Effects of Mercerization of Bamboo Strips on Mechanical Properties of Unidirectional Bamboo–Novolac Composites

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ABSTRACT: Bamboo strip reinforced novolac resin composites were fabricated using bamboo strips that were treated with varying concentrations of sodium hydroxide solution at a constant filler loading (25%). The mechanical properties of various composites (flexural modulus, toughness, tensile strength, and elastic modulus) were determined. The physical characteristics, such as the wetting ability of the alkali treated reinforcements, were increased because of alkali treatment. With increasing concentrations of alkali, a higher percent loss in weight occurred. The mechanical properties were increased with increasing mercerizing strength. Maximum improvement in properties was achieved with 16–20% of caustic treated reinforcements. An FTIR study indicated aryl alkyl ether formation with —OH groups of cellulose and methylol groups of novolac resin. Beyond 20% there was degradation in all strength properties because of the failure in the mechanical properties of the reinforcements. A correlation was found to exist between the mechanical properties and the developed morphology. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 238–244, 2006

Key words: reinforcement; composite; mercerization; mechanical properties; interface morphology

INTRODUCTION

Natural fibers have proved to be a renewable and cheaper substitute than synthetic fibers such as glass and carbon, which are conventionally used as reinforcements in making structural components. Lignocellulose-based natural fibers offer low density, high specific strength, and stiff reinforcement. They are relatively more abundant in nature and more eco-friendly and have a CO_2-neutral life cycle in contrast to their synthetic opponents.[1–4] Studies have been reported on composites with natural fibers, such as jute, sisal, coir, hemp, pineapple leaf, banana, straw, broom, luffa, and wood fibers, which are considered to be lignocellulosic natural fibers.[5–12] Compared to studies on other natural fiber reinforced composites, however, less effort has been made on bamboo fiber reinforced composites.[13–19] Among the known natural fibers, bamboo has the lowest density[20] and high mechanical strength.[21]

The present work investigates the modifying influences of bamboo strips on the mechanical properties of composites made out of treated bamboo strips and novolac resin compared to those made out of untreated ones and the same novolac resin in relation to variations in the caustic concentration during treatment.

The basic chemical constituents of bamboo are cellulose, hemicellulose, and lignin. In bamboo, cellulose and hemicellulose are present in the form of hollocellulose, which amounts to more than 50% of the total chemical constituents. Most of the cellulose is present as fiber. Actually, bamboo is a natural composite material in which cellulose fibers are reinforced in the lignin matrix along the length of the bamboo culms, providing it with maximum strength in that direction. Bamboo has a very low surface energy and consequently low wetting characteristics.[14]

McLaughlin and Tait[22] carried out extensive studies on various plant species and presented a physical description of the mechanism of failure in tension of cellulose-based fibers. They predicted that the tensile strength and mean Young's modulus would increase with increasing cellulose content and decreasing microfibrillar angle.

Jain et al.[14] reported that bamboo has 60% cellulose with a considerably higher percentage of lignin, its microfibrillar angle being relatively small (10–12°). These facts about bamboo support its high tensile strength. By considering these important properties of bamboo, it was selected as a reinforcement. It has maximum strength along the fibers and minimum strength across the fibers.

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Phenolic resin is a versatile matrix to reinforce with various fibers because of its cheapness and ease of manufacture. Here, wetting of bamboo strips by resin is carried out in molten novolac resin containing a hardener so that wetting and curing of the matrix resin may take place simultaneously. The melt viscosity of the resin at its fusion point (before gelling starts) and the surface or surface tension of the strip play a major role in attaining strong interfacial bonding. Novolac is selected as a matrix in order to minimize expected blister formation that is associated with the carrier solvent as in the case with solvent laden resol and to avoid the extra step of dipping for a prolonged period to achieve saturated impregnation, which is a time consuming step for a resin dissolved or dispersed in a liquid medium like resol. The melt viscosities of novolac resins at higher temperatures are very low.[23]

The fiber and matrix must cooperate for a composite to be an effective load bearing system. This cooperation between the fibers and the matrix will not exist without the presence of the interface. The interface acts as a "binder" and transfers load between the matrix and the reinforcing fibers. Further, because each fiber forms an individual interface with the matrix, the interfacial area is very large. The interface therefore plays a key role in controlling the mechanical properties of a composite.

