The Effect of Alkalization and Fiber Loading on the Mechanical Properties of Bamboo Fiber Composites, Part 1: – Polyester Resin Matrix

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ABSTRACT: Bamboo strips [10 cm × 1.5 cm × (1−1.5) mm] were treated with caustic solutions for 1 h at different concentrations e.g., 0, 10, 15, 20, and 25%. Bamboo strips reinforced polyester resin composites were fabricated by hand-lay-up technique using both alkali-treated and untreated bamboo strips, using a room temperature curing system for the polyester resin. This study aims at the evaluation of the influence of caustic concentration on the mechanical properties of bamboo strips reinforced polyester resin composites at a constant 50% loading of reinforcement. Maximum improvement in property was achieved possibly with 20% of caustic treated strip reinforcements. Beyond 20%, there was degradation in all the strength properties because of failure in mechanical properties of the reinforcements itself. The effect of fiber loading variation upon mechanical properties was also studied. It was observed that superior mechanical properties were obtained with 60% filler loading. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 489–495, 2009

Key words: fibers; matrix; mechanical-properties; interface; morphology

INTRODUCTION

Now-a-days a growing interest in natural-fiber based composites is mainly due to their high specific modulus, light weight, low cost, and resistance to deforestation in addition to the other usual advantages. Bamboo is one of the important natural fibers that are getting continuously more and more attention for its diversified use as a potential reinforcement in polymer composites both in academic and industrial research. Amada et al. have reported on the structure variation in bamboo with cross-section and height.[1] Jain et al. studied the mechanical properties of bamboo.[2] The results of these studies revealed that the mechanical properties of bamboo vary along and across the cellulose fibers. Despande et al. have developed methods for extraction of bamboo fibers and evaluated their mechanical properties.[3] Das and Chakraborty have investigated the effect of mercerization on the mechanical properties of bamboo,[4] thermal properties of bamboo, and fine structure and morphology of bamboo fiber.[5,6] They have studied about the effect of mercerization on the mechanical and impact properties of bamboo strips powdered novolac resin composites[7,8] with a fixed fiber loading.

A strong adhesion between resin and fiber is required for effective stress transfer and load distribution throughout the interface. Good adhesion is usually a result of good wetting of the fibers by the matrix, as well as the formation of a chemical bond (if any) between the fiber surface and the matrix. Taking the advantage of plenty of reactive group's present, modification of cell wall using proper surface modifier is to be done to increase the scope utilization of natural fibers as reinforcement. Mercerization is one of the most conventionally used treatments for natural fibers so as to increase the fiber's wetting ability by extracting the noncellulosic substances mainly hemicellulose, pectin, and others. The effect of alkali treatment of the natural fiber on the properties of natural fiber reinforced polyester composites have been studied by many researchers[1] and reported that surface texture modification of fibers leads to the effectiveness of alkali treatment. D'almeida reported that considering the cost factor, polyester composites fabricated with high strength natural fibers can even compete with glass fiber-mat polyester matrix composites.[9] Gassan and Bledzki[10] reported about alkali-treated jute fiber reinforced thermosets. Composite strength and stiffness generally increased as a consequence of the improved mechanical properties of the fiber by NaOH treatment

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under isometric conditions. Aziz and Ansell[11] made composites with alkali treated hemp and kenaf fiber and polyester resin and analyzed their mechanical and thermal properties. A general trend was observed whereby alkalized long fiber composites gave higher flexural modulus and flexural strength compared with the composites made from as-received or native fibers. Jain et al.[2] have reported on mechanical properties of bamboo fiber polyester composites. Rajulu et al.[12] developed short bamboo fiber reinforced styrenated polyester composites were with varying fiber content. The density, void content, weight reduction, tensile strength, and flexural strength of these composites were determined. These composites possess good tensile and flexural strength. The density of these composites was found to decrease with increasing fiber content. In these reports,[12–14] no surface treatment was used. Reports on bamboo composites where different surface treating agents were used to modify the interface are, however, scanty.

The aim of the present work is to modify bamboo fiber surface by alkali treatment and to explain the effect of surface modification of fiber on the different mechanical aspects of the bamboo fiber-polyester resin composites. The explanation is to be given on the basis of interaction between resin and the fiber, which has also been modified by alkali treatment. Again, the effect of filler variation has also been studied.

