Dynamic Mechanical Analysis and Morphological Studies of Glass/Bamboo Fiber Reinforced Unsaturated Polyester Resin-Based Hybrid Composites

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ABSTRACT: Hybrid composites based on isophthalate polyester and vinyl ester resin were fabricated with glass and bamboo fibers. 25, 50, and 75 wt % of glass fibers were replaced by bamboo fibers of the optimized glass fiber reinforced composites and were subjected to dynamical mechanical analysis to determine the dynamic properties as a function of temperature and frequency. The storage modulus E' was found to decrease with the increase of weight fraction of bamboo fibers. Loss modulus was also found to decrease with loading while the damping property was found to increase marginally. Scanning electron micrographs of flexural fracture surfaces of composites demonstrated fiber-matrix bonding. Cole–Cole analysis was made to understand the phase behavior of the composite samples. Kubat parameter was calculated to study the adhesion between matrix and fibers of the fabricated composites. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: E382–E387, 2012

Key words: bamboo fiber; glass fiber; USP resin; dynamic mechanical properties; hybrid composites; phase morphology

INTRODUCTION

A dynamic mechanical analyser, commonly referred to as just DMA, measures the stiffness and damping properties of a material. The stiffness depends on the mechanical properties of the material and its dimensions. It is frequently converted to a modulus to enable sample intercomparisons. Damping is expressed in terms of tan δ and is related to the amount of energy a material can store. DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behavior is observed.[1] One of the targets of the researchers across the world is to investigate, develop, and construct high-performance building materials from renewable resources. The renewable raw materials save the valuable nonrenewable resources and are environmentally sound and do not cause health problems. Natural fibers have already established a track record as simple filler material in automobile parts. Natural fibers like coir, jute, oil palm, sisal fibers have all been proved to be good reinforcement in thermoset and thermoplastic matrices.[2–5] In our previous study, we have found that the replacement of glass fiber, upto a certain extent, by bamboo fibers to be an effective reinforcement in polyester matrix.[6]

Researchers have examined the dynamic mechanical behavior of coir fiber-reinforced natural composites.[7] They have observed an increase in loss modulus and damping factor, which indicated lower heat dissipation in the gum. It was also found that composites with poor interfacial bonding tend to dissipate more energy than that with good interfacial bonding. In another study involving bio-fibers, the dynamic and static mechanical properties of randomly oriented, intimately mixed banana and sisal hybrid-fiber reinforced polyester composites were reported.[8] Maximum stress transfer between the fiber and matrix was obtained in composites having a volume ratio of banana and sisal as 3 : 1. The storage modulus was found to increase with fiber volume fraction above the glass transition of the composites.

The dynamic mechanical properties of a composite material depend on the fiber content, presence of the additive like filler, compatibilizer, fiber orientation, and the mode of testing. The three important parameters that can be obtained during a dynamic mechanical test are: (1) storage modulus, which is a measure of the maximum energy, stored in a material during one cycle of oscillation. It also gives an idea of stiffness behavior and load bearing capability; (2) loss modulus, which is proportional to the amount of energy that has been dissipated as heat

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by the sample; and (3) mechanical damping term tan δ, which is the ratio of the loss modulus to the storage modulus and is related to the degree of molecular mobility in the polymer material. The other useful quantities characterized by DMA are storage and loss compliance, dynamic and complex viscosity, creep compliance, and the stress–relaxation modulus. Dynamic tests over a wide range of temperature and frequency are especially sensitive to all kinds of transitions and relaxation processes of the matrix resin and also to the morphology of the composites. Data and information generated may then be employed as a means of finger-printing polymer systems and for locating glass transition temperature. The glass transition temperature (T_g) can be defined as the maximum of the transition in the loss modulus curve or in the loss tangent curve. It is usually interpreted as the peak of tan δ or loss modulus curve that is obtained during a dynamic test conducted at low frequency.[1,9]

