Dynamic Mechanical Analysis of FRP Composites Based on Different Fiber Reinforcements and Epoxy Resin as the Matrix Material

P. GHOSH,[1] N. R. BOSE,[2] B. C. MITRA,[3] S. DAS[3]

[1] Department of Polymer Science & Technology, Calcutta University, 92 Acharya Prafulla Chandra Road, Calcutta—700009, India

[2] Central Glass and Ceramic Research Institute, Calcutta—700032, India

[3] Indian Jute Industries Research Association, Calcutta—700088, India

Received 16 July 1996; accepted 2 December 1996

ABSTRACT: Three-ply composite laminates prepared from E-glass or N-glass chopped strand mats (CSMs) and jute (J) fabrics as reinforcing agents and amine-cured epoxy resin as the matrix material were subjected to dynamic mechanical thermal analysis at a fixed frequency of 1 Hz over a temperature range of 30–180°C. The volume fraction of fibers ranged between 0.21 and 0.25. The reinforcing effect for the three fibers is in the order E-glass > N-glass ≫ jute. Glass-reinforced composites show a higher storage modulus (E') than that of jute-reinforced composites. The E' values of glass–jute hybrid composites lie between those of glass-reinforced and jute-reinforced composites. Odd trends in temperature variability of the loss modulus (E'') and the damping parameter, tan δ, and in the glass transition temperature (T_g) for the three different unitary and four different hybrid composites are interpreted and understood on the basis of odd differences in (1) the chemical nature and physical properties of the three different fibers (E-glass, N-glass, and jute), (2) the void content and distribution, (3) the thermal expansion coefficients of the main phases in the composites, (4) the degree of matrix stiffening at or near the fiber–matrix interface, and (5) the extents of matrix softening in the zone next to the interface. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2467–2472, 1997

Key words: FRP composites; dynamic mechanical analysis of composites; glass fiber–jute fiber hybrid composites; epoxy resin matrix

INTRODUCTION

Dynamic mechanical analysis (DMA) at a selected fixed frequency over a range of temperature has grown as a useful analytical technique[1–5] for characterization of polymeric materials—homopolymers, copolymers, blends, and composites—and their evaluation for consideration in stress- and safety-sensitive applications. Such studies enable the determination of the temperature dependencies of the dynamic moduli, stress relaxation, mechanical loss, and damping phenomena. Data and information generated may then be employed as a means of fingerprinting polymer systems and for locating glass transition and associated features. Dynamic mechanical thermal analysis (DMTA) also enables one to investigate the phase structure and morphology and to draw useful conclusions about the state of the matrix polymer and odd physicochemical effects includ-

Correspondence to: P. Ghosh.

Table I Compositions and Some Properties of Oven-dry E-glass, N-glass, and Jute (J) Fibers Used in Making Composites

Constituents	Fiber: E-Glass	Fiber: N-Glass	Constituents	Fiber: Jute
Chemical composition (wt %)				
SiO_2	54.30	68.41	α-Cellulose	60.70
Al_2O_3	15.20	5.22	Lignin	12.50
CaO	17.20	7.12	Hemicellulose	23.14
MgO	4.70	0.19	Fats and waxes	1.00
Na_2O	0.60	7.84	Ash	0.79
K_2O	—	3.46	Nitrogenous matter	1.87
B_2O_3	8.00	6.25		
Others	—	1.51		
Properties of fibers				
Specific gravity	2.54	2.50		1.30
Tensile strength (MPa)	1500–3400	1000–3000		442
Specific tensile strength (MPa)	590–1348	400–1200		340
Tensile modulus (GPa)	70–80	60–70		56
Specific tensile modulus (GPa)	27–30	24–28		43
Price (Rs./kg) (glass CSM and jute fabric)	170	120		25

ing the development of transcrystalline morphology at the fiber–matrix interface for thermoplastic matrix systems and modification of the network structure for FRP composites based on thermosets.