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. Mercerization is one of the most conventionally used treatments for natural fibers in order to increase the fibers' wetting ability by extracting the noncellulosic substances, mainly wax and pectin, among others. It has been successfully applied to enhance fiber–matrix adhesion in different systems such as jute–epoxy[24] and wood flour–unsaturated polyester resin[25] composite materials.

In this study, the effect of mercerization of bamboo strips on the mechanical properties and morphology of bamboo–novolac resin composites is investigated.

EXPERIMENTAL

Materials

Dried bamboo strips with average dimensions of 100 × 15 × (1.1–1.5) mm (culm length × width × thickness) were obtained from a local source. The strips were dipped in NaOH solution at seven different concentrations (2, 5, 10, 15, 20, 25, and 50%) for 1 h at ambient temperature (25°C). After this treatment, the strips were copiously washed with distilled water and subsequently neutralized with 2% H_2SO_4 solution; the neutrality of the resulting solution was tested with litmus. The strips were then dried in an oven at 105°C until a constant weight was obtained. Novolac resin premixed with hexamethylene tetramine (Hindustan Adhesive and Chemical) was used as the matrix resin. A hand-operated electrically heated hydraulic press (Moore) was used for preparing the composite sheet. A mold with internal dimensions of 100 × 60 × 30 mm (length × width × height) was used to manufacture the composites.

Fabrication of composites

Composites were fabricated with 25 vol % fibers in strip form in the phenolic matrix in each case by placing the bamboo strips on a bed of novolac resin. This bed was made by using half of the total quantity of novolac used inside the mold, and the other half was used to cover the upper layer of the bed of bamboo strips. A mold release agent (silicon oil) was smeared onto the mold surfaces before loading to facilitate the removal of the composites. Molding was done at 180°C under 15-atm pressure for 5 min; a 15-s breathing period was allowed to release air and entrapped gaseous product from the condensation of the novolac resin after attaining the mold temperature.

Testing

Wetting ability test

A drop of water was placed separately on the treated strips (for every concentration of NaOH) and the untreated ones. The drop was allowed to fall from a burette (0.05 mL). The time required to wet a 1-cm distance (previously marked) was noted with a stopwatch.

Percent loss in weight

The strips were weighed separately before and after treatment, followed by the necessary washing and drying. The percentage losses in weight were the average weight (kg) of strips before treatment (W_1) and the average weight (kg) of strips after treatment with a particular concentration of alkali and drying (W_2), which were calculated as follows:

$$\text{average loss in weight (kg)} = (W_1 - W_2)$$

$$\text{percentage loss in weight} = (W_1 - W_2) \times 100/W_1$$

The averages of five samples were considered for each alkali concentration.

Tensile test

Rectangular specimens of bamboo–novolac composite samples ($60 \times 12.5 \times 3$ mm^3) were cut from the composite sheets and then tested according to ASTM

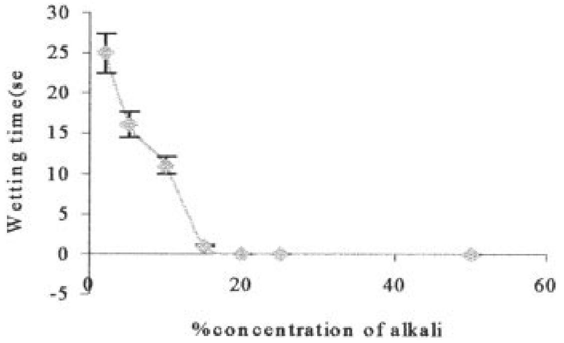


Figure 1 The influence of mercerization on the wetting ability of bamboo strips.

D 638. Specimens were tested to failure under tension at a crosshead speed of 5 mm/min using an Instron 4304 tensile tester. Five specimens without any visual micropores or nicks were tested for each type of sample. The tensile strength and elastic modulus of these samples were recorded.

Flexural test

Three-point bend tests were performed with the bamboo–novolac composite samples of dimensions 60 × 12.5 × 3 mm^3 according to ASTM D 790. A crosshead speed of 1.2 mm/min was used. The span length was 4 cm and the thickness of the sample was 3 mm.

FTIR analysis

FTIR spectroscopy was performed for both cured novolac resin and composites made of 20% alkali treated bamboo strips and novolac resin in a JASCO FTIR 460+ spectroscope. Analysis was carried out with pellet samples made out of composite dust and KBr in a range of 500–3500 cm^{-1}.