Wielage et al.[10] studied the dynamic mechanical properties of flax and hemp fiber-reinforced polypropylene composites. The authors found that the increasing mobility of the molecules is counteracted by the fibers, which leads to an increase in storage modulus with fiber loading. The loss factor was found to behave reciprocally. The characterization of soy protein-reinforced by styrene–butadiene rubber composites using DMA was reported by Jong.[11] The addition of soy protein to the rubber composites generated a significant reinforcement effect. Sreekala et al.[12] investigated the viscoelastic properties of oil palm fiber/phenol formaldehyde and oil palm fiber/glass hybrid phenol formaldehyde composites as a function of fiber content and hybrid fiber ratio. The incorporation of oil palm fiber lowered the glass transition temperature. The glass transition temperature of hybrid composite was found to be lower than that of the unhybridized composites. Storage modulus of the hybrid composites was also found to be lower than that of the unhybridized oil palm fiber/PF composite. Activation energies for the relaxation processes in different composites were calculated. Activation energy was found to increase upon fibrous reinforcement. A number of studies as seen above have been reported on the dynamic mechanical behavior of synthetic fibers and natural fiber-reinforced polymer matrix composites but that of hybrid fiber-reinforced composites has been few and need to be addressed in detail. The advantages of using a hybrid composite containing two or more types of different fibers are that the advantages of one type of fiber could complement what are lacking in other. As a result, a balance in performance and cost could be achieved through proper material designing.

In this article we have studied the dynamic mechanical analysis and morphology of bamboo/glass fiber-reinforced composites of unsaturated polyester (USP) resin containing 50 wt % of fibers out of which 0, 25, 50, or 75 wt % of glass fibers has been replaced by 5-mm-long bamboo fibers. Cole–Cole analysis was made to understand the phase behavior of the composite samples. Kubat parameter was calculated to study the adhesion between matrix and fibers of the fabricated composites.

EXPERIMENTAL

Materials used

C′POL-301, i.e., isophthalate polyester resin was procured from Crest Composites and Plastics Private Limited, India and used as matrix resins in these studies. The density of the cast resin is 1.108 g/cm^3.

Bamboo fibers were isolated from the bamboo strips that were made from the different segment of bamboo. A combination of chemical and mechanical methods was used for extracting bamboo fibers. The bamboo strips were soaked in 0.1*N* or 1*N* aqueous solution of NaOH for 72 h. After that the strips were washed thoroughly with water. Then the strips were dried at room temperature for 1 h and were placed between two flat platens of a hydraulic press subjected to a constant load of 10 tons for 10 s. Finally, the bamboo strips were boiled in water in a pressure cooker for 30 min and fibers were then separated out manually.

Composites fabrication

Laminates were fabricated using glass fibers (length: 5 mm; density: 2.5 g/cm^3) or bamboo fibers (length: 5 mm; density: 1.46 g/cm^3). Laminates were prepared by thorough mixing of fibers and resin and then placing it in a glass mould at room temperature using 1.5 phr of both accelerator (3% solution of cobalt octoate) and catalyst [50% solution of methyl ethyl ketone peroxide (MEKP) containing 9% active oxygen] for isophthalate resin-based laminates.

Hybrid composites were fabricated by using 50 wt % of glass and bamboo fibers. Composites of USP resin containing 50 wt % of fibers out of which 0, 25, 50, and 75 wt % of glass fibers has been replaced by 5-mm-long bamboo fibers were prepared and are designated as AH-0, AH-1, AH-2, and AH-3, respectively.

Measurements

DMA measurements were carried out in TA instruments (model DMA 2980). The experiments were performed under dual cantilever bending mode at frequency of 1, 10, and 100 Hz. The sample dimension was 56 mm × 13 mm × 3 mm. The samples were tested in the temperature range from 20 to 250°C and the heating rate was 2°C/min. Fractured surface of composites with different fiber loading specimens obtained during flexural test[6] were observed in a scanning electron microscope (CARL ZEISS EVO-50) to study the morphology of the composite samples. The acceleration voltage used was 20 kV and the magnification was 1700× for all samples. The samples were coated with a thin layer of gold by using a vacuum sputtered before SEM observations.

