Fabrication, Characterization, and Evaluation of *Luffa cylindrica* Fiber Reinforced Epoxy Composites

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Because of the increasing awareness of the environment and energy issues, as well as advances in technology, the areas of application for annual plant fiber functional materials are expanding. In this work, two chemical treatments, alkalization (2 h agitation with 5% NaOH) and furfurylation (graft furfuryl alcohol followed by oxidation with (1N) NaClO$_2$ solution), were conducted on *Luffa cylindrica* fiber surfaces. The grafting of furfuryl alcohol followed by oxidation-generated quinines showed better results than alkaline treatment with respect to enhancement of surface area and hydrophobicity as well as wax, lignin, and hemicellulose extraction. The efficiency of chemical treatments was verified by elemental analysis and FTIR spectroscopy. Differential scanning calorimetry, thermo-gravimetric analysis, scanning electron microscopy, water absorption, and mechanical tests were performed to determine the thermal, mechanical, and morphological properties of untreated and chemically treated luffa fiber reinforced epoxy composites. Microstructures of the composites were examined to determine the mechanisms for the fiber-matrix interaction, which affects the thermal stability, water absorption, and mechanical behavior of the composites. The data from the water absorption process of composites at various temperatures were analyzed using a diffusion model based on Fick's law.

INTRODUCTION

Natural fibers such as jute, flax, ramie, hemp, coir, sisal, banana, bagasse, and pineapple are known to be very strong and can be effectively utilized for composites in various applications (Acharya *et al.* 2011). Natural fibers have the advantages of low density, low cost, worldwide availability, renewability, biodegradability, ease of preparation, lower energy consumption, and relative non-abrasiveness over traditional reinforcing synthetic fibers (Khalil *et al.* 2007; Bledzki *et al.* 2010; Asasutjarit *et al.* 2009). Their softness is also an advantage in relation to common synthetic fibers like glass fibers. Moreover, natural fibers are environmentally friendly and neutral with respect to the CO$_2$. However, the main disadvantages of natural fibers in composites are the poor compatibility between fiber and matrix and the relative high moisture sorption (Ghali *et al.* 2011). Therefore, chemical treatments considered in modifying the fiber surface properties including alkali, silane, acetylation, benzoylation, acrylation, maleated

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coupling agents, isocyanates, permanganates, and others have been reviewed (John and Anandjiwala 2008). The chemical treatment of fiber aimed at improving the adhesion between the fiber surface and polymer matrix may not only modify the fiber surface but also increase fiber strength. Water absorption of composites is reduced and their mechanical properties are improved (Boynard and D'almeida 2000; Edeerozey *et al.* 2007; Li *et al.* 2007; Weyenberg *et al.* 2003).

In this respect, this study concentrated on the use of *Luffa cylindrica* fiber that is easily available because of its natural distribution, along with some inherent advantages over other fibers for its renewability, biodegradability, natural network (special arrangements), high strength, and initial modulus (Boynard and D'almeida 2000). Luffa cultivation worldwide has been steadily increasing in the past 20 years in response to the rising demand for renewable fiber sources and clean agricultural practices. It is obtained from the fruit of two cultivated species of the genus *Luffa* in the cucurbitaceous family, *Luffa cylindrica* (smooth fruit) and *Luffa acutangula or aegyptiaca* (angled fruit). Luffa fiber is not a single filament like glass fiber, but rather a bundle of cellulose fibrils making a fibrous vascular system in a hierarchical structure. It is found in tropical and subtropical countries of Asia (India, China, Pakistan, and Indonesia), Africa, and South America. The young and greenish fruit is eaten as a vegetable all over the world. The ripe and dried fruit is the source of *Luffa cylindrica* or luffa fiber, vegetable sponge, or sponge gourd and is used as an industrial fiber as shown in Fig. 1. Parts of the plant are used to create bath or kitchen sponges, a natural jaundice remedy (juice), home insulation, furniture, and various other products (Demir *et al.* 2006; Seki *et al.* 2011).

Fig. 1. A photograph of *Luffa cylindrica* fiber

A large number of polymers that have good performance as matrix materials provide a wide range of properties and therefore offer a large variety of composite materials (Hoareau *et al.* 2004). Compared to thermoplastic materials such as polyethylene, polypropylene, polyamides, *etc.*, thermoset compounds have a superior thermal stability and lower water absorption (Trindade *et al.* 2005). At this moment, the conventional thermoset matrix such as epoxy (EP) fulfills the requirements of excellent adhesion, surface coatings, engineering composites, and resistance to chemical attack and to moisture. Apart from these, EP has the following traits: it has better electrical

insulation properties; minimum pressure is needed for fabrication of products; there is an absence of volatility on heat curing; and there is negligible shrinkage compared to other thermosets such as vinyl ester and polyester resin.

The luffa fiber surface has many alcohol groups, limited (acidic) carboxylic groups, reducing (aldehydic) groups, and phenol groups that provide ample scope for chemical anchorage of epoxide group segments on resin. Chemical treatments of luffa fibers using sodium hydroxide and furfuryl alcohol induced by oxidation-generated quinines were carried out in this research. An important point to consider is that the reagents used in chemical treatment cannot be too expensive, and ideally, the treatments must involve a minimum number of compounds obtained from nonrenewable sources. The main idea of this experiment was to observe the conversion of polar hydrophilic functional groups of the fiber to hydrophobic functional groups with increased adhesion with the matrix. The modified fibers were characterized by FTIR spectroscopy and elemental analysis. The thermal, mechanical, and morphological properties of chemically treated luffa fibers reinforced epoxy composites were compared with those obtained for untreated luffa fibers reinforced epoxy composites. The unsteady state of diffusion method based on Fick's law was used for all the composites in this study to determine the diffusion coefficient by measuring the change of the composite weight as a function of time until reaching equilibrium weight.

EXPERIMENTAL

Materials

Luffa cylindrica fiber was obtained from Tristar products limited, Noida, India. The as-received luffa fiber was cut carefully to separate the inner fiber core (central core) from the outer mat core. Only the outer mat core was used in this study. The inherent properties of *Luffa cylindrica* fiber are given in Table 1 (Akgul *et al.* 2013; Espert *et al.* 2004; Tanobe *et al.* 2005). The diglycidyl ether of bisphenol A (DGEBA) based epoxy resin with an epoxy value of 0.51 and a density of 1.1 to 1.5 g/cm^3, supplied by Dow Chemicals, Mumbai, India under the trade name Araldite, was used as the matrix material in the fabrication of composites. The hardener of the grade HV 953 IN is an aliphatic polyamine supplied by Dow Chemicals. Both the resin and hardener were used as received. The typical properties of epoxy resin are shown in Table 2. Chemicals used for the surface modification of fiber — sodium hydroxide, furfuryl alcohol, sodium chlorite, acetone, and other reagents were obtained as analytical grade from Central Drug Houses (CDH) Pvt. Ltd. New Delhi, India.

