Effects of Alkalization and Fiber Loading on the Mechanical Properties and Morphology of Bamboo Fiber Composites. II. Resol Matrix

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ABSTRACT: Resol resin composites reinforced with alkali-treated bamboo strips were fabricated with a hand-lay-up technique. This study was aimed at the evaluation of the influence of the caustic concentration on the mechanical properties of bamboo-strip-reinforced resol composites with a constant 50% loading of the reinforcement. The treatment of bamboo fiber in a solution of sodium hydroxide with increasing concentration percentages resulted in more and more rigid composites; as a result, the strength and modulus values exhibited improvements. The maximum improvement in the properties was possibly achieved with 20% caustic treated reinforcements. An infrared study indicated the formation of aryl alkyl ether with —OH groups of cellulose and methylol groups of resol. Beyond 20%, there was degradation in all the strength properties due to the failure of the mechanical properties of the reinforcement itself. A correlation was found to exist between the mechanical properties and the morphology that developed. Another set of composites with variable loadings of 20% alkali treated fiber (40, 50, and 60%) was fabricated, and a 60% fiber loading showed the best mechanical properties. J Appl Polym Sci 112: 447–453, 2009

Key words: composites; fibers; interfaces; mechanical properties; morphology

INTRODUCTION

Their natural abundance, much higher strength per unit of weight versus most inorganic fillers, lower density, and biodegradable nature make natural fillers attractive as reinforcements of engineering polymer systems.[1] Bamboo is one of the important natural fibers and has diversified use as a potential reinforcement in polymer composites in both academic and industrial research. Amada et al.[2] reported on structural variations in bamboo with the cross section and height. Jain et al.[3] reported that the mechanical properties of bamboo vary along and across the cellulose fibers. Despande et al.[4] developed methods for the extraction of bamboo fibers and evaluated their mechanical properties.[4] Das and Chakraborty[5–7] investigated the effect of mercerization on the mechanical and thermal properties, fine structure, and morphology of bamboo fibers. They also studied the effect of mercerization on the mechanical and impact properties of bamboo strip–novolac resin composites.[8,9]

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Phenolic resin is a versatile matrix that can be reinforced by various fibers. Because of its cheapness, ease of manufacturing, and affinity to lignocellulosic fibers, a phenol–formaldehyde resin, resol, was selected as the matrix. Many workers have reported the successful fabrication of resol-based natural fiber composites. Zárate et al.[10] used vegetable fibers such as cotton, sisal, and sugar cane bagasse as reinforcements in a resol matrix and evaluated the influence of the fiber volume fraction on the flexural properties and density of the composites. Cotton and sugar cane bagasse composites present a fiber volume fraction at which the flexural strength and modulus are maximum. However, sisal composites show a continuous rise in the flexural strength and modulus as the fiber volume fraction increases up to 76%, which is the highest concentration studied. Scanning electron microscopy reveals good adhesion between the fiber and matrix in the composites. Sreekala et al.[11] prepared composites from short oil palm empty fruit bunch fibers and a resol-type phenol–formaldehyde resin. The effect of the fiber length and fiber loading on the mechanical properties was studied. Tensile, flexural, and impact properties of the composites were analyzed. They found that the mechanical properties of the phenol–formaldehyde resin were improved by the incorporation of oil palm empty fruit bunch fibers.

Certain drawbacks such as incompatibility with the hydrophobic polymer matrix, a tendency to form aggregates during processing, and poor resistance to moisture greatly reduce the potential of natural fibers as reinforcements in polymers. Interfacial bonding is 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 advantage of the many reactive groups present, modification of the cell wall with the proper surface modifier can be performed to increase the scope of utilization of natural fibers as reinforcements. Mercerization or alkali treatment is one of the most conventionally used treatments for natural fibers, increasing the wetting ability of fibers by extracting noncellulosic substances, mainly wax, pectin, and others, and it has been reported by many authors.[12–17] De et al.[18] evaluated the thermal properties, water absorption, and swelling behavior of water-leached and alkali-treated chopped-grass-fiber-reinforced resol composites. They carried out an alkali treatment of the grass fiber by varying the concentration of sodium hydroxide. A composite prepared from 1% alkali treated grass fiber and 55% resin showed the highest tensile strength, whereas a composite prepared from 5% alkali treated grass fiber and 55% resin showed maximum flexural properties. In this work, an attempt has been made to explain the different mechanical aspects with respect to the developed fiber–matrix interface morphology. Gassan and Bledzki[19] reported thermosets reinforced with alkali-treated jute fiber. The composite strength and stiffness generally increased as a result of the improved mechanical properties of the fiber by NaOH treatment under isometric conditions. Ray et al.[20] studied the correlation between the microstructure and mechanical strength. They found that 10% NaOH could remove the adhered matrix with a little effect on the fibers, whereas 20% or stronger alkali reduced the strength of the fiber. An alkali treatment was successfully applied by Das and Chakraborty[5–7] and Das et al.[8,9] to develop bamboo fiber composites.

