Effect of Layering Pattern on Dynamic Mechanical Properties of Randomly Oriented Short Banana/Sisal Hybrid Fiber–Reinforced Polyester Composites

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ABSTRACT: Dynamic mechanical test methods have been widely employed for investigating the structures and viscoelastic behavior of polymeric materials to determine their relevant stiffness and damping characteristics for various applications. Randomly oriented short banana/sisal hybrid fiber–reinforced polyester composites were prepared by keeping the volume ratio of banana and sisal 1 : 1 and the total fiber loading 0.40 volume fraction. Bilayer (banana/sisal), trilayer (banana/sisal/banana and sisal/banana/sisal), and intimate mix composites were prepared. The effect of layering pattern on storage modulus (E'), damping behavior (tan δ), and loss modulus (E'') was studied as a function of temperature and frequency. Bilayer composite showed high damping property while intimately mixed and banana/sisal/banana composites showed increased stiffness compared to the other pattern. The Arrhenius relationship has been used to calculate the activation energy of the glass transition of the composites. The activation energy of the intimately mixed composite was found to be the highest. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2168–2174, 2005

Key words: composites; stiffness; polyesters; matrix; mechanical properties

INTRODUCTION

In recent years, rapid growth has occurred in the consumption of fiber-reinforced polymer composites, which yield a unique combination of high performance, great versatility, and processing advantages at favorable cost.[1] Natural fibers, environmentally friendly materials, are potentially user friendly and have been proved to be good reinforcement in polymeric matrices.[2–8] Natural fiber–reinforced polyester composites have been evaluated both for strength, performance, and cost and have proved to be competitors for glass fiber/polyester composites. Hybridization of two different fibers has proved to be an effective method to design materials suited for various requirements.[9] The aging studies of bamboo/glass fiber–reinforced polymer matrix hybrid composites showed that the reduction in tensile strength and modulus for the hybrid composites is nearly half those of the unhybridized composites.[10,11] Earlier studies by Thomas et al.[12–14] proved that banana as well as sisal fibers can be used as effective reinforcements in a polyester matrix. These fibers were hybridized with glass fibers to obtain better mechanical performance.[15,16]

The viscoelastic or dynamic properties of polymeric materials are of considerable practical significance for several reasons, particularly if they are determined over wide ranges of frequency and temperature. They can yield insight into various aspects of material structure, provide a convenient measure of polymer transition temperatures, and may influence other important properties such as fatigue and impact resistance. The dynamic properties are also of direct relevance to a range of unique polymer applications concerned with the isolation of vibrations or dissipation of vibrational energy in engineering components. The dynamic properties are generally expressed in terms of storage modulus, loss modulus, and damping factor, which are dependent on time and temperature. Generally the introduction of a filler in a polymeric matrix leads to a reduction in mobility of the macromolecular chains in the vicinity of filler. This is evident from the increase in the temperature of the main relaxation associated with the glass transition. Therefore, the extent of fiber/mareix interaction and structure/property relationship could be understood from DMA. Valea et al.[17] investigated the influence of cure condi-

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TABLE I
Physical Properties of Banana and Sisal Fiber

Physical property	Sisal fiber	Banana fiber
Density (g/cc)	1.41	1.35
Cellulose content (%)	60–65	63–64
Lignin content (%)	10–14	5
Microfibrillar angle (°)	20	11
Lumen size (μm)	11	5

tions and the exposure to various chemicals on the dynamic mechanical properties of several vinyl ester and unsaturated polyester resins containing glass fiber. Exposure to aromatic solvents was found to modify the viscoelastic character of these materials. Bledzki and Zhang[18] investigated the dynamic mechanical thermal behavior of jute fiber–reinforced epoxy foams. It was observed that the temperature of the log decrement peak for the jute fiber–based composites was shifted by about 5°C, in comparison with that of pure epoxy resin. Dynamic mechanical analysis of unsaturated polyester resin modified with (poly)organo siloxanes was done by Valeria and Marie[19] and they concluded that 1,3-amino-propyl-triethoxy silane (APTS) was incorporated into the resin by reaction of its amino group with glycidyl methacrylate (GMA), generating a graft copolymer, which has its flexibility improved by the addition of a chain extender. Thermal and DMA analysis of sisal/polystyrene composites was studied in our research group and showed that the T_g values of composites are lower than that of unreinforced PS.[20] Mechanical properties and viscoelastic behavior of Basalt fiber–reinforced PP have been investigated by Botev et al.[21] The effect of compatibilizer on the structure–property relationships of kenaf-fiber/polypropylene composites has been investigated by Feng et al.[22] They found that better adhesion between polymer matrix and kenaf resulted in the blends having an increased temperature modulus.