EXPERIMENTAL

Material

Matrix resin

General purpose polyester resin (Firebond 333) of medium reactiviy in liquid form was supplied by Ruia Chemical, Kolkata, India and was used as the matrix resin. The resin is clear with slightly pale yellow colour. The properties of the liquid resin are as follows.

- Viscosity at 30°C: (500–600) cps.
- Specific Gravity at 30°C: 1.12–1.13
- Acid value (mg KOH/g resin): max 20.
- Volatile content: 34–36%.
- Storage life of uncatalyzed resin in the dark at 30°C: Minimum 3 months.

Curing agent

A room temperature curing system based on methyl ethyl ketone peroxide and cobalt napthenate were used and was procured from Ruia Chemical, Kolkata, India. Cobalt napthenate was used as the catalyst. The weight of both the reagent used was ~ 1% of the amount of resin taken. The setting time required was 15 min.

Reinforcement

Bamboos belonging to the variety *Bamboosa balcua* were supplied by FOSET (Forum of Scientist, engineers and Technologists), West Bengal, India. Dried bamboo strips with average dimension of 100 × 15 × (1.1–1.5) mm^3 were dipped in NaOH solution of five different concentrations (w/v) (10, 15, 20, and 25%) at liquor ratio 15 : 1 for 1 h at ambient temperature. After this treatment, the strips were copiously washed with distilled water and subsequently neutralized with 2% H_2SO_4 solution, and then the strips were dried in an oven at 105°C till a constant weight was obtained.

Fabrication of composites

Required amount of resin were weighed properly. Then cobalt napthenate and methyl ethyl ketone peroxide were added successively and mixed thoroughly. Then the bamboo strips were properly dipped in the mixture and quickly arranged in the mould using hand-lay-up technique. The mould was then placed in a compression moulding unit under pressure (5 kgf/cm^2) and kept for over night. Post curing was done in an oven at 80°C. The sample sheets were ejected from the mould at the room temperature and preserved for 7 days in humidity controlled room at room temperature. Sampling was then done for various testing. A mould with internal dimensions of 100 × 60 × 3 mm^3 (length × width × height) was used to manufacture the composites. The filler loading was kept constant at 50%.

Another system was studied with polyester resin and 20% alkali-treated strips with filler loading of 40, 50, and 60%. Then the composites were fabricated following the same method. Table I represents the designation of the fabricated composites.

TESTING

Tensile test

Five specimens of composites (60 × 12.5 × 3 mm^3) were tested with an Instron 4304 tensile tester

TABLE I
Table for Sample Designation

Concentration of alkali used for treatment of bamboo strips	Fiber loading (%)	Sample designation
0	50	BSPES-U50
10	50	BSPES-1050
15	50	BSPES-1550
20	50	BSPES-2050
25	50	BSPES-2550
20	40	BSPES-2040
20	60	BSPES-2060

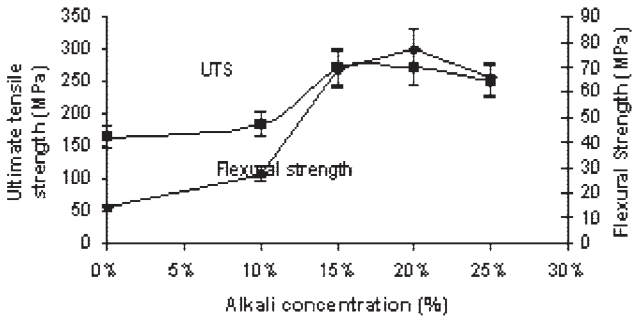

Figure 1 Influence of alkali concentration on tensile strength and flexural strength of bamboo-polyester composites.

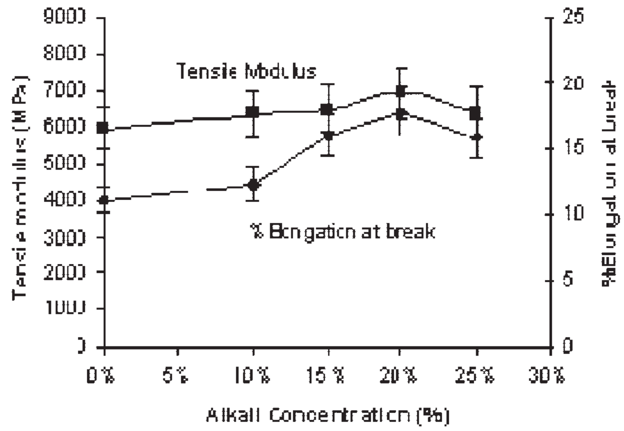

Figure 2 Influence of alkali concentration on tensile modulus and % elongation at break of bamboo-polyester composites.

according to ASTMD638 using a cross-head speed of 5 mm/min and span length of 4 cm.

