

Mechanical and Dynamic Mechanical Properties of Jute Fibers–Novolac–Epoxy Composite Laminates

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ABSTRACT: A study was done of jute composite using a polymer matrix of epoxidized Novolac resin (ENR), diglycidyl ether of bisphenol A (DGEBA)–based epoxy, and their blends with different weight percentages of the resins. It was found that on blending ENR with DGEBA, the storage moduli at room temperature are enhanced by about 100% or more in the case of 30 and 40% ENR-containing matrices, whereas the enhancement in the case of 20 and 12% ENR-containing matrices is only 50% that of the pure matrix. It was also observed that the $\tan \delta$ peak heights of the composites containing 30 and 40% ENR are closer to that of 20% ENR-containing composite. The probable explanation drawn on the basis of experimental findings of DMA and mechanical analysis is that by blending ENR with DGEBA epoxy it is possible to manufacture jute composites with increased stiffness without sacrificing their ductility. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2800–2807, 2002

Key words: storage modulus; loss modulus; damping coefficient; synergistic effect; fiber–matrix interaction

INTRODUCTION

Epoxy resins have been widely used as engineering plastics because of their high-performance characteristics, such as good mechanical, thermal, and electrical properties. To use epoxy resins properly, it is important to understand their structure–property relationship. A considerable amount of research work has already been done in this field on the relation between the properties of the cured epoxy resins and the structures of the epoxy resin compounds; however, these studies were mostly made on the basis of bisphenol A–type resins using various kinds of hardeners.

Recently, because high-performance epoxy resin is strict in its requirements, polyfunctional

epoxy has been offered in practical fields. In particular, epoxidized Novolac resin (ENR) is largely used as electronic encapsulation material because of its well-known thermal resistance properties. Because the structures of ENR exert a significant influence on the properties of the cured resins, it is necessary to understand their structure–property relationship.

Despite various advantages, epoxy needs modifications to overcome the following disadvantages:

1. Limited solubility in polar solvents.
2. Higher costs because of the cost of bisphenol A.
3. Maximum service temperature of only about 80°C.

From the very beginning of epoxide resin technology research, constant effort has been devoted

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to obtain resin systems that maintain their properties at higher temperature. One approach was to increase the crosslink density in the cured polymer network, either by use of polyfunctional resins having average epoxide content greater than 2% or by using curing agents of higher functionality. The ENR mostly used in practice has 3.6 epoxide groups per molecule ($n = 1.6$ in general formula). Care must be taken that no unreacted phenolic groups remain in the resin because this would limit storage stability and cause volatiles to be evolved during cure. Depending on the cure temperature and the choice of the amine curing agents, strengths as high as 3000 psi at room temperature and over 1000 psi at the range of -55 to 150°C were reported in the literature.¹

On blending ENR with diglycidyl ether of bisphenol A (DGEBA), the essential thermal stability of the ENR resin is preserved, while the crosslinking possibility of the epoxide group can be concomitantly utilized, as seen from the molecular structure of the polyglycidyl ether.^{1,2} Incorporation of more aromatic rings in the chain enhances the thermoresistant profile of the system. Thus such materials partake of the nature of both components and show greatly improved high-temperature performance compared with that of a straight-chain epoxy.

The importance and popularity of fiber-filled (natural or synthetic) epoxy composites are attributed to their unusually high strength and stiffness for a given weight of material. In recent years, greater emphasis has been rendered in the development of fiber-filled epoxy composites based on natural fibers with a view to replace glass fibers, either solely or in part, for various applications. The scope for using jute fibers in place of traditional glass fibers stems from the lower specific gravity and workable specific modulus of the jute fiber (1.45 and 19 GPa, respectively). Moreover, the much lower cost and renewable nature make it an attractive fiber for use as a reinforcing material in the fiber-filled composites. Again the nonabrasive nature of the jute fiber permits higher fiber loading in the composite without the fear of extensive damage to compounding and molding equipment that occurs when much harder glass fiber is used.

For characterization of polymeric materials—homopolymers, copolymers, blends, and composites—and their evaluation for consideration in stress and safety-sensitive applications, dynamic mechanical analysis (DMA) at a selected fixed

frequency over a range of temperature has advanced as an increasingly useful technique.³⁻⁵ Dynamic mechanical tests, in general, give more information than other tests about a composite material. Dynamic tests, over a wide range of temperature and frequency, are especially sensitive to all kinds of transitions and relaxation processes of matrix resin and also to the morphology of the composites. 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 (T_g) and associated features. Dynamic mechanical thermal analysis also enables one to investigate the phase structure and morphology to draw useful conclusions about the state of the matrix polymer and odd physicochemical effects, including 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.