In the present study, banana and sisal fibers were selected to hybridize and reinforce a polyester matrix to develop cost-effective, high-performance composites. The intrinsic properties of banana and sisal fibers are given in Table I, which are taken from the literature. Fibers having high cellulose content and low microfibrillar angle possess high tensile properties. The cellulose contents of both of these fibers are almost the same. However, banana fiber has a microfibrillar angle of 11°, which is less compared to sisal (20°). Hence, the inherent tensile properties of banana fiber are higher than sisal. The spiral angle, as well as lumen size, of sisal fiber is higher than banana, which causes high impact strength in sisal–reinforced composites. Therefore, banana and sisal fibers can be selected to hybridize and reinforce polyester and a combination of properties of both the fibers can be achieved in the hybrid composites. Short randomly oriented banana/sisal hybrid fiber polyester composites, having a volume ratio of banana and sisal of 1 : 1, were prepared at a total volume fraction of 0.40 and their mechanical performance under dynamic conditions was studied The effect of layering patterns such as bilayer (banana/sisal), trilayer (banana/sisal/banana and sisal/banana/sisal), and intimate mix composites on storage modulus, loss modulus, and damping peaks was investigated. Fiber–matrix interaction was analyzed from the dynamic mechanical data.

EXPERIMENTAL

Materials

Banana (*Musa sepentium*) and sisal (*Agave-sisalana*) fibers were obtained from Sheeba Fibers and Handicrafts, Poovancode, Tamilnadu, India. The physical properties of banana and sisal fiber are given in Table I. Isophthalic polyester resin HSR 8131 obtained from M/s. Bakelite Hylam Ltd., Hyderabad, India was used as the matrix. The properties of the resin are given in Table II.

Preparation of composites

Chopped banana and sisal fibers of 30 mm length were used to prepare the composites. A hand lay-up method, followed by compression molding, was adopted for composite fabrication. The curing of polyester resin was done by the incorporation of 1 vol %

TABLE II
Typical Properties of Liquid Resin

Appearance	A clear pale yellow liquid
Viscosity at 25°C (cps) Brookefield viscometer	650
Specific gravity at 25°C	1.11
Typical properties of cured unreinforced resin (specimens cured for 24 h at 30°C followed by postcuring for 4 h at 80°C)	
Tensile strength (MPa)	33
Flexural strength (MPa)	70
Impact strength (kJ/m^2)	9

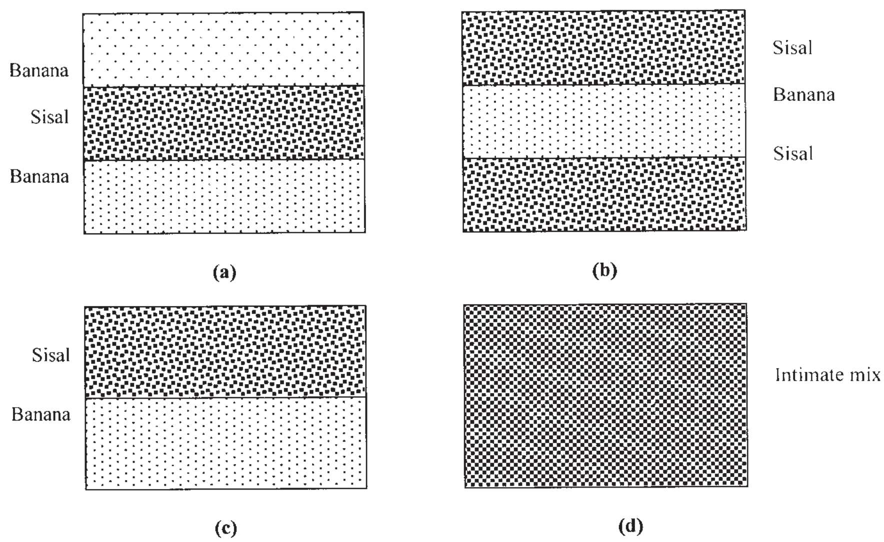

Figure 1 Schematic representation of different layering patterns of hybrid composites (a) banana/sisal/banana, (b) sisal/banana/sisal, (c) bilayer (banana/sisal), and (d) intimate mix.

