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THERMOMECHANICAL PROPERTIES OF JUTE/BAGASSE HYBRID FIBRE REINFORCED EPOXY THERMOSET COMPOSITES

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Natural fibres are partly replacing currently used synthetic fibres as reinforcement for polymer composites. Jute fibre bundles were high-cellulose-content modified by alkali treatment, while the bagasse fibre bundles were modified by creating quinones in the lignin portions of fibre surfaces and reacting them with furfuryl alcohol (FA) to increase their adhesiveness. The effects of different fibre bundle loading and modification of bagasse fibre surfaces in hybrid fibre reinforced epoxy composites have been studied. The role of fibre/matrix interactions in chemically modified hybrid composites were investigated using Differential Scanning Calorimeter, Differential Thermo Gravimetry, and a Universal Tensile Machine and compared with those of unmodified bagasse fibre bundles incorporated with modified jute fibre bundles reinforced hybrid composites. Fibre surface modification reduced the hydrophilicity of fibre bundles, and significantly increased mechanical properties of hybrid composites were observed in conjunction with SEM images. The SEM analysis of the fibre and the composite fractured surfaces have confirmed the FA grafting and shown a better compatibility at the interface between chemically modified fibre bundles and epoxy resin. This paper incorporates interesting results of thermomechanical properties and evaluation of fibre/matrix interactions.

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INTRODUCTION

Conventional fibre-reinforced composites are typically manufactured with carbon or glass fibres that are incorporated into unsaturated polyester or epoxy resin. These composites show high mechanical and thermal properties, so they are widely used in various applications from aerospace to sports. These advantages, on the other hand, can lead to environmental problems in disposal by incineration. Thus, in order to overcome these problems, there is keen interest in environmentally friendly composites that employ natural fibres as reinforcement (Nishino et al. 2003).

Jute is a lignocellulosic bast fibre obtained from the bark of two cultivated species of the genus *Chorchorus*, *Chorchorus capsularis* and *Chorchorus olitorius*. It is polar, owing to the presence of various polar groups in the chemical structure. Jute Fibre (JF) bundle has some inherent advantages over other fibres for its renewable nature, biodegradability, high strength, and initial modulus. However, the major disadvantages of JF bundles are due to their coarseness, stiffness, low extensibility, wash shrinkage, ready

susceptibility to microbial attack, and poor abrasion resistance. In order to minimize or even eliminate some of the major disadvantages, attempts have been made to use modified jute fibre bundle with modified and unmodified bagasse short fibre bundles in hybrid composites (Sarkar and Adhikari 2001).

Sugarcane bagasse is a plentiful lignocellulosic waste typically found in tropical countries that process sugarcane, such as Brazil, India, Cuba, and China. It is called bagasse or cane-chuff, and it is obtained as the left-over matter after liquor extraction in a sugar factory. About 54 million tons of bagasse is produced annually throughout the world. In general, sugar factories generate approximately 270 kg of bagasse (50% moisture) per metric ton of sugarcane (Xu et al. 2006). The Bagasse Fibre (BF) bundles are unusually coarse and stiff material. It is used either as a fuel for the boilers by the sugar factory or as a raw material for the manufacture of pulp and paper products, various types of building boards, and certain chemicals. It is suitable for making nonwoven products. Application of agro-industrial residues in industries on the one hand provides alternative substrates, and on the other hand helps in solving pollution problems, which their disposal may otherwise cause. These agricultural residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass (Sun et al. 2004). The chemical compositions of pure bagasse fibre bundles are cellulose (52.42%), lignin (21.69%), hemicellulose (25.8%), ash (2.73%), and ethanol/dichloro methane extract (1.66%) (Rezayati-Charani and Mohammadi-Rovshandeh 2005).

Several studies have been carried out to understand the structure, mechanical properties, and the effect of chemical modification on bagasse fibre bundles. However, the traditional uses of bagasse husk consume only a small percentage of the potential total world production of bagasse husk. Hence, research and development efforts have been underway to find new applications for bagasse, including utilization of bagasse as reinforcement in polymer composites (Satyanarayana et al. 1981). In the mixture of two components of diverse chemical natures of any dimension or shape, the larger the contact area (interfaces) among them, the greater the possibility of an interaction of physical, chemical, and physico-chemical nature between the two components. In all cases, the interaction between the dispersed phase and the matrix phase depends on not only the extension of the contact area, but also on the affinity between the components. The affinity can be intensified, for instance, either by physical or chemical modifications applied to the surface of the fibre bundles (Yosomiya et al. 1990). An important point to consider is that the reagents used in chemical modification cannot be too expensive, and ideally, the modifications must involve a minimum of compounds obtained from nonrenewable sources. In the present work, jute fibre bundles were taken as bi-directional cross ply fabrics. They were modified by sodium hydroxide solution, which is a relatively inexpensive and effective way to increase mechanical properties. A new selective chemical modification of the surface of BF bundles has been considered. This modification is based on the selective oxidation of guaiacyl and syringyl units of lignin, generating ortho- and para- quinones able to react by Diels-Alder reaction with furfuryl alcohol that is commercially prepared by reduction of furfural, which in turn is obtained from agricultural residues (Frollini et al. 2004; Trindade et al. 2004).

A large number of polymers that have good performance as matrix materials provide a wide range of properties and, therefore, a large variety of composite materials (Chawla 1994). Over 75% of all polymeric matrices in composites are thermoset

polymers in which the resins are cross-linked by heat, pressure, and/or addition of catalyst during the curing (Matthews and Rawlings 1994). Epoxy resins are very used in plastic as structural adhesives and automotive industries, and due the versatility imparted by the strained oxirane ring, their applications in the aerospace industry is growing. They have a lower cost compared with many other high performance resins like PEEK (poly (ether ether ketone)), which makes this material more attractive for applications at large scale. Epoxy resins are of interest as adhesives and composite matrices due to their good shelf life, ease of processability, and excellent network mechanical properties. Resulting networks also show good solvent and corrosion resistance and are extremely versatile. Properties of the resin and cured network can be tailored for specific applications by varying both the epoxy chemistry and the cross linking agent used to cure the epoxy (Lee and Neville 1967; Ellis 1993).

Extensive research has been carried out in order to understand the nature of the interfacial bond and its characterization. The adhesion between fibre and matrix is a major factor in determining the response of the interface and its integrity under stress. Additionally the interface may be more vulnerable to moisture and solvents than are fibre and matrix. The fracture of an interface between two materials depends on the geometry, the constitutive properties of the adherents and details of bonding across the interface. If the interface is weak, effective load distribution is not achieved and the mechanical properties of the composites are impaired. On the other hand, a strong interface can assure that the composite is able to bear load even after several fibres are broken, because the load can be transferred to the intact portions of broken as well as unbroken fibres.

In practical applications, there should be good tensile and compressive strength in composites. Jute fibre bundle has good tensile properties due to its high content of cellulose, while bagasse fibre bundle has comparable compressive strength due to its better damping behavior. Therefore, instead of making single-fibre reinforced composites, jute/bagasse hybrid fibre reinforced composites have been made, which will impart superior properties.

The use of natural fibres as reinforcing agents of epoxidised phenolic novolac (EPN) resin reduces production costs, as the resin is substituted by fibre bundles, and improves the properties of the resin, such as mechanical strength. Recently, EPN resin, reinforced with unmodified/modified bagasse fibre bundles incorporated with modified jute fibre bundles reinforced hybrid composites were prepared and characterized (Wambua et al. 2003; Paiva and Frollini 2002).