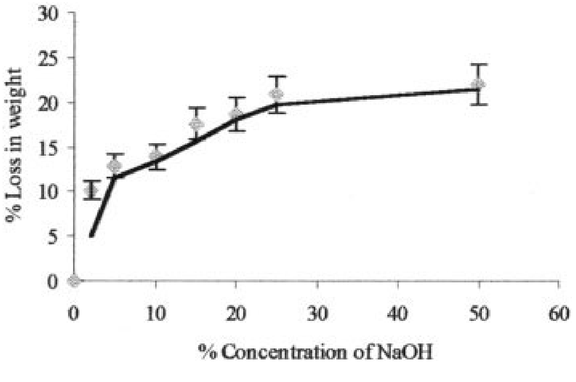


Figure 2 The influence of mercerization on the percent wet loss of strips due to mercerization.

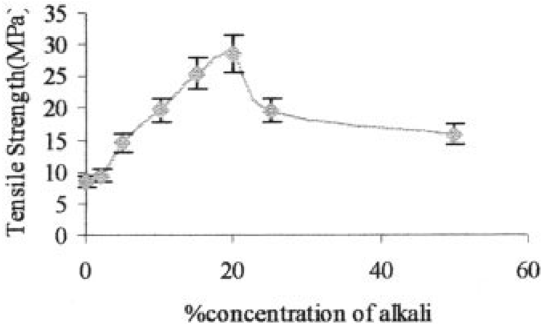


Figure 3 The influence of mercerization on the tensile strength of bamboo–novolac composites.

Analysis of morphology of resin–fiber interfaces by scanning electron microscopy

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

RESULTS AND DISCUSSION

Wetting ability test

Water possesses a very high surface energy (~72.06 dyne/cm), which is well known. Most of the organic resins and solutions have a surface energy that is much lower than that of the water used for testing the wetting ability of bamboo strips. A surface capable of being wetted by water will definitely allow the water to spread over and through the surface. Figure 1 shows that an increasing NaOH concentration increases the wetting ability of the strips; that is, the surface tension is lowered. It was expected that wax, pectin, and any other oily and greasy matter present in the strips, which are effective in lowering the surface tension, are removed by NaOH treatment. This decrease in surface tension is conducive to the subsequent wetting and spreading of the molten novolac resin over the bamboo strips used as reinforcement.

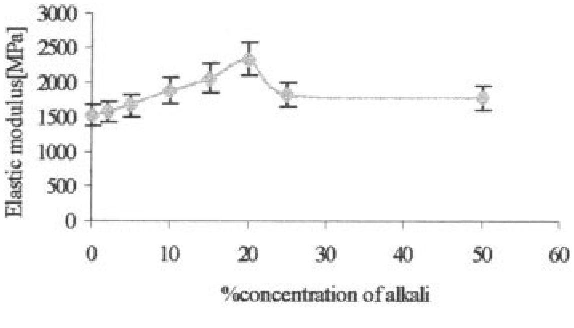


Figure 4 The influence of mercerization on the elastic modulus of bamboo–novolac composites.

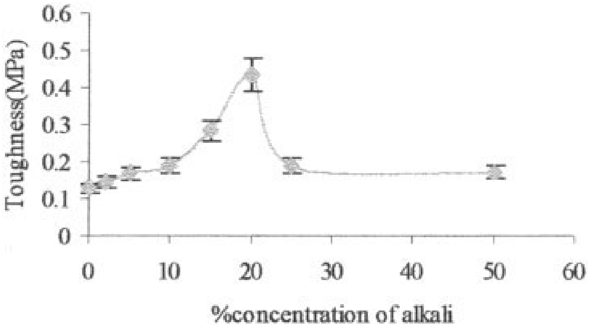


Figure 5 The influence of mercerization on the toughness of bamboo–novolac composites.

Percent loss in weight of bamboo strips

Figure 2 displays percent losses in weight of bamboo strips as a function of the NaOH concentration. The loss in weight is attributed to the gradual and steady removal of more and more hemicelluose and lignin with increasing concentrations of NaOH solution. Thus, the effectiveness of the caustic solution in terms of exposing the α-cellulose (mainly responsible for reinforcement) and consequent interaction with the reactive sites of novolac increases with an increase in concentration.

