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

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SYNOPSIS

Unidirectional (UD) hybrid composite laminates based on glass fibers (GF) and high performance polyethylene fibers (PEF) were prepared with partially polymerized methyl methacrylate (MMA) at room temperature, followed by heating at 55°C (well below the softening point of PEF) for 2 h. The total volume fraction of fibers of the hybrid composite was held constant and the proportion of PEF or GF was varied. The viscoelastic behavior of the hybrid composite was studied through dynamic mechanical analysis at different relative volume fractions of PEF. Parameters such as storage modulus (E'), loss modulus (E''), and loss factor or damping efficiency (tan δ) were determined in a resonant frequency mode. All the properties were compared between the hybrid composites. It was found that the glass transition temperature (T_g) increased to a higher region with the increase in relative volume of PEF. It was also observed that the efficiency of the hybrid composite increased with the increase in relative volume of PEF. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The present trend of polymer scientists is to prepare thermoplastics and thermosetting composites of increasing mechanical behavior, light weight, low cost, and covering different static and dynamic fields of application. By permutation and a combination of various fibers and polymers, a wide range of composites, having unique properties for versatile applications, as alternatives to conventional materials like metals, woods etc. have been prepared.

Investigation of dynamic mechanical properties, particularly dynamic modulus and internal friction, over a wide range of temperatures is quite useful in studying the polymer composite structure.[1-4] The dynamic mechanical properties of the unidirectional (UD) composites are dependent on the volume fraction of fibers[5,6] and the fiber orientation,[7,8] so that the performance of a structural material can be judged by dynamic mechanical thermal analysis in the direction of fiber alignment at different volume fractions of fibers.

Polyethylene fibers (PEF) possess unique mechanical properties in terms of high strength-to-weight ratios and stiffness-to-weight ratios.[9] Moreover these PEF possess a relatively high energy to break compared to carbon, aramid, and glass fibers (GF).[10] Due to these unique properties, PEF has high potential for use in composite structures, notably where good damping properties are required.[10-15] GF, a well-known reinforcing fiber, can be considered as a pure elastic material so that damping efficiency of GF is effectively zero.[2] Thus, elastic GF is being used in combination with viscoelastic PEF to obtain a good balance of damping behavior.

A few workers used PEF as one of the reinforcing fibers in hybrid composites, but these works are mainly based on the use of thermoset matrix. Composites made from thermoplastic polymeric matrices potentially offer several advantages compared to those of thermosetting resins.[16,17] Thus, one could expected a unique structural material based on the use of poly(methyl methacrylate) (PMMA), a thermoplastic polymer, as the matrix in PEF-GF reinforced hybrid composite laminates.

The purpose of this work is to obtain fundamental information concerning the viscoelastic properties in dynamic conditions of UD-PEF-GF reinforced

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PMMA hybrid laminates at different relative volume fractions of PEF. All the viscoelastic properties are also compared among the different hybrid composites.

EXPERIMENTAL

Fibers and other reagents used are as follows:
1. PEF (Spectra 900, 1200 den) supplied by Allied-Signal Corporation, Petersburg, FL;
2. GF (433 BF-225) supplied by Owens Corning Fiberglas Corporation, Granville, OH;
3. MMA supplied by Western Chemical Corporation, Calcutta, India;
4. benzoyl peroxide (BZ_2O_2) supplied by Loba-Chemie Indo-austranal Corporation, Bombay, India; and
5. N,N dimethyl aniline (NDA) supplied by E. Merck Limited, Bombay, India.

MMA was purified by standard technique,[18,19] and BZ_2O_2 was recrystallized from chloroform[20] 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 composites was treated with chromic acid following the literature.[10,21,22] The surface of the GF was already treated with a standard treatment and used directly for making composites. The wetting characteristics of PMMA on treated and untreated GF and PEF were studied by contact angle determination as found in the literature.[23-25] Improved wetting was found when the treated fibers were investigated.[26]

The UD plies were made in a dust free chamber on a glass sheet using partially polymerized MMA as the resin with the amine-peroxide (NDA-BZ_2O_2) initiator system in bulk at room temperature.[27] Laminated structures were prepared by stacking these plies of PEF and GF unidirectionally in the mold, and the composites were made by using the same resin at room temperature until it solidified within the mold. Shrinkage was controlled 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. A detailed description of the preparation of laminates is given elsewhere.[26]

The lay-up sequence and relative proportion of PEF in hybrid laminates are given in Table I. Total volume fraction was held constant at 35.6%, and the proportion of PEF was varied from 0 to 100% with steps of approximately 25%.