EXPERIMENTAL

Materials

Sugarcane bagasse was locally collected from agricultural fields of Jharkhand (India) after the sugarcanes had been pressed to separate molasses from filter mud (2007 crops), and the bagasse was used for the preparation of sugar and alcoholic products. The residual fibre bundles called "bagasse" or "cane-chuff" were first dried in the sunlight and then cut into small pieces of 2 mm length. The cut bagasse fibre (BF) bundle was further dried in a cabinet oven with air circulation for 16 h at 60 $^{\circ}$C. Jute Fibre (JF) bundle was obtained from Fort-Gloster Jute Mill, Howrah, India. The epoxidised

phenolic novolac (EPN) resin was prepared in our laboratory. Phenol and 37% w/w Formalin, both from E.Merck, India were used as received for novolac preparation. Epichlorohydrin and sodium hydroxide were used for epoxidation of novolac resin and purchased from S.D.Fine Chemicals, India. Di-ethylene Triamine (DETA) was used as a hardener for the EPN resins. Acetone, toluene, sodium chlorite, furfuryl alcohol, cyclohexane, ethanol and other chemicals were obtained as analytical grade of CDH make, India. The physical properties of jute and bagasse fibre bundle are given in Table 1 (Bledzki et al. 1996; Nangia and Biswas 2003; Rahman and Khan 2007; Shibata et al. 2005; Reis 2006; Rasul et al. 1999; El-Tayeb 2008), and the typical properties of liquid EPN resin are given in Table 2 respectively.

Table 1. Physical Properties of Jute and Bagasse Fibre Bundles

Physical Properties	JF bundles	BF bundles
1. Density (gm/cc)	1.45	0.55-0.70
2. Cellulose content (%)	60-65	40-52
3. Hemicelluloses content (%)	20-24	20-26
4. Lignin content (%)	12-14	20-26
5. Microfibrillar angle (^{o})	8.1	10-22
6. Diameter (μm)	90-115	300-400
7. Tensile Strength (MPa)	393-773	170-290
8. Young's Modulus (GPa)	19-26.5	15-19
9. Elongation at break (%)	1.16-1.8	3-7
10. Aspect ratio (L/D)	152-365	100-140

Table 2. Typical Properties of Liquid EPN Resin

1. Appearance	A clear pale yellow liquid
2. Specific gravity at 25 ^{o}C (gm/cc)	1.119
3. Epoxy equivalent number	191
4. Gel point in minutes	20
5. Solid content (%)	84
6. Tensile strength (MPa)	31
7. Flexural strength (MPa)	67
8. Impact strength (kJ/m^2)	9

Filler/Reinforcement Treatment

Alkali treatment of JF bundles

Jute fibre bundle was cut to 100x100 sq. cm. dimensions and soaked in a 5% NaOH solution at 30 ^{o}C, maintaining a liquor ratio of 15:1. The material was kept immersed in the alkali solution and sonicated in an ultrasonic bath for 2 hours. The fibre bundles were then washed several times with distilled water to remove any NaOH sticking to the fibre surface, neutralized with dilute acetic acid, and finally washed again with distilled water. A final pH of 7 was maintained. The Jute fibre bundle was then dried at room temperature for 48 h, followed by air-oven drying at 70 ^{o}C for 5h. (Ray et al. 2002).

$$\text{JF bundle—OH} + \text{NaOH} \rightarrow \text{JF bundle —O}^-\text{Na}^+ + \text{H}_2\text{O} + \text{surface impurities} \quad (1)$$
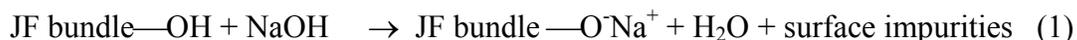
The product of this reaction was named as modified JF bundle.

Two-stage treatments of BF bundles

(i) Oxidation of BF bundles: - The BF bundles were extracted by a Soxhlet apparatus with cyclohexane/ethanol, 1:1 v/v, for 48 h and then with water for 24 h. The fibre bundles were dried in an air-circulated oven (60 °C) until constant weight. The fibre extraction with cyclohexane/ethanol allows removal of waxes from the fibre bundle surfaces, preventing weakening of the interactions at the interface fibre matrix of these compounds. Oxidation of fibre bundles was performed with a chlorine dioxide-water solution:

$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + 2H_2O + Cl^- \tag{2}$$

In the experimental procedure, the molar solutions of sodium chlorite and acetic acid were prepared in distilled water according to the above mentioned equation and mixed in a closed system to generate chlorine dioxide. Here acetic acid acts as an acid only, which gives hydrogen ion in solution, oxidizing sodium chlorite to produce chlorine dioxide gas act as an oxidizing agent. After reaction, the fibres, which had turned yellow-red, were washed with water until neutrality, and they were named as oxidized bagasse fibre bundles (BF_{ox}) bundles.

(ii) Grafting of furfuryl alcohol (FA) on oxidized bagasse fibre bundles: The BF_{ox} bundles impregnated with furfuryl alcohol were heated at 100 °C for 4 h in a specially designed reaction vessel with an outlet and inlet for passage of N_2. The volume of FA added into the vessel containing the total volume of BF_{ox} bundles was taken in a ratio of 20:1. The excess of FA was removed by Soxhlet extraction using ethanol for 8 h. Then the fibre bundles were dried for about 24 h at 45 °C, and weight gains due to reaction were determined on the basis of the original and final oven-dried fibre bundle weights. The percent graft yield for bagasse fibre bundle was observed to be 17% (Rout et al. 2002). The fibre bundle was named as FA grafted bagasse fibre (BF_{ox-FA}). The percentage of grafting was calculated using the following equation:

$$\% \text{ Graft yield} = \frac{\textit{Dry weight grafted BF} - \textit{Dry weight unmodified BF}}{\textit{Dry weigh unmodified BF}} \times 100 \tag{3}$$

Cellulose is the most essential component of all natural fibres. It is a linear, crystalline polymer, and hydrophilic in nature. Its basic unit is 1-4 β,D-glucose or anhydro D-glucose. On the other hand, lignins are amorphous, highly complex and hydrophobic in nature. They are mainly composed of p-hydroxy phenyl propane, guaiacyl, and syringyl units. Schematic representations of the structures of (A) lignin (partial structure), (B) cellulose, and (C) poly (furfuryl alcohol) are shown in Fig. 1.
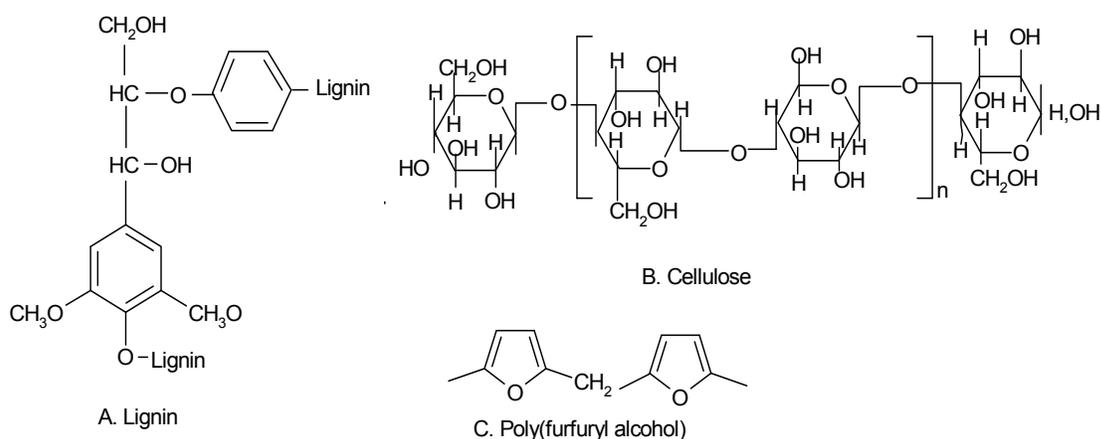
Figure 1. Schematic representation of the structure of (A) lignin, (B) cellulose, and (C) poly (furfuryl alcohol)