Mechanical tests

The various mechanical properties of the composites made from bamboo strips treated with varying concentrations of NaOH versus the untreated strips are depicted in Figures 3–6. There is a steady and sharp increase in each of the mechanical parameters under study with increasing concentrations of caustic treatment on bamboo fiber strips. Another striking feature of these various curves is the sharp decline in each individual mechanical aspect under consideration, beyond 20% caustic exposure. With increasing mercerizing agent strength the interfibrillar region gradually loses more and more hemicellulose and lignin, becoming less dense and less rigid, thereby making the fibrils more capable of rearranging themselves and undergoing reorientation and recrystallization along the direction of tensile deformation.[4] Therefore, now when they are stretched, such rearrangements among the fibrils result in better load sharing within them, thus resulting in higher and higher strength. Alkali treatment leads to an increase in percent crystallinity index up to 20% alkali concentration and then randomness appeared because of degradation of long chain cellulose molecules at a higher concentration of alkali.[26] Here, the mechanical properties also fall beyond 20% alkali concentration.

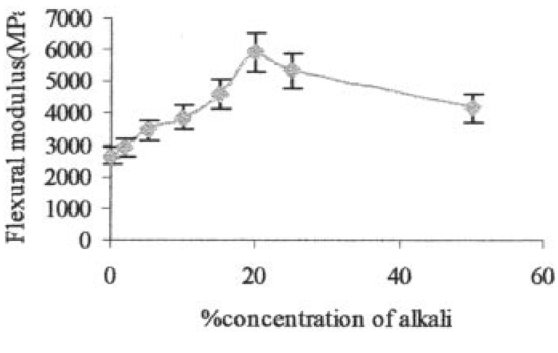


Figure 6 The influence of mercerization on the flexural modulus of bamboo–novolac composites.

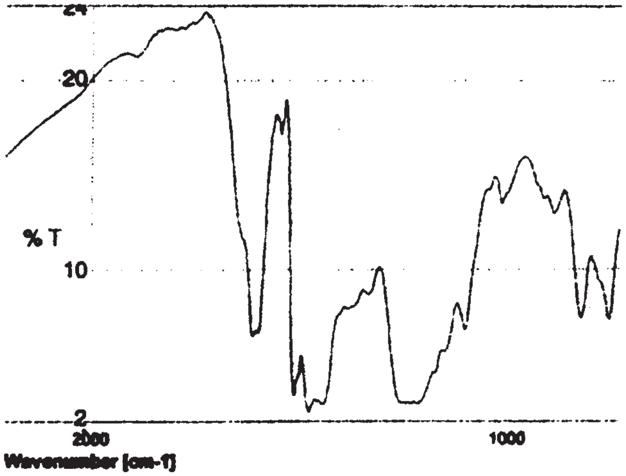


Figure 7 Scanning electron micrographs of (a) untreated bamboo fiber novolac composite and (b) 2, (c) 5, (d) 10, (e) 15, (f) 20, (g) 25, and (h) 50% alkali treated bamboo fiber novolac composites.

Mercerization renders a rough surface topography, as is revealed by scanning electron micrographs [Fig. 7(a–h)]. More and more disentangled fibers (i.e., more