Kubat parameter (K_p) was calculated using the Eq. (1)[13,14] to find out the interfacial adhesion between the fibers and the polymer matrix.

$$\text{Kubat parameter } (K_P) = [\{\tan\delta_c/(V_m \tan\delta_m)\} - 1]$$

where tan δ_m and tan δ_c are the tangent δ (damping) of the matrix and composite, respectively. V_m is the volume fraction of the matrix in the composites. The value of K_p approaching to 0 corresponds to the strong interfacial bonding between the matrix and the fibers in the composites.[13]

RESULTS AND DISCUSSION

Storage modulus

It is very well known that the dynamic storage modulus in many structural applications is very important. A clear understanding of the storage modulus-temperature curve obtained during a dynamic mechanical test provides valuable insight into the stiffness of a material as a function of temperature. This curve is useful in assessing the molecular basis of the mechanical properties of materials since it is very sensitive to structural changes such as molecular weight, degree of cross linking, and fiber-matrix interfacial bonding.[9]

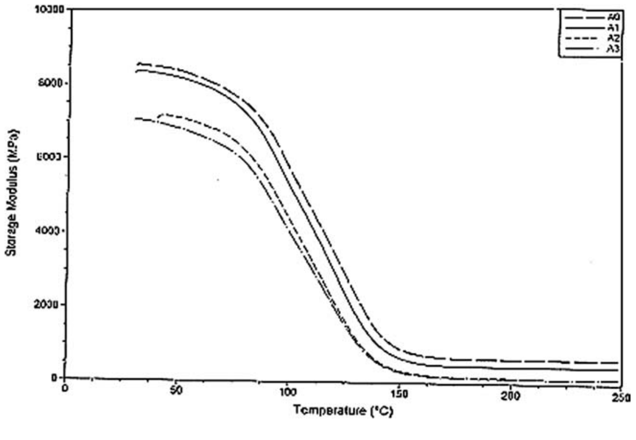

Figure 1 The variation of storage moduluś (E') with temperature at a frequency of 10 Hz.

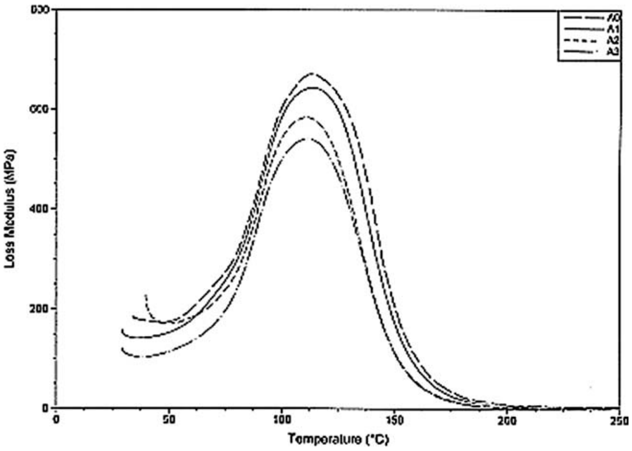

Figure 2 Variation of log (E') with fiber replacement at different temperatures.

The variation of storage modulus with temperature at a frequency 10 Hz for different loading is shown in Figure 1. Variation in storage modulus occurs due to the effect of replacement of glass fibers by bamboo fibers. In the case of optimized glass fiber reinforced USP resin composites, it was found that the storage modulus is higher than the hybrid composites. The decrease is prominent in the glassy state below T_g while there is not much effect in the rubbery plateau region.

It is important to mention that the modulus in the glassy state is determined primarily by the strength of the intermolecular forces and the way the polymer chain is packed.[15] Figure 2 shows the variation of log(E') with fiber replacement at different temperatures of 40, 80, 110, 140, and 160°C. In all cases, E' value decreases gradually. The decrease is lesser in case of 25 wt % replacement of glass fiber. Apparently it seems to us that the hybrid composite is giving –ve results but it is not so, as the values were compared with the glass fiber reinforced composite, not with the pure resin.[15,16] The value of storage modulus of hybrid composite is higher than the pure resin.[9]

Loss modulus

The loss modulus (E'') is defined as the amount of energy dissipated or lost as heat per cycle of sinusoidal deformation, when different systems are compared at the same strain amplitude. It is the viscous response of the material. The loss modulus is most sensitive to the molecular motions. Figure 3 shows the variation of loss modulus with the replacement of glass fibers by the bamboo fibers. It is seen from the figure that the loss modulus peak values decreased marginally with increase of bamboo fibers

