

Dynamic Mechanical Study on Unidirectional Polyethylene–Carbon Fibers: PMMA Hybrid Composite Laminates

NIRMAL SAHA, AMARNATH BANERJEE

Department of Polymer Science and Technology, University of Calcutta, 92 A.P.C. Road, Calcutta-700009, India

Received 20 March 1997; accepted 12 September 1997

ABSTRACT: Unidirectional (UD) composite laminates based on carbon fibers (CF) and high-performance polyethylene fibers (PEF) were prepared with partially polymerized methyl methacrylate (MMA) at 25°C, followed by heating at 55°C (well below the softening point of PEF) for 2 h. The viscoelastic behavior of the composite was studied through dynamic mechanical analysis at different volume fractions of the fibers. Several parameters such as the storage modulus (E'), loss modulus (E''), and loss factor or damping efficiency ($\tan \delta$) were determined between 40 and 160°C in a resonant frequency mode. The glass transition temperature (T_g) increased to a higher region with increase in the volume of PEF in the hybrid laminates. It was also observed that the efficiency of the composite decreases with increase in the volume fraction of the fibers. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1631–1637, 1998

Key words: polyethylene–carbon fibers; hybrid composite; poly(methyl methacrylate) matrix; dynamic mechanical behavior

INTRODUCTION

It is interesting to note that composites, both thermoplastics and thermosetting ones, are becoming more popular and interesting to the scientist due to their high mechanical performance, lightweightness, low-cost, and applicability under static and dynamic conditions. By permutating and combining various fibers and polymers, a wide range of composites having unique properties for versatile applications, as alternatives to conventional materials like metals and wood, have been prepared. A limited number of reports are available about studies on the dynamic mechanical properties of hybrid composites.

Now it is worthwhile to study the polymer composite structure and to investigate the dynamic

mechanical properties, particularly the dynamic modulus and internal friction, over a wide range of temperatures.^{1–4} It is known that the dynamic mechanical properties of the unidirectional (UD) composites are dependent upon the volume fraction of the fibers^{5,6} and the fiber orientation.^{7,8} Hence, the performance of a structural material can be judged by dynamic mechanical thermal analysis in the orientation of the fiber alignment at different volume fractions.

The PEF possess unique mechanical properties in terms of high strength-to-weight ratios and stiffness-to-weight ratios.⁹ Moreover, high-performance polyethylene fibers (PEF) possess a relatively high energy to break compared with glass, aramid, and carbon fibers (CF).¹⁰ Due to these unique properties, PEF have a high potential for applications in composite structures, notably when good damping properties are required.^{10–15} A limited number of workers have used PEF as reinforcing fibers, but these works are based mainly upon the thermoset matrix. Composites

Correspondence to: A. Banerjee.
Contract grant sponsor: CSIR.

Journal of Applied Polymer Science, Vol. 67, 1631–1637 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/091631-07

based upon thermoplastic polymeric matrices potentially offer several advantages compared with those based upon thermosetting resins.^{16,17} Thus, one could expect a unique structural material based on the use of poly(methyl methacrylate) (PMMA), a thermoplastic polymer, as the matrix in PEF–CF-reinforced composite laminates.

The main theme of this work was to obtain fundamental information concerning the viscoelastic properties in the dynamic condition of UD-PEF-reinforced PMMA laminates (PEFRC), CF-reinforced PMMA laminates (CFRC), and CF-PEF-reinforced PMMA hybrid laminates at different volume fractions of the fibers.

THEORETICAL

If the mechanical damping of a filled polymer results only from the inherent damping of its constituents, then the damping of a UD composite can be approximated by¹⁸

$$\tan \delta_c = V_f \tan \delta_f + (1 - V_f) \tan \delta_m \quad (1)$$

where $\tan \delta_c$ and $\tan \delta_m$ are the $\tan \delta$'s of the composite and matrix, respectively, and V_f is the volume fraction of the fibers. CF can be considered as a pure elastic material; hence, the damping efficiency of CF is effectively zero² and eq. (1) can be rewritten as

$$\frac{\tan \delta_c}{\tan \delta_m} = (1 - V_f) = V_m$$

where V_m is the volume fraction of the matrix.

EXPERIMENTAL

Fibers and other reagents used are as follows: (1) PEF (spectra 900, 1200 den) supplied by Allied Signal Corp. (St. Petersburg, FL); (2) CF (Indcarf-30, 6K) supplied by Indian Petrochemicals Co. (Boroda, India); (3) MMA supplied by Western Chemical Corp. (Calcutta, India); (4) benzoyl peroxide (Bz_2O_2) supplied by Loba-Chemie Indoaustranal Corp. (Mumbai, India); and (5) *N,N*-dimethylaniline (NDA) supplied by E. Merck (Mumbai, India).