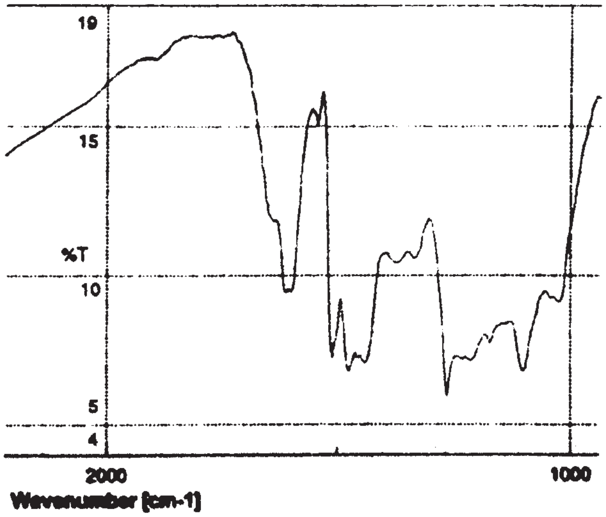
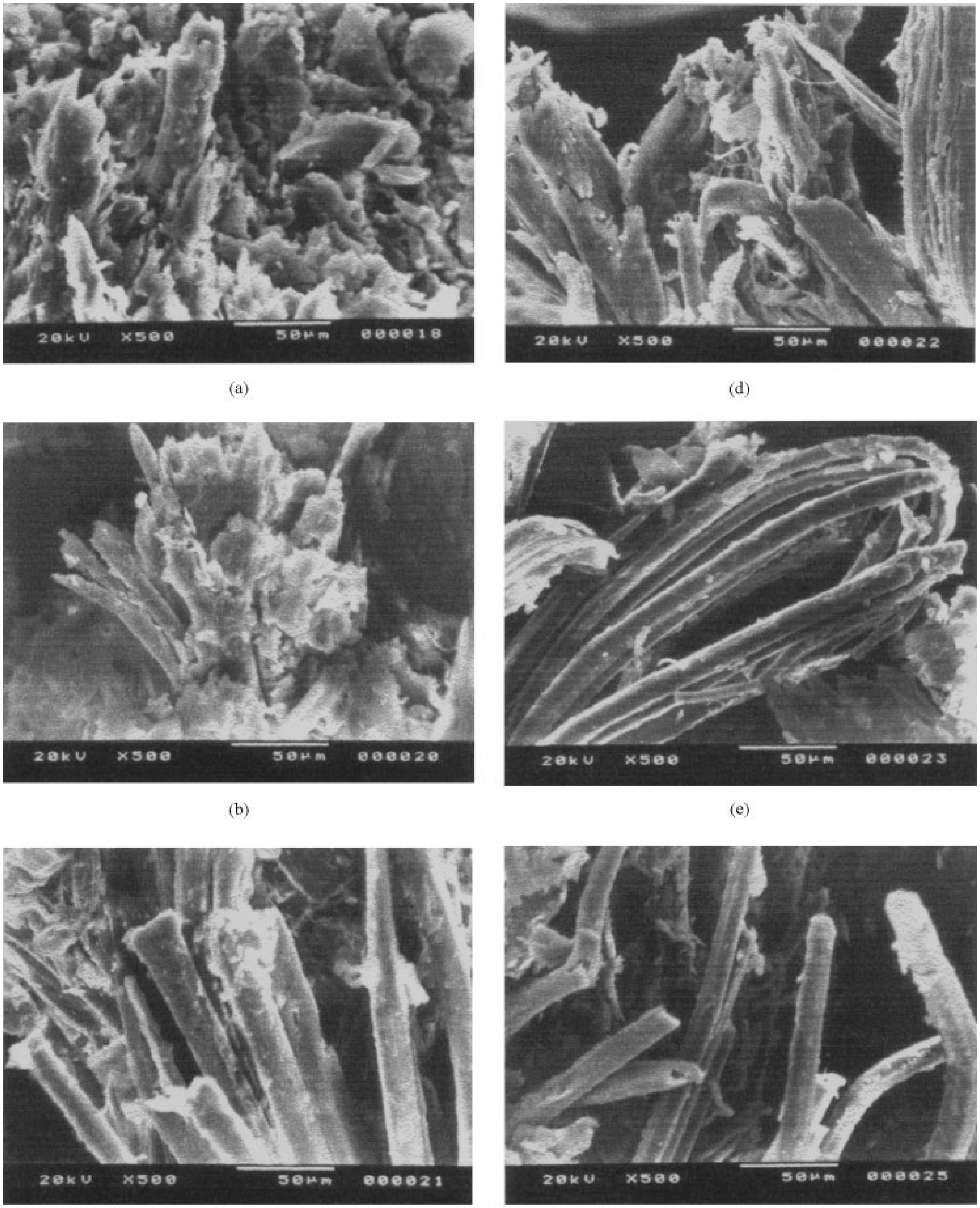


Figure 8 FTIR spectroscopy of the cured novolac resin.