EXPERIMENTAL

Materials

Matrix resin

A lamination-grade resol resin in a liquid form was supplied by Hindustan Adhesive & Chemical (Calcutta, India) and was used as the matrix resin. The viscosity of the liquid resin was 50 cps at room temperature. The recommended curing temperature and shelf life were 150°C and 45 days, respectively.

Reinforcement

Dried bamboo strips with average dimensions of 100 mm × 15 mm × 1.1–1.5 mm were dipped in NaOH solutions (10, 15, 20, or 25%) for 1 h at the ambient temperature. After this treatment, the strips were copiously washed with distilled water and subsequently neutralized with a 2% H_2SO_4 solution, the neutrality being tested through the testing of the resulting solution with litmus. The strips were then dried in an oven at 105°C until a constant weight was obtained. Adhesive-grade resol in a liquid form was used (Hindustan Adhesives & Chemicals).

TABLE I
Sample Designations

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

Fabrication of the composites

Accurately weighed amounts of treated and untreated bamboo strips were impregnated thoroughly with a calculated amount of the resol resin. The filler loading was previously kept constant at 50% for various concentrations of alkali. After proper impregnation, they were sun-dried carefully for complete drying, and thus the resol-impregnated bamboo strips were prepared for further processing.

Another set of prepegs was made with 20% alkali treated strips with variations in the filler loading (40, 50, and 60%) in a similar manner.

Prepegs of bamboo strips were then placed in a male–female-type mold, which was preheated at 145°C to ensure complete mold filling. Then, the mold was placed in a compression-molding machine at 145°C. Molding was performed at 150°C under 10 kgf/cm^2 for 5 min (15 s was the breathing time to release air and entrapped gaseous products from the condensation of the novolac resin after the mold temperature was attained). Then, the mold was taken out of the machine, and the sheet was collected for testing. Table I presents the designations 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 according to ASTM D 638 with a crosshead speed of 5 mm/min and a span length of 4 cm.

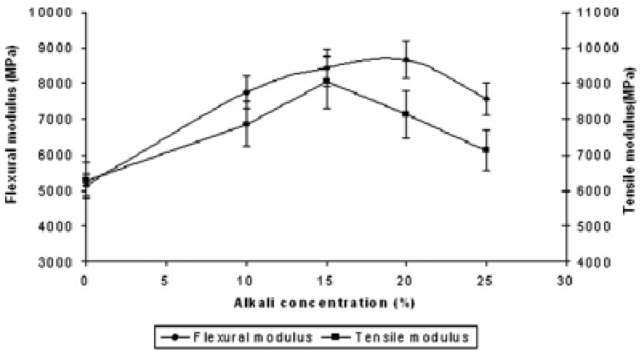

Figure 1 Influence of the alkali concentration on the tensile modulus and elongation at break of bamboo–resol composites.

Flexural test

Three-point-bending tests were performed with 60 × 12.5 × 3 mm^3 composite samples according to ASTM D 790 with an Instron model 4304 instrument. A crosshead speed of 1.2 mm/min was used. The span length was 4 cm.

Impact testing

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

Fourier transform infrared (FTIR) analysis

FTIR spectroscopy was performed for both the cured polyester resin and bamboo strip–polyester resin composites with a Jasco FT/IR 460+ spectroscope (Mumbai, India). It was carried out with a pellet sample made of composite dust and KBr. The range was 500–3500 cm^{-1}.