The possible proposed products made by chemical reaction between ortho or para quinones and FA from Diel's Alder reaction are shown in Fig. 2.
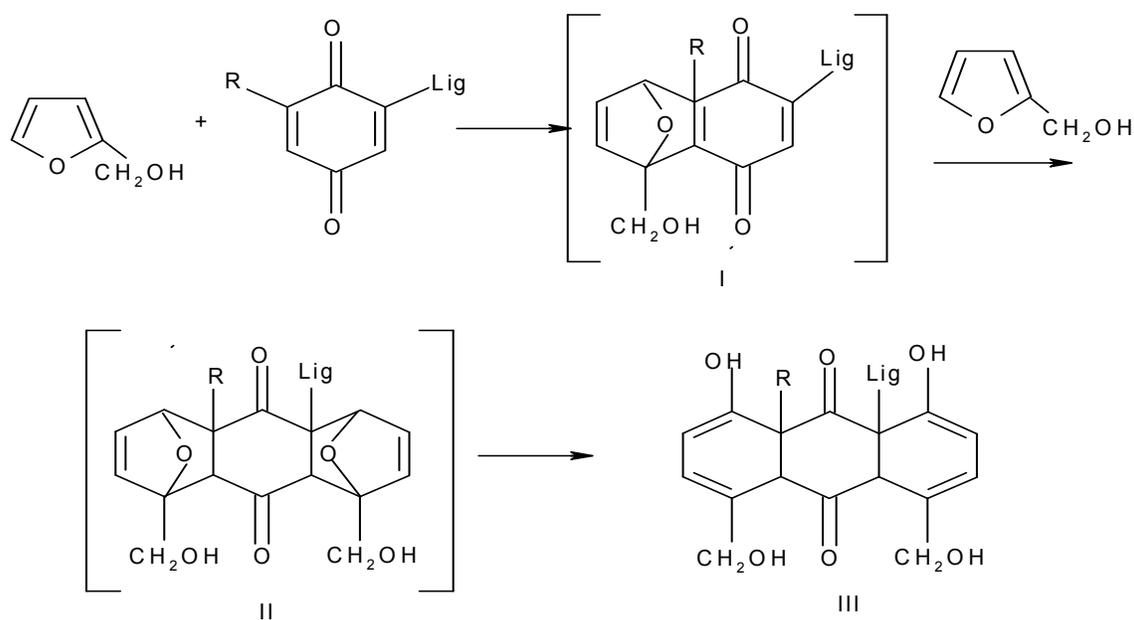
Figure 2. The adducts of lignin generated para-quinones and furfuryl alcohol

Preparation of Epoxidized Phenolic Novolac (EPN) Resin

The Novolac resins were first prepared, and their epoxidation was carried out by following the specific procedure as described earlier (Datta et al. 2002). The chemical reaction involved in the epoxidation of novolac resin is shown in Fig. 3. Reacting a known quantity of resin with HCl in pyridine medium and measuring the unreacted acid by back titration with standard alkali, the epoxy equivalent was calculated. The epoxy equivalent was found to be 191 gm-equivalent/mole.

Epoxidized Phenolic Novolac [EPN] Resin
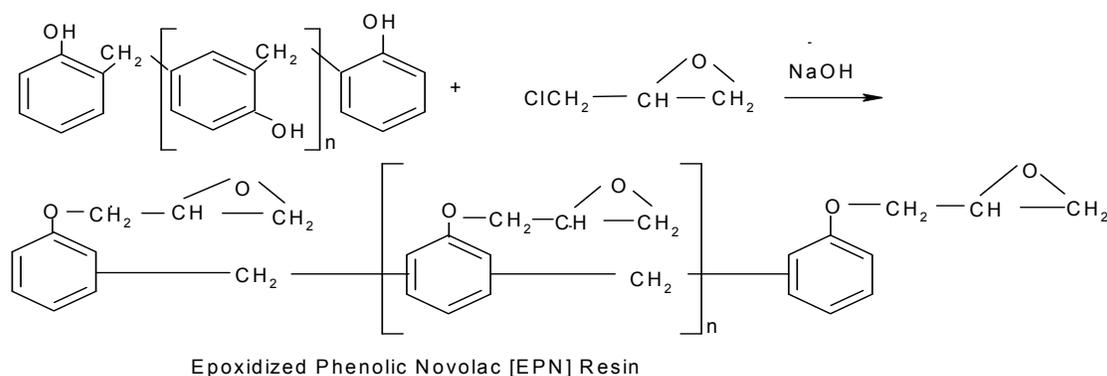
Figure 3. The chemical reaction involved in the epoxidation of novolac resin with NaOH

Composite Preparation

The hybrid composites containing unmodified and modified short BF bundles of 2 mm length in varying volume percent with modified bi-directional JF bundles were fabricated for investigation. Thermoset matrix materials were obtained by mixing EPN and hardener (DETA) in suitable acetone solvent in stoichiometric ratio in a three-necked round bottom flask through mechanical stirring at 50 ^{o}C for 1 h. The volume ratio of the resin and hardener was 90:10 in 100 ml of acetone (acting as a thinner). Composites were prepared with bagasse as short fibre (2mm) randomly and evenly distributed in between the two layers of JF bundles as trilayers (jute/bagasse/jute) and then impregnated with the EPN resin. Keeping the combined fibre volume as 30% and the volume percent of the jute:bagasse as 100:00, 80:20, 65:35, 50:50, 35:65, and 00:100, several hybrid composites were prepared. Composites with a single fibre type such as a trilayer of JF bundles (discontinuous short jute fibre of 2 mm length in between the two layer of jute fabrics as volume percent 100:00) and a trilayer of short BF bundles of 2 mm in length (short BF/ short BF / short BF as volume percent 00:100) were also prepared as cited above, and their mechanical behaviors were compared to those of hybrid fibre reinforced epoxy composites.

A prepregnation route was followed for the preparation of composites. Hand lay-up technique followed by compression molding was adopted for composite fabrication. JF bundles of uniform thickness and BF bundles of particular length were impregnated in EPN resin. In the preparation of hybrid composites, JF bundles were taken as bi-directional fabrics acting as reinforcement, and BF bundles were taken as short fibre of 2 mm length (in particle form) acting as filler materials in hybrid composite due to smaller sizes. The prepreg was kept at room temperature for 24 h, and then it was cured by means of hydraulic press at 120 ^{o}C temperature and 5 tones per unit area of pressure for half an hour as 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 post curing of composite was done at 80 ^{o}C in air-dried oven for 5 h. unreinforced cured EPN samples (specimens cured for 24 h at room temperature, followed by post-curing for 5 h at 80 ^{o}C) were also prepared.

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METHODS OF CHARACTERIZATION

Chemiluminescence Spectrofluorophotometer

The fluorescence measurements were obtained with a Spectrofluorophotometer, Shimadzu Corporation, Kyoto, Japan (model - RF-5301 PC). The instrument is used to measure fluorescence wavelength maximum radiated by irradiating the excited light to the sample, performing qualitative and quantitative analysis. The wavelength scan range was 220-900 nm with zero order light having accuracy ±1.5 nm. The experiment was done in fast mode of scan speed using a xenon lamp as a light source.

Differential Scanning Calorimeter (DSC)

The DSC thermograms were taken from TA Instruments, USA, model DSC Q_{10} in nitrogen atmosphere (Gas flow rate-50 ml/ minute) and at constant heating rate of 10°C/min from 0°C to 400°C in an aluminum pan crimped with a pinhole. Fibre samples weighing between 3 and 5 mg were used. DSC has been used to study the variations in transition temperature on the fibre surface.