(a) (d)

(b) (e)

(c) (f)

Figure 9 FTIR spectroscopy of the bamboo–novolac composite (20% alkali treated bamboo strips).

fibrillation) were obtained with increasing alkali concentration, although it does not give any suitable idea of the particular treatment that promotes better modification of the surface of the fibers. It may be expected that novolac resin, by virtue of its low melt viscosity, attains increased flow before the incipient crosslinking and enters into voids and crevices (troughs) on the rough long fiber strips, which is further augmented because of lowering of the surface energy with an increasing extent of mercerization; thus, it becomes more and more mechanically entangled after crosslinking. Furthermore, the low viscous novolac melt containing reactive methylol groups not only undergoes a crosslinking reaction within itself but also reacts with the available free —OH groups of the cellulose chains, thus leading to reasonably good mechanical properties.

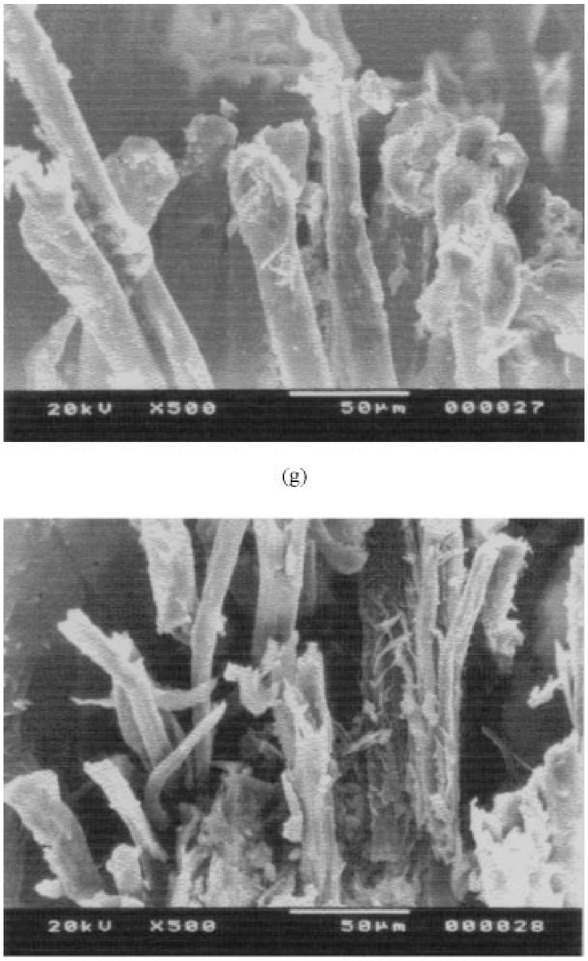
Alkali treatment leads to fibrillation, which increases the effective surface area available for contact with the matrix. In other words, mercerization reduces the fiber diameter and thereby increases the aspect ratio,[27] which offers better fiber–matrix adhesion and contributes to improved mechanical properties as the NaOH treatment increases from 2 to 20%. Increased fibrillation at still higher concentrations of NaOH (>20% in our case) leads to the development of random breakdown of the cellulose chains and thus to a sharp fall in properties.

FTIR analysis

Cured novolac (Fig. 8) and composites made of 20% alkali treated bamboo fibers and novolac (Fig. 9) were subjected to FTIR analysis. A sharp peak at 1260 cm^{-1} was observed in the composite (IR-2), which is absent either in the cured novolac resin (IR-1) or in the alkali treated bamboo strip fiber. Usually aryl alkyl ethers give rise to two bands: an asymmetric C—O—C stretch near 1250 cm^{-1} and a symmetric stretch near 1040 cm^{-1}.[28] Therefore, it can be assumed that the transmission near 1260 cm^{-1} for the composite under investigation is associated with ether linkage formation. The reactive methylol groups present in the novolac resin might be facing two simultaneous reactions, one with the hexamethylene tetramine curative and one with the relatively more abundant and accessible —OH groups (one primary and two secondary) present in the alkali treated cellulose of bamboo strip fibers. This possibly leads to synergism in the mechanical properties as observed earlier. The symmetric stretching at 1039 cm^{-1} may be considered as supporting evidence of such ether linkage formation.

CONCLUSION

The mechanical properties of bamboo–novolac composites were improved by mercerization of bamboo strips. The improvement was up to a 20% concentration of alkali and then the properties deteriorated. Changes in the fiber structure and topography led to improved mechanical properties of the composites. However, a 20% alkali concentration showed maximum value of the mechanical properties of composites under the corresponding experimental condition. At higher concentration the mechanical properties deteriorated because of degradation of the fiber.



(g)

(h)

Figure 9 (*Continued from the previous page*)

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