Reports on DMTA studies on E-glass fiber-reinforced epoxy resin-based composites are available.[1,2] Results on similar studies for N-glass fiber-reinforced or jute fiber-reinforced composites and for jute fiber–glass fiber hybrid composites based on epoxy resin as the matrix material are reported in the present article.

EXPERIMENTAL

Materials

E-glass chopped strand mat (CSM) was supplied by FGP Limited, India. N-glass CSM was prepared in our laboratory (CGCRI, Calcutta) and woven jute fabric was obtained from the local market. Chemical composition, some physical properties, and the present price level of E- and N-glass CSMs and of jute fabric used are shown in Table I. G, J, E, and N symbolize glass in general, jute, E-glass, and N-glass, respectively.

Epoxy resin, viz., diglycidyl ether of bisphenol A (DGEBA), and a relevant curative, triethylene tetramine (TETA), were obtained from Hindustan Ciba Geigy Ltd. TETA was used to the extent of 15% of DGEBA.

Methods

Composite Making

For improved adhesion with the epoxy resin matrix, the two glass fibers used were pretreated with a silane coupling agent (γ-methacryloxypropyl trimethoxy silane, grade A174 from Union Carbide, USA), and jute fabric was used after defatting following established procedures.[6,7]

Different 3-ply combinations of E-glass CSM, N-glass CSM, and jute (J) fabric having top, middle, and bottom fiber layers for three unitary composites designated as EEE, NNN, and JJJ and for four glass–jute hybrid composites designated as EJE, NJN, JEJ, and JNJ were used for reinforcing the epoxy resin matrix. A hand-lamination technique was employed in each case. The green laminate was squeezed between two Mylar films using a pressure of a hand roller so as to minimize voids and to avoid accumulation of excess matrix resin as far as possible.

The hand-pressed laminates free from excess resin were allowed to cure for 72 h at room temperature (30°C) and finally postcured in an oven

Table II Composite Code for 3-Ply Laminates Showing Volume Fraction of Fiber Used, Flexural Properties, and Temperatures Corresponding to E''_{max} and tan δ_{max}

	Composite Number and Code[a]			Volume Fraction (× 100) of Fiber in Composite			Flexural Data[b]		Temperature (°C)		
				Glass	Jute	Total	FS (MPa)	FM (GPa)	E''_{max}	tan δ_{max}	ΔT[c]
1	Cured epoxy resin (unreinforced)			—	—	—	80.8	2.6	128	135	7
2	E	E	E	25.5	—	25.5	178.7	7.6	115	118	3
3	N	N	N	25.8	—	25.8	167.5	6.6	118	123	5
4	J	J	J	—	23.5	23.5	82.4	3.6	128	135	7
5	E	J	E	11.80	9.4	21.2	161.6	5.7	128	130	2
6	N	J	N	12.0	9.4	21.4	144.7	5.4	118	122	4
7	J	E	J	6.7	15.0	21.7	84.8	3.9	128	132	4
8	J	N	J	6.8	15.0	21.8	88.9	4.3	115	118	3

[a] E = E-glass CSM, N = N-glass CSM, and J = jute fiber providing the reinforcements.
[b] FS = flexural strength; FM = flexural modulus.
[c] Difference between temperatures under columns 7 and 8.

at 80°C for 4 h and 100°C for 2 h. Test pieces of 60 × 12 mm size (thickness varying between 2 and 4 mm) were cut out from the laminates for dynamic mechanical analysis. The weight percentage or volume fraction of the fiber mats or fabrics in the composites was calculated considering the specific gravity of each material and area density data of mats and fabrics and of the trimmed laminates.

Dynamic Evaluation

A DuPont dynamic mechanical analyzer (Model 983) was employed for dynamic evaluation of the FRP test pieces using a fixed frequency (1 Hz) over a temperature range of 30–180°C (303–453 K) in an atmosphere of N_2.

