carried out to increase the fiber–phenolic polymer interactions at the interface. This modification was based on a selective oxidation of guaiacyl and syringyl units of lignin, into *ortho*- and *para*-quinones and other muconic derivatives, able to react by Diels–Alder reaction with furfuryl alcohol. The chemical modification of fibers facilitated the diffusion of the prepolymer (EPN resin) in the lignocellulosic fiber network, leading to a more intense fiber/matrix interactions during the curing step, and consequently also facilitating the establishment of physical interactions and/or possibly of fiber/matrix chemical bonds. As a result, the composites reinforced with surface-modified fibers have shown better mechanical properties (strength, modulus, and impact strength). The properties of matrix and fiber are very important aspects in achieving good mechanical properties of the composites. The variation of tensile and flexural properties of jute–coir hybrid fibers reinforced EPN composites is shown in Figure 2 as a function of the coir fiber content. Both tensile and flexural properties of the modified hybrid fibers reinforced composites are found to be superior to those of the composites made with unmodified fibers. The surface modifications of the fibers is promoted the diffusion of prepolymer (EPN resin) through the fiber network before curing, the interactions at interface are intensified and a material probably with greater possibility of matrix to fiber load transfer is obtained.

For unmodified fiber reinforced composites, the lack of adequate impregnation of prepolymer into fibers limits interfacial bonding between unmodified fiber surface and matrix, which could reduce the transmission of stress to the bulk of material through the interface and hence, inducing the crack propagation at the weak interface. However, the tensile and flexural properties of the composites are significantly increased with increasing the modified coir fiber loading up to 50 vol %, followed by decreased at higher fiber content (65 vol %). The tensile and flexural strength is increased by 78% and 61%, respectively, when the modified coir fiber loading increased from 0 to 50 vol %, whereas the tensile and flexural modulus increased by 74% and 56%, respectively. The deterioration of these mechanical properties at higher coir fiber loading (>50 vol %) is probably due to fiber–fiber agglomeration that caused to weaken the fiber–matrix interface. The composites made with unmodified jute–coir fibers as reinforcement exhibited same increasing trend of tensile and flexural properties as the coir fiber loading increase from 0 to 35 vol% and, subsequently decreased at 50 and 65 vol% (Fig. 2). The result indicates the poor fiber-loading capacity of the unmodified fibers compared to that of the modified fibers,