Table 1. Physical Properties of *Luffa cylindrica* Fiber

Chemical constituents (%)		Physical properties of luffa fiber	
Cellulose (%)	63.0±2.5	Density (gm/cc)	0.92±0.10
Lignin (%)	11.69±1.2	Diameter (μm)	270±20
Hemicelluloses (%)	20.88±1.4	Aspect ratio	340±5
Ash (%)	0.4±0.10	Microfibrillar angle (^{0})	12±2

Table 2. Typical Properties of Epoxy Resin

Properties	Evaluation
Appearance	A milky white liquid
Specific gravity at 25 °C (gm/cc)	1.12
Viscosity at 25 °C (centipoises)	550
Gel point in minutes	26
Solid contents (%)	84
Tensile strength (MPa)	6.9
Tensile modulus (MPa)	166
Impact strength (kJ/m^2)	1.1

Surface Treatment of *Luffa cylindrica* Fibers

Alkali treatment of luffa fiber

Luffa fiber mat was prepared into 100 mm x 100 mm dimensions. It was initially washed with distilled water to remove dirt and other water-soluble impurities. The cleaned luffa fibers were then immersed in a 5% NaOH solution and sonicated for 2 h at 50 °C in an ultrasonicator bath (model UD80SH2L) of M/s (Analytical Instruments Consortium, Kolkatta, India). The fiber was taken out from the NaOH solution, neutralized with dilute acetic acid solution (2N), and finally washed with distilled water. A final pH of 7 was maintained. The luffa fibers were then dried at room temperature for 48 h, followed by air-oven drying at 70 °C for 5 h.

It is known that the alkalization treatment removes impurities and increases the fiber surface adhesion characteristics with the resin. The removal of surface impurities on plant fibers is advantageous in fiber-matrix adhesion because it facilitates both mechanical interlocking and bonding reactions.

Oxidation of luffa fiber

The raw fibers (2 g) were oxidized with an aqueous chlorine dioxide (ClO$_2$) solution (18 mL, 1.88 mmol), which was prepared by reactions between sodium chlorite and acetic acid in aqueous medium. After the oxidation reaction, the yellow-red colored fibers were washed with deionised-water until neutrality.

Grafting of furfuryl alcohol (FA) on oxidized luffa fiber

The oxidized luffa fiber (2 g) impregnated with furfuryl alcohol (11.35 g) was heated at 100 °C for 2 h in the presence of N$_2$ gas. Excess furfuryl alcohol was removed by washing with ethanol followed by drying the fibers at 50 °C for 24 h. This fiber was designated as FA-grafted luffa fiber.

Fabrication of composite materials

A hand lay-up technique followed by compression molding was adopted for composite fabrication. Treated and untreated luffa fiber mats were separately impregnated with epoxy resin in a mold of dimensions 100 mm x 100 mm x 3 mm for fabricating the composites. In each composite, the weight ratio of matrix to fiber was maintained at 70:30.

The curing of resin was done by the incorporation of epoxy resin and amine hardener in a weight ratio of 70:30 in 100 mL of acetone which acted as a thinner or diluent. The prepared matrix solution was also degassed before pouring. The composite was allowed to set for 24 h at room temperature. Thereafter, the composite was compression-molded at 5 MPa and 100 °C for one hour followed by post-curing at 105 °C for half an hour in an oven. Before making the composite, the press machine was degassed to remove air bubbles and voids. Single layers were added successively in order to produce a 3 mm thick composite laminate.

A neat epoxy matrix (unfilled) sample was also prepared to compare the properties of untreated and treated luffa composites. The test specimens for mechanical, thermal, and water absorption properties were cut from the composite laminates according to ASTM standards.

Characterization of Fiber, Epoxy Resin, and Composites

Elemental analysis

The elemental analysis of untreated and various treated *Luffa cylindrica* fibers was undertaken with an elemental analyzer (Model: Vario EL III; Make: M/s Elementar, Germany). The estimation of five elements, *i.e.* carbon, hydrogen, nitrogen, oxygen, and sulfur was undertaken. The resulting O/C ratio is summarized in Table 3.

FT-IR spectroscopy

A Fourier transform infrared spectrophotometer (FTIR, model-IR Prestige-21, Schimadzu Corporation, Japan) was used for the structural determination of functional groups and compounds. FTIR spectra in the solid state using potassium bromide (KBr) pellets of untreated, alkali treated, oxidized, and FA-grafted luffa fiber were recorded. This technique consisted of cutting the fiber samples into small pieces with scissors and then sieving through a 120-mesh screen, followed by preparation of KBr pellets by mixing about 1 mg of sample with 100 mg of high-purity infrared-grade KBr powder (Aldrich). The KBr was previously oven dried to reduce the interference of water. The spectra were recorded in the range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and 20 scans were carried for each specimen in transmittance mode. The overlay of the spectra is shown in Fig. 2.

Differential Scanning Calorimetry (DSC) analysis

The DSC analysis of the pre-cured matrix resin and composites was carried out in a DSC Q$_{10}$ thermal analyzer (TA Instruments, New Castle, DE, USA) under a nitrogen atmosphere (50 mL/min). DSC was used to analyze the curing reaction of luffa fiber with epoxy resin at a heating rate of 10 °C/min from 20 to 400 °C, by taking 8 to 10 mg of the sample in a standard aluminum hermetic liquid sample pan, secured by the crimping of a standard aluminum cover. An indium standard was used for instrument calibration, including baseline slope, cell constant, and temperature. The measured DSC thermograms are shown in Fig. 3.

Thermo-gravimetric (TGA) analysis

Dynamic TGA of pure epoxy, untreated, and chemically treated composites was executed in a DTG-60 (Schimadzu Corporation, Kyoto, Japan) from 30 to 700 °C in a platinum pan at a heating rate of 10 °C/min under flowing nitrogen atmosphere (30

mL/min) to find the thermal stability of materials. For each scan 8–10 mg of composite sample was taken. The results of TGA thermograms are presented in Fig. 4 and Table 4.

Mechanical properties

A tensile test was carried out with rectangular specimens (width 10 mm, thickness 3 mm) using a universal tensile machine (model 3366, Instron, London, UK) with a 500 kN capacity, a gauge length of 80 mm, and a crosshead speed of 1 mm/min, as per ASTM D 638 (Daniel and Ishai 2006). All tests were conducted at room temperature and 50% relative humidity. For pure epoxy and its composites, six tests were executed with each sample. The standard specimens were visually inspected before measurement and were found to be free from pores and nicks. The results are described in Fig. 5a and b.

The impact strength is used to determine the amount of energy that is required to break the specimens. The impact strength of the pure epoxy and its composites was measured with a standard Charpy, Izod impact testing machine (model IT 1.4; Fuel Instruments, Mumbai, India), according to ASTM D 256 (Daniel and Ishai 2006). The measurements were done on unnotched samples (70 mm x 10 mm x 3 mm) with an impact speed of 1 m/s, a hammer weight of 4.580 kg, height 203.70 mm, and energy of 1.4 joules. The test specimen was supported by a vertical cantilever beam and was broken by a single swing of a pendulum which struck the face of specimen, and the impact strength was noted on the dial meter fitted to the machine at room temperature. For each specimen, six measurements were recorded and mean values were reported. The investigation of impact strength is shown in Fig. 5c.

Scanning Electron Microscopy (SEM)

To study the morphological features of fiber-matrix interface in the composite samples, the tensile test samples were fractured in liquid nitrogen after 15 to 20 min of freezing in liquid nitrogen. The fractured surfaces were coated with a thin layer of metallic gold in an automatic sputter coater (JEOL JFC-1600) to make the surface conductive and analyzed by a scanning electron microscope (JEOL JSM 6390 LV). The SEM image was captured at the following specifications: accelerating voltage, 20 KV; image mode, secondary electron image; working distance, 20 mm; and magnification, 500X. The surface morphologies of fiber sample before and after chemical treatments were also observed using the same microscope. The resulting image is shown in Fig. 6.