Differential Thermo Gravimetry (DTG)

The DTA and TGA thermograms of hybrid composites containing unmodified and modified BF bundles with modified JF bundles were made under the constant flow rate (30 ml/ minute) in a nitrogen atmosphere at a continuous heating rate of 5°C/minute from ambient to 600°C by using a DTG-60 (Schimadzu Corporation, Kyoto, Japan) instruments. DTG was used to characterize the thermal stability of hybrid composites. Composites weighing between 5 and 10 mg were used.

Mechanical Properties

A Universal Tensile Machine (UTM) from Instron, United Kingdom, (model-3366) was used for measuring the mechanical properties of composites.

Tensile Properties

The tensile properties such as tensile strength, tensile modulus, and percent elongation at break were determined. ASTM method D 638 was followed. A crosshead speed of 5 mm/min was maintained. All tests were conducted under ambient conditions in an environmentally controlled room. The specimens for tensile measurements were cut in a dumbbell shape of 50 mm in span. The width and thickness of each specimen were measured and recorded. The standard specimens were visually inspected before measurement, and were found to be free from pores and nicks. The data reported were averages of at least six measurements, and the standard deviations of the results were found to be within ±5 of the mean values.

Flexural Properties

The flexural strength modulus was also determined using the above-mentioned universal tensile machine as per ASTM D 792 procedure. The test speed was maintained at 1.5 mm/minute. In each case six specimens were used, and the average values were reported. The standard deviations of the results were found to be within ±7 of the mean values.

Impact Properties

The impact properties of a material represent its capacity to absorb and dissipate energies under impact. The impact strength was calculated using an Izod impact testing machine, model IT 1.4 with the specification of energy range of 0 to 1.4 J, hammer weight 4.580 kg, and height 203.70 mm from Fuel Instruments, Maharashtra, India. Izod impact strength was determined using ASTM D256. The unnotched samples for measurements were cut to 70X10X3 mm dimensions. In all cases, 12 specimens were tested, and average values were reported. The standard deviation was ±7 of the mean values.

Scanning Electron Microscopy (SEM)

The SEM studies were conducted using JEOL-JSM 6390 LV with the following specifications: accelerating voltage, 20 KV; image mode, secondary electron image; working distance, 20mm. The test samples were mounted on aluminum stubs and gold coated to avoid electrical charging during examination. The morphological changes observed on the fibre surfaces of unmodified and modified natural fibers were scanned into 1000 times of magnification. The fracture morphology of the composites was also observed to scan the fracture ends of tensile specimens of the composites.

RESULTS AND DISCUSSION

Fluorescent Studies

Fluorescence spectra were obtained by spectrofluorophotometer, using 5 and 1.5 nm band pass settings for excitation and emission spectra, respectively. The measurement wavelength was set at 220-750 nm, and the excitation wavelength was 335 nm. Firstly, the oven-dried unmodified and oxidized BF bundles were ground into fine powder of particle size 2μm or less and were dissolved in 1,4-dioxan-water (9:1, v/v) mixture having concentration $1x10^{-5}$ moles/litre. The solvent mixture dissolves the lignin portions of fibre bundles, but limits the wavelength to above 240 nm, due to absorption of energy by dioxan's functional groups. The fluorescence spectrum was measured before and after oxidation. In Fig. 4, from analysis of overlap spectra, it was observed that the peaks at 410 and 455 nm were in accordance with fluorescence properties of unmodified and oxidized BF bundles, respectively. The peak at 410 nm is attributable to the natural fluorescence of lignin moieties of fibre sample in dioxan solution. The oxidized BF bundles showed a shoulder near 370 nm and an intense peak at 455 nm, supporting the formation of complex quinonoid structures, as expected from Diels-Alder reactions between ortho-quinones and conjugated dienes (Trindade et al. 2005).

Thermal Analysis

The thermal properties of unmodified and chemically modified jute and bagasse fibre bundles were analyzed by differential scanning calorimeter (DSC). The changes observed when the unmodified jute and bagasse fibre bundles were compared to chemically modified fibre bundles confirm the relation between the presence of the peaks and the polymer enthalpy relaxation processes. The epoxy hybrid composites reinforced

by unmodified and chemically modified BF bundles with modified JF bundles were analyzed by differential thermogravimetry (DTG).
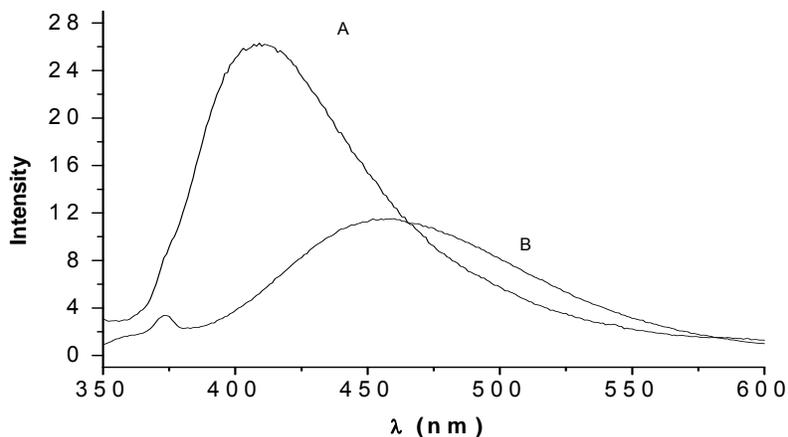
Figure 4. The overlapping of fluorescence spectra of (A) unmodified BF and (B) oxidized BF bundles

DSC Analysis

The overlay results of DSC thermograms of unmodified and chemically modified jute and bagasse fibre bundles are shown in Fig. 5. In all the DSC thermograms, different endothermic and exothermic peaks can be seen, and the corresponding ΔH values are given in Table 3. Among them, the peak at around 100 ^{o}C corresponds to a loss of absorbed moisture. In the DSC thermograms of unmodified JF bundles (Fig. 5A), an endothermic peak due to moisture loss at 105.65 ^{o}C was observed, but in case of modified JF bundles, the moisture loss peak was shifted to a lower temperature at 87.61 ^{o}C (Fig. 5B). This is due to the increased surface area of modified JF bundles facilitating easier evaporation (Ray et al. 2002; Razera and Frollini 2004), while in case of modified BF bundles, the moisture loss peak were shifted towards higher temperature from 80.17 ^{o}C to 95.80 ^{o}C in oxidized BF and to 108.08 ^{o}C in FA grafted BF bundles (Fig. 5, C through E, respectively). These peaks could be considerably smoothed, reducing the diameter for oxidized BF related to the release of water and other volatiles. These endothermic peaks are related to enthalpy relaxation (Trindade et al. 2005).

In unmodified JF bundles, the exothermic peak at 295.28 ^{o}C and the endothermic peak at 361.27 ^{o}C were caused by the decomposition of hemicelluloses and α-cellulose, respectively. In case of modified JF bundles, the α-cellulose decomposition peak changed from endothermic to an exothermic peak and appeared at high temperature (395.27 ^{o}C). It is, therefore, apparent that the removal of the non-cellulosic constituents such as hemicelluloses, pectin etc. during alkali treatment leading to the destruction of the chemical linkages between the constituents might have some influence in inverting the α-cellulose degradation peak from endothermic to exothermic (Ray et al. 2002). In modified JF bundles, an endothermic peak appeared at 214.13 ^{o}C; this is probably due to oxidation of lignin moieties (Sinha and Rout 2009).