Morphology analysis

A JEOL JSM 5200 (Kolkata, India) scanning electron microscope was used to study the fracture surfaces of the composite samples that were subjected to flexural testing. Before the analysis, the samples were sputtered with a gold–palladium alloy and stuck onto a stub with adhesive tape.

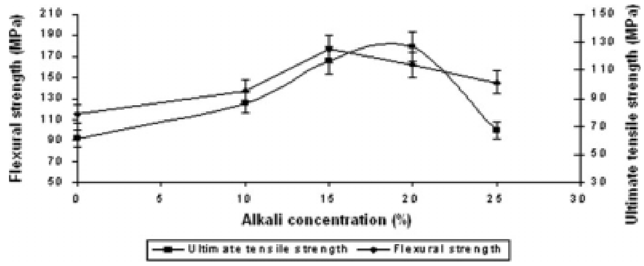

Figure 2 Influence of the alkali concentration on the tensile strength and flexural strength of bamboo–resol composites.

RESULTS AND DISCUSSION

The effect of alkali treatment on the mechanical properties of bamboo–resol composites has been studied, and the results are depicted in Figures 1–3. The treatment of bamboo fiber in solutions of sodium hydroxide with increasing concentration percentages resulted in more and more rigid composites, and every parameter displayed in the figures exhibited an improvement. With changes in the alkali concentration, the elongation at break (%) for the composites decreased continuously, indicating the rigidity of the composites. The treatment improved the value of the flexural strength from 78.68 MPa for BSRC-U50 to 125.077 and 114.117 MPa for BSRC-1550 and BSRC-2050, respectively. The values for BSRC-1550 and BSRC-2050 were more or less comparable. A similar trend was observed for the flexural modulus and toughness: the maximum improvements were observed with BSRC-2050, and the BSRC-2050 composite exhibited optimum properties. A similar observation was also made by Das et al.[8] with mercerized bamboo and novolac resin composites.

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,

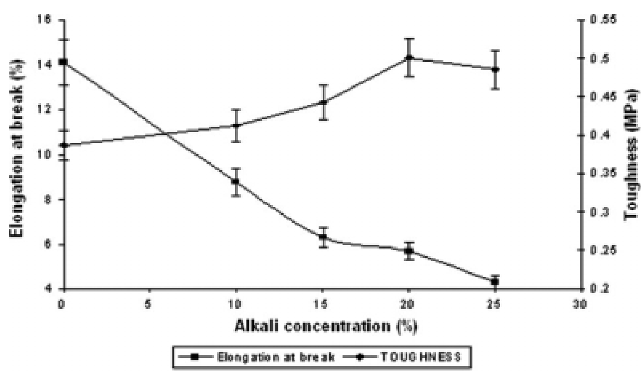

Figure 3 Influence of the alkali concentration on the toughness and flexural modulus of bamboo–resol composites.

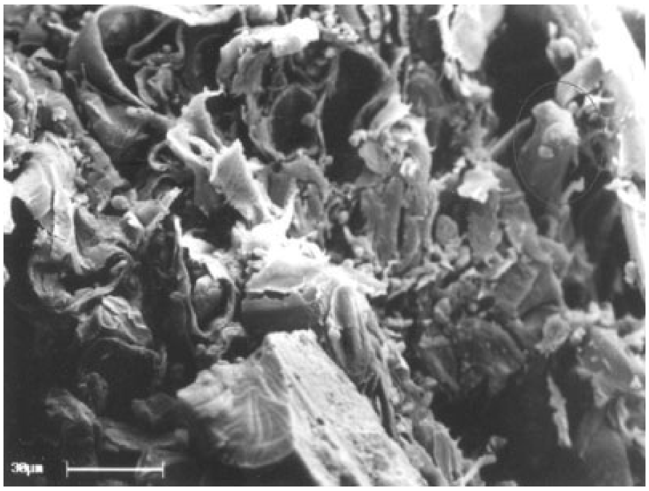

Figure 4 Scanning electron micrograph of an untreated bamboo fiber–resol resin composite.