MMA was purified once before use by a standard technique^{19,20} and Bz_2O_2 was recrystallized

Table I Layup Sequence and Volume of PEF and CF in Hybrid Composites

Layup Sequence ^a	Designation	V_f	
		PEF	CF
[CSC]	H-1	0.090	0.085
[SCS]	H-2	0.180	0.043

^a C, CF; S, PEF ply.

from chloroform²¹ and dried in a vacuum. The purification of NDA was achieved by distillation under reduced pressure before use.

The PEF used for the preparation of the composites were treated with chromic acid, following Peijs et al.¹⁰ and Ladizesky and Ward.^{22,23} The surface of the CF were already treated by a standard treatment used directly for making composites. The wetting characteristics of PMMA on treated and untreated CF and PEF were studied by contact-angle determination, following Yamaki and Katayami,²⁴ Sellitti et al.,²⁵ and Tissington et al.²⁶ Improved wetting was found when the treated fibers were investigated.²⁷ In this work, only treated fibers were used.

The UD plies were made in a dust-free chamber on a glass sheet using partially polymerized MMA as the resin with an amine–peroxide (NDA– Bz_2O_2) initiator system in the bulk at room temperature.²⁸ Laminated structures were prepared by stacking these plies of PEF and CF unidirectionally in the mold and the composites were made by using the same resin at room temperature until it solidified within the mold, and shrinkage was controlled by using extra resin in the mold. Finally, the composite was heated to a temperature of 55°C for 2 h to ensure the completion of MMA polymerization. UD laminates were prepared up to three plies for PEF (designated as S_1 – S_3 , respectively) and CF (designated as C_1 – C_3 , respectively). The layup sequence and volume of PEF and CF in the hybrid laminates are given in Table I. A detailed description of the preparation of laminates was given elsewhere.^{27,29–34}

The dynamic mechanical properties were measured by using a Dupont 983 DMA. The samples (10-mm width, 1.70-mm thickness) were tested in the resonant frequency mode with an oscillation amplitude of 0.20 mm and were mounted in the vertical clamps at a clamping distance-to-thickness ratio of 11. The analyses were performed in

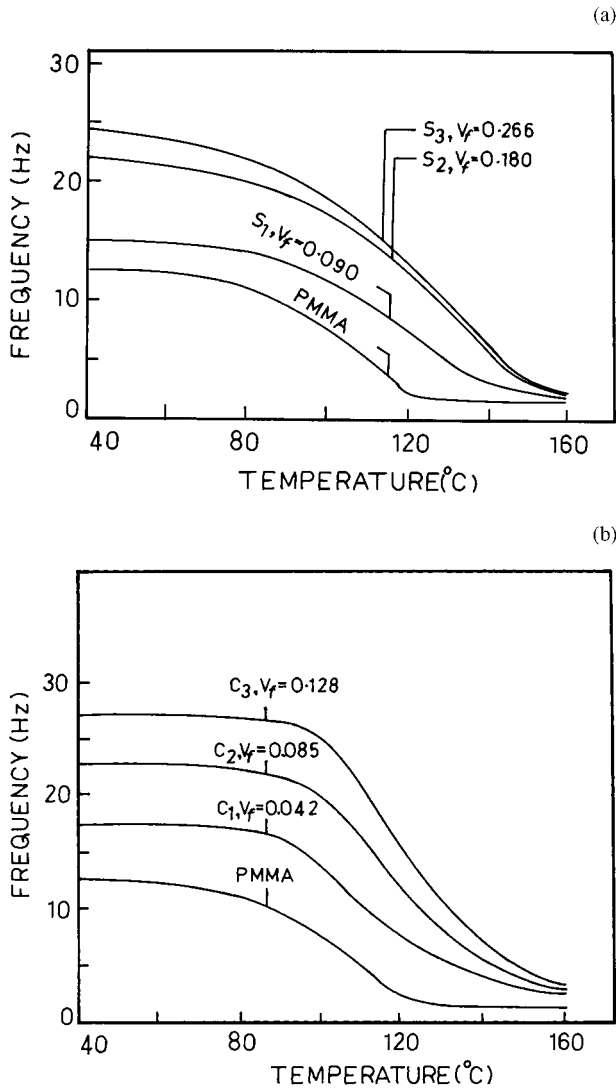


Figure 1 Variation of resonant frequency with temperature: (a) PEFRC; (b) CFRC.

a nitrogen atmosphere at the heating rate of 5°C/min. In all cases, six specimens were tested and average values are reported.