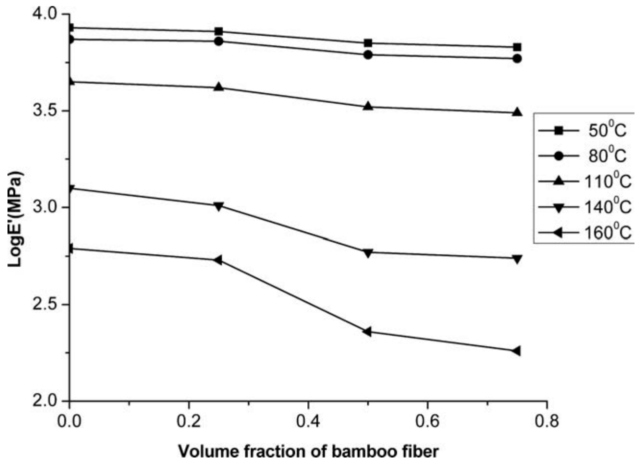

Figure 3 Change in loss modulus (E'') with the replacement of glass fibers by the bamboo fibers.

content. The peak height shows a regular decrease with increase of bamboo fibers content. This happened because the natural bamboo fiber is stiffer than the glass fiber.

Tan δ

Tan δ is a damping term that can be related to the impact resistance of a material. Since the damping peak occurs in the region of the glass transition where the material changes from a rigid to a more elastic state, it is associated with the movement of small groups and chains of molecules within the polymer structure, all of which are initially in Ref. 9. In a composite system, damping is affected by the incorporation of fibers. This is due mainly to shear stress concentration at the fiber ends in association with the additional viscoelastic energy dissipation in the matrix material.

Figure 4 shows the effect of temperature on the tan δ. Decrease in interfacial bonding in composites occurs as observed by the increase in the tan δ values. The higher the damping at the interfaces indicates the poorer the interface adhesion. When there is closer packing of the fibers crack propagation will be prevented by the neighboring fiber. The effective stress transfer occurs in the case of composites with 25 wt % replacement of glass fibers by bamboo fibers. The variation of tan δ with temperature of composite has been analyzed with respect to fiber loading and frequency. Incorporation of bamboo fibers reduces the tan δ peak height by restricting the movement of the polymer molecules. Magnitude of the tan δ peak is indicative of the nature of the polymer system. The replacement of glass fibers by bamboo fibers decreases the T_g value of the composites as the thermal stability of bamboo fiber is lower. The result is consistent with the E' values obtained. However, the replacement by bamboo fibers reduces the magnitude of the tan δ peak more than shifting the T_g. Kubat parameter (K_p) of the composites calculated from the eq. (1) is given in the Table I. It is observed that Kubat parameter (K_p) of the AH0 is lower than that of AH1, AH2, and AH3. However the value of K_p of AH1 is close to AH0 whereas the K_p value of AH2 and AH3 is far higher than that of AH0. The decrease in the interfacial adhesion of the composite was due to the decrease in volume fraction of the matrix. When the specified percentage of glass fiber was replaced by bamboo fibers, the resulting hybrid composite was having higher volume fraction of fibers as compared to the neat glass fibers reinforced composites due to the lower density of the bamboo fibers than that of glass fibers. In consequence of this the volume fraction of the matrix gradually decreased in the composites, hence the interfacial adhesion was also decreased.

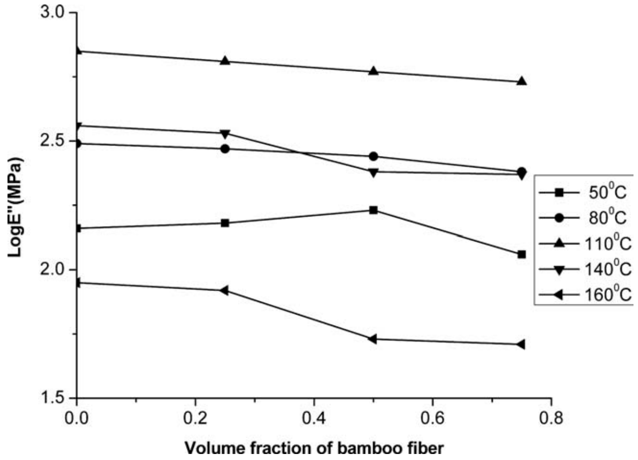

Figure 4 Effect of temperature on the tan δ of the hybrid composites.