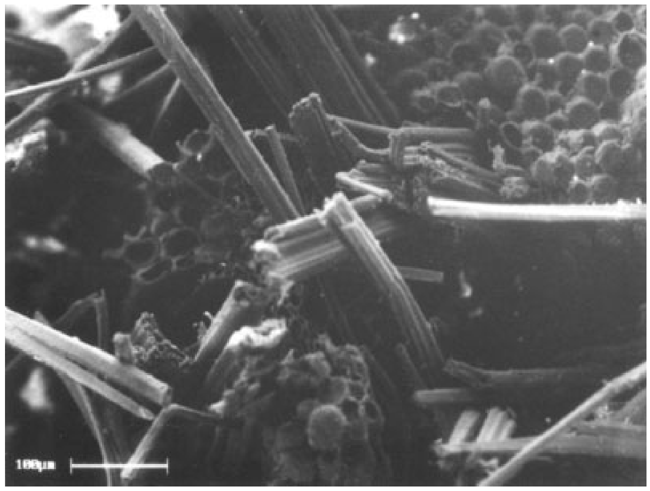

Figure 5 Scanning electron micrograph of a 10% alkali treated bamboo fiber–resol resin composite.

expanding the dimensions of the molecules. Subsequent rinsing with water and neutralization by acid will remove the linked sodium ions and convert the cellulose into a new crystalline structure, that is, cellulose II, which is thermodynamically more stable than cellulose I. 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[8] by removing the noncellulosic substances from the bamboo strips. This decrease in the surface tension is conducive to the subsequent wetting and spreading of the resin over the bamboo strips used as reinforcements, and this also results in good interfacial adhesion. There are more free —OH groups of cellulose after mercerization, which can effectively react then with the matrix. Furthermore, the reactive groups of the resol resin not only undergo a crosslinking reaction within themselves but also react with the available free —OH groups of the cellulose chains and thus lead to reasonably good mechanical properties as the availability of free —OH groups of cellulose chains and access to them are increased with increasing alkali treatment.

The removal of hemicellulose releases the initial strain between the cellulose chains, which are normally separated by the hemicellulose/lignin matrix. As a result of alkali treatment, the formation of new hydrogen bonds leads to closer packing of the cellulose chains.[5] This phenomenon is responsible for the increased average density and mechanical properties of samples due to alkali treatment.[7] Therefore, the combined effect of good interfacial bonding and the use of reinforcing agents with improved mechanical properties, that is, alkali-treated strips, successfully led to a composite sample with improved mechanical properties. Similar observations were made by Ray and coworkers[13,17] during the fabrication of composites of a vinyl ester resin with untreated and alkali-treated jute fibers with various fiber loadings ranging from 0 to 35%. The composites were characterized for their mechanical, dynamic mechanical, thermal, impact fatigue, and microstructural properties. The flexural strength and flexural modulus of 4-h treated fiber-reinforced composites with a 35% fiber loading were increased by 20 and 23%, respectively, in comparison with the untreated one. Rout et al.[21] in their work on the surface modification of coir fibers involving alkali treatment, bleaching, and vinyl grafting studied the mechanical properties of coir–polyester composites. Among all the modifications, bleached (65°C) coir–polyester composites showed better flexural strength, whereas 2% alkali

Figure 6 Scanning electron micrograph of a 20% alkali treated bamboo fiber–resol composite.

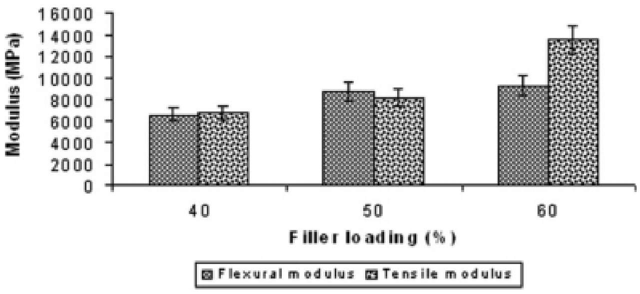

Figure 7 Influence of the filler loading on the modulus of 20% alkali treated bamboo fiber–resol composites.