RESULTS

The composite codes and volume fraction of fibers used in each composite are shown in Table II.

Storage Modulus (E') and Loss Modulus (E'')

Variations in E' and E'' values with variation of temperature (30–180°C) are shown in Figures 1 and 2. Plots in Figure 1 clearly reveal that the room temperature (30°C) value for the storage modulus (E') of the epoxy matrix resin (curve 1) is enhanced by more than 200% on reinforcement with glass fiber CSMs, the enhancement being distinctly higher for use of E-glass CSM (laminate EEE, curve 2) than for use of N-glass CSM (laminate NNN, curve 3) as the reinforcement. En-

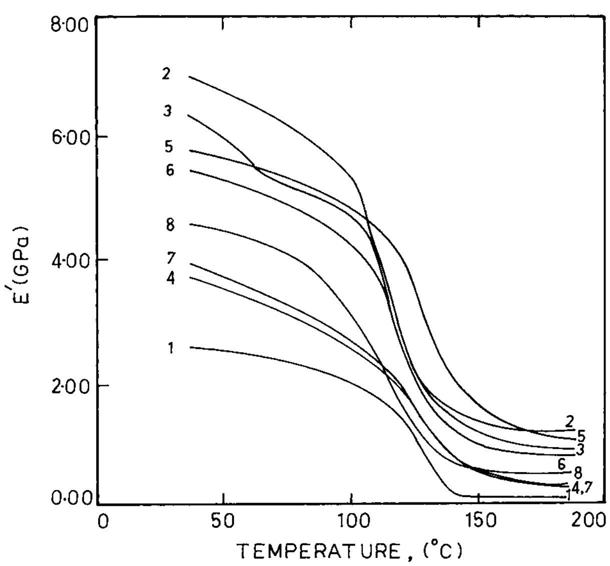

Figure 1 Plots of storage modulus, E', vs. temperature, °C, for cured epoxy resin (curve 1) and relevant 3-ply composite laminates: (curve 2) EEE; (curve 3) NNN; (curve 4) JJJ; (curve 5) EJE; (curve 6) NJN; (curve 7) JEJ; (curve 8) JNJ.

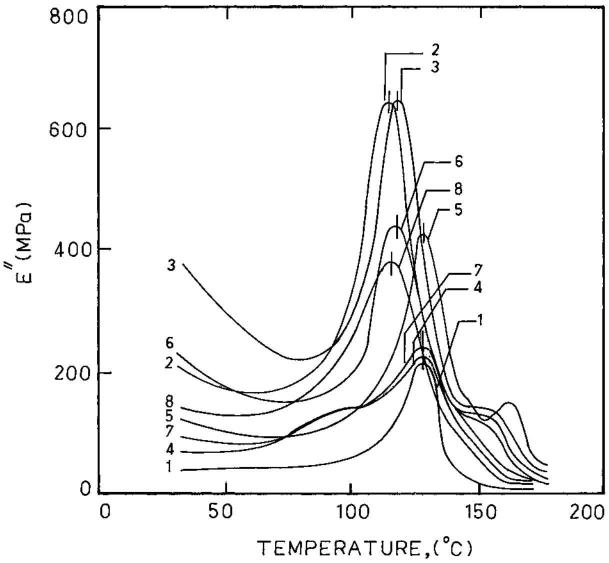

Figure 2 Plots of loss modulus, E'', vs. temperature, °C, for cured epoxy resin and relevant 3-ply composite laminates (identity of curves as in Fig. 1).