RESULTS AND DISCUSSION

Figure 1 displays the sample's resonant frequency (related to the Young's or elastic modulus) as a function of temperature. For both the composites (CFRC and PEFRC) and matrix PMMA, the modulus decreases with increase in the temperature over the whole range of the experiments. The variation of E' with temperatures at different V_f is

shown in Figure 2. It is seen that E' increases with increase in V_f at all temperatures due to the inherent stiffness imparted by the fibers that allows efficient stress transfer.

The modulus enhancement of the composites is demonstrated by the reduced storage modulus (E'_c/E'_m , where E'_c and E'_m are the E' of the composite and matrix, respectively) values. The non-linear variation of the reduced modulus with V_f is observed at higher V_f (Fig. 3). At higher V_f , the fiber interaction takes place, and either they tend

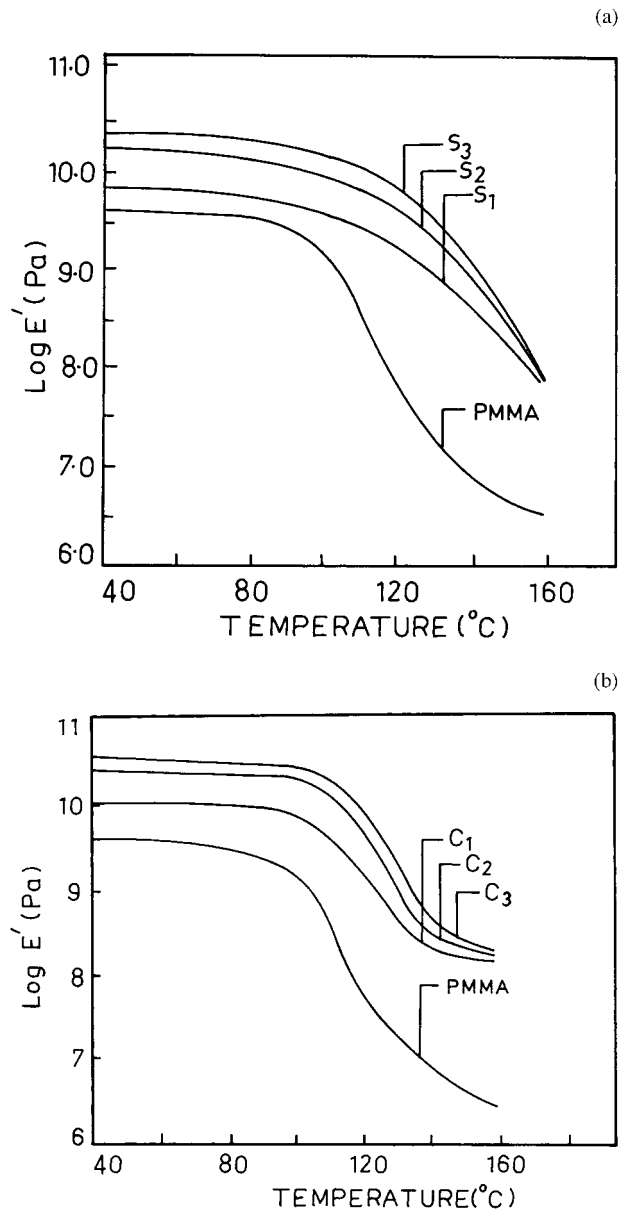


Figure 2 Variation of storage modulus with temperature: (a) PEFRC; (b) CFRC.

to bundle up among themselves or touch each other physically, due to that the hand layup technique may sometimes produce a random nature of fiber distribution in the matrix. Due to either of these facts, the proper and uniform penetration of the matrix does not take place throughout the fiber surfaces, causing inefficient stress transfer at the