The enthalpies associated with moisture desorption, as well as the decomposition of α-cellulose and hemicellulose, showed an increasing trend from unmodified to modified conditions. The closer packing of the cellulose chains could cause the increase in enthalpies from unmodified to modified conditions. It is reported that the increased H-bonding between the closely packed cellulose chains tends to stabilize the structure and increased the enthalpy values. Similar explanation could be suitable to explain the present behavior of the unmodified and chemically modified, jute and bagasse fibre bundles (Hoareau et al. 2004, Ray et al. 2001).

The BF bundles showed completely different behavior from the jute fibre bundles. The unmodified BF bundles showed one endothermic and one exothermic peak. The endothermic peak at 80.17 ^{o}C is due to moisture loss while the exothermic peak at 201.53 ^{o}C may be due to the oxidation of lignin (Sinha and Rout 2009).

The oxidized BF bundles showed two endothermic peaks at 95.80 ^{o}C and 182.27 ^{o}C and one exothermic peak at 332.46 ^{o}C. The peak at 95.80 ^{o}C is due to moisture loss. However, this peak was observed at 80.17 ^{o}C in case of unmodified BF bundles. This shifting may be due to smoothening of fibre surface by releasing water and other volatiles, reducing its diameter. This shifting may also be attributed to oxidation of fibre bundles (Hoareau et al. 2004). The endothermic peak at 182.27 ^{o}C may be due to degradation of remaining fatty ester product of waxy layer. The exothermic peak at 332.46 ^{o}C is due to degradation of cellulose in BF bundles and formation of char.

Similarly, the FA grafted BF bundles showed one endothermic peak at 108.08 ^{o}C and two exothermic peaks at 216.70 ^{o}C and 298.62 ^{o}C, respectively. In comparison to unmodified and oxidized BF bundles, the high temperature of moisture desorption peak at 108.08 ^{o}C is due to improved wetting of the fibres by the resin and stronger bonding at the interface. The reaction of oxidized BF bundles with FA shifted the exothermic peak maximum at 298.62 ^{o}C, and a new exothermic peak appeared, probably due to furan derivatives (Fig. 5E). The macromolecule in BF structure has been observed to change considerably after modification with FA (Hoareau et al. 2004).

DTG Analysis

The overlay of TGA and DTA thermograms of unmodified and modified BF bundles with modified JF bundles reinforced epoxy hybrid composites are shown in Fig. 6. In TGA thermograms, there were three distinct zones of degradation observed. The initial zone corresponded to a small loss in weight due to evaporation of absorbed moisture, and it appeared nearly at 70-80 ^{o}C. The middle zone was associated with a sharp loss in weight after onset of the thermal decomposition process, and the third zone corresponded to ultimate thermal degradation. From DTA thermograms, the ultimate degradation peak temperature was noted. The percent residue of each hybrid composites from TGA thermograms at 600 ^{o}C was also noted in Table 4.

In thermograms A and C of Fig. 6, the middle zone of the thermograms, around 250-400 ^{o}C, were almost same. These features were caused due to degradation of hemicellulose and α-cellulose. The residual char left at 600 ^{o}C increased from 21 to 39% in the case of modified hybrid composites. From the thermograms B and D, the increase in degradation temperature from 438.16 to 475.86 ^{o}C in the case of modified BF bundles with modified JF bundles reinforced hybrid composites was observed. A similar observation was reported by Saha et al. (1991). An increase in residual char formation

and increase in degradation temperature indicated that this might be caused by an increased rate of formation of free radicals that are stabilized by condensed carbon ring formation in the char residue.
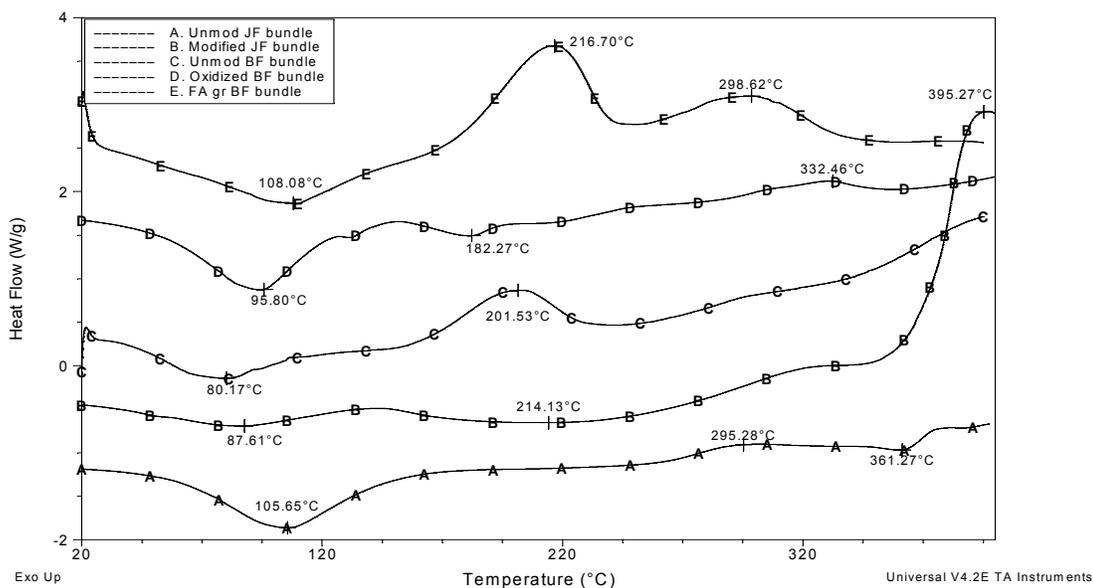

Figure 5. Overlay of DSC thermograms of the following: A. unmodified JF, B. modified JF, C. unmodified BF, D. oxidized BF, and E. FA grafted BF bundles

Table 3. Results of Differential Scanning Calorimeter (DSC) Analysis of Unmodified and Modified, Jute Fibre and Bagasse Fibre Bundle

Sample	Peak temperature (^{o}C)	Nature of peak	ΔH (J/g)
A. Unmodified JF bundle	105.65	Endothermic	-254.4
	295.28	Exothermic	53.93
	361.27	Endothermic	-29.15
B. Modified JF bundle	87.61	Endothermic	-245.1
	214.13	Endothermic	-98.36
	395.27	Exothermic	247.8
C. Unmodified BF bundle	80.17	Endothermic	-40.19
	201.53	Exothermic	44.32
D. Oxidized BF bundle	95.80	Endothermic	-236.7
	182.27	Endothermic	-20.41
	332.46	Exothermic	30.99
E. FA grafted BF bundle	108.08	Endothermic	-165.8
	216.70	Exothermic	99.45
	298.62	Exothermic	162.18