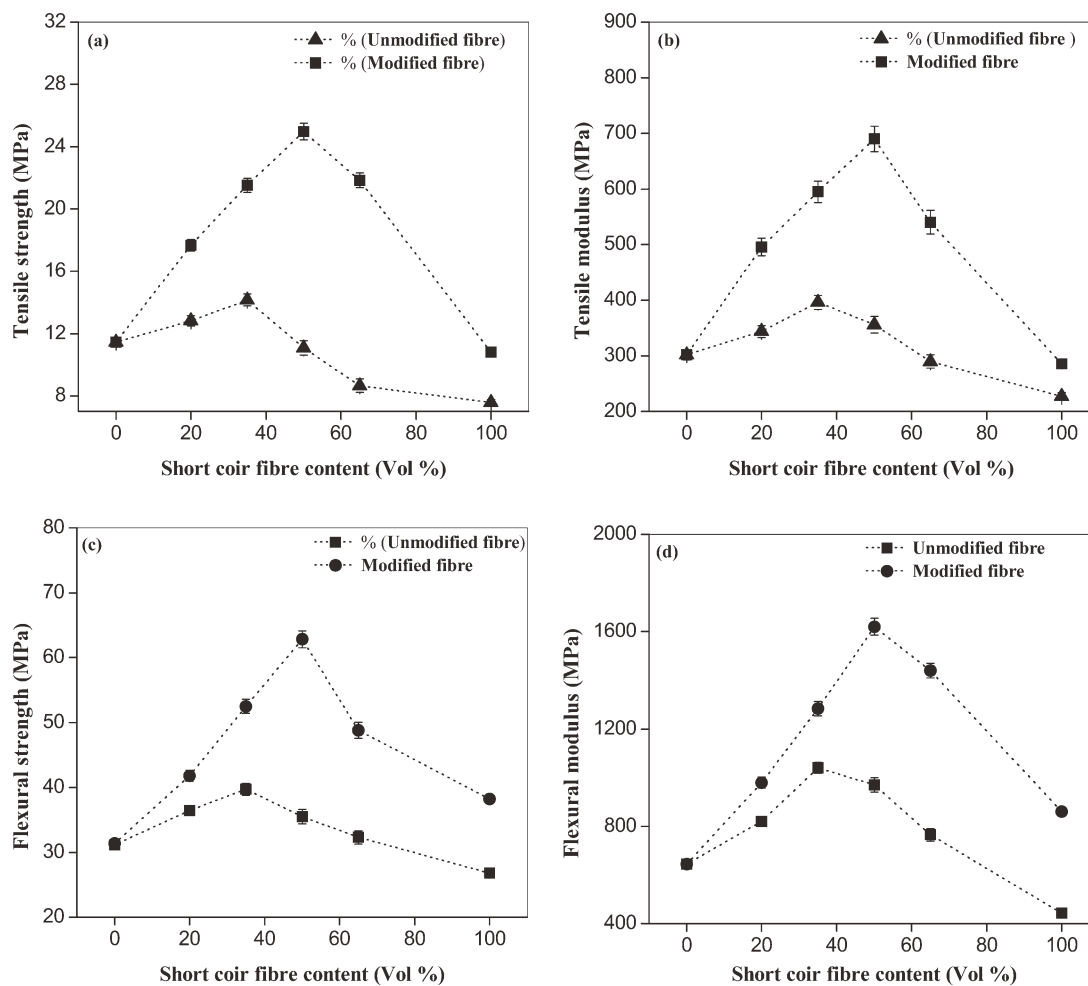


Figure 2 Tensile (a, b) and flexural (c, d) properties of the jute-coir hybrid fibers reinforced EPN composites.

which is attributed to inferior interfacial adhesion between unmodified fiber and matrix. In case of unmodified fiber reinforced composites, the tensile and flexural strength increased by only 23% and 27% respectively, as the coir fiber loading in the composite increased from 0 to 35 vol %. Therefore, surface modification of the fibers not only improved the mechanical performance of the composites, but also effectively increased the fiber loading capacity of the matrix.

The effect of modified and unmodified coir fiber loading on impact strength of the different formulated jute-coir hybrid fiber reinforced EPN composites are graphically presented in Figure 3. As observed in Figure 3, the impact strength of the unmodified fibers reinforced composites is higher than that of the composites made with modified fibers. Numerous microfailure mechanisms could occur during impact loading.²⁵ In this study, the increase in stiffness and rigidity of the fibers due to their chemical treatments seems to be an important factor affecting the impact strength of the corresponding composites. A weak interface, as expected for

unmodified fibers reinforced composites, could lead to crack in the matrix or at interface before the load transfer mechanism have occurred in all the

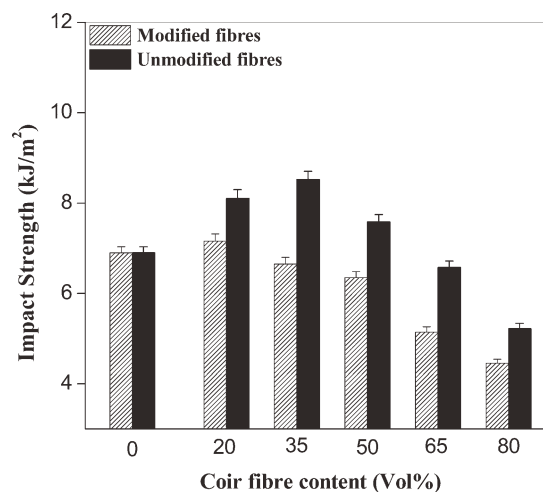


Figure 3 Variation of impact strength as a function of coir fiber loading (modified and unmodified) for jute-coir hybrid fibers reinforced EPN composites.

extension as possible, leading them to lower impact strength. However, in this study, a somewhat weak adhesion of unmodified fibers to matrix lead to an opposite effect, contributing to higher impact properties. For modified fiber reinforced composites, the more stress transfer from fiber to matrix leads to faster crack propagation at the matrix phase. Nevertheless, the impact strength of the pure EPN thermoset, i.e., 1.2 kJ/m^2 , is remarkably increased by incorporation of unmodified or modified jute-coir hybrid fibers. Hence, the necessary energy to break the samples was higher for the composites than for the pure EPN, confirming that the jute-coir hybrid fibers act as a reinforcement of EPN matrix.