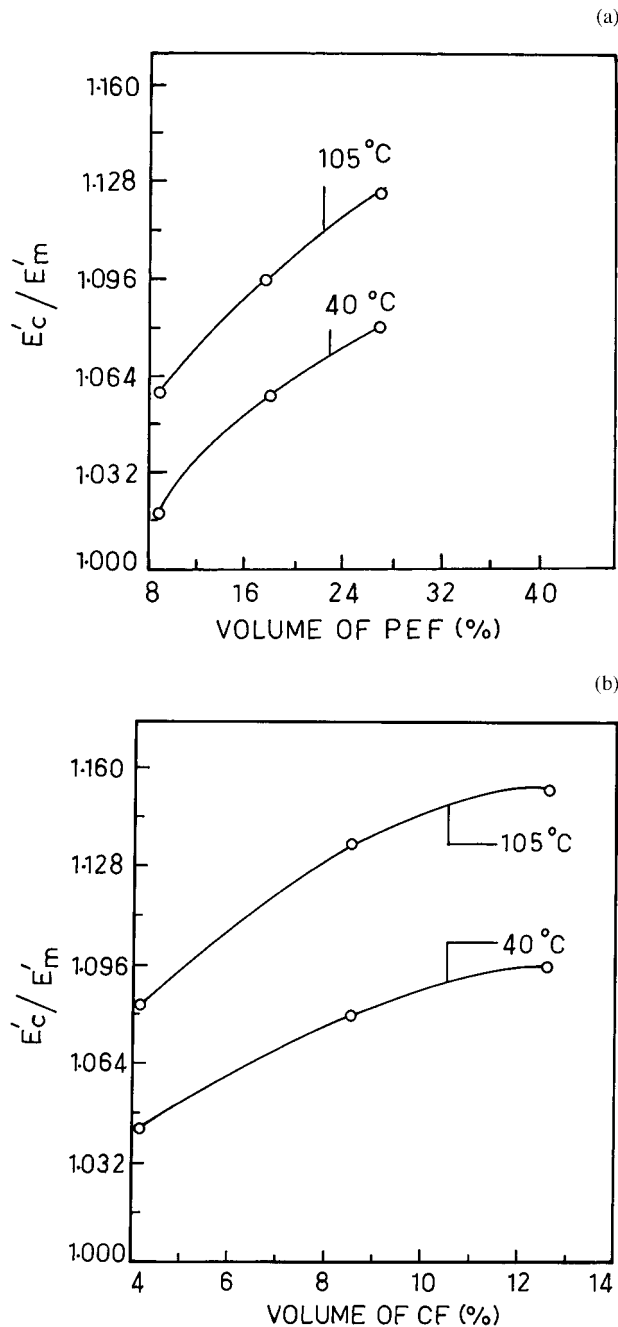


Figure 3 Variation of reduced modulus with volume fraction of fibers: (a) PEFRC; (b) CFRC.

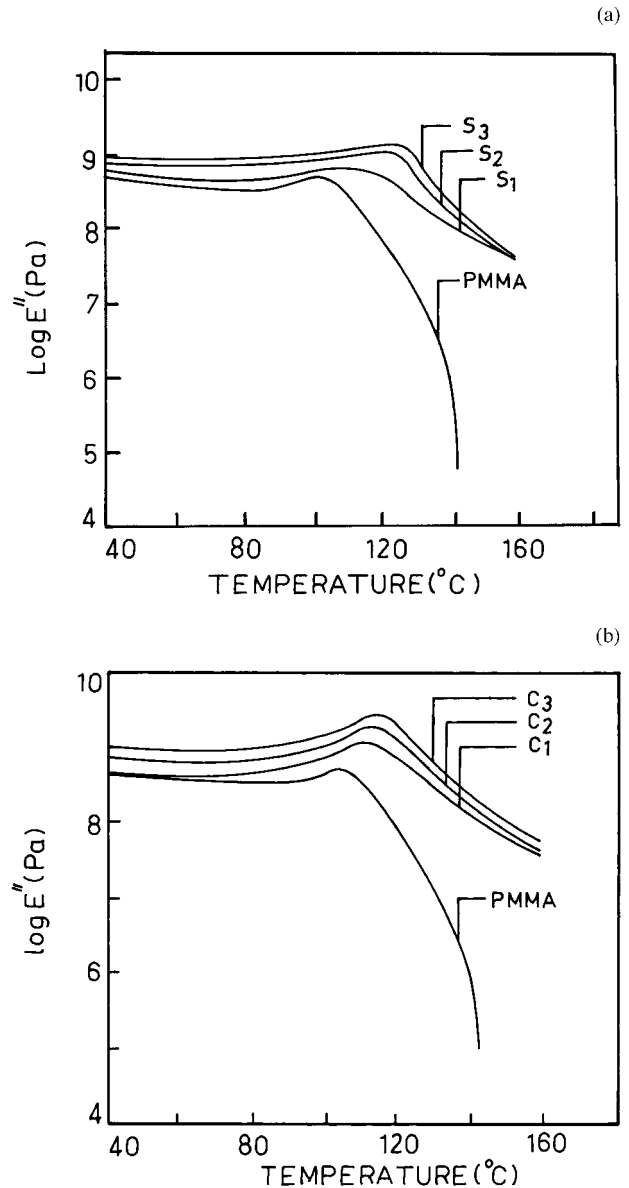


Figure 4 Variation of loss modulus with temperature: (a) PEFRC; (b) CFRC.

interface.^{35,36} These facts can be understood from the nonlinear behavior of curves at higher V_f .