methyl ethyl ketone peroxide (MEKP) catalyst; 1 vol % cobalt naphthenate (accelerator) was also added. Keeping the combined fiber volume fraction as 0.40 and the volume ratio of the two fibers as 1 : 1; intimately mixed, trilayer (banana/sisal/banana and sisal/banana/sisal), and bilayer (banana/sisal) composites were prepared. A sketch of the different configurations is given in Figure 1. Mats of chopped fibers were prepared, air dried at 50°C for 5 h, and impregnated with polyester resin in a mold having dimensions of 150 mm × 150 mm × 3 mm. Curing was done at room temperature for 24 h under a constant pressure of 1 MPa. To prepare different layering patterns, different layers of mats were prepared separately, placed together, and then impregnated with the resin. Neat polyester samples (polyester resin cured with MEKP and cobalt naphthenate, without incorporating fibers) were also prepared.

Tensile measurements

The tensile measurements of banana and sisal fibers were carried out in an FIE universal testing machine with a gauge length of 30 mm and cross-head speed of 1 mm/min. 30 samples were tested and the average properties were calculated. The diameter of the fibers was also measured using a Leica (DMLP) polarizing light microscope. The diameter of banana fiber is less than that of sisal, which can be observed in Table III.

Dynamic mechanical analysis

Rectangular specimens having dimensions of 60 mm × 10 mm × 3 mm were used for the dynamic mechanical experiments. A dynamic mechanical thermal analyzer, NETZSCH DMA 242, was used for the evaluation of dynamic moduli and mechanical damping (tan δ). Three point-bending modes were used. The temperature range over which properties were measured was 30–150°C at a heating rate of 5°C/min. The tests were carried out at frequencies of 2, 20, and 50 Hz.

RESULTS AND DISCUSSION

Dynamic mechanical properties of fiber-reinforced composites depend on the nature of the matrix material and the distribution and orientation of the reinforcing fibers and the nature of the fiber–matrix interfaces and of the interphase region. Even a small change in the chemical and physical nature of the fiber for a given matrix may result in notable changes in the overall dynamic mechanical properties of composites.

Effect of layering pattern on storage modulus (E')

Fillers have an active role in increasing the modulus of polymeric materials. Figure 2 shows the effect of layering patterns on the storage modulus values with temperature of the hybrid composites at a frequency

TABLE III
Tensile Properties and Diameter of Banana and Sisal Fiber

Property	Sisal fiber	Banana fiber
Tensile strength (MPa)	350 ± 7	550 ± 6.7
Youngs modulus (GPa)	12.8	20
Elongation at break (%)	6–7	5–6
Diameter (μm)	205 ± 4.3	120 ± 5.8