Thermomechanical properties of hybrid composites

Dynamic mechanical measurements over a wide temperature range are useful for understanding the viscoelastic behavior and provide valuable insight into the relationship between the structure and properties of composite materials. The storage modulus is useful in assessing the molecular basis of the mechanical properties of a material because it is very sensitive to structural changes, such as fiber-matrix interfacial bonding.²⁶ Figure 4(a) shows the variation of storage modulus (E') with temperature for pure EPN and different formulated EPN/jute-coir fiber hybrid composites. At the temperature range of 60–160°C, the values of the storage modulus dropped as the temperature increased as shown in Figure 4(a). The storage modulus improved significantly with the incorporation of chemically jute or coir or jute-coir hybrid fibers to pure EPN over the whole range of testing temperatures as a result of the reinforcement imparted by the fiber, which allowed stress transfer to occur at the interface. A much enhanced storage modulus of the composites is obtained for the jute-coir hybrid fibers (jute:coir 80 : 20, 65 : 35, 50 : 50, and 35 : 65) rather unhybridized composites (jute:coir 100 : 0 and 0 : 100). In the case of jute-coir hybrid fibers reinforced EPN composites, the E' values of the hybrid composites significantly increased with increasing the FA-grafted coir fiber content and the maximum values of storage modulus is obtained for 50 : 50 jute-coir fiber combination in the composites. This situation could be explained as a result of strong interfacial adhesion or chemical bonding between FA-grafted coir fibers and the EPN matrix. At the loading of coir fiber more than 50 vol %, i.e., EPN/35 : 65 jute-coir fiber composites, the storage modulus values are somewhat decreased, which is probably due to fiber-fiber agglomeration and consequent inferior fiber-matrix interfacial adhesion at higher fiber loading. The storage modulus provides an idea of the stiffness behavior and load-bearing capability of a composite material. Therefore, it is

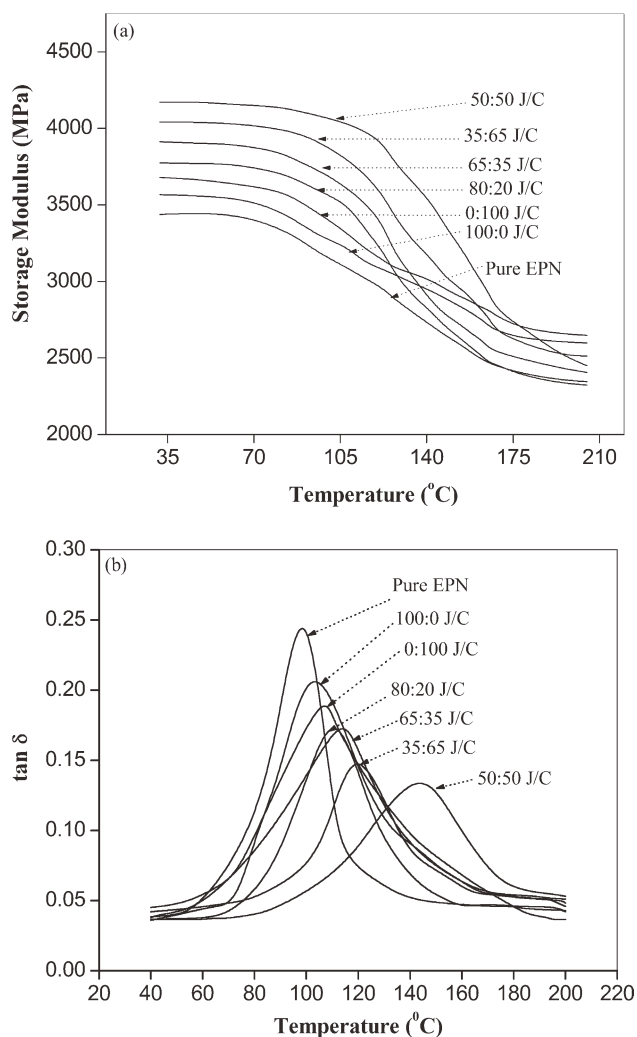


Figure 4 Variation of (a) storage modulus and (b) $\tan \delta$ of the pure EPN and the EPN/jute-coir hybrid composites as a function of temperature.

expected that the 50 : 50 jute-coir hybrid fibers reinforced composites would have greater load-bearing ability than would other hybrid composites.