The variation of E'' with temperature is shown in Figure 4. The maximum heat dissipation occurs at the temperature where E'' is at a maximum, indicating the T_g of the system.³⁷ It was observed that by incorporating fibers the T_g is shifted to a higher region (T_g of PMMA is 105°C). Incorporation of the fiber inhibits the molecular segmental motion of the chains of PMMA at the transition region, yielding a higher value of T_g .

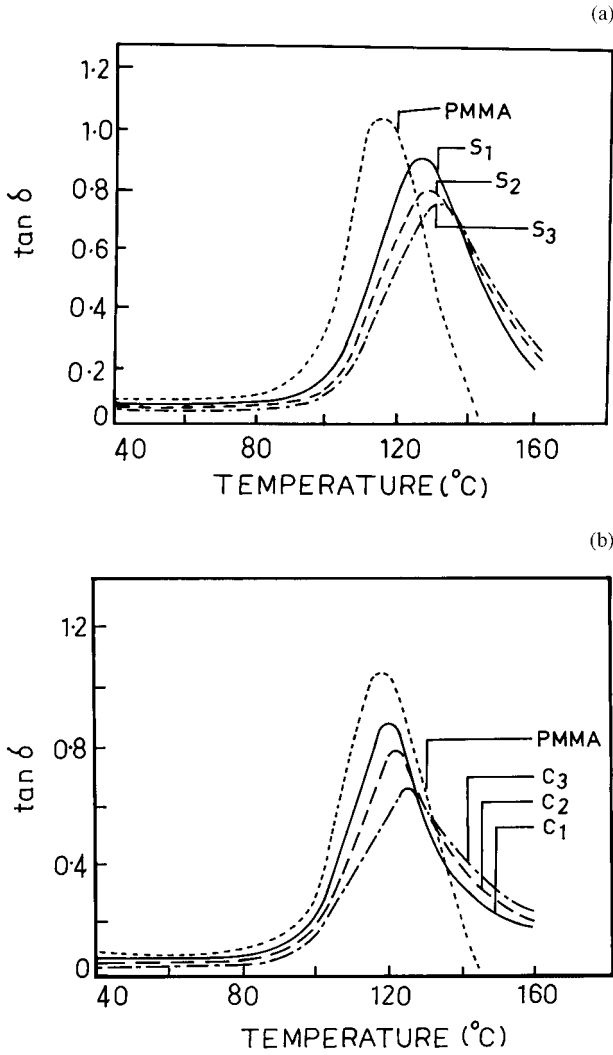


Figure 5 Variation of $\tan \delta$ with temperature: (a) PEFRC; (b) CFRC.

Figure 5 shows the variation of $\tan \delta$ with temperature for various composites compared with the matrix. It is seen that the introduction of fibers has reduced the peak height and the position of the peak has been shifted to a higher temperature with the increase in V_f . This is due to the restriction of segmental motion of PMMA by the fibers as discussed earlier. The most pronounced effect of incorporating and increasing the fiber concentration in the matrix is the broadening of the transition region. This effect is probably due to the hindrance of the relaxation process within the composites on the incorporation of the fibers.

The variation of reduced $\tan \delta$ ($= \tan \delta_c / \tan \delta_m$) with V_f is shown in Figure 6. Curves in these figures include theoretical and experimental data.