Water absorption test

Water absorption tests were conducted as per ASTM D 5229 (Daniel and Ishai 2006). Before testing, the weight of each specimen was measured. Three specimens of each formulated composite were immersed in distilled water at various temperatures (23, 50, and 100 ^{o}C, respectively). The specimens were removed from the water after a certain period of time and wiped with a soft tissue paper before the weight was measured. The weight of the specimens was taken and they were then immersed in water again. The water absorption test was continued for several hours until a constant weight of the specimens was reached. The results are reported in Fig. 7. The percentage of water absorption [WA (%)] is calculated by using the calculation formulla (1):

$$WA\ (\%) = \frac{\text{Weight of water absorbed composite - weight of dry composite}}{\text{Weight of dry composite}} \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Chemical Treatment of Fiber Surface

Sodium hydroxide (NaOH) chemical treatment disrupts hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax, and hemicelluloses of the fiber cell wall, depolymerizes cellulose, and exposes the short-length cellulose fibril. The ionization of hydroxyl groups of fibers into alkoxide increases the fiber strength and stiffness and hence, increases mechanical properties (Demir *et al.* 2006; Seki *et al.* 2011). The weight changes of the fibers after alkali treatments were determined gravimetrically and a loss of weight was observed near 2%.

Furfuryl alcohols (FA) were chosen as reagents because these alcohols can be obtained from renewable waste biomass. The untreated luffa fiber was selected for grafting furfuryl alcohol followed by oxidation with sodium chlorite generating *ortho-* and *para*-quinones on its surface. By visual inspection, it was observed that the fibers turned yellow-red after the oxidation reaction. It was then washed with water until neutrality. The grafting of FA chain structure onto luffa fiber is exemplified in scheme 1. In this modification, the polymeric coating layer so obtained by FA treatment acts as coupling agent between epoxy and luffa fibers. Similar results were also obtained on other natural fibers (Hoareau *et al.* 2004; Trindade *et al.* 2005). The reaction with $-ClO_2$ and furfuryl alcohol was studied and percent graft yield for luffa fiber was calculated as 12% by using Eq. 2:

$$\text{Graft Yield (\%)} = \frac{\text{Dry weight of FA grafted luffa fibers - Dry weight of untreated luffa fibers}}{\text{Dry weight of untreated luffa fibers}} \times 100 \quad (2)$$
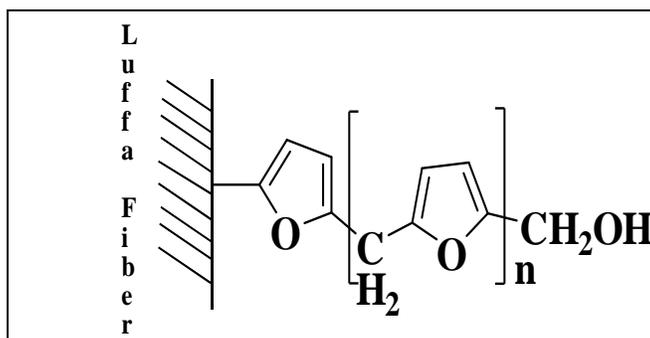
Scheme 1. The grafting of furfuryl alcohol chain on to untreated luffa fiber surfaces

Elemental Analysis of Fiber

An elemental analyzer was used to determine the atomic concentrations of untreated and chemically treated luffa fiber, and the results are tabulated in Table 3. Some significant differences in the carbon (C) and oxygen (O) percentages were found between untreated and treated luffa fibers. The O/C ratio for untreated fiber was 0.58. This ratio is an indication that there was still lignin on the surface. When this ratio reaches 0.83, the sample is said to be pure cellulose, whereas when it is in the range 0.31 to 0.40, it is said to be pure lignin (Toth *et al.* 1993). The value was increased to 0.66 for alkali-treated fibers; this may be expected due to the removal of some parts of lignin and

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hemicellulose content and an increase in the cellulose content. This ratio was 0.67 for oxidized luffa fiber while this value reached a maximum of 0.71 for FA-grafted fiber.

Table 3. Results of Elemental Analysis

Sample	%C	%H	%N	%O	%S	O/C ratio
Untreated luffa	56.47	5.45	0.09	32.61	0.50	0.58
Alkali treated luffa	53.62	4.55	0.08	35.33	0.48	0.66
Oxidized luffa	53.01	4.37	0.08	35.57	0.37	0.67
FA-grafted luffa	53.87	5.13	0.08	38.2	0.22	0.71

It can be concluded that during the oxidation treatment, the polymerized parts of the fiber, such as lignin and carbohydrates, were oxidized to generate *ortho-* and *para-* quinines, muconic esters, and some other active groups, which increased the concentration of oxygen and hence, enhanced the O/C value. The possible reaction of generated reactive site (*ortho-* and *para-* quinines) with furfuryl alcohol ordered the arrangement of the fiber surface due to the polymeric coating and increased the molecular orientation of cellulose, thus enhancing the O/C value of FA-grafted luffa fiber. A similar observation was also shown on Brazilian luffa fiber with an O/C ratio of 0.57 (Tanobe *et al.* 2005).

Spectral Analysis of Fiber

IR spectra of the untreated, alkali treated, oxidized, and FA-grafted luffa fiber are shown in Fig. 2 from wave number 4000 to 400 cm^{-1}. By comparing the FTIR spectra of untreated and chemically-treated fibers, it is evident that there were some differences in the spectra. The characteristic features of the spectrum of the luffa fiber are due to its constituents such as cellulose, lignin, and hemicelluloses (Khan *et al.* 2005).
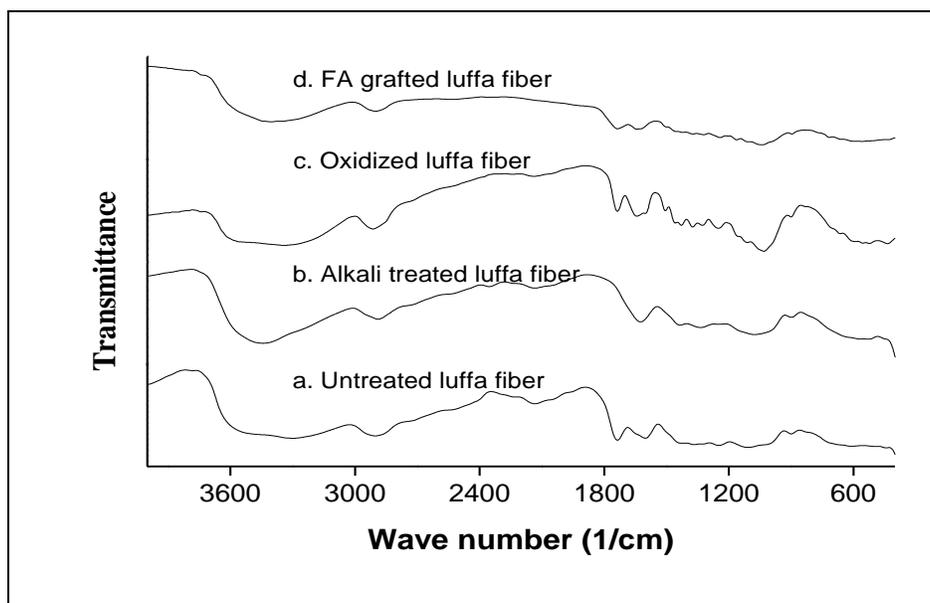
Fig. 2. The FTIR spectra of untreated, alkali treated, oxidized, and FA-grafted luffa fiber

In Fig. 2a, a broad absorption band at the 3650 to 3250 cm^{-1} region is characteristic of polymeric association of the –OH groups and hydrogen bonded –OH stretching vibration present in carbohydrates (cellulose + hemicelluloses) and lignin. It can be noted that the broadness of the –OH band decreased more for alkali treated fiber and less in oxidized fiber, as shown in Fig. 2b and 2c, respectively, when compared to untreated fiber.