The ratio of the viscous to the elastic properties is measured as the mechanical loss or $\tan \delta$. Fibers is considered to be essentially elastic while the polymer and fiber-matrix interface are viscoelastic.²⁷ Therefore, energy dissipation will occur both in the polymer matrix and at the interface with a stronger interface, characterized by loss energy dissipation. The variation of $\tan \delta$ as a function of temperature for different formulated composites is shown in Figure 4(b). The $\tan \delta$, which is corresponding to the damping properties of the composites, is an indication of the molecular motions existing in the materials. The $\tan \delta$ peak value ($\tan \delta_{\max}$) or $\tan \delta$ peak height found to be decreased with increasing FA-grafted coir fiber content in the EPN/jute-coir fiber hybrid composites. The minimum $\tan \delta_{\max}$ value is obtained for the composite containing 50 : 50 jute-

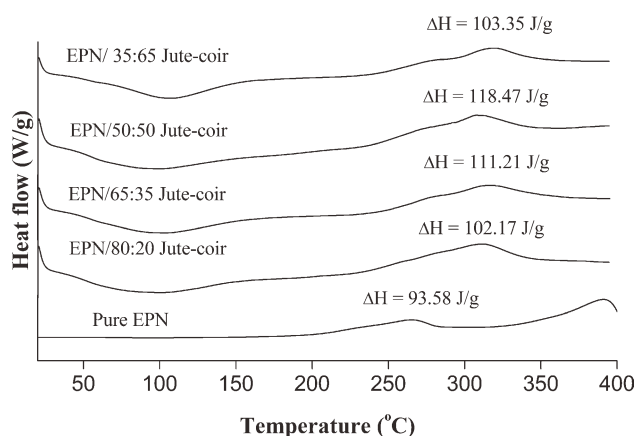


Figure 5 DSC thermograms of pure EPN and its modified jute-coir reinforced hybrid composites.

coir hybrid fibers. The improved interfacial adhesion between FA-grafted coir fibers and polymer matrix tends to reduce the mobility of the polymer chains at the interface and decreases $\tan \delta_{\max}$ values accordingly. The broadening of $\tan \delta$ peak is increased with increasing the coir fibers content (0–50 vol %) in the hybrid composites [Fig. 4(b)], which is due to the increase in the energy absorption caused by strong interfacial adhesion. However, the composites with more than 50 vol % coir fiber loading exhibit little increment of $\tan \delta_{\max}$ values. At higher coir fiber loading (>50 vol %), the ease of fibrillation associated with the lignocellulosic fibers and poor fiber-matrix interfacial bonding are leads to dissipate more energy, which contributes to high magnitude of $\tan \delta_{\max}$ or damping peak. Moreover, with increasing coir fiber content in the composite, the glass transition temperature (T_g) indicated by $\tan \delta$ peak is found to be shifted to higher temperature, due to restriction of polymer chain mobility at the interface.

Curing and thermal behavior of hybrid composites

The curing behavior of the epoxy novolac resin in its pure state and in the composite systems is investigated by DSC analysis. During the DSC scanning, the thermal cure steps of the prepolymer (i.e., EPN) could be detected. Figure 5 shows the DSC thermograms of the uncured EPN resin and the resin with modified jute-coir fibers at different fiber ratio, i.e., jute:coir = 80 : 20, 65 : 35, 50 : 50, and 35 : 65. In Figure 5, one endothermic peak in temperature region of 60–120°C is observed for each formulated composite, which is due to removal of moisture and other volatile matters present in the fibers. Apart from this endothermic peak, one exothermic peak is observed at >250°C, which is related to a curing process of the EPN component. It can be seen from DSC thermograms that the incorporation of modified

fibers resulted in increase in curing temperature of the EPN resin. The shifting of curing temperature toward higher values for composites indicates that the crosslinking of the more hindered EPN prepolymer demands a higher availability of thermal energy, when compared to the pure EPN prepolymer (Fig. 5). The ΔH values related to the cure process were determined from the area of the exothermic peak obtained from DSC analysis, taken in the dynamic mode. The incorporation of fibers is significantly affected the ΔH_{cure} values. The ΔH_{cure} values obtained for composites are higher than that of the pure EPN resin. This is an indication that the crosslinking reaction occurred to a greater extent in the composite system compared that in the pure EPN resin system. In the case of composite materials, the heat of curing (ΔH_{cure}) is found to be increase with increasing volume fraction of coir fiber up to 50 vol %, which indicates the increase of FA-grafted coir fibers loading promotes the extent of curing reactions of EPN matrix resin.