hancement in the E' value for use of only jute (J) fabric as the reinforcement (laminate JJJ, curve 4) is, however, far lower in comparison. For the glass–jute hybrid FRP composites (curves 5–8), the room temperature E' values lie between those of the glass fiber-reinforced composites (EEE or NNN) and the jute fiber-reinforced composite (JJJ). It is interesting to note that for use of a single middle layer of glass CSM with two outer layers of jute fabric, on the one hand, and for use of one middle layer of jute fabric with two outer layers of glass CSM, on the other, the trend of variation in the E' value of the composite over the useful temperature range (30–140°C) becomes prominently reversed as the selection of the glass fiber is switched over from E-glass to N-glass. Thus, for use of a glass CSM in the middle layer (i.e., for the composite designated JGJ), N-glass appears more effective than does E-glass in enhancing the E' value of the composite laminate, while for use of jute fabric in the middle layer (laminate designated GJG), E-glass CSM (producing laminate EJE) appears more effective than does N-glass CSM (giving laminate NJN) in improving the E' value over the useful temperature range.

Figure 2 shows trends of variation of the loss modulus (E'') for the different composite laminates with variation of temperature. Differences in storage and loss modulus values and in the trend of their temperature variability are very narrow or marginal between laminates JJJ and JEJ (curves 4 and 7, respectively, in Figs. 1 and 2). Thus, replacement of the middle layer of jute fabric in the JJJ laminate by a layer of E-glass CSM (to give JEJ laminate) produces a marginal property advantage; moreover, the replacement deserves little justification considering the much higher price and density of E-glass in comparison with jute fiber (Table I). The observed values of E''_{max} appearing over the temperature range 115–128°C for the composite laminates are in the order EEE $\approx$ NNN $\gg$ NJN $>$ EJE $>$ JNJ $\gg$ JEJ $\geq$ JJJ. E''_{max} is the lowest for the unreinforced cured epoxy resin. In comparing the use of E-glass and N-glass in the glass–jute hybrid composites, the temperature of E''_{max} is 10–14°C higher for the use of E-glass. Starting with the NNN laminate, replacement of one layer or even two layers of N-glass CSM by jute fabric in the making of the 3-ply hybrid laminates as in Table II does not cause much of a shift in the temperature of E''_{max}, even though the peak E'' value follows a decreasing trend as glass (CSM) layers are taken off successively and correspondingly replaced by jute fabrics (Fig. 2). Considering the peak E'' value and the temperature at which the peaks appear for comparable hybrid composites (Fig. 2), it is apparent that N-glass lends a more controlling influence than does jute in the N-glass–jute hybrid laminates while jute imparts a greater controlling influence in the E-glass–jute hybrid laminates.

Mechanical Damping Parameter (tan δ)

Trends of change in the variation of the mechanical damping parameter tan δ ($= E''/E'$) with variation of temperature for the different composite laminates are shown in Figure 3. The temperature corresponding to the (primary) peak for each composite laminate and for the cured epoxy resin shown in Figures 2 and 3 indicates a glass transition point (T_g) for the resin matrix in the system. In each case, the T_g value indicated from the damping parameter peak (tan δ_{max}) is higher[8] than that indicated from the corresponding loss modulus peak (E''_{max}) (Table II). The temperature difference (ΔT) between E''_{max} and tan δ_{max} for a given composite/material system is minimum (2°C) for the laminate EJE and maximum (7°C) for the unreinforced cured epoxy resin and for the JJJ laminate. In tune with common experience, the temperatures for $(dE'/dT)_{max}$ and E''_{max} for each composite material coincide with one another (Figs. 1 and 2).