These results reflect the decrease of phenolic/aliphatic hydroxyl groups in the fiber polymer after treatments such as alkali and ClO_2 oxidation reaction. The broadness and the peak intensity of the –OH band for FA-grafted fibers (Fig. 2d) was also found to be less than the untreated fibers, which indicates the involvement of the hydroxyl group of furfuryl alcohol in the polymerization reaction forming a polymeric coating of polyfurfuryl alcohol on fiber surface.

No significant change was observed in the spectra between untreated and the FA-grafted luffa fibers. A small peak at 2900 cm^{-1} was attributed to the C-H stretching vibrations of methyl and methylene groups of cellulose and lignin, respectively, in all the spectra of luffa fiber.

Figure 2a shows the bands at 1738 cm^{-1} from carbonyl group stretching, at 1608 cm^{-1} from the free carbonyl band, at 1373 cm^{-1} from the O-H in plane bending, at 1420, 1318, and 1246 cm^{-1} from CH deformation, at 1204 cm^{-1} from C-O stretching, at 1157 cm^{-1} from the skeletal stretching vibrations including the C-O-C stretching, and at 1104 cm^{-1} from ring vibration.

In Fig. 2b, for alkali treated fibers, the intensity of the bands at 1373 cm^{-1} from O-H in plane bending was reduced because of the formation of glycoside bonding. Also, the intensity of bands at 1738 cm^{-1} from carbonyl group stretching was reduced or almost absent due to hemicellulose removal. The decrease of the intensity of a band at 1608 cm^{-1} can be explained by the removal of OH bending in the absorbed water molecules by alkalization (Han and Jung 2008).

After ClO_2 oxidation, as shown in Fig. 2c, a decrease in intensity is observed for the aromatic band of cellulose and lignin unit and an increase in band intensity is observed for the carboxyl stretching at around 1740 cm^{-1} confirming the formation of quinines on the fiber surface. This confirmation is also supported by visual inspection of the color change of the fiber during oxidation and consequent grafting of furfuryl alcohol. In Fig. 2d, the spectra of FA-grafted fiber exhibits a less resolved spectrum due to the polymeric coating layer on the fiber surfaces (Saw *et al.* 2011).

Influence of Fiber Surface Modification on Composites Thermal Properties

The thermal behavior of the epoxy resin in its pure state and in the composite systems was investigated by DSC analysis. During the DSC measurements, the thermal cure steps of the prepolymer (*i.e.*, epoxy matrix) could be detected. Figure 3 shows the DSC thermograms of pre-cured epoxy based composites containing untreated, alkali treated, and furfuryl alcohol grafted luffa fibers and that of pre-cured pure epoxy resin. In the DSC thermograms, all composites show two transition peaks, one endothermic at around 100 ^{o}C and one exothermic peak at >200 ^{o}C, whereas one exothermic peak at a comparatively higher temperature (>370 ^{o}C) appears for pure epoxy resin.
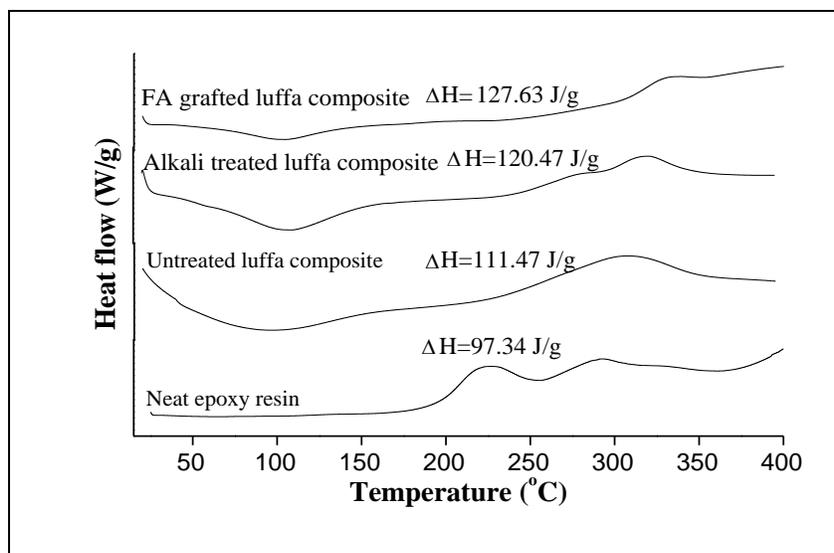
Fig. 3. DSC thermograms of pure epoxy and its composite systems

For the untreated luffa composites, the endothermic peak at around 100 ^oC was due to the removal of moisture and other volatile matter present in the fibers, while this peak shifted at a higher temperature for chemically treated luffa composites *i.e.* at 106 ^oC for alkali treated and 110 ^oC for FA-grafted luffa composites. There was no endothermic peak for the pure epoxy composite, and a flat baseline was observed indicating no moisture on its surface. An exothermic peak was obtained for curing reactions of the epoxy matrix. It can be observed from Fig. 3 that the ΔH_{cure} (enthalpy of curing reaction) values for the composite samples was found to be higher compared to that observed for pure epoxy resin. The higher values of ΔH_{cure} for composites indicated the involvement of more thermal energy for crosslinking the epoxy pre-polymer in the composite systems compared to that in the case of pure epoxy pre-polymer resin, which might be due to hindrance of polymer chain mobility by the fibers. The enthalpies values (ΔH_{cure}) 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 significantly affected the ΔH_{cure} values. In the case of composite materials, the enthalpy of curing reaction (ΔH_{cure}) was found to increase with chemically treated fiber in comparison to untreated fiber. The ΔH_{cure} was slightly greater in furfuryl alcohol grafted luffa composites than alkali treated composites, indicating that furfurylation of fibers significantly promoted the crosslink degree of the epoxy matrix.

Table 4. TGA Data Obtained for Pure Epoxy and its Composites

Sample	^1T_o (^oC)	$^2T_{max}$ (^oC)	^3T_f (^oC)	% Residue
Pure epoxy	223.42	256.2	700	0.5
Untreated luffa composites	258.71	277.96	700	4.84
Alkali treated composites	273.58	284.37	700	23.76
FA-grafted composites	334.41	362.23	700	29.33
^{1} onset degradation temperature, ^{2} temperature of maximum rate of mass loss, ^{3} final degradation temperature.				
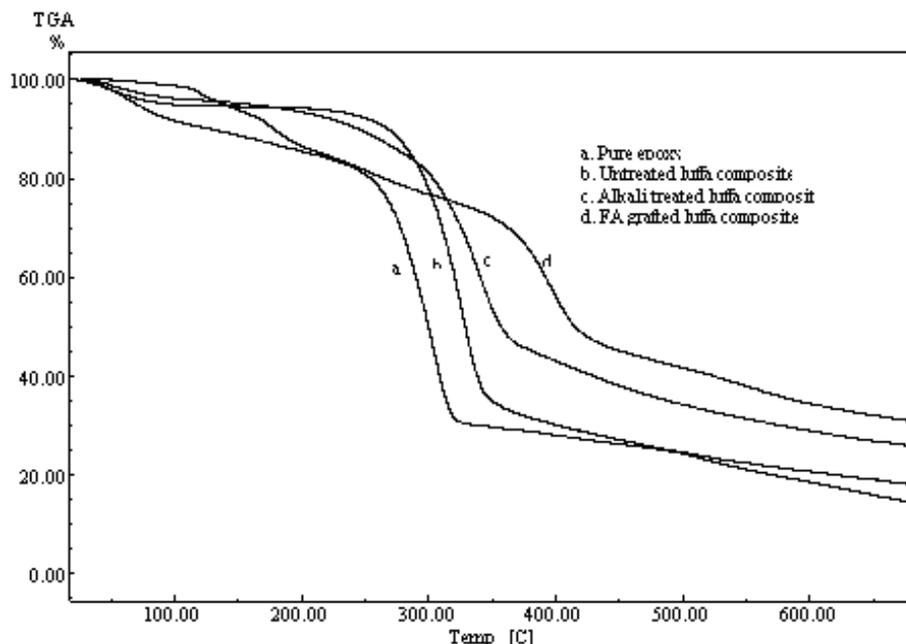
Fig. 4. Thermogravimetric analysis of pure epoxy and its composite systems