Cole–Cole plots

Using the Cole–Cole method, structural changes taking place in cross-linked polymers after fiber addition to polymeric matrices can be studied. The magnitude of polarization, which can be represented by the Debye and Onsager[17] equations, within a material is represented by dielectric constant. To describe the viscoelastic response of polymers, the single

TABLE I
Kubat Parameter (K_p) of Glass/Bamboo Fiber Reinforced USP Resin Composites

Sl No.	Sample	Volume fraction of matrix (V_m)	Kubat parameter (K_p)
1.	AH-0	0.693	0.026
2.	AH-1	0.657	0.099
3.	AH-2	0.625	0.440
4	AH-3	0.595	0.606

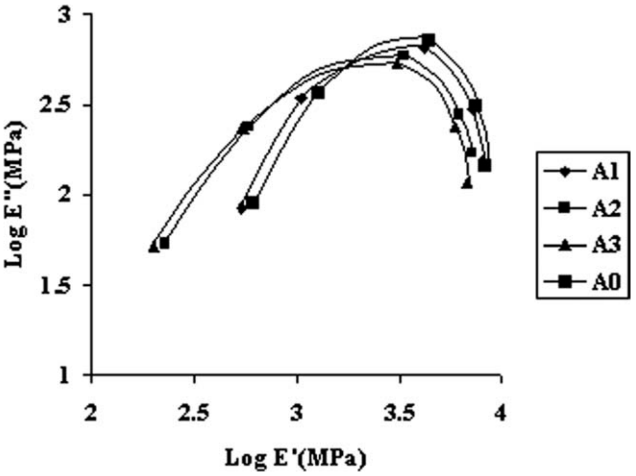

Figure 5 Cole–Cole plot.

relaxation peaks are not adequate. Cole–Cole is a particular treatment of dielectric relaxation data obtained by plotting E'' against E', each point corresponding to same frequency.[17]

The dynamic mechanical properties when examined as a function of temperature and frequency are represented on the Cole–Cole complex plane,

$$E = f(E')$$

where E = Young's modulus of the composites; f = function and E' = Real (storage) part of the complex modulus.

Figure 5 shows the Cole–Cole plot, where the loss modulus data log E'' are plotted as a function of the storage modulus log(E''). The nature of the Cole–Cole plot is reported to be indicative of the nature of the system. Homogeneous polymeric systems are reported to show a semicircle diagram.[18] The Cole–Cole diagrams presented in the figure are imperfect semicircles the shape of the curve points towards the relatively good fiber–matrix adhesion.[9]

Morphology

Figure 6 shows the SEM micrographs of glass fiber-reinforced composites of USP resin composites containing 50 wt % of glass fibers of which (a) 0, (b) 25, (c) 50, and (d) 75 wt % replaced by bamboo fibers. It can be seen from the SEM micrographs that there is better fiber/matrix bonding in composites with 50% glass fiber loading [Fig. 6(a)]. Whereas fiber/matrix debonding is evident in composites with 50 and 75% of glass fiber replaced by bamboo fibers [Fig. 6(c,d)]. This happened because the matrix volume decreased as explained in the tan δ section. However the fiber–matrix adhesion in