EXPERIMENTAL

Materials Used

1. Novolac resin, obtained from local market (softening point 84°C , by the ring and ball method).
2. Epichlorohydrin, manufactured by S.D. Fine -Chemicals, Ltd., laboratory reagent (LR) grade.
3. NaOH, manufactured by Merck (Darmstadt, Germany), LR grade.
4. Toluene, manufactured by International Chemicals (India), LR grade.
5. Room-temperature aromatic polyamine-based curative EH-400, from SIP Industries Ltd., India.
6. Epoxy resin [diglycidyl ether of bisphenol A (DGEBA), EPG-180], from SIP Industries Ltd., India.
7. Jute fabric from Fort Gloster Jute Mill, Howrah, India.

Preparation of Novolac-Epoxy Resin

A precalculated quantity of Novolac was added to a conical flask fitted with a reflux condenser in an

inert atmosphere, and to which a calculated quantity of epichlorohydrin was added, slow heating with continuous stirring dissolved the Novolac in the solution. Then 40% NaOH was added to the solution over a period of about 3 h, maintaining the temperature at 100°C. After the addition of the total amount of NaOH solution, the mixture was heated for sometime further at 100°C and then cooled down to room temperature. Then the whole viscous mass was taken in a separating funnel and was extracted with toluene (1:1 v/v) by shaking for about 1 h to perform complete extraction of the epoxidized Novolac resin, which was indicated by the conversion of the toluene layer from a clear to a brown viscous liquid. The NaCl crystals were removed by washing the resin with distilled water and dried. The epoxidized Novolac was isolated by evaporating the toluene.

Fabrication of Composite Sheets

A weighed amount of resin (blend of ENR soluble in acetone and DGEBA), admixed with a relevant room-temperature curing aromatic polyamine-based curative, was applied on both sides of jute fabric by hand layup technique. Four layers of green laminates were squeezed between two Mylar films using the 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 at 80°C for 6 h. The volume fraction of fiber was maintained at 30% in all cases. Test pieces of 60 × 12 mm size (thickness 1.7) were cut out from the laminates for DMA.

Mechanical Properties

Tensile testing of the samples was carried out at $25 \pm 0.5^\circ\text{C}$, using a dumbbell-shape test specimen in an Instron Universal Testing machine (model 4301). The specification of the dumbbell is as follows: gauge length, 20 mm; width, 6 mm; and thickness, 1.7 mm with end tabs and loaded with serrated jaw wedge grips. A strain rate of 5 mm/min was used throughout the investigation. In all cases, 12 specimens were tested, and average values are reported.

Dynamic Mechanical Properties

A DuPont dynamic mechanical analyzer (model 983; DuPont, Boston, MA) was employed for dy-

amic 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 AND DISCUSSION

Dynamic Mechanical Analysis

Dynamic storage modulus (E') is the most important property to assess the load-bearing capability of a composite material. The ratio of the loss modulus (E'') to the storage modulus (E') is known as a mechanical loss factor ($\tan \delta$), which quantifies the measure of balance between the elastic phase and the viscous phase in a polymeric structure. This can relate to impact properties of a material. Generally, the $\tan \delta$ peak (at low frequency) is at a temperature 10–20°C above the T_g , as measured by dilatometer or differential thermal analysis (DTA). The temperature of maximum loss modulus E'' is very close to T_g .

Storage Modulus (E')

Figure 1 shows variations in E' values with temperature (30–180°C). The plots clearly reveal that storage modulus of ENR shows 100% enhancement compared to that of DGEBA-based epoxy composite, both reinforced with 30% jute fabric. It is interesting to note that on blending ENR with DGEBA-based epoxy, the storage moduli at room temperature are enhanced by about 100% or more in the case of 30 and 40% ENR-containing matrices, whereas the enhancement in the case of 20 and 12% ENR-containing matrices is only 50% of the pure matrix. On the other hand, the degree of storage modulus loss resulting from thermal transition in the temperature range of 35–100°C is smaller (35%) for jute composites based on only ENR compared to that based on DGEBA-based epoxy resin (90%). It is also evident that the degrees of modulus loss of the jute composites with 40, 30, and 20% ENR are 36, 40, and 40%, respectively, but interestingly it is 60% with 12% ENR. These observations are as expected because the crosslink density of epoxidized Novolac is much higher compared to that of pure epoxy matrix; thus with increasing temperature the slippage is greater in the pure epoxy matrix compared to that in the epoxidized Novolac-based matrix, resulting in higher E' loss.