Flexural test

Three point bend tests were performed with the composite samples of dimensions 60 × 12.5 × 3 mm^3 according to ASTM D790 using an Instron model 4304. A cross-head speed of 1.2 mm/min was used. The span length was 4 cm.

Impact testing

Five specimens of each of treated and untreated bamboo and bamboo strips-novolac composite samples with dimensions 60 × 12.5 × 3 mm^3 were cut out and then tested according to ASTM D 256 using a pendulum impact tester (Ceaft Italy) fabricated on the basis of the principles of the Izod impact tester. Specimens were tested without notch and until failure because introducing a notch at right angle to the plane of the unidirectional composites involves cutting of the fibril layers. The impact loads were applied at right angles to the fabric. The orientation was so chosen to represent the lateral impact to structural composites in commercial use.

FTIR analysis

FTIR Spectroscopy was made for both cured polyester resin and bamboo strips-polyester resin composites in a FTIR spectroscope (JASCO- FT/IR- 460+). It was carried out with the pellet sample made out of composite dust and KBr. The range used was 500–3500 cm^{-1}.

Morphology analysis

A ZEOL scanning electron microscope (JSM 5200) was used to study the fracture surface of the composite samples, which were subjected to flexural test. Prior to the analysis the samples were sputtered with Au/Pd alloy and stuck on a stub by adhesive tape.

RESULTS AND DISCUSSIONS

Figures 1–3 show comparative results of the various mechanical properties of the composites with constant fiber loading and varying concentration of alkali treatment. The data given are the average of five samples in each case. All the mechanical properties demonstrate sharp increase with increasing concentrations of caustic treatment on bamboo fiber strips. After 10% alkali concentration, the UTS (Fig. 1) value is increased by sufficiently high value up to 15% of alkali concentration, and then it becomes almost similar with the value corresponding to 20% alkali concentration. The increase in %elongation at break of composite may be attributed to the flexibility of ester linkage of polyester resin as with increasing alkali treatment fibers undergo more interaction with resin. (Fig. 2). Flexural strength and modulus (Fig. 3) show maximum values for BSPES-20. Toughness increases linearly with alkali concentration up

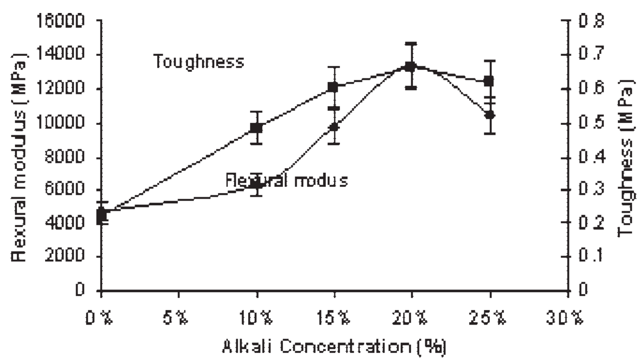

Figure 3 Influence of alkali concentration on toughness and flexural modulus of bamboo-polyester composites.

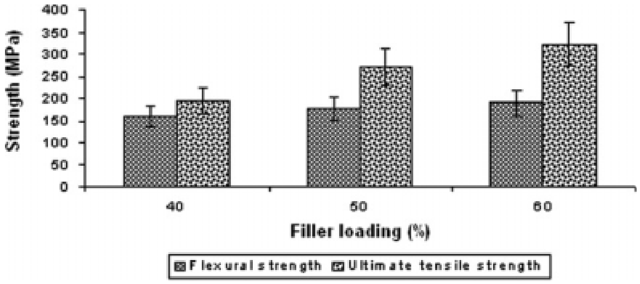

Figure 4 Influence of filler loading on of strength 20% alkali-treated bamboo fiber-polyester composites.