The thermal stability of epoxy composites that were untreated or reinforced with chemically treated luffa fiber in pure and dry nitrogen atmosphere was evaluated by thermogravimetric analysis (TGA) and compared with that of pure epoxy matrix. The TGA curves obtained for pure epoxy and various treated and untreated fiber reinforced epoxy composites are presented in Fig. 4. The thermal degradation of all the samples took place within the programmed temperature range of 30 to 700 $^{\circ}$C. The onset temperature of degradation (T_o), temperature of maximum rate of mass loss (T_{max}), and final decomposition temperature (T_f) are noted in Table 4.

It can be seen from Fig. 4 and Table 4 that the initial small weight loss at around 100 °C corresponded to the volatilization of moisture and other volatile products present in the samples. The thermal decomposition of the composites started at comparatively higher temperatures than that of the pure epoxy matrix. The decomposition of pure epoxy started at a temperature of 238 °C and nearly 100% decomposition occurred at 700 °C, whereas the composites started losing weight in the range of 255 to 335 °C and a certain quantity of charred residue of carbonaceous products was left. This indicates that the incorporation of fibers into epoxy polymer enhanced the thermal stability of the composites, which was due to an increase in strength and stiffness of the fibers. It can be noted from Table 4 that the T_o and T_{max} values for the composites were increased with FA-grafted luffa fiber loading in the composites, which indicates that the strong interfacial bonding between grafted luffa fiber and epoxy matrix enhanced the thermal stability of the composites. In composite materials, the percent residue at 700 $^{\circ}$C is found to be higher than that obtained for pure epoxy matrix. This also ensures a higher thermal stability in the composite systems.

Effect of Fiber Surface Modification on Composites Mechanical Properties

The mechanical properties can also give indirect information about interfacial behavior in the composite system, because the interaction between the components has a great effect on the mechanical properties of the composites. The mechanical properties

were evaluated for the pure epoxy and the composites containing both untreated and treated fiber, as shown in Fig. 5. The tensile strength, tensile modulus, and impact strength of the pure epoxy were recorded as 6.9 MPa, 166 MPa, and 1.1 kJ/m^2, respectively, as shown in Table 2. All mechanical tests showed that treated fiber composites withstood more fracture strain than untreated fiber composites. The variation in mechanical properties such as tensile and impact properties of epoxy/luffa composites were evaluated.

Table 5. Mechanical Properties of Untreated and Chemically Treated Luffa Fibers

Fiber samples	Tensile strength (MPa)	Tensile modulus (MPa)	% Extension
Untreated luffa fibers	178.20	4263.84	3.12
Alkali treated luffa fibers	192.70	5184.62	1.86
FA-grafted luffa fibers	226.40	5865.70	1.74

The effect of chemical treatments on tensile strength and modulus of luffa fiber reinforced epoxy composites was investigated, as shown in Fig. 5a and b, respectively. The tensile properties of the composite were influenced by the strength and modulus of the fibers as reported in Table 5. Chemical treatment of the fiber improved chemical bonding and helped it to withstand high tensile load by the composites made of them (Sabeel and Vijayarangan 2008; Saw *et al.* 2012). The extent of improvement in mechanical properties for FA-grafted fiber reinforced composites was higher than that observed for alkali treated fiber composites. For FA-grafted fiber composites, the tensile strength and modulus was increased by 100% and 123%, respectively, when compared to untreated fiber reinforced composites. However, in the case of alkali treated fiber reinforced composites, the tensile strength and modulus increased by only 64% and 75%, respectively.

The impact strength can only be improved by increasing the frictional stress between the fiber and the matrix. The total energy dissipated in the composite before final failure occurs is a measure of its impact resistance or toughness. Major microfailure mechanisms operating during impact loading of the composite include initiation and propagation of matrix cracking, fiber-matrix debonding, and fiber breakage and fiber pullout. Impact strength of the fiber reinforced polymer composites depends on the nature of the fiber, polymer, and fiber-matrix interfacial bonding. Comparing the impact strength values of pure matrix and its fiber reinforced composites, it can be inferred that for all composites, the presence of untreated and treated luffa fibers increased the impact strength, that is, the composites had better energy absorbing capacity compared to that of pure epoxy matrix. The chemically treated fiber composites had higher values of impact strength than untreated fiber composites, as shown in Fig. 5c. The increase in stiffness and rigidity of the chemically treated luffa fibers due to their chemical treatments seemed to be an important factor affecting the impact strength of the corresponding composites. The impact strength of alkali treated luffa fiber reinforced composites was observed to be higher than that of the FA-grafted fiber reinforced composites. The impact strength was increased by 73% for alkali treated luffa composites and 38% for FA-grafted luffa composites when compared to untreated fiber reinforced composites. The strong interface adhesion between FA-grafted fiber and epoxy matrix resulted in more stress transfer from