Therefore, from DTG analysis, it may be concluded that the thermal stability of unmodified BF bundles was improved by chemical modification. The thermal decomposition in the third zone, as shown in TGA thermograms, was the result of complex reactions. One of the degradation mechanisms that might be expected was decomposition of aromatic rings, occurring above 400 ^{o}C. Continuous heating leads to saturation of rings, rupture of lignin C-C bonds, release of methane, CO, and CO_2, and structural rearrangements (Rials and Glasser 1984).
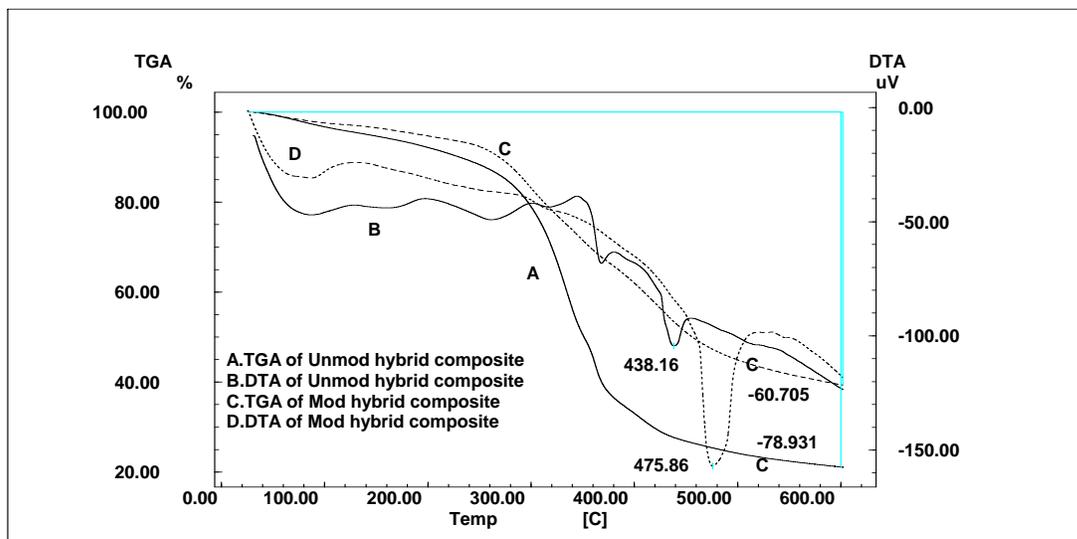
Figure 6. Overlay of DTG thermograms of unmodified and modified BF bundles with modified JF bundles reinforced epoxy hybrid composites

Table 4. Results of Differential Thermo Gravimetry (DTG) of Unmodified and Modified BF Bundles with Modified JF bundles Reinforced Hybrid Composites

Sample	Peak temperature (^{o}C)	% Char residue
1. Unmodified hybrid composite	438.16	21
2. Modified hybrid composite	475.86	39

Mechanical Properties

The importance of mechanical properties is to quantify the reinforcing potential of the particular system. However, mechanical properties can also give indirect information about interfacial behavior in composites, because the interaction between the components has a great effect on the mechanical properties of the composites. The properties of composites were strongly influenced by short bagasse fibre bundles loading. The effect of fibre ends plays an important role in the fracture of hybrid composites. Thus, it is very important to optimize the fibre loading for a particular fibre/matrix system so that maximum properties can be achieved. The improvement in properties is more pronounced in the modified BF bundles with modified JF bundles reinforced epoxy hybrid composite than that of unmodified BF bundles with modified JF bundles

reinforced epoxy hybrid composite (Joseph et al. 2002). The tensile, flexural, and impact behavior were evaluated, and the results are shown in Table 5.

It is evident from Fig. 7, A and B respectively, that as soon as volume % of the BF bundles increased from 0 to 50%, the Tensile Strength (TS) and Tensile Modulus (TM) increased. But as soon as volume % of the BF bundles increased above 50%, tensile strength and tensile modulus decreased considerably. This was due to the fact that higher loading of BF bundles leads to greater fibrillation, owing to the relatively larger quantity of fibre ends available for crack initiation. This could lower the effective stress transfer at the interface. TS and TM of the modified BF bundles with modified JF bundles reinforced epoxy hybrid composite was higher than unmodified BF bundles with modified JF bundles reinforced epoxy hybrid composite because after surface modification of BF, bonding between fibre and resin increased. The tensile strength of modified BF bundles with modified JF bundles reinforced epoxy hybrid composites improved by 43% when % of BF bundles increased from 20% to 50% in composites.

From Figure 7C, the variation in % elongation at break was higher in FA grafted BF bundles with modified JF bundles reinforced composite. When the percentage of BF bundles was 50% in unmodified and modified BF bundles with modified JF bundles reinforced epoxy composite, % elongation at break was 5.18 and 8.35 respectively. The addition of short BF bundles increased the ductility of composite materials. High failure strain of BF bundles provides a better strain compatibility between the fibres and matrix. The value of failure strain decreased on addition of BF bundles beyond the loading limit i.e. more than 50%.

Flexural Strength (FS) and Flexural Modulus (FM) of the unmodified and modified BF bundles with modified JF bundles reinforced epoxy hybrid composite at different % of BF bundles are shown in Fig. 7, D and E respectively. In this case also as soon as % of the BF bundles increased above 50%, FS and FM of the unmodified and modified BF bundles with modified JF bundles reinforced epoxy hybrid composites decreased. When flexural properties of unmodified and modified BF bundles with modified JF bundles reinforced composites were compared, it was observed that flexural properties of the chemically modified BF bundles with modified JF bundles reinforced composites were much higher than unmodified BF bundles with modified JF bundles reinforced composites. Flexural Strength of modified BF bundles with modified JF bundles reinforced epoxy hybrid composites improved by 52% when % of BF bundles increased from 20% to 50% in composites.

Impact strength is defined as the ability of the material to resist fracture under stress applied at high speed. The impact strength of hybrid composites containing unmodified and modified bagasse fibre bundles with modified JF bundles is presented in Fig. 7F. The impact properties of composite materials were directly related to their overall toughness. The impact performance of fibre-reinforced composites depended on many factors, including the nature of the constituent, fibre/matrix interface, the construction and geometry of the composite, and test conditions. The impact failure of a composite occurs by factors such as matrix fracture, fibre breakage, fibre/matrix debonding, and fibre pull out. Nevertheless, fibre breakage has been found to be an important energy dissipation mechanism in fibre reinforced composites. The applied load transferred by shear to fibre bundles may exceed the fibre/matrix interfacial bond strength, and fibre breakage occurs. The fractured fibres may be pulled out of the matrix,

which involves energy dissipation. It is observed that impact strength gradually increases with increasing content of bagasse fibre bundles (Cao et al. 2006). Composites with FA grafted BF bundles improved the impact strength 59% when the % of BF bundles was increased from 20% to 50%.

All of the above observations suggest that optimum mechanical properties are obtained at higher JF bundles loadings and more specifically when JF and BF bundles are in the ratio of 50:50.
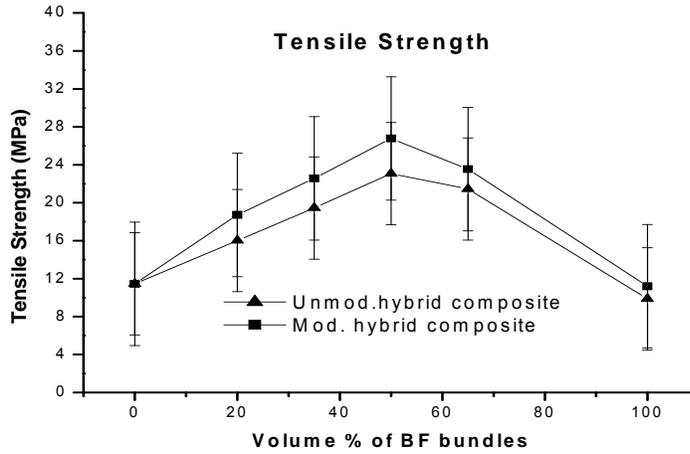
Table 5. Results of Mechanical Properties of Unmodified and Modified BF Bundles Incorporated with Modified JF Bundles Reinforced Epoxy Hybrid Composites