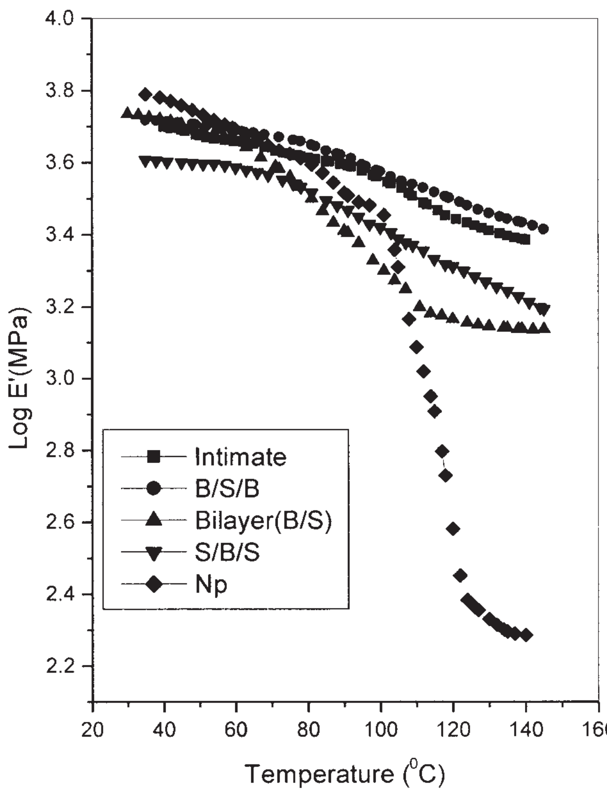

Figure 2 Effect of layering pattern with temperature on storage modulus of the hybrid composites at a frequency of 20 Hz.

of 20 Hz. The storage modulus of neat polyester (Np) can also be seen in Figure 2. In all cases storage modulus was found to be decreased with temperature. At low temperature the E' values of the matrix and the composites are very close, i.e., at low temperature fibers do not contribute much to imparting stiffness to the material. In the case of the neat polyester sample, there was a sharp fall in E' on passing through the glass transition temperature (T_g), due to the increased molecular mobility of the polymer chains above T_g. The drop in the modulus on passing through the glass transition temperature was dramatically reduced for reinforced composites compared to the neat resins, which shows the greater reinforcing effect of banana and sisal fiber on the modulus above T_g than below it. This can be attributed to the combination of the hydrodynamic effects of the fibers embedded in the viscoelastic medium and to the mechanical restraint introduced by the fibers at high concentrations, which reduce the mobility and deformability of the matrix.[23] The dynamic modulus curves of the filled systems showed a higher E' value than the unfilled sample above the T_g region in the rubbery plateau. B/S/B represents a trilayer composite having banana as the skin and sisal as the core material and S/B/S represents a trilayer composite having sisal as the skin and banana as the core material. Intimately mixed composites and bilayer composites can also be seen. B/S/B and intimately mixed composites had almost the same values of E' at T_g. But, above T_g, the E' value was slightly greater in B/S/B. The effectiveness of fillers on the moduli of the composites can be represented by a coefficient C[24] as

$$C = \frac{(E'_G/E'_R)\ \text{composite}}{(E'_G/E'_R)\ \text{resin}} \tag{1}$$

where E'_G and E'_R are the storage modulus values in the glassy and rubbery region, respectively. The higher the value of the constant C, the lower the effectiveness of the filler.

The measured E' values at 45 and 130°C (for polyester) were employed as E'_G and E'_R, respectively. The values of C obtained for different composites are given in Table IV. The value of C is minimum for B/S/B and intimate mix composites. The value of C is maximum for the bilayer composite. The high stiffness of these composites (B/S/B and intimately mixed) is in agreement with their tensile properties reported in our earlier studies.[25] Above T_g, the E' value of S/B/S was comparatively lower than B/S/B and intimately mixed composites. The E' value of the bilayer composite was very low compared to the others, showing more molecular motions in it and poor stress transfer between fiber and matrix. Since sisal has lower tensile properties compared to banana (Table III), the stiffness of the composite will be decreased when sisal is used as the skin material. Since the diameter of sisal fiber is less than that of banana fiber, the surface area of the

TABLE IV
Tan δ Peak Height and Peak Width, Coefficient (C), Tanδ_{max}, (T_g), E''_{max} (T_g), and Activation Energy of Different Layering Patterns

Composite	(C)	Tan δ peak height (cm)	Tan δ peak width (cm)	T_g from tan δ_{max} at 20 Hz (°C)	T_g from E''_{max} at 20 Hz (°C)	Activation energy (kJ/mol)
Gum	—	12	2.5	106	100	53
Bilayer	0.7	6.5	3.7	99	84.9	48
B/S/B	0.65	2.7	5.4	123	110.5	65
S/B/S	0.67	3.3	5.6	117	104	54
Intimate mix	0.65	2	5.6	122	114	68