The polymers with high thermal stability are always challenging criteria to every industry for enhancement of durability of the products. TGA was used to investigate the thermal stability of the EPN/jute-coir hybrid composites in nitrogen atmosphere and compared with that of pure EPN matrix. The results of this analysis are presented in Figure 6 and Table III. It is observed that the thermal degradation of all the samples has taken place within the programmed temperature range of 30–700°C. The pure EPN matrix mainly exhibit one step thermal degradation started at 223.4°C with a maximum degradation rate at 256.2°C corresponds to weight loss of polymer. In the case of jute-coir fiber reinforced EPN composites, the initial small weight loss at around 100°C is corresponding to the volatilization

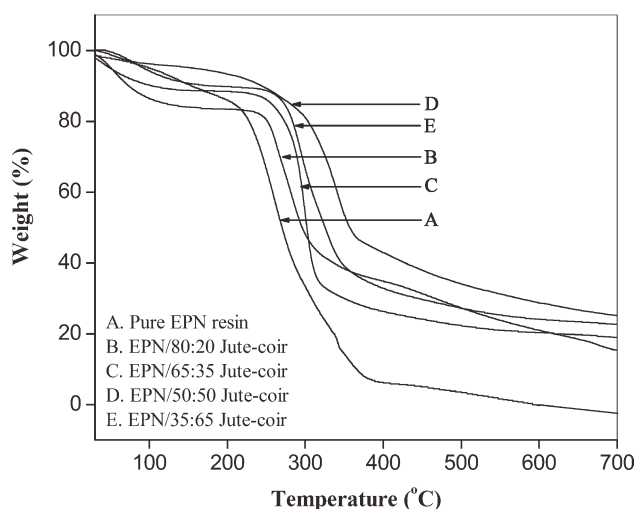


Figure 6 Thermogravimetric analysis of EPN resin and its jute-coir reinforced hybrid composites.

TABLE III
TGA Data Obtained for Pure EPN and Its Formulated Hybrid Composites

Sample	T_0 (°C) ^a	T_{max} (°C) ^b	T_f (°C) ^c	% Residue
Pure EPN	223.4	256.2	700	0.5
EPN/80:20 jute-coir	247.7	278.9	700	15.35
EPN/65:35 jute-coir	261.6	294.3	700	18.96
EPN/50:50 jute-coir	274.7	336.7	700	25.19
EPN/35:65 jute-coir	274.4	306.2	700	22.78

^a Onset degradation temperature.

^b Temperature of maximum rate of mass loss.

^c Final degradation temperature.

of moisture and other volatile products present in the samples and the second step weight loss at $>245^\circ\text{C}$ is associated with degradation of fibers and matrix components. For the composites, both onset and maximum degradation temperatures (T_0 and T_{max}) are found to significantly higher than those observed for pure EPN (Table III). It indicates that the thermal stability of EPN matrix is remarkably increased by hybrid fiber reinforcement, which is due to heat deflection property of fibers. It can be noted from Table III that the T_0 and T_{max} values for the composites are increased with increasing the grafted coir fiber loading in the composites, which

indicates the strong interfacial bonding between grafted coir fibers and EPN matrix enhance the thermal stability of the composites. For EPN/jute-coir fiber composites, the percent residue at 700°C is found to higher than that obtained for pure EPN matrix. This also ensures a higher thermal stability in the composites.

Morphological studies of tensile fracture surfaces of composites

The fracture surfaces of the composites were observed using scanning electron microscopy (SEM), as shown in Figure 7. Matrix cracking, fiber breakage, and fiber-matrix debonding are some of the failure mode observed during cryogenic fracture of the composite samples. The observed fiber pull-out phenomenon in the fracture surfaces of the composites is a kind of index of the adhesiveness between the fibers and the matrix resin. It can be seen from Figure 7 that for the composites with fiber loading of less than 50 vol %, the fibers are found well embedded in the matrix and less number of fiber pull outs (less number of holes) were observed. It can also be noted for these composites that the fiber failed by tearing, but no complete interfacial failure was observed; indicating that adhesion between the