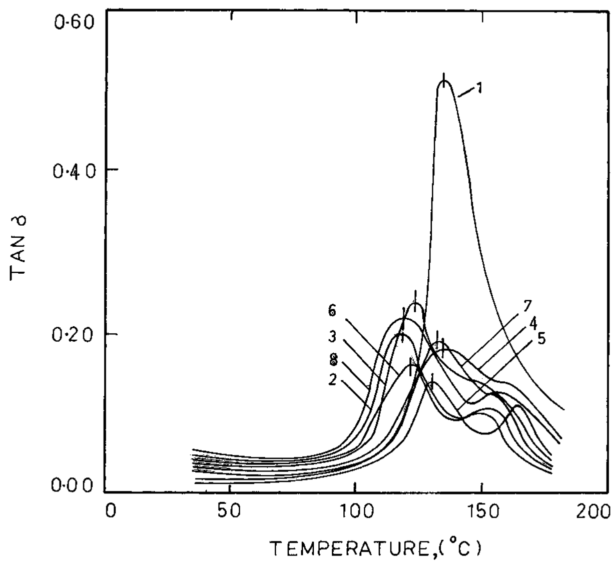

Figure 3 Plots of tan δ vs. temperature, °C, for cured epoxy resin and relevant 3-ply composite laminates (identity of curves as in Fig. 1).

Figure 3 clearly indicates that the relatively high viscoelastic damping character (tan δ value) for the cured epoxy resin becomes substantially lowered[5] on reinforcement with glass and jute fibers in the order jute > E-glass > N-glass. Among the different glass–jute hybrid composite laminates, minimum damping is given by the EJE hybrid composite laminates. Use of jute fiber contributes to a lowering in the damping character in general. Hybrid composites based on E-glass CSM produce a measurably lower intensity of damping than do corresponding composites based on N-glass CSM, apparently due to the higher inherent stiffness (modulus) character of E-glass and, consequently, a higher degree of stiffening of the matrix in its presence.

Glass Transition Temperature (T_g)

Accepting that E''_{max} rather than tan δ_{max} is a closer indicator[8] of T_g and judging from the E''_{max} temperatures (Fig. 2 and Table 2), it is clear that the T_g value of the unreinforced cured epoxy matrix resin (128°C) remains practically unchanged in the composite laminate if only jute or jute–E-glass combinations are used as the reinforcing agent. Use of only glass (E- or N-glass) or jute–N-glass combinations as fiber reinforcements, however, causes a lowering in the T_g value by about 10–14°C, thus expectedly infusing an enhanced toughening effect.

DISCUSSION

Properties of FRP composites, more importantly, their dynamic properties, are likely to depend as much on the nature and distribution of the matrix materials and the reinforcing fibers as on the nature of the fiber–matrix interfaces and of the interfacial regions. Even a small change in the chemical and physical nature of the fiber for a given matrix resin and in relative weight proportions of the fiber and matrix may result in notable changes in the overall properties of the composite. The observed odd differences in the dynamic properties of the 3-ply unitary composites based on E-glass CSM, N-glass CSM, and jute fabric and of the hybrid composites based on different glass–jute combinations for epoxy resin providing the matrix must be viewed in the light of the above considerations. Between E-glass and N-glass, each having a coat of the same coupling agent that ensured nearly comparable compatibilizing interactions between the outer part of the layer of the coupling agent and the matrix resin, the interactions and nature of anchorage between the inner part of the layer of the coupling agent and the outer surface of the E- or N-glass fibers are likely to be measurably different in view of notable differences in the chemical compositions of the two glasses as shown in Table I. Data on the initial mechanical properties (flexural strength and modulus), (Table II and Refs. 9 and 10) on the resistance to hydrothermal degradation under boiling conditions in different chemical environments for E-glass and N-glass fiber-based epoxy and other resin composites indicate that while E-glass fiber produces higher reinforcing effects apparently due to higher inherent strength and modulus of the fiber (Table I) N-glass fiber reinforcement imparts much higher stability to the composites with respect to hydrothermal degradation as reflected from the higher degree of retention of strength and modulus.[9,10] Favorable compositional features of N-glass (much higher SiO_2 and alkali metal contents) foster improved anchorage of the silane coupling agent on the fiber surface and thereby ensure improved fiber–matrix bonding via the coupling agent.