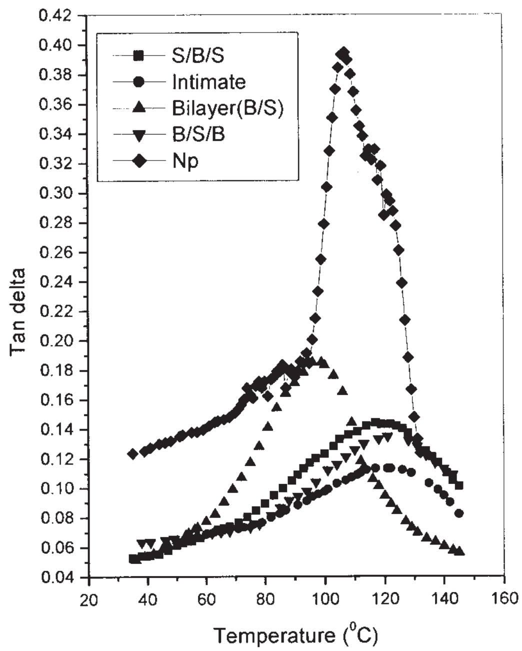

Figure 3 Effect of layering pattern with temperature on tan δ values of the hybrid composites at a frequency of 20 Hz.

fiber per unit area of the composite is less in the case of sisal. Hence, stress transfer between the fiber and matrix is decreased.

Effect of layering pattern on the mechanical loss factor (tan δ) with temperature

The variation of tan δ values of the above composites with temperature at a frequency of 20 Hz is given in Figure 3. It was observed that the tan δ peak obtained at 106°C (T_g) of the unfilled sample was very high. It is associated with the glass transition of polyester resin. With the incorporation of fibers, the tan δ peak was lowered as expected. This is due to the decrease in volume fraction of the matrix by the incorporation of fibers. The peak height and peak width values are given in Table IV. A wider and lower tan δ peak was obtained for intimately mixed composites. When fibers are intimately mixed with each other, better dispersion takes place and stress is transferred from fiber to matrix easily without the failure of the matrix.[26] In B/S/B, the peak height was slightly higher, but peak width was closer to the intimately mixed composite. The peak height of the bilayer composite was found to be very high and its peak width was very small. This indicates poor fiber/matrix adhesion and is consistent with its E' values. The positive shift in T_g value shows the effectiveness of the fiber as a reinforcing agent. Elevation of T_g is taken as a measure of interfacial interaction. The T_g values are given in Table IV. B/S/B and intimately mixed composites showed the highest values of T_g with S/B/S and bilayer composites following. The shifting of T_g of polyester to higher temperatures is associated with the decreased mobility of the polymer chains due to their interaction with the fibers.

Effect of layering pattern on loss modulus (E'') with temperature

The loss modulus (E'') is a measure of the viscous response of the material, which indicates the energy dissipated by the system. The effect of temperature on the loss modulus of the neat polyester sample as well as the composites at a frequency of 20 Hz can be observed in Figure 4. The maximum heat dissipation occured at the temperature where E'' was maximum, indicating the T_g of the system.[27] Above T_g, the E'' value of B/S/B was the highest and that of the bilayer was the lowest. The effect of filler was prominent above the glass transition temperature in this case also. The E''_{max} (T_g) of the different composites can be seen in Table IV. The highest T_g is observed for the intimately mixed composite, followed by B/S/B, S/B/S, and bilayer composites.

Effect of frequency

The viscoelastic properties of a material are dependent on temperature, time, and frequency. The storage