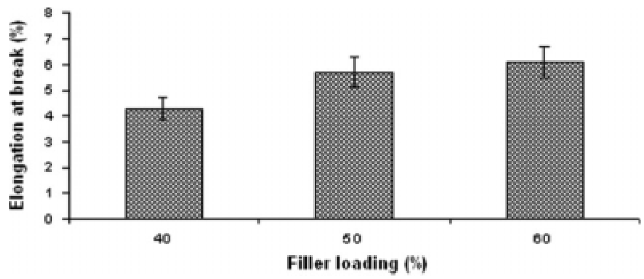

Figure 9 Influence of the filler loading on the elongation of break of 20% alkali treated bamboo fiber–resol composites.

treated coir–polyester composites showed significant improvements in the tensile strength.

An examination of fractured surfaces with a scanning electron microscope (Figs. 4–6) has revealed that the debonding of bamboo strips from the polymer matrix is greater in the case of BSRC-U50. This indicates that with an increasing alkali concentration, the dissolution of alkali-sensitive materials leads to destruction of the network structure of fibers and thus splits the fibers into disentangled fibrils. In other words, alkali treatments lead to fiber fibrillation. Any lignocellulosic material is composed of multicellular fibers. Each unit cell of a fiber consists of small cellulose microfibrils, which are surrounded by and cemented together with lignin and hemicellulose. Although the length of each cell is very small, they are held to each other in a longitudinal direction, thereby producing a long, continuous fiber. The neighboring units are also attached among themselves, producing a meshlike structure. Alkali treatment leads to the destruction of the total structure first by removing the cementing material, and it splits the fiber into finer filaments. These treated, fibrillated fibers form stronger bonds at the interface, showing minimum fiber pullout from the resin matrix and showing maximum pullout of fibrillated fibers from the hemicellulose–lignin matrix.

The variation in the mechanical properties with the volume fraction percentage of 20% alkali treated bamboo fiber reinforcements is shown in Figures 7–10. As phenolic resin itself is a brittle resin, with an increasing fiber loading, the elongation at break (%) of the composites continuously increases.[8] As the fraction of the load-bearing component of the composites increases, the mechanical properties are also increased, being optimum for BSRC-2060.

The work of fracture values of the bamboo–resol composites reinforced with bamboo strips treated with alkali solutions of various concentrations and untreated bamboo strips are shown in Figure 11. From the graph, it is clear that the treated fiber composites had better toughness than the untreated one. However, there is variability in the results. Among the treated composites, BSRC-2050 showed the best results. Beyond that, there was deterioration in all the strength properties due to degradation of the cellulose fiber by stronger alkali exposure.[8,20]

It is known that with good interfacial bonding, crack propagation along the fiber–matrix interface is restricted, the energy absorbed to propagate the crack is low, and the value of work done due to fracture is also low. Bamboo itself is a lignocellulosic composite in which cellulose fibers are embedded in a lignin–hemicellulolose matrix. In the case of an untreated composite, the interfacial bonding between the cellulose fiber and hemicellulose/lignin matrix is maximum. With increasing alkali treatment, as more and more matrix material is removed, the interfacial bonding weakens, and this consequently leads to increased toughness of the composite.

Alkali treatment appears to reduce the fiber diameter by the removal of the binding material and

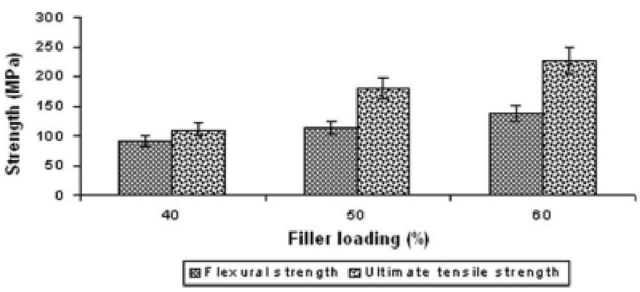

Figure 8 Influence of the filler loading on the strength of 20% alkali treated bamboo fiber–resol composites.