Table I   Lay-Up Sequence and PEF Fraction of Hybrid Laminates

Lay-Up Sequence	PEF Fraction (%)
[GGGG]	0 (All GF)
[GSGG]	25.4
[SGSG]	50.6
[SSGS]	74.7
[SSSS]	100 (All PEF)

G, GF ply, S, PEF ply.

The dynamic mechanical properties were measured by using a Dupont 983 DMA. The samples (10 × 1.70 mm) were tested in 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 analysis was performed in nitrogen at the heating rate of 5°C/min. In all cases, six specimens were tested and average values are reported.

RESULTS AND DISCUSSION

The variation of E' with temperature at different relative volumes of PEF is shown in Figure 1. It is seen that E' remarkably increases with the incorporation of fibers in the PMMA matrix that is due to the fact that inherent stiffness is imparted by the fibers that allows efficient stress transfer. Comparing the different hybrid laminates, E' increases with the increase in relative volume of the PEF at the glassy region. This is due to the fact that the modulus of elasticity (E) of PEF is higher than that of GF (E is 103 GPa for PEF and 70 GPa for GF). But at the rubbery region E' decreases with the increase in relative volume of PEF. It is also observed that the rate of fall of E' with respect to temperature (or time) at the higher temperature region increases with the increase in relative PEF fraction. At this region the viscoelastic fiber PEF becomes rubbery, resulting a decrease in E'. The above behavior is reflected in Figure 2. The E' increases almost linearly at 40 and 105°C (glass transition temperature, T_g, of PMMA) with the relative PEF fraction. But at 160°C E' decreases with an increase in relative PEF fraction.

The modulus enhancement of hybrid composites with relative PEF fraction is also demonstrated by the relative storage modulus (E'_c/E'_m, where E'_c and E'_m are the E's of composite and matrix, respectively) values (Fig. 3). The nonlinear variation of
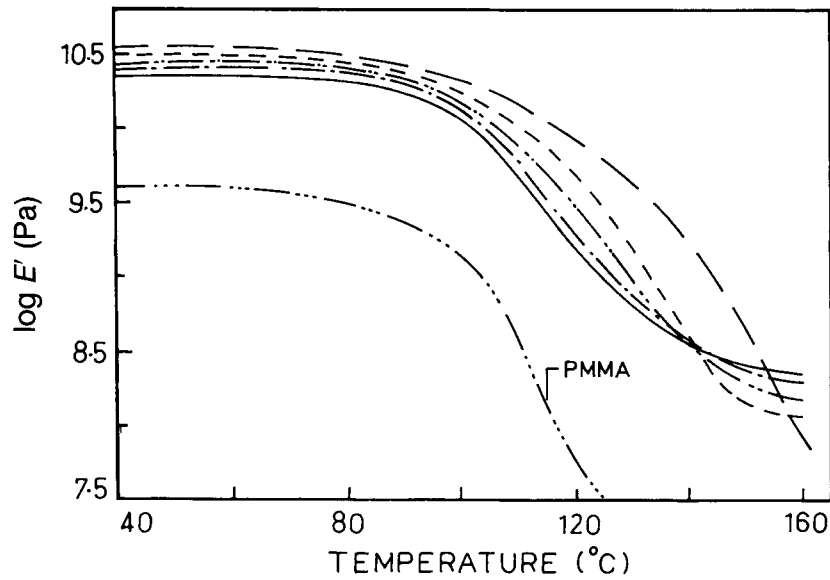
Figure 1   Variation of storage modulus with temperature. (—) 0% PEF; (-·-) 25.4% PEF; (-··-) 50.6% PEF; (---) 74.7% PEF; (- -) 100% PEF.