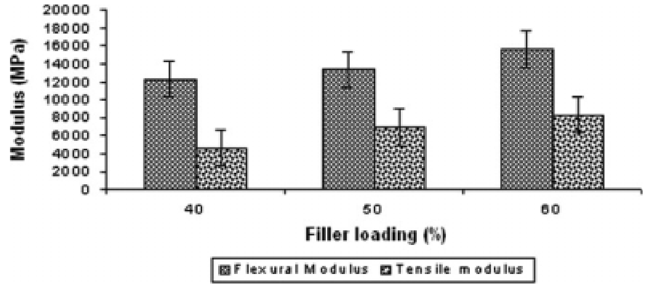

Figure 5 Influence of filler loading on modulus of 20% alkali-treated bamboo fiber-polyester composites.

to 20% of alkali concentration and decreases at 25% alkali concentration.

Das and Chakraborty reported about the improvement of mechanical properties of alkali-treated bamboo strips[4] and also of novolac resin composites with alkali-treated bamboo strips[7] in their earlier works. In both the cases, the improvement is up to around 20% and beyond that the properties deteriorate. Ray et al. also observed improvement of mechanical properties during the study of alkali-treated jute and vinyl-ester resin composite.[15] They used 5% alkali solution for treatment with varying time and fiber loading. Improvement of mechanical properties of starch-based resin and short bamboo fiber composite with alkali treatment of fiber has been reported by Takagi and Ichihara.[13]

With increasing strength of mercerizing agent, the improvement of aforementioned properties can be justified by the enhancement of wetting ability of fiber due to removal of surface impurities and binding material present in the bamboo, a well established natural composite, with alkali. Increase of wetting ability was earlier reported by Das et al in their work of bamboo-novolac resin composite.[7] The effect of alkali on cellulose fiber is a swelling reaction, during which the natural crystalline structure of the cellulose relaxes and the OH-groups of the cellulose are converted into ONa-groups, expanding the dimensions of molecules. Subsequent rinsing with water and neutralization by acid will remove the linked Na-ions and convert the cellulose to a new crystalline structure, i.e., cellulose-II, which is thermodynamically more stable than cellulose-I.[6]

$$\text{Cellulose} - \text{OH} + \text{NaOH} \rightarrow \text{Cellulose} - \text{ONa} + \text{H}_2\text{O}$$

$$\text{Cellulose} - \text{ONa} + \text{H}^+ \rightarrow \text{Cellulose} - \text{OH} + \text{Na}^+$$

The alkali solution influences not only the cellulosic components inside the plant fiber but also the noncellulosic components. The treatment has been shown to improve the properties possibly because it lowers the surface tension of the bamboo strip surface[7] by removing the noncellulosic substances from bamboo strips. This decrease in surface tension is conducive to the subsequent wetting and spreading of the resin over the bamboo strips used as reinforcement, which also results in good interfacial adhesion. There is more number of free-OH groups of cellulose after mercerization which can effectively react then with the matrix. In natural fiber, smaller cellulose fibrils are strongly bonded together with binding material (namely, hemicellulose and lignin) to form a continuous cellulose fiber. Alkali treatment leads to dissolution of those binding material resulting in fibrillated fiber with enhanced aspect ratio which in turn possesses high surface energies, which augments strong interaction at the interface in between fiber and matrix is obtained. Hence, improvement of interfacial adhesion leads to an increase in the mechanical parameter of composites. Gassan and Bledzki reported about the increased aspect ratio of jute fiber and improvement of mechanical properties during study of alkali-treated jute fiber and polyester composites.[10] Again alkali destroys the H-bonding network in between the components of bamboo, and thus, leads to an increase in the number of free-OH groups after the treatment. This also helps to form a strong interaction at the interface. However, with higher percentage of alkali, it was observed that beyond 20% alkali concentration randomness appeared because of degradation of long-chain cellulose molecules itself and as a result the properties of composites suffered deterioration.[7,14]

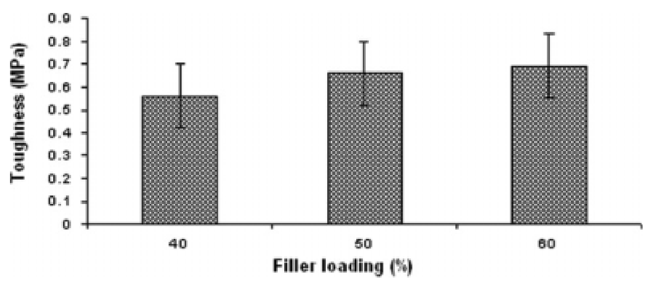

Figure 6 Influence of filler loading on toughness of 20% alkali-treated bamboo fiber-polyester composites.