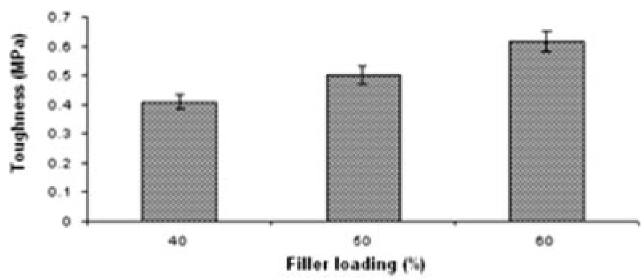

Figure 10 Influence of the filler loading on the toughness of 20% alkali treated bamboo fiber–resol composites.

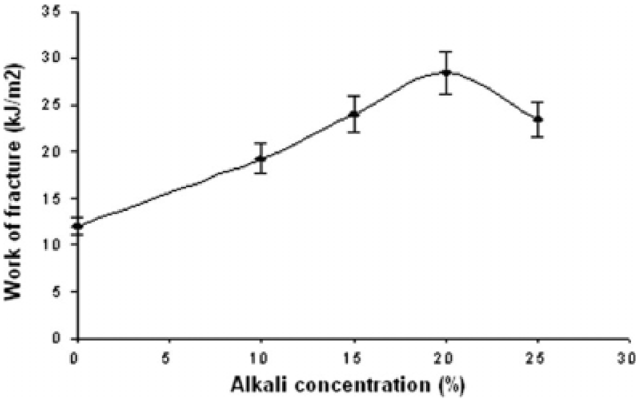

Figure 11 Influence of the alkali concentration on the work of fracture of bamboo–resol composites.

thereby appears to increase the aspect ratio;[19] this offers better fiber–matrix adhesion due to better wetting, as explained previously. Here, as the interfacial bonding between the resin and bamboo strips increases continuously with increasing alkali treatment, it is expected that the crack propagation along the fiber matrix along the interface will be low; as a result, the work of fracture value will be low. However, the interfacial friction between the fiber and resin matrix is not the only contributing factor here; the interface of the cellulose fiber and hemicellulose/lignin matrix also plays a dominating role as we use bamboo strips here, which are lignocellulosic composites. With increasing alkali treatment due to the removal of binding material from the bamboo fiber, there is a continuous decrease in adhesion between the cellulose fiber and hemicellulose/lignin matrix, resulting in longer fiber pullout, and this causes a higher work of fracture value.

Figure 12 presents the variation of the work of fracture for 20% alkali treated bamboo fiber and resol composites with various filler loadings. As the loading of bamboo fiber (which contributes to good work of fracture values after alkali treatment and offers a better impact property to the resin) increases, with an increased amount of reinforcement, the work of fracture value increases, showing a maximum for BSRC-2060.

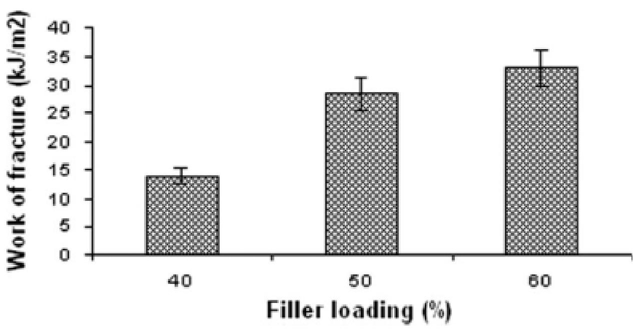

Figure 12 Influence of the filler loading on the work of fracture of 20% alkali treated bamboo fiber–resol composites.

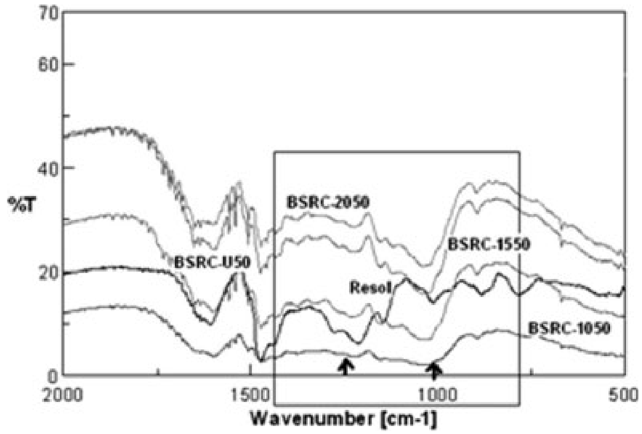

Figure 13 Infrared spectra of the cured resol resin and bamboo fiber–resol resin composites.