Storage Modulus vs Temperature

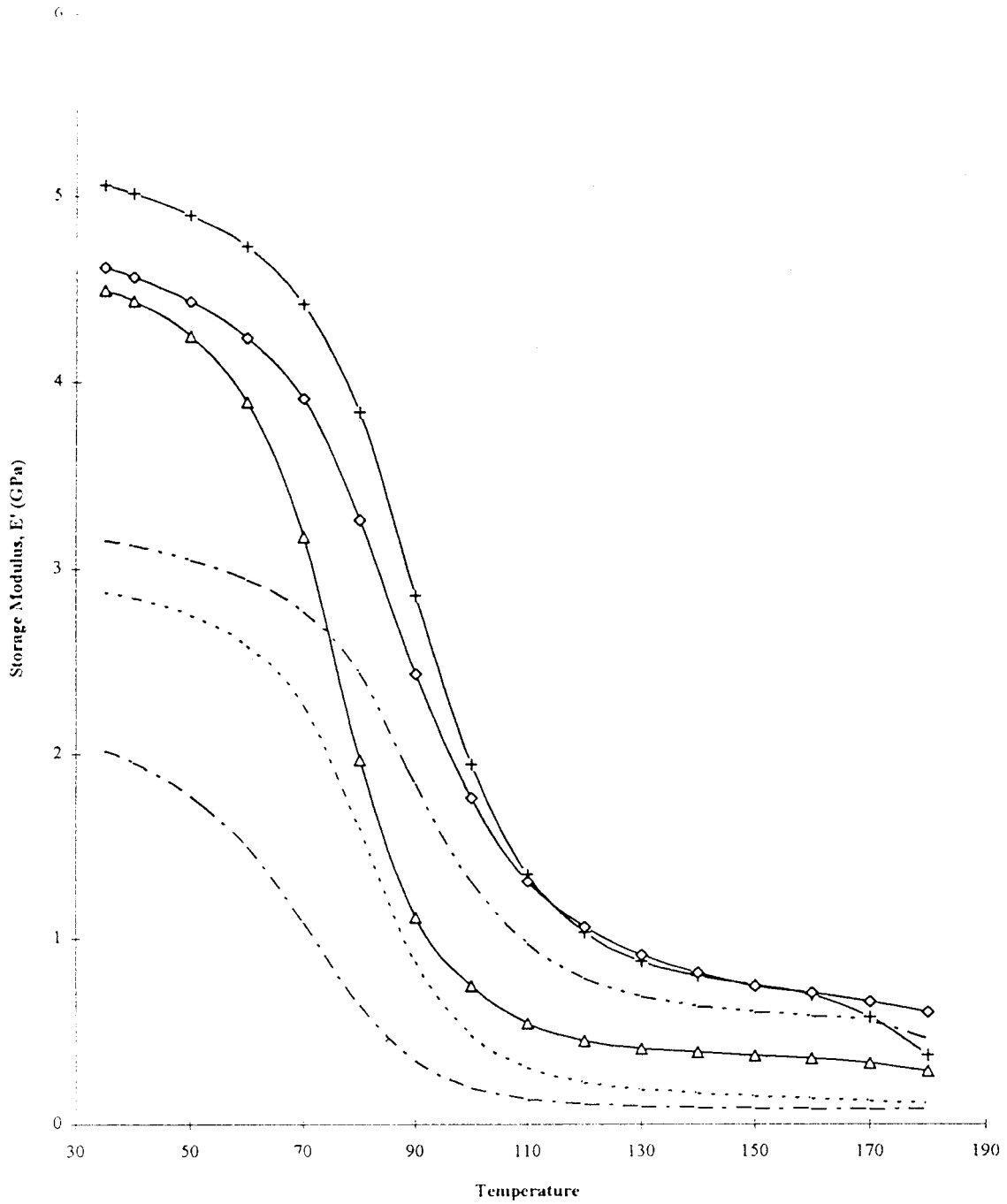


Figure 1 Variation of storage modulus E' with temperature for different percentages of Novolac-epoxy composites: -·-, 0%; - - -, 12%; - · · -, 20%; - + + -, 30%; -◇-, 40%; -△-, 100%.