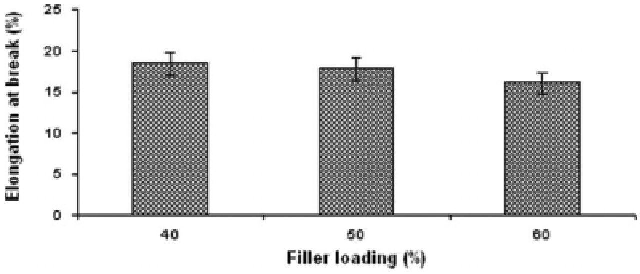

Figure 7 Influence of filler loading on % elongation of break of 20% alkali-treated bamboo fiber-polyester composites.

From Figures 4–7, it can be concluded that as the weight percent of 20% alkali-treated bamboo strips was increased from 40 to 50%, significant increase in the properties under discussion occur, and this improvement is more pronounced when the fiber incorporation is maximum with respect to the present study. Fiber shares the major portion of the load acting on a composite structure. It is referred as the reinforcing phase, or reinforcement, as it enhances or reinforces the mechanical properties of the matrix. So, as per our expectation, it is evident from the graphs that higher the amount of fiber present, more improvement of flexural and tensile properties occurred.

Figures 8–10 represent the scanning electron micrograph of flexural fractured surface of untreated, 10% alkali treated, and 20% alkali-treated bamboo strips reinforced polyester composite samples. It is evident that (Figs. 9 and 10) mercerization renders a rough surface topography compared with the untreated one (Fig. 8). SEM of BSPES-U50 reveals that there minimum pull-out of cellulose fibril and they are bonded together (marked portion). Again, there are areas where sudden break up of fiber has taken place showing fiber lumen. Dissolution of alkali sensitive material leads to fibrillation of fiber showing longer cellulose fiber pull-out from hemicellulose-lignin matrix. As a result, incase of SEM pictures of BSPES-1050 and BSPES-2050 fiber pull-out increases and with BSPES-2050 that leads to more entanglement of fibrils (marked fibrillated fiber) removing more amount of binding material between cellulose fibrils. These give a tentative support to conclusion of the aforementioned explanation on mechanical properties.

Figure 11 represents the value of work of fracture of all the composites obtained from impact test vs. alkali concentration. It can be improved by reducing the friction stress between the fiber and the matrix

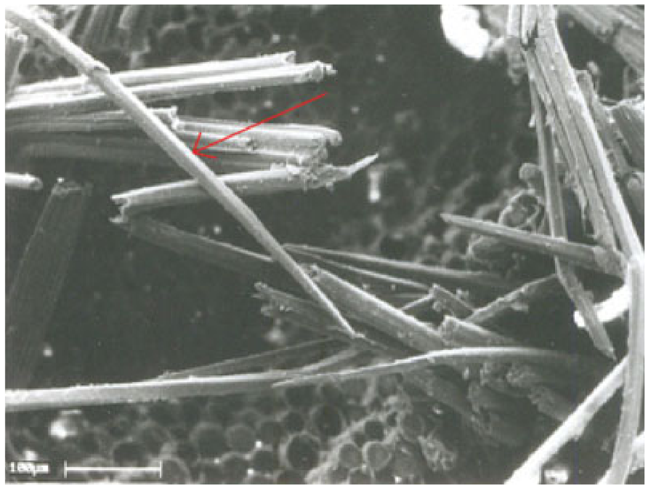

Figure 9 Scanning electron micrograph of 10% alkali-treated bamboo fiber-polyester resin composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

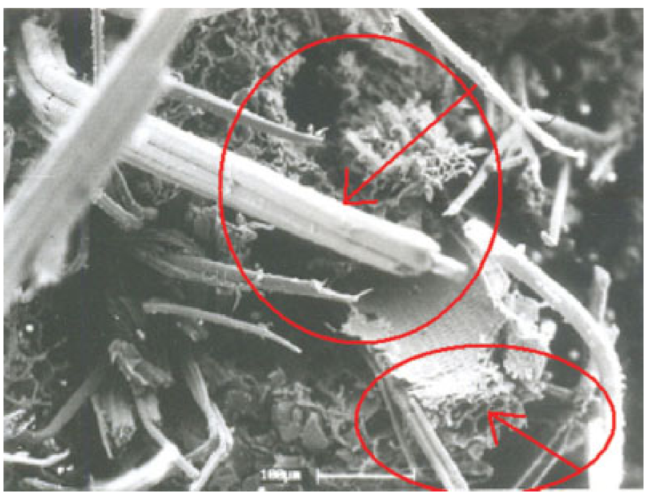

Figure 8 Scanning electron micrograph of untreated bamboo fiber-polyester resin composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