From Figure 13, it is clear that a change in the region between 1250 and 1000 cm^{-1} takes place with composites made from bamboo fibers treated with alkali solutions of various strengths and with untreated composites in comparison with the cured resol resin. From the literature, it is known that aryl alkyl ether usually gives rise to two bands, asymmetric C—O—C stretching near 1250 cm^{-1} and symmetric stretching near 1040 cm^{-1}.[22] The stretching at about 1239 and 1040 cm^{-1} in the infrared spectra presented in the figure indicates the formation of aryl alkyl ether between the resol matrix and —OH groups of cellulose of bamboo fibers, instead of the self-condensation of resol, which can well explain the improvements in various properties.

CONCLUSIONS

An overall improvement in all the properties of bamboo–resol composites was observed with the mercerization of bamboo fiber. The improvement seems to occur in the alkali concentration range of 15–20%. A change in the fiber structure due to mercerization leads to an improvement in the crystallinlty[5] and mechanical properties of the fiber as well. Again, modification of the surface topography by alkali treatment leads to an improved aspect ratio of the fibers and consequent interfacial adhesion between the matrix and reinforcement. The effect is the contributory factor for improved mechanical properties of the fabricated composites.

References

1. Bledzki, A. K.; Gassan, J. Prog Polym Sci 1999, 24, 221.
2. Amada, S.; Ichikawa, Y.; Munekata, T.; Nagase, Y.; Shimuzu, H. Compos B 1997, 28, 13.
3. Jain, S.; Kumar, R.; Jindal, U. C. J Mater Sci 1992, 27, 4598.

4. Despande, A. P.; Rao, M. B.; Rao, C. L. J Appl Polym Sci 2000, 76, 83.
5. Das, M.; Chakraborty, D. J Appl Polym Sci 2008, 107, 522.
6. Das, M.; Chakraborty, D. Ind Eng Chem Res 2006, 45, 6489.
7. Das, M.; Chakraborty, D. J Appl Polym Sci 2006, 102, 5050.
8. Das, M.; Pal, A.; Chakraborty, D. J Appl Polym Sci 2006, 100, 238.
9. Das, M.; Chakraborty, D. Polym Compos 2007, 28, 57.
10. Zárate, C. N.; Aranguren, M. I.; Reboredo, M. M. J Appl Polym Sci 2000, 77, 1832.
11. Sreekala, M. S.; Thomas, S.; Neelakantan, N. R. J Polym Eng 1997, 16, 265.
12. Ray, D.; Sarkar, B. K. J Appl Polym Sci 2001, 80, 1013.
13. Ray, D.; Sarkar, B. K.; Basak, R. K.; Rana, A. K. J Appl Polym Sci 2002, 85, 2594.
14. (a) Ray, D.; Sarkar, B. K.; Rana, A. K.; Bose, N. R. Compos A 2000, 32, 119; (b) Ray, D.; Sarkar, B. K.; Bose, N. R. Compos A 2002, 33, 233.
15. Ray, D.; Sarkar, B. K.; Das, S.; Rana, A. K. Compos Sci Technol 2002, 62, 911.
16. Bisanda, E. T. N. Appl Compos Mater 2000, 7, 164.
17. Gassan, J.; Mildner, I.; Bledzki, A. K. Compos Mater 1999, 35, 435.
18. De, D.; Adhikari, B.; De, D. Polym Adv Technol 2007, 18, 72.
19. Gassan, J.; Bledzki, A. K. Compos Sci Technol 1999, 59, 1303.
20. Ray, A. K.; Mondal, S.; Das, S. K.; Ramachandrarao, P. J Mater Sci 2005, 40, 5249.
21. Rout, J.; Misra, M.; Tripathy, S. S.; Nayak, S. K.; Mohanty, A. K. Comp Sci Tech 2001, 61, 1303.
22. Dyer, J. R., In Application of Absorption Spectroscopy of Organic Compounds, Prentice-Hall of India Private Limited: Delhi, India, 1997; p33.