Loss Modulus (E'')

Figure 2 shows trends of variation of E'' for the different composite laminates with variation of temperature. The maximum heat dissipation occurs at the temperature where E'' is at a maximum, indicating the T_g of the system.⁶ It can be seen that loss modulus peak temperature of DGEBA-based epoxy/jute composite is lower (72°C) compared to that of ENR-based jute composite (81°C).

Again, by blending ENR and DGEBA-based epoxy, the values of loss moduli peaks are shifted toward higher temperatures. It is interesting to note that the jute composites with 12, 20, and 30% ENR have T_g of 88, 97, and 99°C, respectively, whereas 40% ENR-based jute composite has a lower T_g (93°C).

It is evident from these observations that, although ENR offers more rigid networks after curing, its fiber–matrix interaction may be poor compared to that of DGEBA-based epoxy resin. This explains why 40% ENR-based composite has lower stress at maximum load (Table I) and also a lower T_g compared to that of 20 and 30% ENR-based composites. The possible explanation may be the synergistic effect of good fiber–matrix interaction attributed to DGEBA and higher extent of crosslinking to the presence of ENR.

Tan δ

Figure 3 shows tan δ versus temperature plots for different jute composite laminates. It was previously reported^{4–6} that the incorporation of stiff fibers reduces the tan δ peak height by restricting the movement of polymer chains. It is also seen that the tan δ peak heights of jute composites with 12, 20, 30, and 40% ENR are reduced compared to that of pure DGEBA based epoxy/jute composite and only ENR-based jute composite. The tan δ peak height of ENR-based jute composite is smaller than that of DGEBA-based epoxy/jute composite, which is probably the result of the higher crosslinking density of the ENR matrix.

It is observed in many cases that the improvement of stiffness markedly reduces the ductility.^{6,7} However, through blending ENR with DGEBA-based epoxy resin it is possible to manufacture jute composites with increased stiffness without sacrificing their ductility. Thus it is observed that temperatures corresponding to the maximum tan δ of 30 and 40% ENR-based jute composites are closer to that of 20% ENR-based jute composite.

CONCLUSIONS

The lignocellulosic jute fiber, having been given no coating of coupling agent and bearing many alcoholic groups, limited (acidic) carboxylic groups, reducing (aldehydic) groups, and phenolic groups, provides ample scope for chemical anchorage of epoxide group segments on it through reaction with some of these groups present at the fiber surface. 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-cured Novolac–epoxy networks. However, the extent of network formation and the adhesion properties of matrix with the fibers are the major factors for determining overall dynamic properties of the composites.

It is evident from these observations that, even though ENR resin offers more rigid networks after curing, its fiber–matrix interaction may be poor compared to that of DGEBA-based epoxy resin. As a result of this, 30 and 40% ENR-based composites have lower temperatures corresponding to their maximum tan δ peak compared to that of the 20% ENR-containing system. The possible explanation may be the synergistic effect of good fiber–matrix interaction attributed to DGEBA and the higher extent of crosslinking resulting from presence of ENR.

The proximity of the stiff fiber and preferential adsorption of readily diffusible constituents (usually the low molecular weight curative) 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. At the same time this may lead to some softening of the matrix in the zone next to the interface because of the notable depletion of the amine curative. The differential opposing effects⁴ 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.

The observed odd effects about the dynamic properties of blends of epoxy resin–jute-based composites detailed here should be viewed in the light of the differences in the uncertain nature and degrees of interactions at the fiber–matrix interfaces designed in different odd combinations with respect to selection of matrix blend systems. Subtle variations in reinforcing fiber selection, layout design, or sequence conditions may lead to