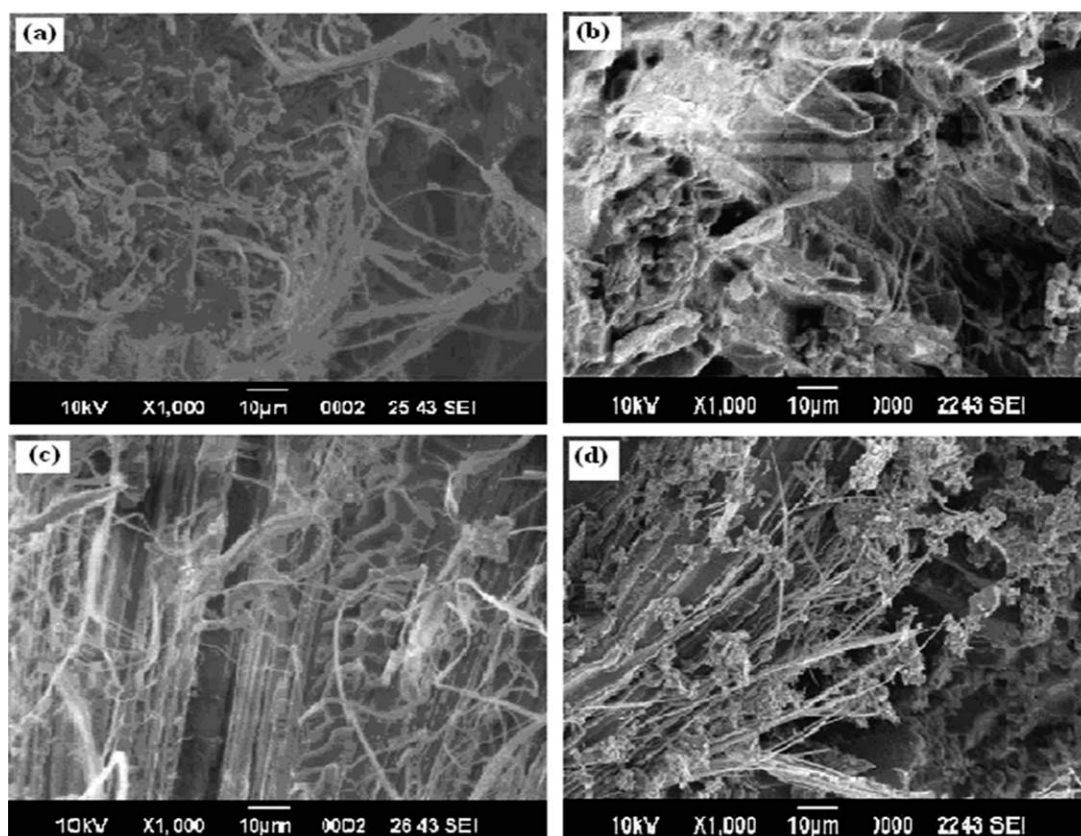


Figure 7 The SEM micrographs of the EPN-based hybrid composites containing jute-coir fiber ratio of (a) 80 : 20, (b) 65 : 35, (c) 50 : 50, and (d) 35 : 65.

chemically modified fibers and EPN matrix was quite good for reinforcing. There is substantial EPN matrix adhering to the fiber surfaces; indicating that the interfacial bond strength is fairly high due to little difference in surface energies between the fibers and the matrix. A significant number of fibers pull-out is observed for the composites reinforced with 65 vol % coir fibers [Fig. 7(d)]. The cracks are easily propagated through the resin matrix showing that little resistance has been offered because of poor interfacial bonding. This feature might be observed due to poor adhesion and more fiber agglomeration or fiber–fiber contact.

Water absorption properties of unhybridized and hybridized EPN/jute-coir fiber composites

The EPN-based jute-coir fibers composites were characterized with respect to water absorption at two different temperatures. The water absorption of the composites is not only influenced by the nature of the individual components such as reinforced fiber and matrix but also by the factors like porosity and volume fraction of hybrid fibers. Water diffuses through the composite materials by two possible mechanisms: (1) direct diffusion of water molecules through the microgaps between polymer chains and (2) through capillary transport into the gaps and flaws at the interfaces between fiber and matrix. The extent of water diffusion depends on the internal material states, e.g., debonding at the fiber–matrix interface, matrix cracking and inherent absorption property of the constituent materials, etc., and environmental conditions. Figure 8(a,b) shows the variation of the water absorption with increasing time for different formulated EPN/jute-coir composites modified and unmodified jute-coir fibers at different temperature i.e., 25 and 50°C, respectively. The water absorption in the composite increased sharply with time up to 24 h, and this was followed by a gradual approach to a saturation point (or equilibrium sorption), beyond which no more water was absorbed till 120 h. The percent water absorption of the composites is expectedly increased with increasing temperature, and also the saturation point is achieved more quickly. It can be seen for unhybridized composite (jute:coir = 100 : 0 and 0 : 100) that the water absorption tendency is significantly reduced for the composites reinforced with modified fibers compared that of the composites made with unmodified fibers. This could be attributed to lowering of the hydrophilicity of the modified fibers compared to unmodified fibers, and also the better fiber–matrix bonding between the modified fibers and EPN matrix. The amount of water absorbed by the composite depended on the quantities of microcavities present, which in turn were affected by