fiber to matrix that lead to faster crack propagation at the matrix phase resulting in a lower value of impact strength.
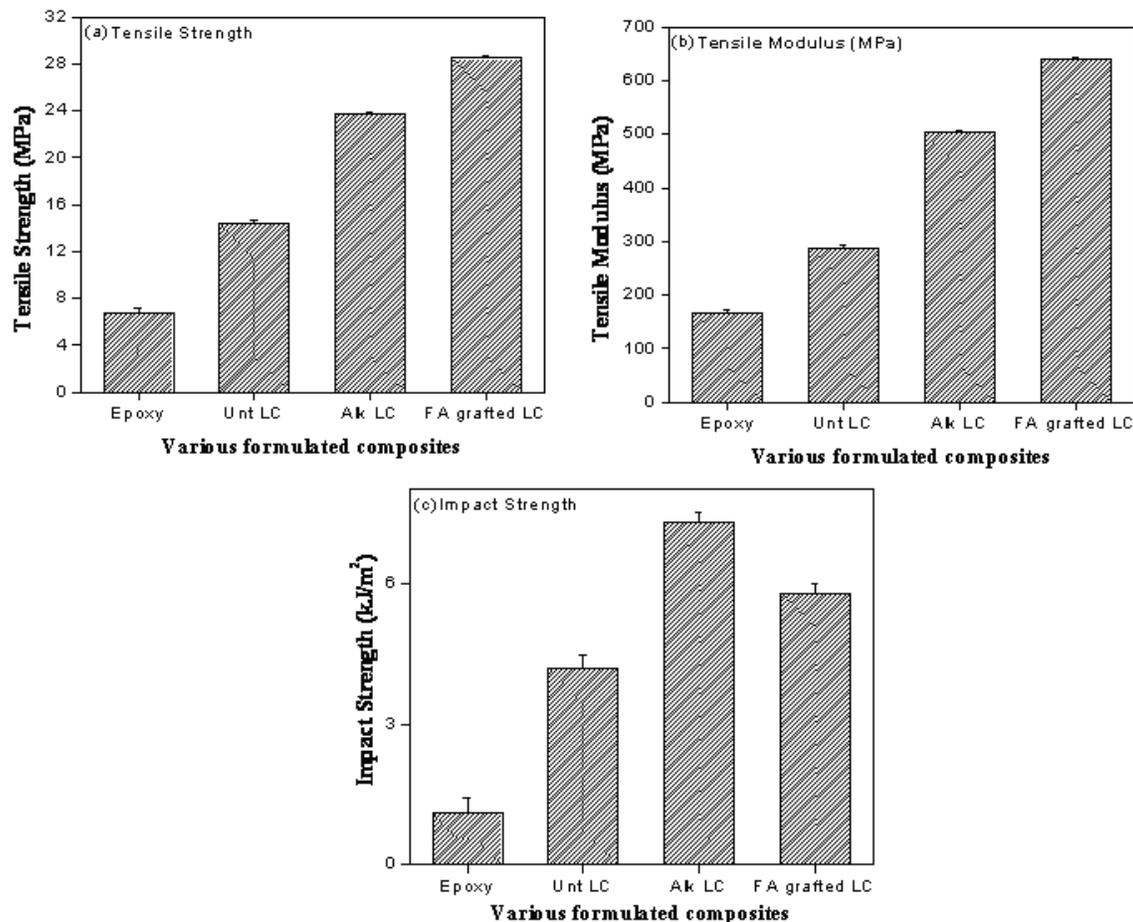
Fig. 5. Mechanical properties of pure epoxy and its composite systems [Unt LC – Untreated luffa composites; Alk LC – Alkali treated luffa composites; FA-grafted LC – Furfuryl alcohol grafted luffa composites]

Morphological Studies of Fiber and Tensile Fractured Composite Surfaces

SEM provides an excellent technique for the examination of fiber surface morphology. Figure 6 (micrographs a through c, respectively) shows the SEM micrographs of untreated, alkali treated, and FA-grafted luffa fiber. The fiber shape seemed to be in long strips with a non-flat surface. A large number of grooves or channels ran more or less parallel along the longitudinal direction of fibers. Waxes, oils, and small particles provided a protective layer on the fiber surface, as can be observed in Fig. 6a. Figure 6b shows a larger number of surface cracks and separation of the fiber bundle, compared to Fig. 6a. Very interestingly, the intercellular gaps are clearly distinguished and the unit cells are partially exposed, which was not obvious in the untreated luffa fiber. These features might have resulted from the partial removal of wax and oily substances and loss of cementing materials such as lignin and hemicelluloses during treatment with sodium hydroxide (Acharya *et al.* 2011). In Fig. 6c, the grafting of furfuryl alcohol around the fiber surface extending the capabilities of fiber with resin is

clearly seen. After furfurylation, the fiber surface became smooth and uniform, and reduced in its diameter. This might have been due to the loss of a natural protecting wax layer, lignin, and hemicellulose.

The mechanical properties of composites were corroborated with the morphological evidence. The SEM photomicrographs of the cryogenically created tensile fracture surfaces of various luffa composites are displayed in Fig. 6 (micrographs d to f). Significant differences were observed in the interfacial characteristics of the composites containing both untreated and treated fiber. The SEM micrographs in Fig. 6d clearly indicate that the interfacial adhesion between the untreated fiber and the matrix was poor due to weak bonding and the absence of any physical interaction between both components. The fibers were pulled out from the epoxy matrix and then the tensile force fractured the matrix and fibers. Holes resulted from debonding along the fiber due to the lack of interaction at the interface, resulting in a poor stress transfer between the matrix and the fiber. However, fracturing the samples did not lead to fracture of the luffa fiber, and the predominant failure mechanism was fiber pullout. The observed fiber pullout phenomenon in the fracture surfaces of the composites is a kind of index of the adhesiveness between the fibers and the matrix resin. It is also well known that epoxy networks display a large shrinkage after curing. This shrinkage reduces the specific volume of the matrix, and due to the weak interfacial interactions, it results in free spaces between the matrix and the filler (Acharya *et al.* 2011).

The chemical treatments of natural fiber decreased the wax, lignin, hemicelluloses, and moisture content and increased the cellulose content and ductility of microfibril to improve its performance characteristics. From Fig. 6e, it is noted that the wetting of alkali treated fiber by the epoxy resin was good due to the existence of a minimum quantity of hemicelluloses and wax contents on the fiber surface. When these composites were subjected to tensile load, the cracks were initiated from the fiber/matrix interface due to a heterogeneous connection. The cracks were propagated along the matrix because the tensile strength of matrix is lower than that of alkali treated fiber (Saw and Datta 2009). Afterwards, the adjacent fibers in the failure plane of composites were interconnected by the cracks. After the complete fracture of the matrix in the failure plane of composite, the applied tensile load was totally carried by treated fibers. Later, the fibers were fractured in the failure plane of the composites, when the applied tensile load was greater that the ultimate tensile strength of fibers. From Fig. 6e, it is obvious that fiber/matrix fractureness were the predominant failure mechanisms rather than fiber/matrix debonding and fiber pullout due to the existence of a good interfacial bond between alkali treated fiber and epoxy matrix (Collings 1994).

In Fig. 6f, FA-grafted composites were found to show the highest strength and modulus among other composites. The furfurylation of the luffa fiber created a polymeric coating of polyfurfuryl alcohol on the fiber surface, which indicated a better interfacial adhesion between FA-grafted luffa fiber and epoxy matrix. Therefore, the chemical grafting of luffa fiber improved the wettability of the fiber with the epoxy matrix by providing hydrophobic surfaces to the fibers and enhanced the fiber-matrix interfacial bond strength by diffusion of resin matrix into the grafted lignocellulosic network or vice-versa. This interdiffusion depends on the correlation between the cohesive energy of the pre-cured resin matrix and the surface energy of the fiber, among other factors. Furthermore, the introduction of hydroxyl groups on the fiber surface and at the end of the poly(furfuryl alcohol) chains, as well as on the basic sites of the furan rings probably