Loss Modulus vs Temperature

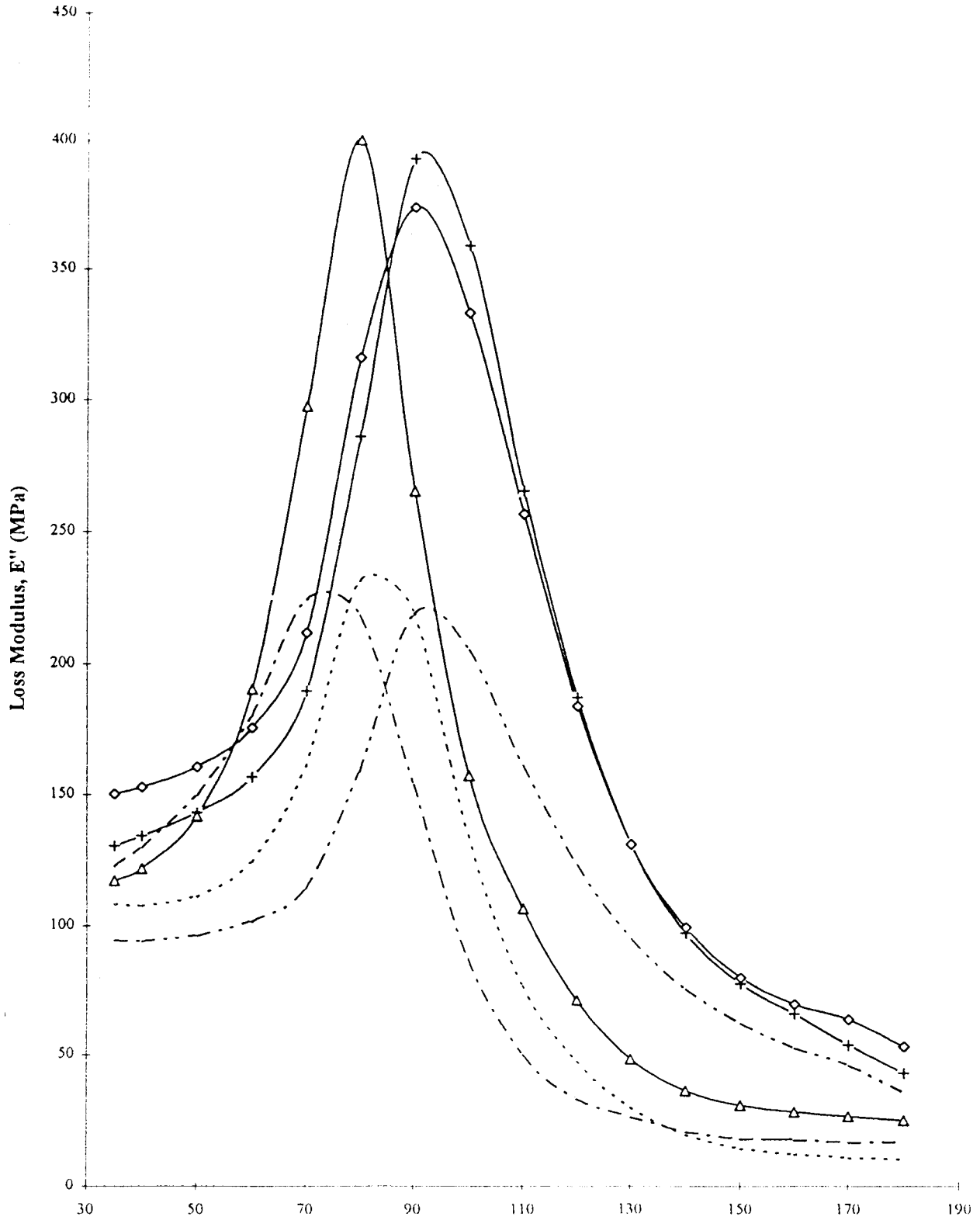


Figure 2 Variation of loss modulus E'' with temperature for different percentages of Novolac-epoxy composites: \cdots , 0%; $---$, 12%; $-\cdot-$, 20%; $+-$, 30%; $-\diamond-$, 40%; $-\triangle-$, 100%.