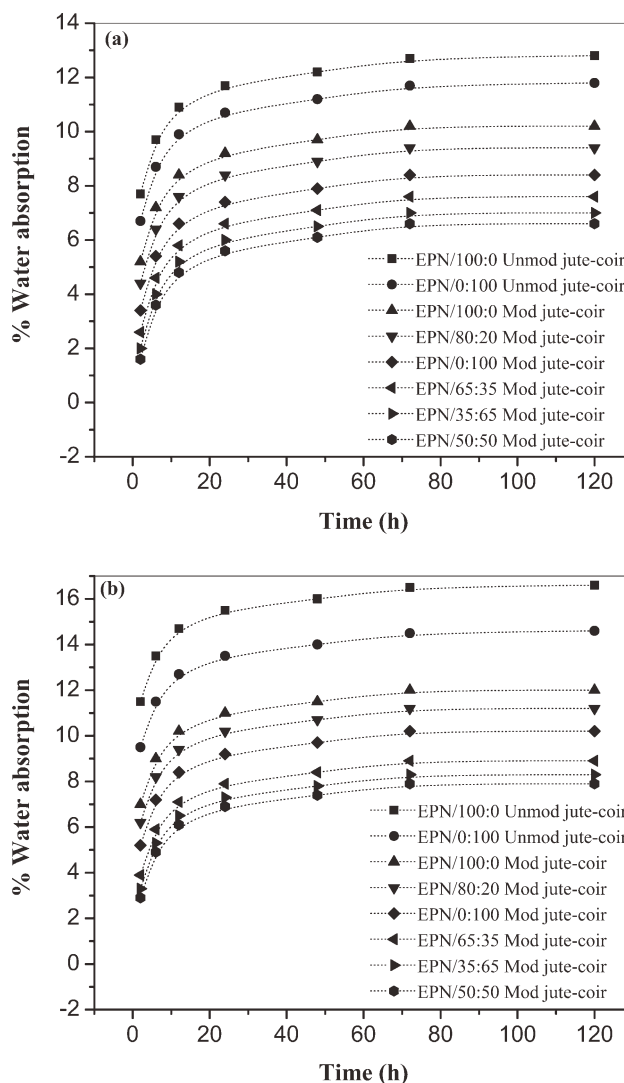


Figure 8 Water absorption curve for unmodified (unmod) and modified (mod) jute-coir fiber reinforced composites at (a) 25°C and (b) 50°C.

interfacial fiber–matrix interactions. The higher the adhesion at the interface, the lower was the quantity of microcavities available for storing water molecules. Furthermore, if the internal ducts of the fibers were more filled with resins, the possibility of storing water molecules decreased even further. As mentioned earlier, the chemical modifications of the fibers improved the interactions between fiber and matrix at the interface and also increased the accessibility of the resin to the inner parts of the fibers, thus reducing the water absorbing capacity of the composite. In the case of jute-coir hybrid fibers reinforced composites, the water uptake (%) decreased with increasing the modified coir fiber loading from 0 to 50 vol % [Fig. 8(a,b)] because of stronger interfacial bonding between the FA-grafted coir fiber and the matrix compared to that between alkali-treated jute–matrix bonding. However, the water absorption

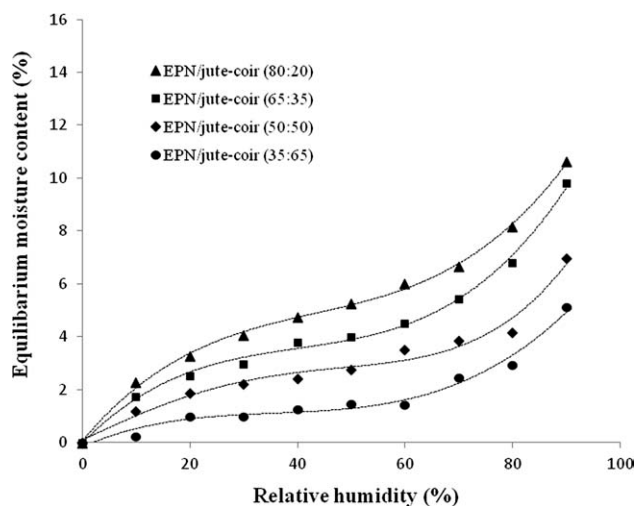


Figure 9 The fitting of experimental (symbol) and theoretical (dotted line) moisture absorption values at different relative humidity for various formulated hybrid composites.