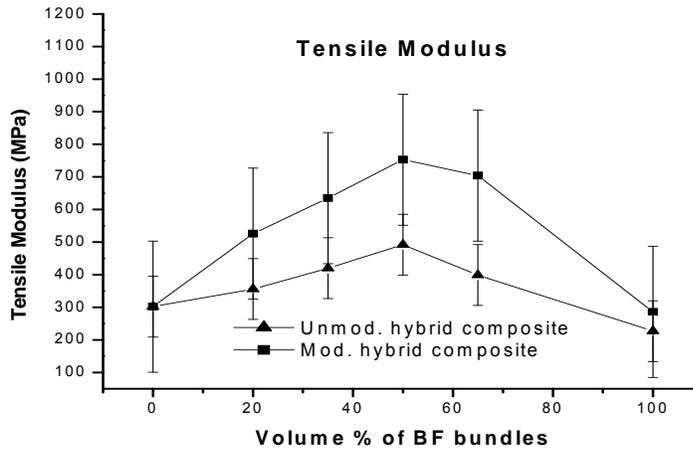|	Unmodified BF bundles with modified JF bundles reinforced epoxy hybrid composites						Modified BF bundles with modified JF bundles reinforced epoxy hybrid composites				
Bagasse %	0	20	35	50	65	100	20	35	50	65	100
T.S. (MPa)	11.45	16.02	19.45	23.07	21.15	9.87	18.72	22.57	26.77	23.54	11.2
T.M. (MPa)	302	356	420	492	399	227	526	635	753	704	286
%E.B.	2.94	3.76	4.39	5.18	4.12	1.78	5.64	6.97	8.35	7.35	2.88
F.S. (MPa)	31.15	36.46	45.32	55.63	51.19	26.78	42.72	54.57	65.22	60.12	30.78
F.M. (MPa)	645	789	1101	1480	1311	502	1178	1484	1748	1518	632
I.S. (kJ/m^2)	6.9	7.46	9.53	10.66	8.33	6.67	10	13.33	15.93	10.93	8.66

SEM Analysis

Scanning electron micrographs (SEM) of single longitudinal surface of unmodified and modified jute fibre are shown in Fig. 8, micrographs A and B, respectively. It can be observed that the filaments in the unmodified JF bundle were packed together but got split after alkali treatment. This might be due to the breaking of the unmodified JF bundles down into smaller ones by dissolution of hemicelluloses, waxes and some other surface impurities. As a result, the surface area available for contact with matrix increased and hence interfacial adhesion increased significantly. A similar observation was also reported previously (Razera and Frollini 2004).

The SEM of single longitudinal surface of unmodified, oxidized, and FA grafted BF are shown in Fig. 9, micrographs A through C, respectively. It can be seen in Fig. 9A that unit cells run longitudinally with more or less parallel orientations. Surfaces contain a large number of pores covered by pithy and waxy materials. The intercellular gaps, in the form of shallow longitudinal cavities, can be clearly distinguished, as the unit cells are partially exposed. The intercellular space is filled up by binder lignin and by fatty substances that hold the unit cells firmly in the fibre.
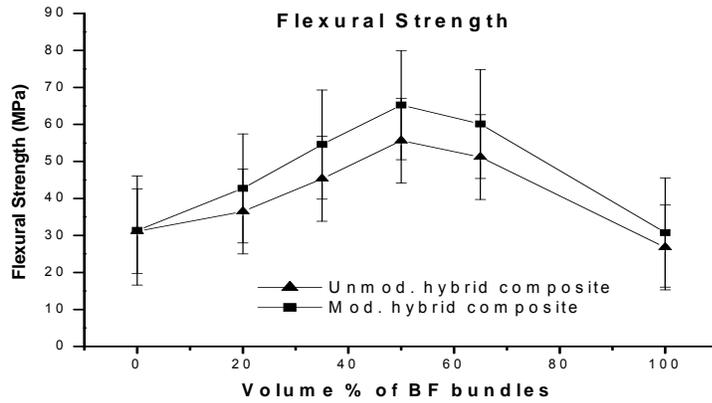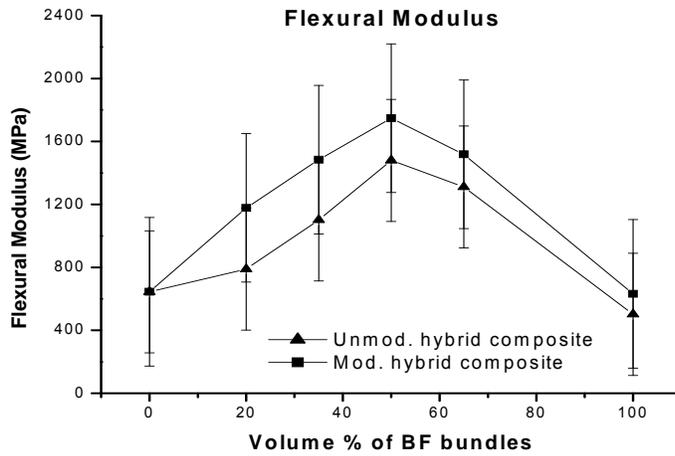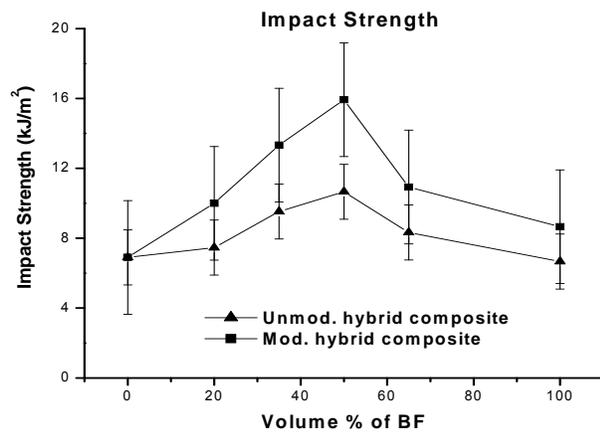
A.

B.
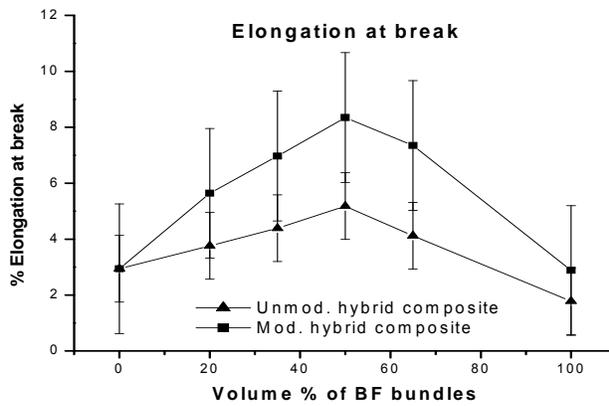
C.

D.

E.

F.

Figure 7. Results of: A. Tensile Strength, B. Tensile Modulus, C. Percent elongation at break, D. Flexural Strength, E. Flexural Modulus, and F. Impact Strength with variable volume percent of unmodified and modified BF bundles incorporated with modified JF bundles hybrid composites

Figure 9B shows a larger number of surfaces cracks, or pit formations, compared to Fig. 9A. These features might result from the partial removal of wax and fatty substances during treatment with the dewaxing solvent mixture. Very interestingly, the parallel unit cells look partially split due to the removal of fatty materials. A micrograph of FA grafted BF, shown in Fig. 9C, revealed that the intercellular gaps were reduced, and FA was bonded onto the fibre surface. FA grafts took place more on the surface of unit cells of fibre (Rout et al. 2002).