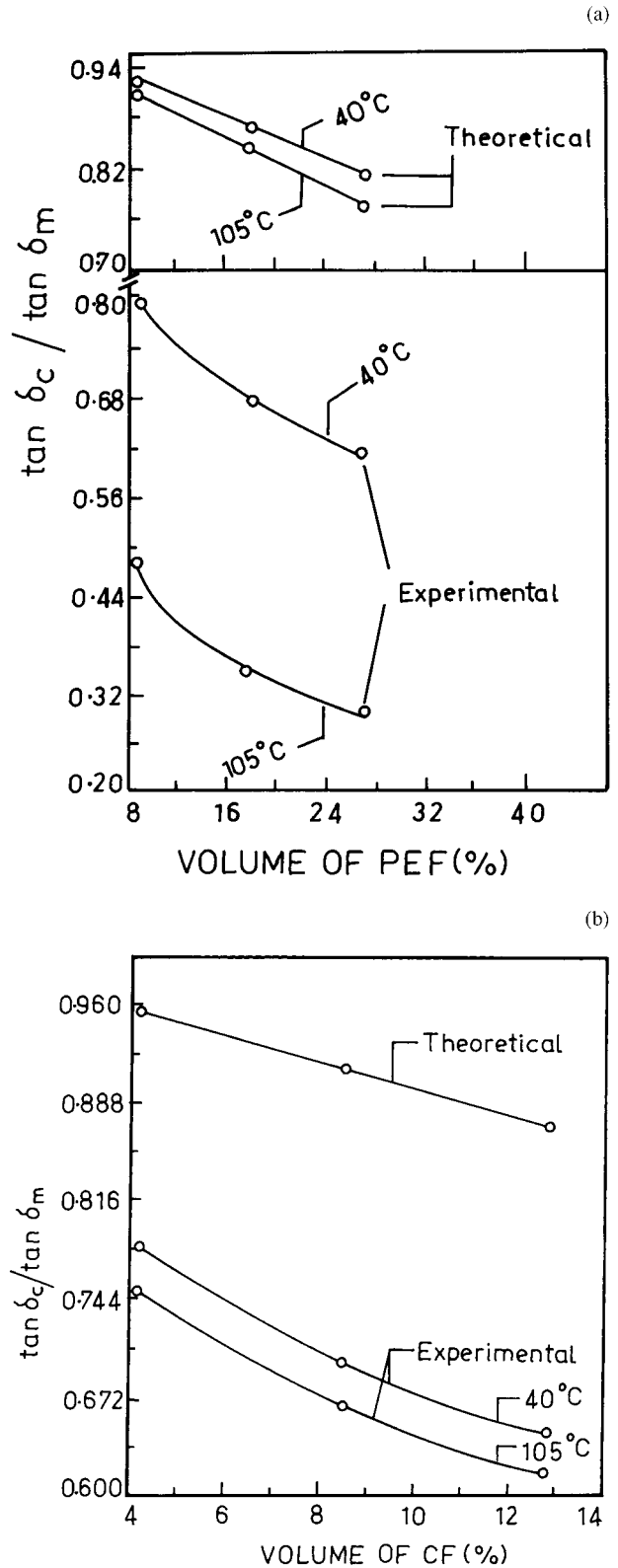


Figure 6 Variation of reduced $\tan \delta$ with volume fraction of fibers: (a) PEFRC; (b) CFRC.

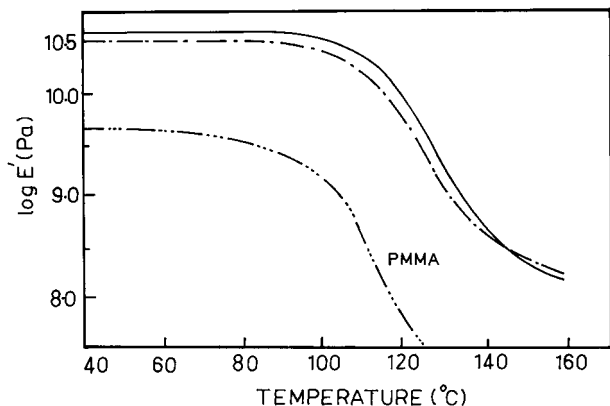


Figure 7 Variation of storage modulus with temperature: (---) H-1; (—) H-2.

The theoretical values of reduced $\tan \delta$ are obtained by using eq. (1) (for the PEFRC, where $\tan \delta_f$ is 0.027 at 40°C and 0.061 at 105°C) and eq. (2) (for the CFRC). All the experimental points lie below the theoretical points, indicating that the presence of reinforcement has led to a greater reduction in the damping efficiency than expected theoretically. The extra reduction can be due to a shell of immobilized matrix PMMA surrounding the individual reinforcing elements. The occurrence of this PMMA shell induces efficient stress transfer around the PMMA fiber interfaces as explained in earlier literature.^{37,38} It was also observed that the experimental curves tend to flatten with an increase in V_f . This is because at higher V_f the fiber–fiber friction takes place and the fiber surfaces are not properly wetted by the matrix.