of the composites containing 65 vol% modified coir fibers is somewhat higher than that of the composites made with lower volume fraction of coir fibers. This might be due to aggregation of the coir fibers or disordered fiber distribution and orientation in the matrix at higher loading (65 vol%) of coir fibers resulting weak fiber–matrix interfacial bonding.

The variation equilibrium moisture content (M_{eq}) as a function of relative humidity for different formulated composites is presented in Figure 9. The obtained results of the moisture absorption measurement were generalized with the Hailwood–Horrobin (H-H) model [eq. (3)]²⁸:

$$M_{eq} = \frac{1800}{W} \left[\frac{k_1 k_2 h}{100 + k_1 k_2 h} \right] + \frac{1800}{W} \left[\frac{k_2 h}{100 - k_2 h} \right] \quad (3)$$

Where M_{eq} is the equilibrium moisture content at a given relative humidity (h), W is the molecular weight of the dry fiber per mole of moisture sorption site, T is the temperature ($^{\circ}\text{C}$), and k_1 and k_2 are constants. The values of k_1 and k_2 are evaluated from the following eqs. (4) and (5):

$$k_1 = 6.34 + 7.75 \times 10^{-4}T - 9.35 \times 10^{-5}T^2 \quad (4)$$

$$k_2 = 1.09 + 2.84 \times 10^{-2}T - 9.04 \times 10^{-5}T^2 \quad (5)$$

For different modified hybrid jute–coir fiber reinforced EPN composites, the moisture absorption plots obtained from fitting the experimental data to the H-H model are presented in Figure 9. The amount of moisture absorption increased with increasing the relative humidity at constant temperature (25°C). It can be observed from Figure 9 that the experimental M_{eq} values for all hybrid compo-

sites followed the same sigmoid pattern with those obtained from the H-H model. However, the experimental values deviated significantly from those predicted by the H-H model. The most deviation observed at relative humidity range of 55–85%. This difference could be attributed to the presence of the EPN polymer that has inferior moisture sorption sites, i.e., hydroxyl groups, than the lignocellulosic fiber materials. The replacement of fiber by synthetic polymer substance in the composites potentially reduced the hydroxyl sites. Moreover, the surface modification of coir fibers with furfuryl alcohol significantly reduced the number of hydroxyl sites (or sorption sites) on the fiber surfaces and making them more hydrophobic in nature through blocking the hydrophilic groups such as hydroxyl groups.

CONCLUSIONS

A novel process was well set for the first time utilized to chemically modify jute and coir fibers as reinforcement in epoxy novolac thermoset hybrid composites. Chemical modification of fiber makes improvement of composite performances. Hybridization of different lignocellulosic fibers has proved to be an effective method to design materials suited for various applications. The chemical modifications of coir fiber with furfuryl alcohol and alkali treatment of jute fiber have significantly improved the interface and properties of the composites. It is observed that the composites reinforced with hybrid jute–coir fibers exhibit superior mechanical, dynamic mechanical, and water absorption properties compared to the unhybridized composites (for 100 : 0 and 0 : 100 jute–coir combination). In contrast to unhybridized fiber, the jute–coir hybrid fibers were significantly promoted the curing process of the matrix resin, as observed from the DSC analysis. The interfacial morphology of the hybrid composites showed better adhesion between FA-grafted coir fiber and matrix at the fiber loading up to 50 vol %, whereas poor fiber–matrix wetting is observed at higher fiber loading. It has been optimized that the 50 : 50 jute–coir hybrid fibers combination showed maximum improvement of thermal and mechanical properties of the composites. The equilibrium moisture content values obtained for different hybrid composites from the experiment followed almost same pattern of that obtained from the H-H model, but the experimental values at various relative humidity levels were deviated from those predicted by the H-H model. The experimental on the basis of aforementioned studies, it can be concluded that an optimal ratio of jute–coir hybrid fibers could effectively reinforce the epoxy novolac resin and enable to achieve satisfactory properties of the composites for various engineering applications.

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