reduced modulus with relative PEF fraction is observed at a higher PEF fraction. The curve becomes steeper with the increasing relative PEF fraction of

the hybrid composite. This may be due to the fact that the brittle nature of GF (i.e., sensitivity to abrasion with handling) makes the composite
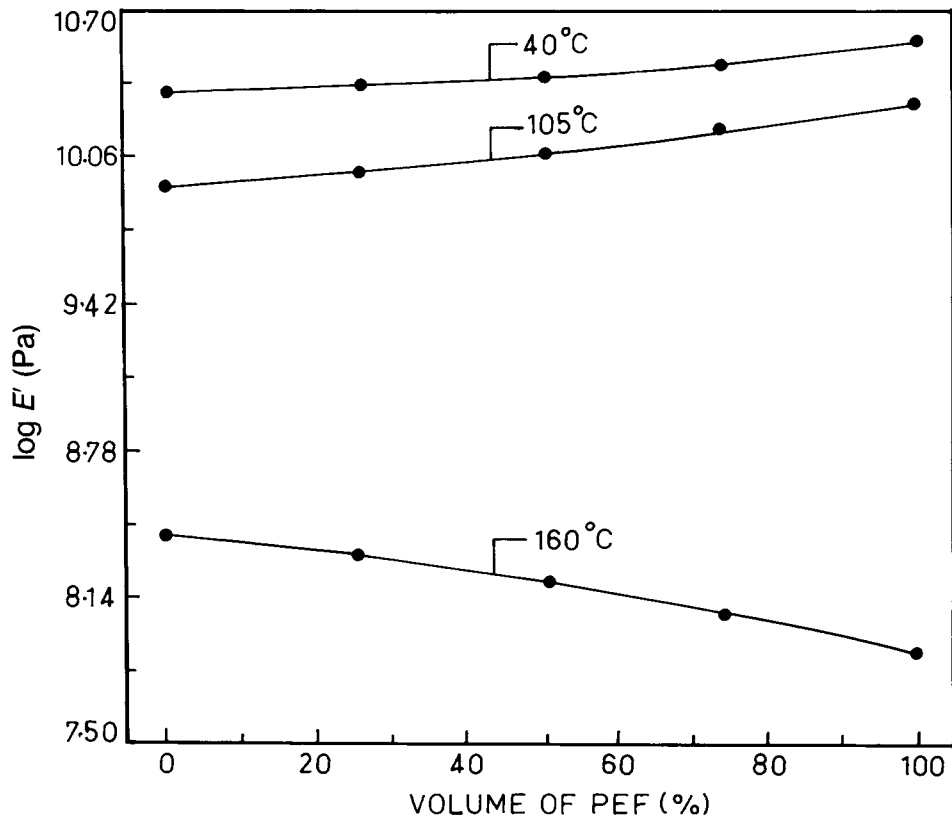

Figure 2   Variation of storage modulus with relative volume fraction of PEF.
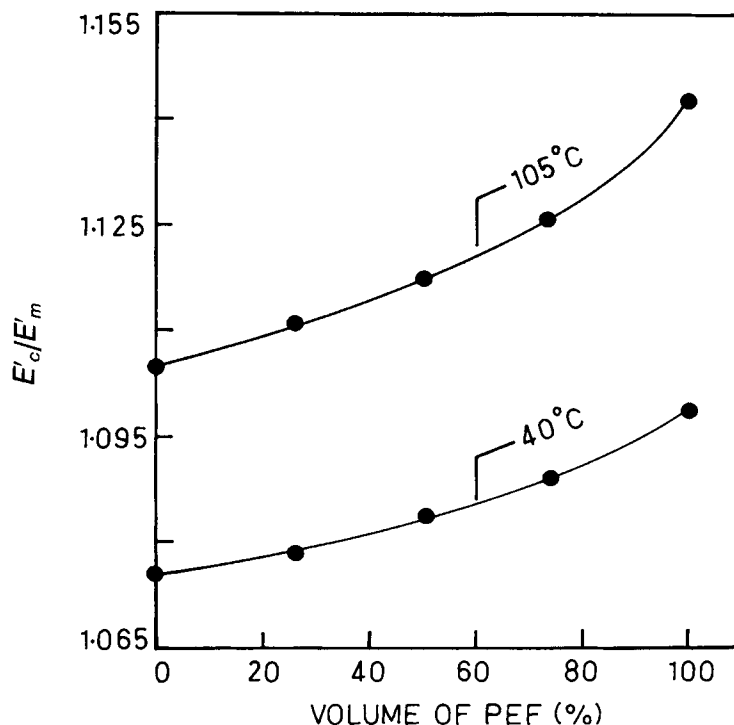
Figure 3 Variation of reduced modulus with relative volume fraction of PEF.

weaker due to breakage of the fiber during manufacturing of the laminates. As a result the curve becomes steeper by replacing the GF with an equal volume of PEF.