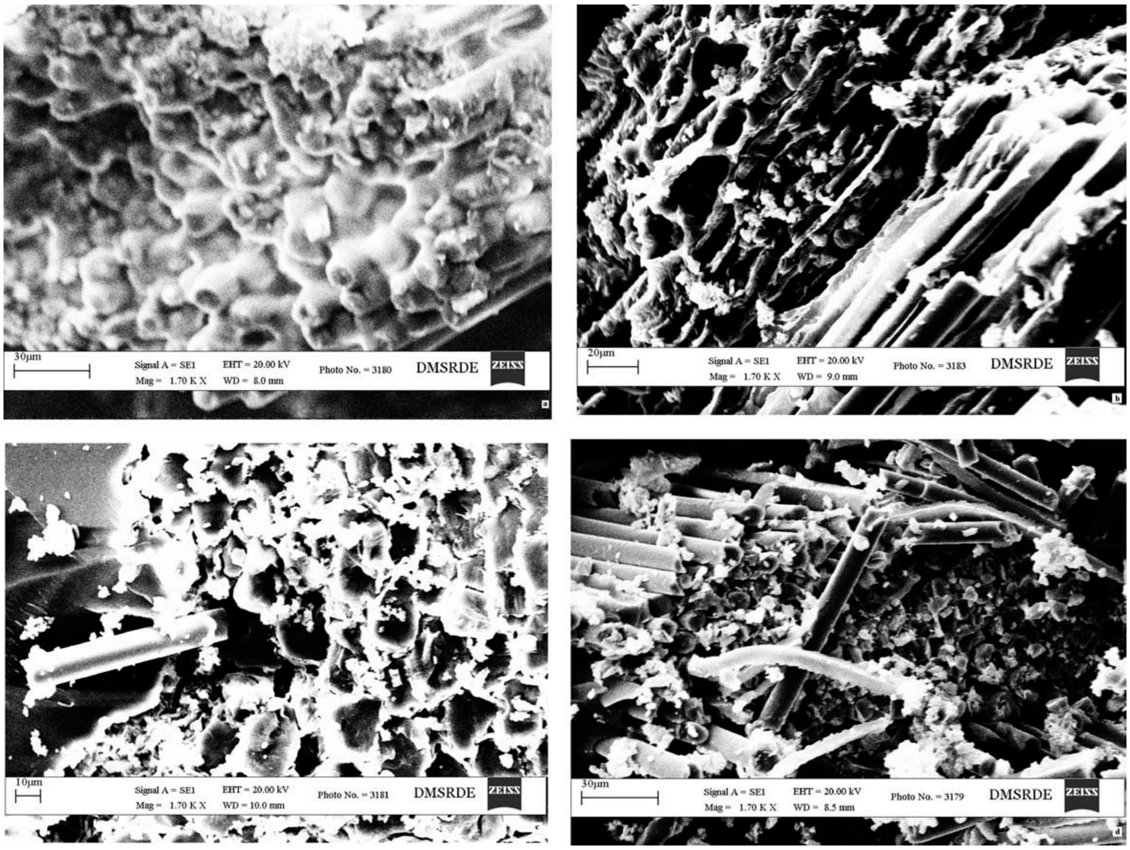

Figure 6 SEM photographs of glass fiber-reinforced composites of USP resin composites containing 50 wt % of glass fibers of which (a) 0, (b) 25, (c) 50, and (d) 75 wt % replaced by bamboo fibers.

the composite with 25% of glass fiber replaced by bamboo fibers [Fig. 6(b)] is observed. It is well known that if the fiber concentration is lower, the packing of the fibers will not be efficient in the composite. In the similar way if the fiber concentration is very high, the matrix would not wet the fibers properly. As a result, debonding of the matrix can happen due to the improper wetting and lower interfacial strength.

CONCLUSIONS

Dynamic mechanical properties of short glass/bamboo fiber reinforced polyester composites are dependent on the volume fraction of the fiber and percentage of glass fiber replaced by bamboo fiber. The storage modulus of the short glass/bamboo fiber reinforced polyester composites decrease with incorporation of fiber below the glass transition temperature and has a positive effect on the modulus at temperatures above T_g. The value of storage modulus of hybrid composite is higher than the pure resin. The peak values of loss modulus decreased marginally with increase of bamboo fiber content due to the stiffness of the bamboo fiber. Decrease in interfacial bonding in composites occurs as observed by the increase in the tan δ values. The higher the damping at the interfaces indicates the poorer the interface adhesion. The least decrease in properties is observed for composites with 25 wt % glass fiber with the bamboo fiber. Critical fiber loading is there in composites above which debonding will happen resulting lower properties due to the improper wetting and low interfacial adhesion, it is clear in the SEM photographs. The critical volume, which can be calculated using the densities of the matrix and the fibers, is determined to be 35% in this study. An imperfect semicircle obtained from Cole–Cole plots showing the heterogeneity of the system and the good interfacial adhesion at 25 wt % glass fiber replacement by bamboo fibers.

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