The variation of E' with temperature for the hybrid laminates is shown in Figure 7. It is clear that E' increases remarkably for hybrid laminates with respect to PMMA. In comparing both the hybrid laminates, E' increases from one PEF ply (H-1) to two PEF plies (H-2) at the glassy region. But at the rubbery region, E' decreases from one PEF ply to two PEF plies. At this region, the viscoelastic fiber PEF becomes rubbery, resulting in a decrease in E' .

In Figure 8, the E'' values of the hybrid laminates are plotted against temperature. From the figure, it is clear that the T_g shifted toward the higher-temperature region as the number of PEF plies increased from one to two. This behavior is probably due to that the coefficient of the thermal expansion of PEF¹⁰ is much higher than that of CF³⁹; as a result, PEF occupies a much higher

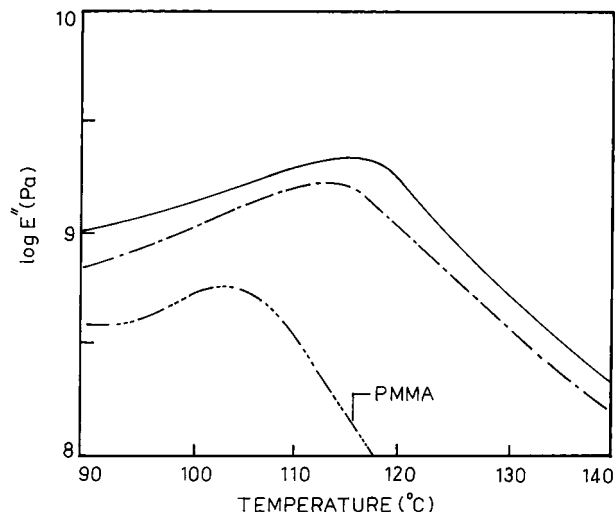


Figure 8 Variation of loss modulus with temperature: (---) H-1; (—) H-2.

volume and puts more constraints on the molecular segmental motion of the PMMA matrix at the transition region.

Figure 9 shows the variation of $\tan \delta$ with temperature for hybrid laminates compared with the matrix. It is seen that the peak height of PMMA was reduced with the incorporation of fibers and the peak temperatures of the hybrid laminates were shifted to higher values compared with those of PMMA. It is also clear from the figure that more broadening of the transition region takes place for hybrid laminates compared with PMMA. The reasons were discussed earlier.

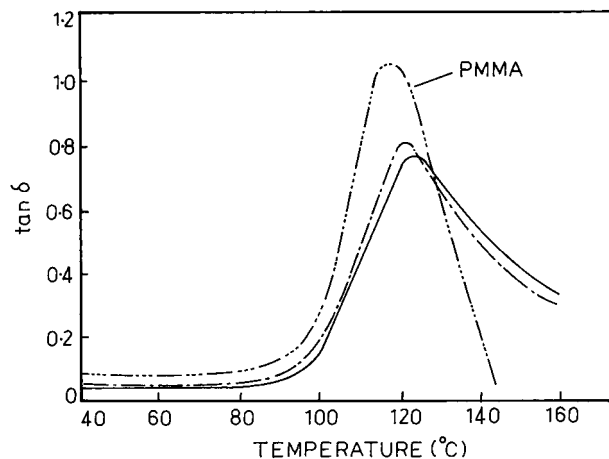


Figure 9 Variation of $\tan \delta$ with temperature: (---) H-1; (—) H-2.

CONCLUSIONS

From the above studies, the following conclusions may be drawn:

1. The E' increases with increase in V_f for both PEF and CF.
2. The T_g of the composite is greater than that of the pure matrix. In hybrid composites, T_g increases with increase in the volume of PEF.
3. The efficiency of the composite reduces with increase in V_f , which was predicted from the nonlinear variation of E'_c/E'_m and $\tan \delta_c/\tan \delta_m$ with V_f .

The CSIR grant to N. S. (SRF) is acknowledged.