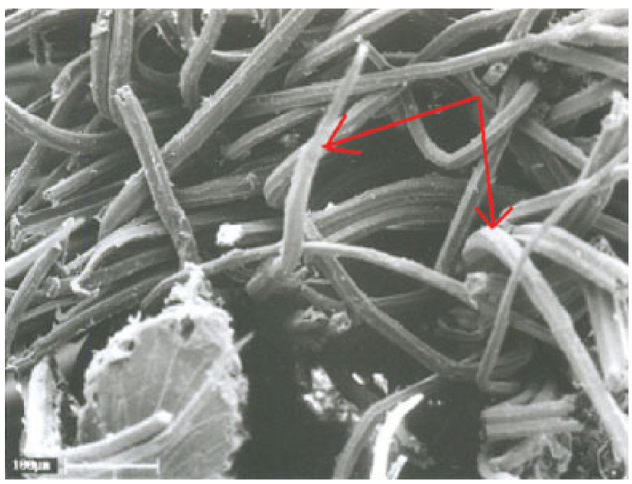

Figure 10 Scanning electron micrograph of 20% alkali-treated bamboo fiber-polyester composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

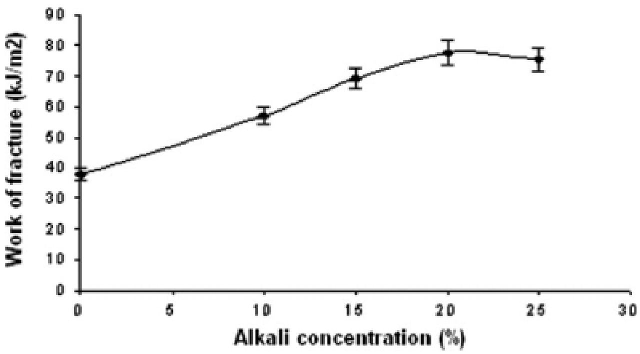

Figure 11 Influence of alkali concentration on work of fracture of bamboo- polyester composites.

in controlled manner. From the graph, it is clear that the treated fiber composites gave better toughness compared with the untreated one. However, there is variability in results. Among the treated composites BSPES-2050 shows the best results. Aziz et al[11] have got better work of fracture value with alkali-treated long kenaf fiber polyester resin composites than that of untreated one. In a treated fiber composite, though the interfacial friction stress between the matrix and the fiber is generally higher when compared with that of untreated ones and usually this cause a drop in toughness. Although the interfacial friction between fiber and the resin matrix is the contributing factor, the interface of cellulose fiber and hemicellulose/lignin matrix also plays a dominating role as we use bamboo strips, which itself is a lignocellulosic composite. With increasing alkali treatment, because of removal of binding material from the bamboo fiber there is a continuous decrease in adhesion between cellulose fiber and hemicellulose/lignin matrix resulting in longer fiber pull-out, and therefore, causes a higher work of fracture value. From Figure 12, it is evident that increase in fiber loading contributes to an increase in work of fracture value or toughness because of the reason as explained earlier.

IR analysis of polyester resin and its composite reinforced with untreated and 20% alkali-treated strips reveals that the main interaction in between resin and fibers is H-bonding. From Figure 13, it is clear that the corresponding peaks obtained in the region between 3,800 cm^{-1} and 3400 cm^{-1} (responsible for —OH stretching vibration) are shifted toward lower region and numbers of peaks for H-bonding are also increased. Peak at 669.17 cm^{-1} is for out of plane bending vibration of intermolecular H-bonded —OH group.[15] A medium peak at 666.285 cm^{-1} and 670.142 cm^{-1} for BSPES-U and BSPES-2050 respectively therefore suggests the formation of H-bonding in between —OH of cellulose and polyester resin whereas in case of polyester resin the peak is at 650.85 cm^{-1} indicating absence of such type of H-bonding. In IR spectra of unsaturated polyester resin a peak at 1633 cm^{-1} is due to $\rangle C{=}C\langle$ stretching vibration.[16] Peak at 1608.34 cm^{-1} is due to $\rangle C{=}C\langle$ stretching vibration of lignin present in bamboo fiber (Fig. 14). It has been reported earlier by Das and Chakraborty[6] that because of alkali treatment the position of the peak was not very much affected