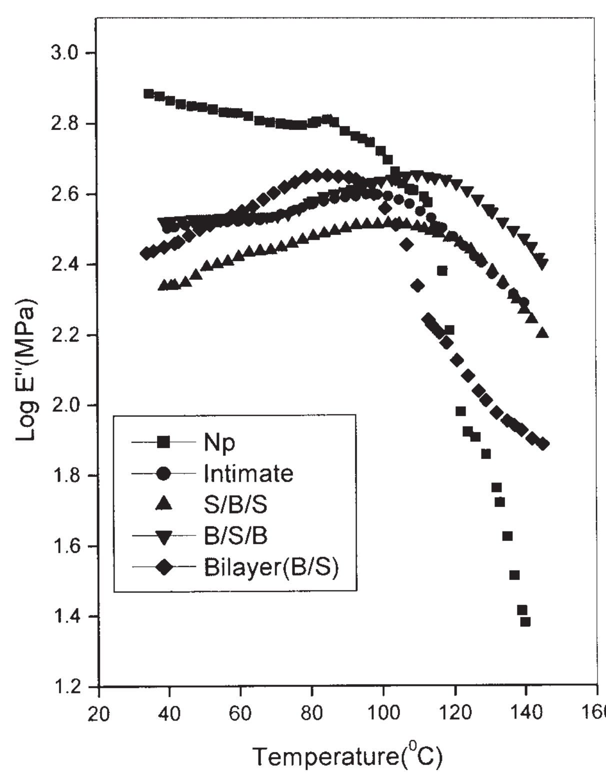

Figure 4 Effect of layering pattern with temperature on loss modulus values of the hybrid composites at a frequency of 20 Hz.

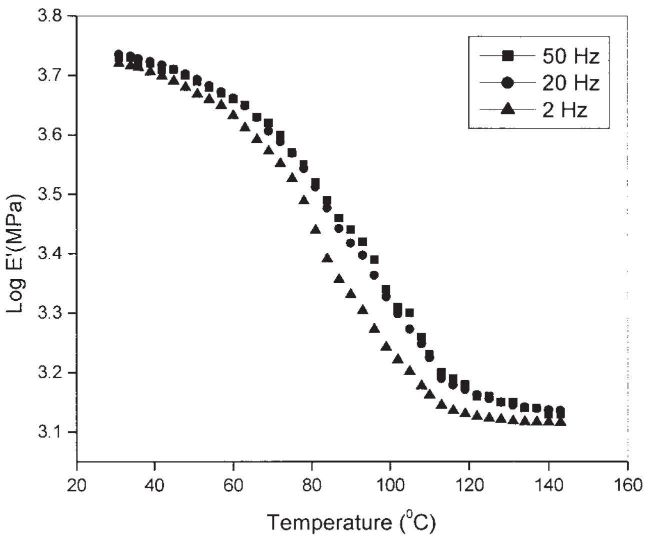

Figure 5 Effect of frequency on storage modulus with temperature of bilayer composite.

modulus, damping peak, and loss modulus are affected by frequency. Figure 5 shows the effect of frequency on storage modulus of the bilayer composite as a function of temperature The modulus values were found to be decreased from 60 to 130°C. It can be observed that there was an increase in storage modulus with increase in frequency, which was more prominent when the frequency was increased from 2 to 20 Hz; after that the modulus value remained unchanged. Modulus measurements performed over a short time (high frequency) result in higher values, whereas measurements performed over long times (low frequency) result in lower values. This is due to the fact that the material undergoes molecular rearrangement in an attempt to minimize the localized stresses.[28] The tan δ values were also affected by frequency. Figure 6 represents the effect of frequency on tan δ of the trilayer (B/S/B) composite. The tan δ peak was shifted to a higher temperature with increase in frequency. The damping peak is associated with the partial loosening of the polymer structure so that groups and small chain segments can move. The tan δ peak, which is indicative of the glass transition temperature, is also indicative of the extent of crosslinking of the system.

Energy of activation for glass transition temperature

The activation energy, ΔE, for the glass transition of the composites can be calculated from the Arrhenius equation

$$f = f_o \exp(-\Delta E/RT) \quad (2)$$

where f is the measuring frequency, f_o is the frequency when T approaches infinity, and T is the temperature corresponding to the maximum of the tan δ curve. Activation energy of the neat polyester sample and the hybrid composites are given in Table IV. Activation energy of the neat polyester sample is only 53 kJ/mol. Intimately mixed and B/S/B showed the highest activation energies, followed by S/B/S and bilayer. This result is also in agreement with the extent of reinforcement.

Cole –Cole plots

The magnitude of polarization within a material is represented by the dielectric constant, which can be represented by the Debye and Onsagar equations.[29] The single relaxation peaks are inadequate to describe the viscoelastic response of polymers. Cole–Cole is a particular treatment of dielectric relaxation data obtained by plotting E'' against E', each point corresponding to one frequency. Structural changes taking place in crosslinked polymers after fiber addition to polymeric matrices can be studied using the Cole–Cole method. The dynamic mechanical properties when examined as a function of temperature and frequency are represented on the Cole–Cole complex plane.