The improved interfacial adhesion in chemically modified composites can be further understood by looking into fracture topography of the composites. Figure 10 (A and B) depicts the scanning electron micrographs (SEM) of tensile fracture surfaces of unmodified and modified BF bundles incorporated with JF bundles reinforced hybrid composites. Figure 10A shows the tensile failure surface of composite containing unmodified BF bundle. The presence of cavities is clearly visible in the figure, and some of the fibres that can be seen are relatively free of the resin material. This indicates that the level of adhesion between the fibre bundles and the matrix is poor, and when stress is applied it causes the fibres to be pulled out from the epoxy matrix easily, leaving behind remnant cavities. The SEM of composites containing modified BF bundles are presented in Fig. 10B. This figure shows short broken fibres projecting out of the epoxy matrix. This indicates that the extent of adhesion between the fibres and epoxy matrix was greatly improved, and when stress is applied, the fibres broke and didn't wholly come out of the matrix. Here we can see the presence of epoxy particles attached to the fibre surface and no considerable cavities, indicating good interfacial adhesion.
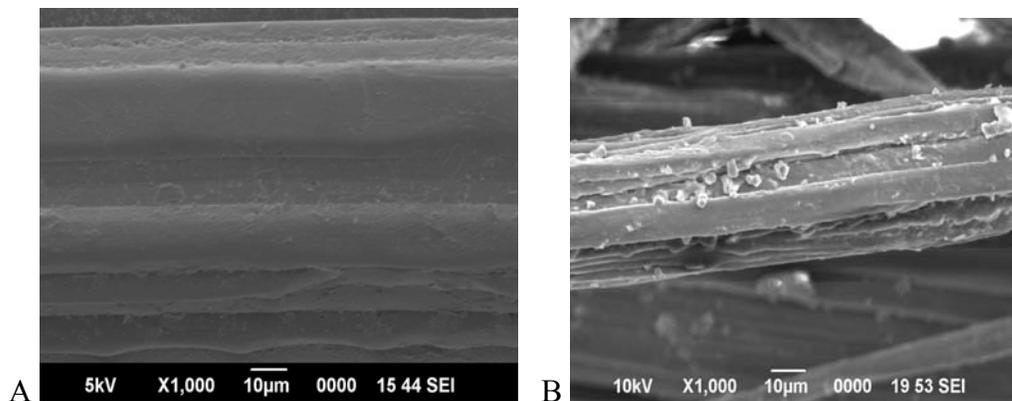

Figure 8. Micrographs of A. Unmodified and B. Modified jute fibre
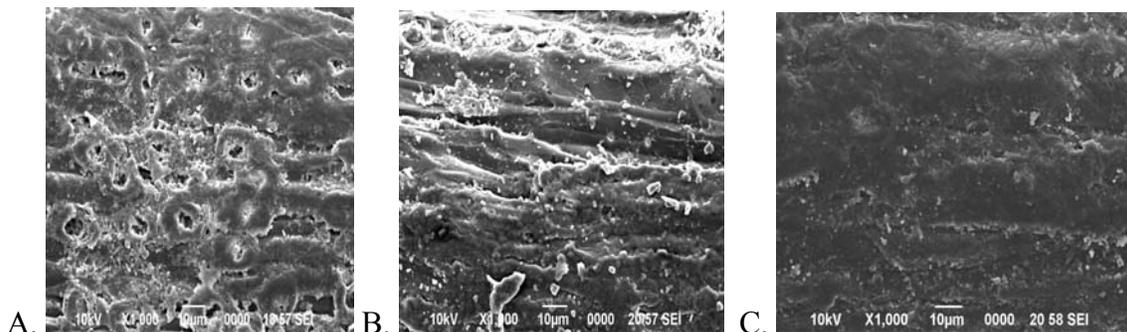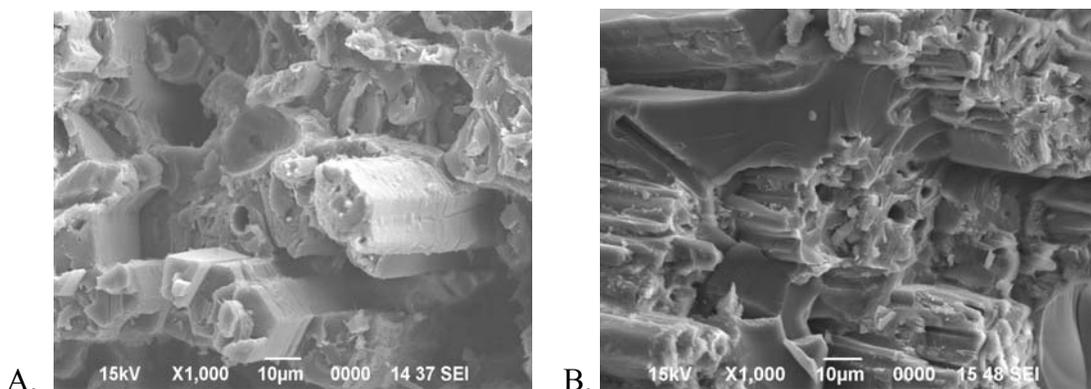

Figure 9. Micrographs of A. unmodified, B. Oxidized, and C. FA grafted Bagasse fibre

Figure 10. Micrographs of A. Unmodified BF bundles and B. Modified BF bundles with modified JF bundles reinforced hybrid composite fracture surface

CONCLUSIONS

The following conclusions are based on the findings reported in this paper:

1. A potential opportunity for the development of new hybrid composites by chemical modification of jute fibre bundles and sugarcane bagasse fibre bundles for epoxy matrix has been presented.
2. The objective of fibre surface modification was to create quinones or some of the unsaturated units in the lignin portions of bagasse fibre bundles, followed by grafting furfuryl alcohol, which is a chemical that is obtained from a renewable source.
3. Chlorine dioxide was used in suitable conditions to oxidize mainly phenolic syringyl and guaiacyl units of the lignin polymer to create quinones or muconic derivatives, which were characterized by spectroflurophotometer.
4. From DSC thermograms, it was observed that there was a shift of an exothermic peak towards a lower temperature by nearly 300 ^{o}C, which confirms that the macromolecule in BF structure was changed considerably after modification with FA.
5. From DTG thermograms, it was observed that thermal stability of hybrid composites increased by increasing residual char left at 600 ^{o}C from 21% to 39% and degradation temperature from 438 to 475 ^{o}C after FA grafting on the BF bundles. The high thermal stability of this hybrid composites place it in the category of tough engineering materials.
6. It was found that FA grafted BF bundles based hybrid composites have higher tensile, flexural, and impact properties than composites based on unmodified BF bundles. SEM features correlated satisfactorily with the mechanical properties of modified BF bundles with modified JF bundles reinforced epoxy hybrid composites.
7. FA grafted BF bundles with modified JF bundles reinforced epoxy hybrid composites improved tensile strength 43%, flexural strength 52% and impact strength 59%, respectively when % of BF bundles increased from 20% to 50%.

8. The short BF bundles could be expected to improve the properties moderately in optimized loading limit. Short fibres show better alignment in the matrix than long fibres, so that onset of fibre-fibre interactions takes place only at higher fibre loading.

9. The optimum mechanical properties are obtained at higher JF bundles loadings and more specifically when JF and BF bundles are in the ratio of 50:50.

10. The decline in mechanical properties at higher fibre loading could be due to poor dispersion, as the amount of BF bundles in resin increased. BF bundles likely interact more with themselves as their content increases.

11. Grafting of FA improves wetting of the fibre with matrix by hydrophobizing the fibre surface and promotes interfacial bonding by diffusion of the chain segments of the grafted molecules into the matrix.

12. This paper provides new direction for the development of chemically modified jute and bagasse fibre bundles reinforced epoxy resin hybrid composites.

13. These hybrid cellular natural fibre-based composites were found to provide an economic and environmentally friendlier alternative to entry-level synthetic composites.

14. Hybrid fibre composites with jute and other fibres rather than synthetic fibres may open up new applications. However, as inferred from the results presented here, significant improvements in strength and fracture characteristics must be realized for this class of materials.

15. It can be predicted that with natural fibre reinforcement, the best properties of synthetic fibre like glass or carbon cannot be achieved, above all because of the big difference between the modulus of elasticity of the glass or carbon and jute/bagasse fibres. However, from the above discussions, we can say that surface-modified natural fibres and epoxy matrix can be molded into cost-effective but value added composite materials.

ACKNOWLEDGMENTS

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