The lignocellulosic fiber jute having been given no coating of a coupling agent and bearing many alcoholic groups, limited (acidic) carboxylic groups, reducing (aldehydic) groups, and phenolic groups provides ample scope for a chemical anchorage of epoxy resin segments on it through reaction with some of these groups present at the fiber surface, the like of which is remotely possible on the glass fiber surfaces. The cellulosic, hemicellulosic, and lignin constituents in the jute fiber, which itself is viewed as a composite material, thus become integral parts of the amine (TETA)-cured epoxy network. As a consequence, the overall modification of the jute–epoxy interface and of the interfacial region of the matrix is such that the jute-reinforced epoxy network composite (volume fraction of jute = 0.24) and the plain epoxy network show nearly comparable or close values for the loss modulus (E'' or $E''_{\max}$ to be more precise) and glass transition temperature (T_g) (Fig. 2 and Table II) while revealing the reinforcing role of jute in the form of relatively high values for the storage modulus (E') and for initial flexural modulus (Fig. 1 and Table II).

The observed odd effects about the dynamic properties of the glass–jute hybrid composites detailed here should be viewed in the light of the differences in the uncertain nature and degrees of interactions at the different fiber–matrix interfaces designed in different odd combinations with respect to selection of the glass CSM type and jute fabric in alternate layers in the 3-ply glass–jute hybrid laminates. Subtle variations in reinforcing fiber selection, layup design, or sequence and processing conditions may lead to odd variations in compatibility zones and the structure buildup of an uncertain presence of voids and odd thermal effects due to differences in the expansion coefficients of the main phases. These features may combine to partly cause odd differences in the dynamic properties of the composites as highlighted by data in Table II and Figures 1–3.

The proximity of the stiff fiber and preferential adsorption of readily diffusible constituents (usually the low molecular weight curatives, such as the amine i.e., TETA used here) on the fiber surface may impose a relatively high crosslink density and hence, lead to the development of a more than expected stiffness level at the fiber–matrix interface. This may at the same time lead to some softening of the matrix in the zone next to the interface due to notable depletion of the amine curative. The differential opposing effects[2] of matrix stiffening and matrix softening as above in different unitary and hybrid composite laminates may also partly explain the odd observed effects in their dynamic mechanical thermal properties. While there is an unmistakable general trend in having a progressively lower loss modulus value with increasing jute content (from GGG through GJG and JGJ to JJJ) in the composite (Fig. 2), the situation is not as clear-cut when changes in the damping parameter (tan δ) is considered even though fiber reinforcement in general causes lowering in the tan δ value of the cohesive mass or the resin matrix.

N.R.B. thanks the Director, C.G. & C.R.I., Calcutta, for encouragement.

REFERENCES

1. J. Milios, V. Kefalas, E. Sidridis and G. Spathis, *Handbook of Ceramic and Composites,* N. P. Cheremisinoff, Ed., Vol. 1, Chapter 6, Marcel Dekker, N.Y., 1990.
2. B. Harris, O. G. Braddel, D. P. Almond, C. Lefebvre and J. Verbist, *J. Mater. Sci.,* **28,** 3353 (1993).
3. M. Akay, *Composite Sci. & Tech.,* **33,** 1 (1988).
4. J. Das, S. Bandyopadhyay and S. Blairs, *J. Mater. Sci.,* **29,** 5680 (1994).
5. C. D. Wingard and C. L. Beatty, *J. Appl. Polym. Sci.,* **41,** 2539 (1990).
6. R. K. Basak, S. G. Saha, A. K. Sarkar, M. Saha, N. N. Das and A. K. Mukherjee, *Textile Res. J.,* **63**(11), 658 (1993).
7. K. L. Lowenstein, *The Manufacturing Technology of Continuous Glass Fibres,* Elsevier, Amsterdam, Oxford, New York, 1983.
8. M. Akay, *Composite Sci. & Tech.,* **47,** 419 (1993).
9. P. Ghosh and N. R. Bose, *J. Mater. Sci.,* **26,** 4759 (1991).
10. P. Ghosh and N. R. Bose, *J. Appl. Polym. Sci.,* **58,** 2177 (1995).