intensified the hydrogen bond interactions between the epoxy polymer and the modified fibers. It is obvious from SEM that the fibers are found well embedded in the matrix and many fewer fiber pullouts (fewer holes) were observed.
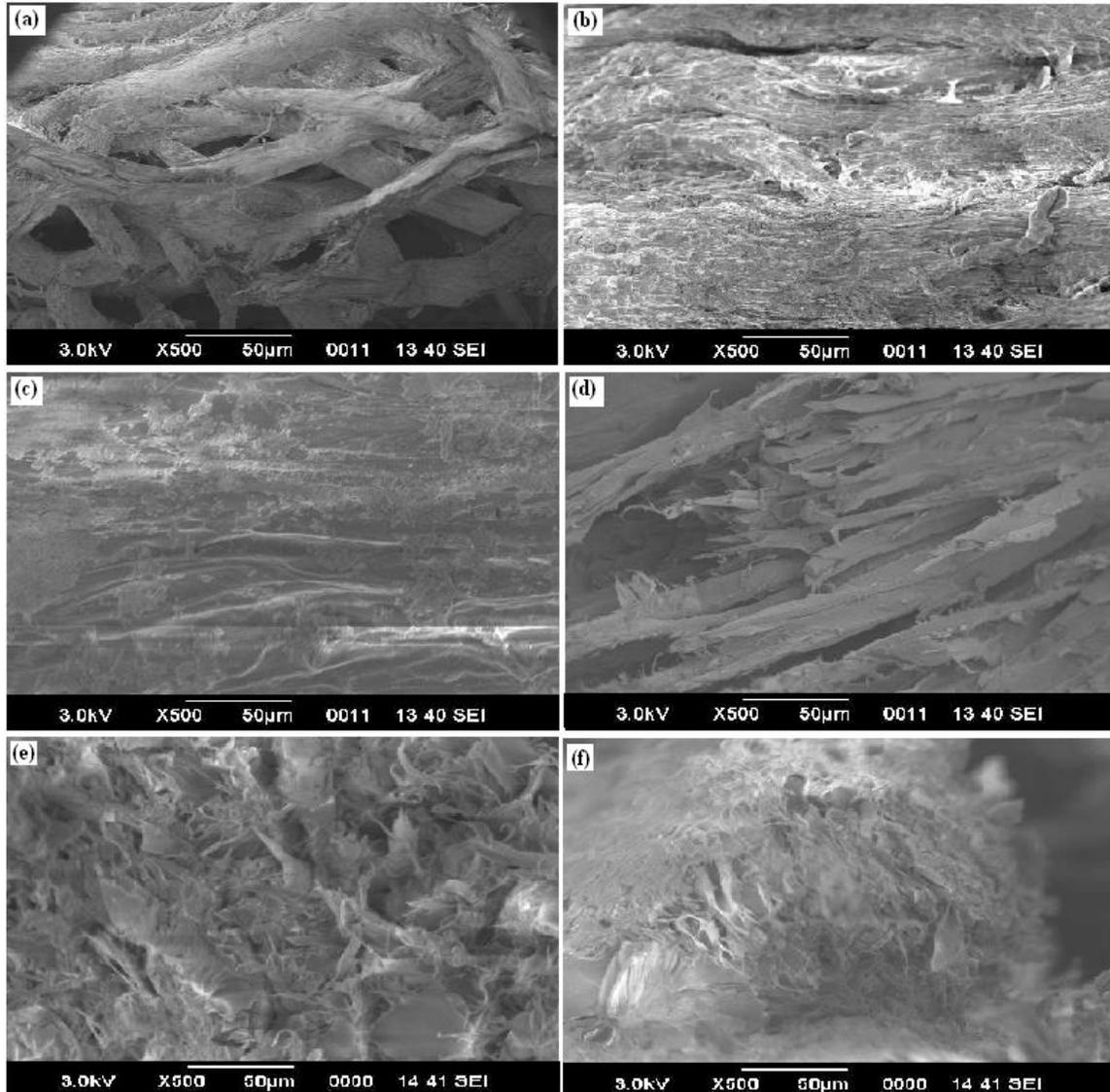
Fig. 6. SEM micrographs of epoxy-based composites with untreated and chemically treated fibers

It can also be noted for these composites that the fiber failed by tearing, but no complete interfacial failure was observed; this indicated that adhesion between the chemically modified fibers and epoxy matrix was quite strong for reinforcing. There is substantial epoxy 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. These results are in accordance with the findings in our previous research work where we analyzed the improvement of the mechanical properties of jute, coir, and bagasse fiber reinforced epoxy novolac composites by modification of the fiber surface (Saw and Datta 2009; Saw *et al.* 2011, 2012).

Kinetics of the Water Absorption

All polymers and composites absorb moisture in humid atmospheres and when immersed in water. Natural fibers absorb more moisture compared to synthetic fibers and polymers. The effect of this absorbed moisture is to degrade properties such as tensile strength (Shen and Springer 1976; Roy *et al.* 2000). Based on experiments on water uptake and assuming one-dimensional diffusion based on Fick's law, several researchers have talked about characteristics of water absorption. When absorption follows Fick's law, it is referred to as "Fickian" diffusion and when it deviates from the Fick's law, it is referred to as "non-Fickian" or anomalous diffusion. Water diffusion in polymeric composites has been shown to be Fickian as well as non-Fickian in character (Camino *et al.* 1997; Joseph *et al.* 2002).

Water absorption into composite materials is conducted by three different mechanisms. The main process consists of diffusion of water molecules inside the micro gaps between polymer chains. The other common mechanisms are capillary transport into the gaps and flaws at the interfaces between fibers and polymer; this is because of incomplete wettability and impregnation, and transport by micro cracks in the matrix formed during the compounding process. In spite of the fact that all three mechanisms jointly are active in case of water exposure of the composite materials, the overall effect can be modeled conveniently considering only the diffusional mechanism (Ghali *et al.* 2011). In this study, the amount of water absorption in all the composites was calculated from the weight difference between the samples exposed to water and the dry samples at three different temperatures of 23, 50, and 100 $^{\circ}$C. These three cases of diffusion can be distinguished theoretically by the shape of the sorption curve represented by Equation (3),

$$\frac{W_t}{W_\infty} = kt^n \tag{3}$$

where W_t is the water content at time t; W_∞ is the water content at the equilibrium; and k and n are constants called linear and angular coefficients, respectively. The value of constant, n, shows a different behavior between cases; for Fickian diffusion, case I, $n = 0.5$, while for case II, $n = 1$ (and for case III, $n > 1$). For anomalous diffusion, n shows an intermediate value ($0.5 < n < 1$). Water absorption in natural fiber reinforced polymer composites usually follows case I Fickian behavior, so further attention was focused on its study. As mentioned before, apart from diffusion, two other minor mechanisms are active in water exposure of composite materials.

The capillary mechanism involves the flow of water molecules into the interface between fibers and matrix. It is particularly important when the interfacial adhesion is weak and when the debonding of the fibers and the matrix has started. On the other hand, transport by microcracks includes the flow and storage of water in the cracks, pores, or small channels in the composite structure. These imperfections can originate during the processing of the material or due to environmental and service effects (Joseph *et al.* 2002). The analysis of the diffusion mechanism and kinetics was performed based on the Fick's theory and the experimental values were adjusted to the Equation (4) derived from Equation (3).

$$Log\left(\frac{W_t}{W_\infty}\right) = \log(k) + n\log(t) \qquad (4)$$

The values of the parameters '*n*' and '*k*' resulting from the fitting are shown for all the samples in Table 6. The absorption of water in natural fiber composites approached the Fickian diffusion case, as the values of *n* were very similar for all the experiments and they were very close to about 0.5. The value of *k* gives information on the affinity between the materials and water molecules. The higher the value of *k*, the stronger is the affinity. The *k* values for the composites reinforced with untreated fibers were 0.35 for all considered temperatures; whereas those for the composites reinforced with chemically treated fibers were in the range 0.1 to 0.17.

The diffusion coefficient is the most important parameter of the Fick's model, as this shows the ability of solvent molecules to penetrate inside the composite structure. For short times ($W_t/W_\infty \leq 0.5$), the following equation can be used (Lin *et al.* 2002),

$$\frac{W_t}{W_\infty} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \qquad (5)$$

where *L* is the thickness of the sample. By Equation 5, the water diffusion coefficient (*D*) is obtained from the slope of the linear part of the plot of W_t/W_∞ vs. $(t)^{0.5}L^{-1}$. Table 6 shows the values of the water diffusion coefficient obtained for the fitting of the linear part to Equation 5. The results for the diffusion coefficient are in agreement with the results reported by other authors (Tajvidi and Ebrahimi 2003).