$$E = f(E') \quad (3)$$

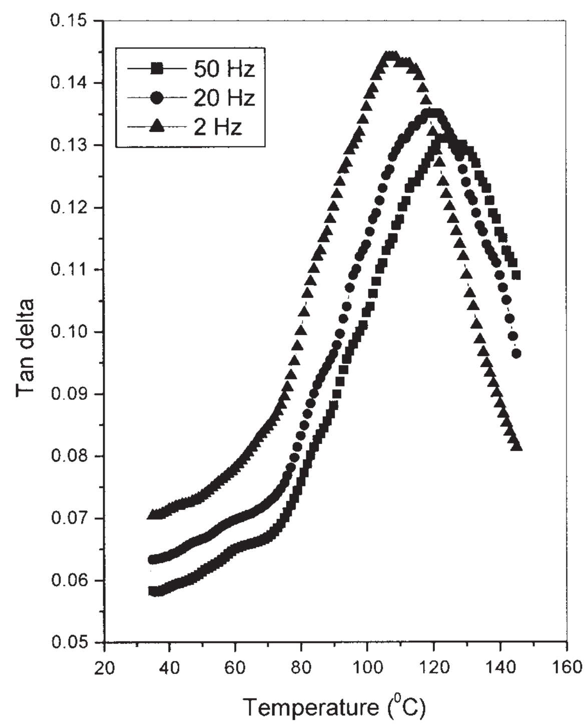

Figure 6 Effect of frequency on tan δ values with temperature of banana/sisal/banana composite.

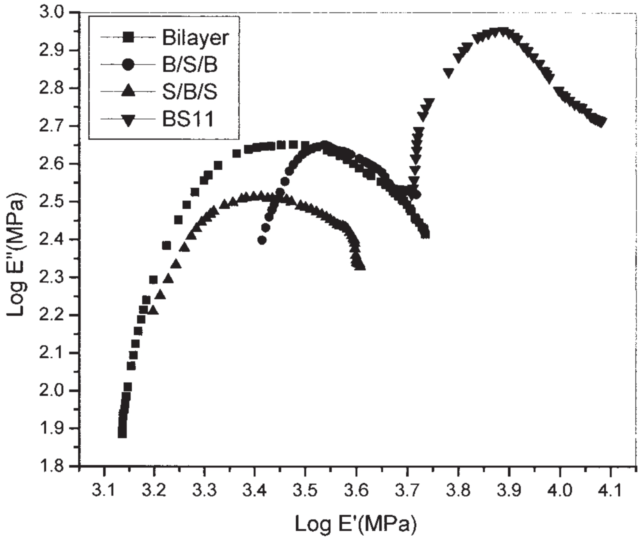

Figure 7 Cole–Cole plots of the hybrid composites having different layering patterns.

Figure 7 shows the Cole–Cole plot, where the loss modulus data log E'' are plotted as a function of storage modulus E'. The nature of the Cole–Cole plots is reported to be indicative of the homogeneity of the system: homogeneous polymeric systems are reported to show a semicirclular diagram.[30] The Cole–Cole diagram of different layering patterns shown in Figure 7 are imperfect semicircles. However, the shape of the curve points toward the relatively good fiber–matrix interaction.

CONCLUSIONS

Dynamic mechanical analysis of short randomly oriented banana/sisal hybrid fiber–reinforced polyester composites was investigated with special reference to different layering patterns of the composites. The effect of temperature and frequency on storage modulus (E'), mechanical damping (tan δ), and loss modulus (E'') was studied by keeping the relative volume fraction of banana and sisal 1 : 1 and the total fiber loading to a 0.40 volume fraction. Above T_g, the storage moduli of the composites were very high compared to neat polyester. The trilayer composite, in which banana was used as the skin and sisal as core material, showed maximum stiffness. The storage modulus of the intimate mix composite is comparable with the composite having banana as the skin material. The bilayer composite showed maximum damping property. Activation energy for the glass transition of neat polyester and composites was evaluated and it was found that intimately mixed and B/S/B had the higher activation energies. Finally, we add that, by hybridizing banana and sisal, we can prepare user-friendly and cost-effective composite materials possessing appropriate stiffness and damping behavior for tailor-made applications. The Cole–Cole plot was constructed and showed good fiber–matrix adhesion.

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