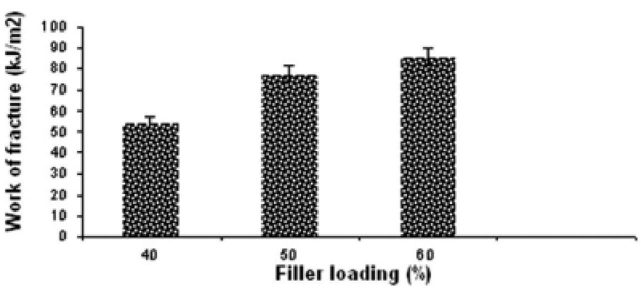

Figure 12 Influence of filler loading on work of fracture of 20% alkali-treated bamboo fiber-polyester composites.

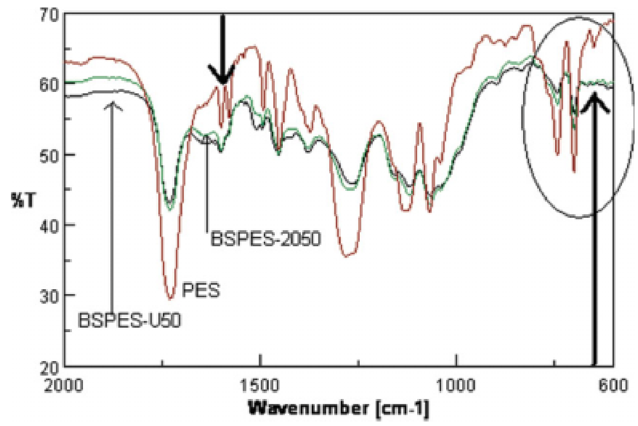

Figure 13 Infra-red spectroscopy of cured polyester resin, untreated bamboo fiber-polyester resin composite and 20% alkali-treated bamboo fiber-polyester resin composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

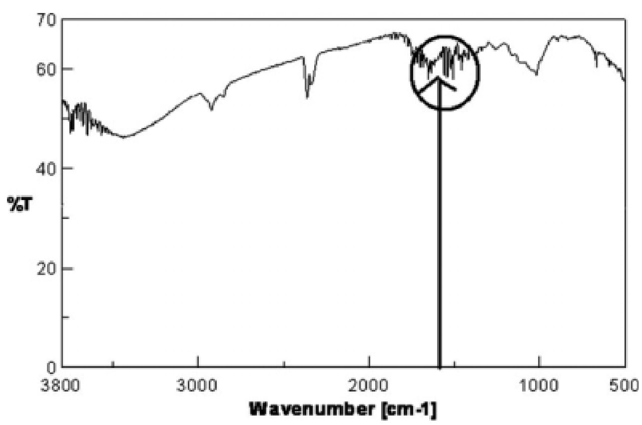

Figure 14 Infra-red spectroscopy of untreated bamboo fiber.

(1612.2 cm^{-1}). However, after composite formation the peak has been shifted to 1625 cm^{-1}. This shifting may be attributed to the involvement of the ⟩C=C⟨ from lignin in the free radical reaction occurred during curing of polyester resin.

CONCLUSION

The mechanical properties of bamboo polyester composites have been studied. Based on the results obtained, the following conclusions can be drawn:

1. UTS, flexural strength, flexural modulus are more strongly affected by alkali treatment than tensile modulus. The increasing trend is continued up to 20% of alkali treatment. With fiber loading variation, superior properties have been achieved with 60% fiber loading.
2. Change in fiber structure, topography leads to the improved mechanical properties of composites. Increased wetting ability of fiber allows resin to penetrate more into the strip where the resin can be involved in more and more entanglement in a better way with the available free-OH groups of alkali-treated fibers.
3. The increase in %elongation at break of composite may be attributed to the flexibility of ester linkage of polyester resin as with increasing alkali treatment fibers undergo more interaction with resin.
4. However, the alkali concentration of 20% shows optimum value of mechanical properties of composites under the corresponding experimental condition. At higher concentration, because of degradation of fiber the mechanical properties deteriorate.
5. As bamboo is a low cost renewable filler of high strength, the bamboo composite made with low-cost polyester resin is also of low cost that can be used for structural application.

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