Table 6. Results of Calculation of *n, k, D* values and Water Absorption Percentage of all Composite Samples at Various Temperatures

Sample	% Water absorption			'D' values		
	23 ^{o}C	50 ^{o}C	100 ^{o}C	23 ^{o}C	50 ^{o}C	100 ^{o}C
Pure epoxy	0.51	0.57	0.61	0.54	0.77	0.92
Untreated composite	12.27	17.74	21.43	9.81	20.6	27.9
Alkali treated composite	7.32	9.82	11.21	6.01	10.3	13.3
FA-grafted composite	5.69	8.87	10.87	3.30	5.64	7.84
Sample	'n' values			'k' values		
	23 ^{o}C	50 ^{o}C	100 ^{o}C	23 ^{o}C	50 ^{o}C	100 ^{o}C
Pure epoxy	0.6202	0.5053	0.4636	0.0415	0.1070	0.1848
Untreated composite	0.5095	0.3831	0.3026	0.2410	0.2928	0.3588
Alkali treated composite	0.5531	0.4325	0.4219	0.1370	0.1562	0.1686
FA-grafted composite	0.5806	0.5545	0.5414	0.1007	0.1344	0.1495

The experimental observation was in good agreement with the theoretical concept. The objective of this work was to relate kinetics and characteristics of the water

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absorption in natural fiber reinforced composite materials. Water uptake leads to the degradation of the fibers and the fiber/matrix interface resulting in a loss of mechanical performance. The differences in mechanical properties due to treated and untreated fiber are reported elsewhere. Results of water absorption are shown in Fig. 7. A similar behavior of water uptake was observed for all the composites. The samples absorbed water very rapidly during the first stages (0 to 50 h), approaching a saturation point (equilibrium sorption) where no more water was absorbed, and the content of water in the composites remained the same. The water absorption of the treated composite reached an equilibrium point after 50 h, while the untreated composite still continued to absorb water slowly (Fig. 7). The rate of absorption was lower for treated composites compared to untreated luffa based composites after 240 h exposure in water. The rate of water absorption decreased in order of untreated being the highest, followed by alkali treated, followed by FA-grafted being the lowest. Untreated luffa fiber based composites exhibit higher rates of water absorption due to the hydrophilic nature of lignocellulose, as well as due to the capillary action in the matrix when fiber composites are exposed to water. This could be possible due to a higher porosity or to the existence of voids formed during processing that could accelerate the diffusion. The high water absorption leads to changes in the dimensional properties of the samples (Sreekumar *et al.* 2009). As a result, cracks and voids may be formed in the matrix due to the swelling of the fibers. This may contribute to the penetration of more water into the composites during prolonged exposure. The untreated luffa composites showed the highest water absorption of 12.27%, 17.74%, and 21.43% at 23, 50, and 100 ^{o}C, respectively.
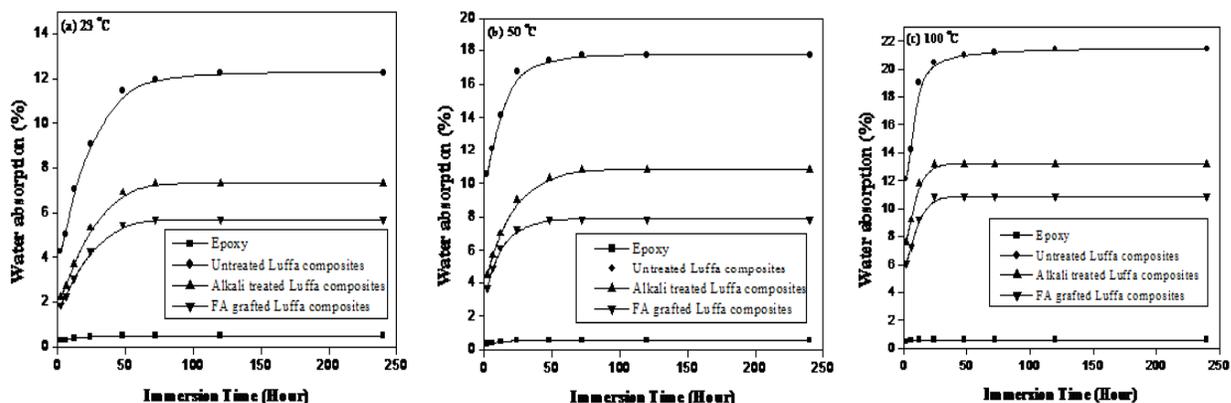
Fig. 7. Effect of fiber surface modification on water absorption of luffa/epoxy composites at various temperatures

A greatly reduced relative water uptake occurred after fiber surface treatment when compared to the untreated material due to good interfacial contact between fiber and matrix, and because the fibers had become more hydrophobic. Chemical treatments of fiber polymer hydroxyl groups reduced water absorption in composites which is attributed to better fiber-matrix interaction (Sreekumar *et al.* 2009). Hence, there were fewer cracks and void formation and decreased porosity in the treated composites. The alkali treated composites showed comparable water absorption of 7.32%, 9.82%, and 11.21% at 23, 50, and 100 ^{o}C, respectively. Thus, the alkalization of luffa fiber reduced the polar groups in fiber by replacing some of the hydroxyl groups on the surfaces of the fibers (Ghali *et al.* 2011). The lowest diffusion rate of FA-grafted luffa composites is due

to improved compatibility between fiber and epoxy resin. The matrix had little effect on the amount of water absorbed as pure epoxy composites demonstrated around the same water content, between 0.5 and 1.0% after 240 h of exposure (Tajvidi and Ebrahimi 2003). The relative rates of water absorption correlate with the effect of different modification upon mechanical properties.

The temperature of the absorption process also influences the water absorption curves. It can be concluded that increased temperature increases the water uptake of the composite materials. When the temperatures of immersion are increased, the saturation time is shortened. For example, for the untreated luffa composites, the saturation time was shortened by 20 h as the temperature was increased from 23 to 50 ^{o}C. This saturation time was further reduced by 10 h for the same composites when temperature was increased from 50 to 100 ^{o}C, as it can be seen in Fig. 7a–c. The increase in temperature led to higher values of the diffusion coefficients for all the composites. Pure epoxy presented the lowest values of diffusion coefficient compared with respective composites with treated and untreated luffa fibers. From the results of the diffusion coefficient, a clear conclusion about the influence of the type of fiber can be extracted. It seems to be that what really influences the water absorption behavior regarding the nature of fibers is the compatibility between fibers and matrix. With this, it appears that FA-grafted luffa composites present good resistance to water absorption, since their diffusion coefficient values are generally the lowest.

CONCLUSIONS

This investigation dealt with a potential opportunity for the development of novel luffa fibers reinforced epoxy composites. The grafting of luffa fibers with furfuryl alcohol and alkali treatment significantly improved the thermal, mechanical, and water resistant properties of the composites, which is important for certain applications such as in outdoor and automotive industries. As evidenced by the fracture surface morphology and the thermal properties, composites reinforced with FA-grafted luffa fiber had high performance stability and durability as furfurylation facilitated more bonding sites of fiber resin interface. Based on the FTIR spectra, it was concluded that the spectral changes with furfurylation were distinctly different from those for alkali treatment. The increase in char residue at 700 ^{o}C from 5% to 29% and prepolymer curing temperature from 258 to 334 ^{o}C, in the case of FA-grafted luffa composites, place it in the category of engineering materials. The advanced graft monomer furfuryl alcohol obtained from renewable waste biomass had many desired features that could be used in various applications. The overall conclusions were to establish that epoxy could be covalently bound to modify luffa fibers and to determine that furfurylated luffa fibers in this way could be used to generate epoxy composites with improved mechanical and thermal properties.

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