Tan Delta vs. Temperature

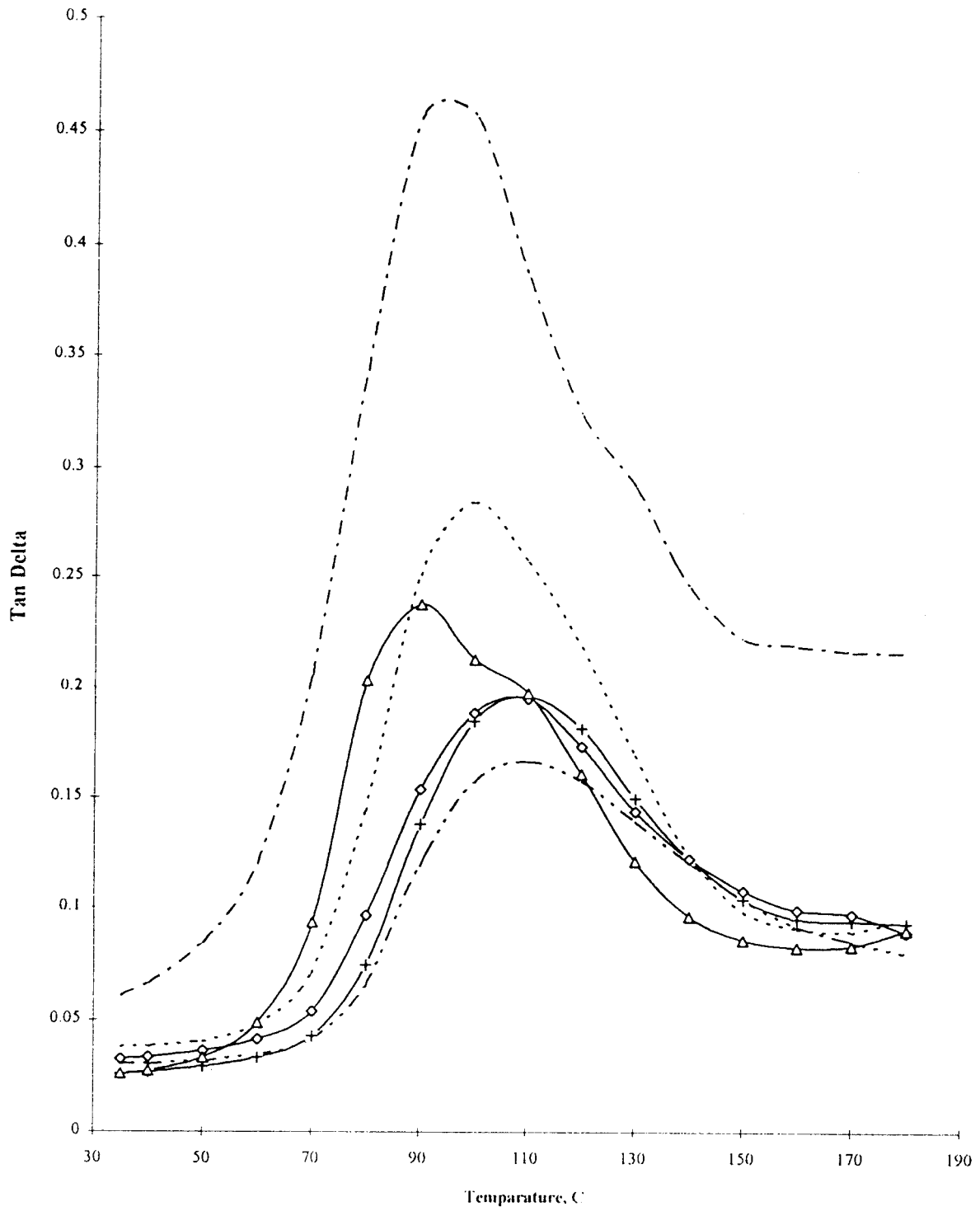


Figure 3 Variation of $\tan \delta$ with temperature for different percentages of Novolac-epoxy composites: - · -, 0%; - · - ·, 12%; - · · ·, 20%; - + - +, 30%; - \diamond -, 40%; - \triangle -, 100%.

odd variations in adhesion zones, buildup of uncertain presence of voids, and odd thermal effects ascribed to the difference in the expansion coefficient of the main phases. These features may combine to cause odd differences in the dynamic properties of the composites as highlighted.

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REFERENCES

1. Lee, N. Handbook of Epoxy Resin; Publisher: City, Year.
2. Potter. Epoxide Resin; Publisher: City, Year.
3. Miliotis, J.; Kefalas, V.; Sidridis, E.; Spathis, G. in Handbook of Ceramic and Composites; Cheremisinoff, N. P., Ed.; Marcel Dekker: New York, 1990; Vol. 1, Chapter 6.
4. Harris, B.; Braddel, O. G.; Almond, D. P.; Lefebvre, C.; Verbist, J. J Mater Sci 1993, 28, 3353.
5. Wingard, C. D.; Beatty, C. L. J Appl Polym Sci 1990, 41, 2539.
6. Otaigbe, J. U. Polym Eng Sci 1991, 31, 104.
7. Ghosh, P.; Mitra, P. S.; Banerjee, A. N. J Polym Sci Polym Chem Ed 1973, 11, 2021.
8. Read, B. F.; Dean, G. D. The Determination of Dynamic Properties of Polymers and Composites; Wiley: New York, 1978.
9. Saha, N.; Banerjee, A. N. J Appl Polym Sci 1996, 62, 1196.