REFERENCES

1. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.
2. T. Murayama, *Dynamic Mechanical Analysis of Polymeric Materials*, 2nd ed., Elsevier, Amsterdam, 1978.
3. B. F. Read and G. D. Dean, *The Determination of Dynamic Properties of Polymers and Composites*, Wiley, New York, 1978.
4. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1975.
5. S. W. Tsai and H. T. Halpin, *Introduction to Composite Materials*, Technomic, Westport, CT, 1980.
6. R. D. Adams and D. F. Short, *J. Phys. D. Appl. Phys.*, **6**, 1032 (1973).
7. R. D. Adams, *Damping Properties Analysis of Composites*, Vol. 1, *Engineered Material Hand Book*, ASTM International, Metals Park, OH, 1987, pp. 207–209.
8. D. F. Adams and D. R. Doner, *J. Compos. Mater.*, **1**, 4 (1967).
9. P. J. Lemstra, R. Kirschbaum, T. Ohta, and H. Yasuda, *Developments in Oriented Polymers—2*, Elsevier, London, 1987, pp. 39–77.
10. A. A. J. M. Peijs, P. Catsman, L. E. Govaert, and P. J. Lemstra, *Composites*, **21**, 513 (1990).
11. A. A. J. M. Peijs, R. W. Venderbosch, and P. J. Lemstra, *Composites*, **21**, 522 (1990).
12. A. A. J. M. Peijs and J. M. M. De Kok, *Composites*, **24**, 19 (1993).
13. D. F. Adams, R. S. Zimmerman, and H. W. Chang, *Soc. Adv. Mater. Process Eng. (SAMPE)*, **21**, 44 (1985).
14. H. W. Chang, L. C. Lin, and A. Bhatnagar, in *Proceedings of the 31st International SAMPE Symposium*, 1986, pp. 859–866.
15. R. F. Gibson, S. R. Vidish, and R. Mantena, in *Proceedings of the 32nd International SAMPE Symposium*, 1987, pp. 231–244.
16. G. K. A. Kodokian and A. J. Kinloch, *J. Mater. Sci. Lett.*, **7**, 625 (1988).
17. J. T. Hoggatt, S. Oken, and E. E. House, *U.S. Air Force Report AFWAL-TR-80-3023*, April 1980.
18. L. E. Nielson, R. A. Wall, and P. G. Richmond, *Soc. Plast. Eng. (SPE)*, **11**, 22 (1955).
19. P. Ghosh, P. S. Mitra, and A. N. Banerjee, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 2021 (1973).
20. P. Ghosh and A. N. Banerjee, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 375 (1975).
21. P. Ghosh, S. Biswas, and U. Niyogi, *J. Polym. Sci. Part A Polym. Chem.*, **24**, 1053 (1986).
22. N. H. Ladizesky and I. M. Ward, *J. Mater. Sci.*, **18**, 533 (1983).
23. N. H. Ladizesky and I. M. Ward, *J. Mater. Sci.*, **24**, 3763 (1989).
24. J. I. Yamaki and Y. Katayama, *J. Appl. Polym. Sci.*, **19**, 2897 (1975).
25. C. Sellitti, S. Vargiu, E. Martuscelli, and D. Fabbra, *J. Mater. Sci.*, **22**, 3477 (1987).
26. B. Tissington, G. Pollard, and I. M. Ward, *J. Mater. Sci.*, **26**, 82 (1991).
27. N. Saha, A. N. Banerjee, and B. C. Mitra, *Polym. Adv. Technol.*, **6**, 637 (1995).
28. P. Ghosh and N. Mukherjee, *Eur. Polym. J.*, **15**, 797 (1979).
29. N. Saha, A. N. Banerjee, and B. C. Mitra, *J. Appl. Polym. Sci.*, **60**, 139 (1996).
30. N. Saha, A. N. Banerjee, and B. C. Mitra, *Polym. Commun.*, **37**, 699 (1996).
31. N. Saha and A. N. Banerjee, *Polymer*, **37**, 4633 (1996).
32. N. Saha and A. N. Banerjee, *J. Appl. Polym. Sci.*, **62**, 1193 (1996).
33. N. Saha and A. N. Banerjee, *J. Appl. Polym. Sci.*, **62**, 1199 (1996).
34. N. Saha, A. N. Banerjee, and B. C. Mitra, *J. Appl. Polym. Sci.*, **60**, 657 (1996).
35. A. Mittleman and I. Roman, *Composites*, **21**, 63 (1990).
36. G. N. Karam, *Composites*, **22**, 84 (1991).
37. J. U. Otaigbe, *Polym. Eng. Sci.*, **31**, 104 (1991).
38. T. Bessel, D. Hull, and J. B. Shortall, *Faraday Spec. Disc. Chem. Soc. (2)*, 137 (1972).
39. A. R. Bunsell, *Fibre Reinforcements for Composite Materials*, Vol. 2, *Composite Materials Series*, Elsevier, Amsterdam, 1988, p. 15.