The variation of E'' with temperature is shown in Figure 4. The maximum heat dissipation occurs at the temperature where E'' is maximum, indicating the T_g of the system.[28] It was observed that by incorporation of fibers in matrix, the T_g is shifted toward the higher region (T_g of PMMA is 105°C). Incorporation of fibers inhibits the molecular segmental motion of chains of PMMA at the transition region, yielding a higher value of T_g. In the case of hybrid composites, the T_g increases with relative PEF fraction; that is, the T_g is shifted from about 112°C (all GF) to about 128°C (all PEF). Hybrid composites with an intermediate volume of PEF had values between these two extremes. The coefficient of thermal expansion of PEF[10] is much higher than that of GF[29] as a result PEF (approaches its melting point, 147°C) occupying a much higher volume with respect to GF and putting more constraints on the molecular segmental motion of the PMMA matrix at the transition region. Probably due to this fact the T_g of hybrid laminates increases with the increase in relative volume of PEF. The situation of simultaneous segmental motion of both the PMMA and PEF is more pronounced as the relative volume

of PEF increases from 0 to 100%. As a result, the peak (where E'' is maximum) becomes less prominent at a higher volume of PEF.

Figure 5 shows the variation of tan δ with temperature for various hybrid composites compared to the matrix. It is seen that the introduction of fibers reduced the peak height of the matrix. It is also found from the figure that the temperature location of the peaks with respect to the matrix has shifted to the higher region with the increase in relative PEF fraction. This may be due to the simultaneous segmental motion of PEF and PMMA as discussed earlier. The most pronounced effect of incorporation of fibers in the matrix is broadening of the transition region. This effect is due to the inhibition of the relaxation process within the composites on incorporation of the fibers.

CONCLUSIONS

From the above studies the following conclusions may be drawn:

1. The E' increases with the increase in relative volume of PEF at the glassy region, but at the rubbery region reverse results are obtained.
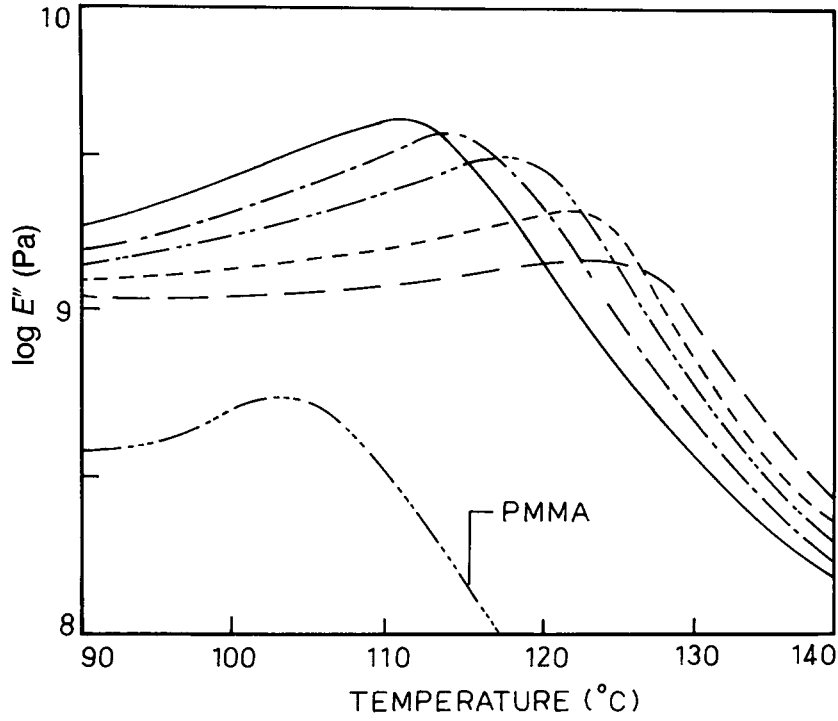
Figure 4   Variation of loss modulus with temperature. Indication of different curves are the same as Figure 1.
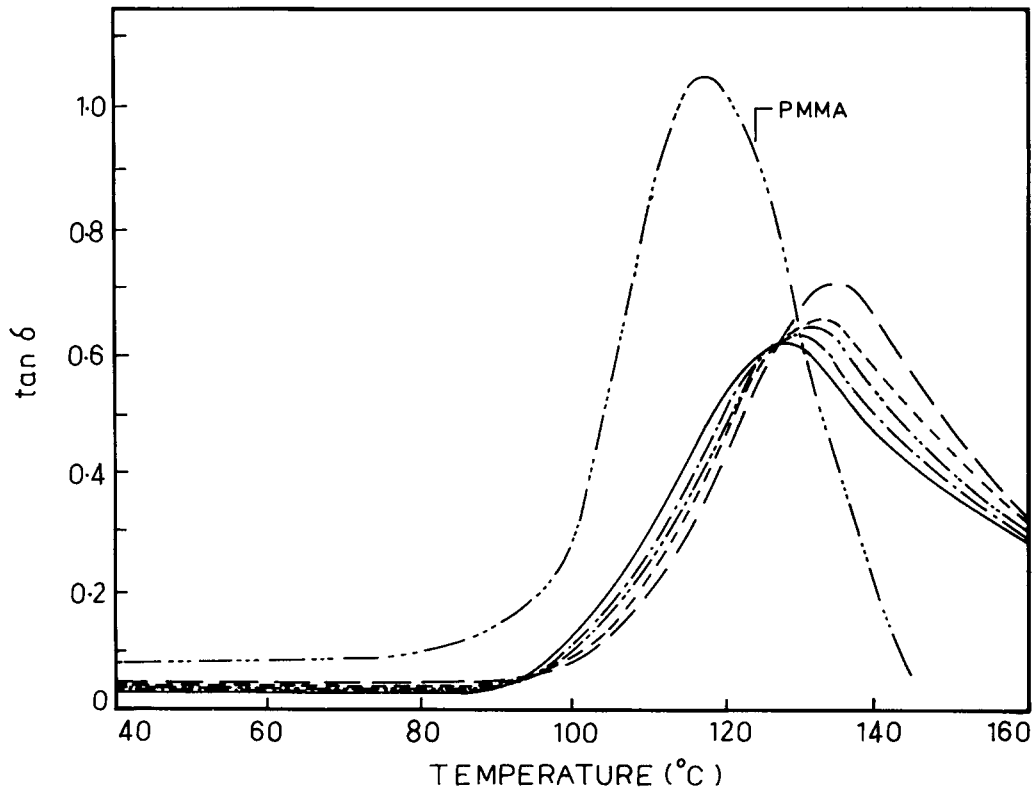

Figure 5   Variation of tan δ with temperature. Indication of different curves are the same as Figure 1.

2. The T_g is shifted to the higher temperature region as the relative volume of PEF is increased from 0 to 100%.

3. Efficiency of the hybrid composite increases with the increase in relative volume of PEF, which was predicted from the nonlinear variation of E_c'/E_m' with PEF fraction.

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 Materials Hand Book*, ASTM International, Metals Park, OH, 1987, p. 207.
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, p. 39.
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. Zimmermann, and H. W. Chang, *SAMPE J.*, **21**, 44 (1985).
14. H. W. Chang, L. C. Lin, and A. Bhatnagar, *31st Int. SAMPE Symp.*, 1986, p. 859.
15. R. F. Gibson, S. R. Vidish, and R. Mantena, *Proc. 32nd Int. SAMPE Symp.*, 1987, p. 231.
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. P. Ghosh, P. S. Mitra, and A. N. Banerjee, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2021 (1973).
19. P. Ghosh and A. N. Banerjee, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 375 (1974).
20. P. Ghosh, S. Biswas, and U. Niyogi, *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 1053 (1986).
21. N. H. Ladizesky and I. M. Ward, *J. Mater. Sci.*, **18**, 533 (1983).
22. N. H. Ladizesky and I. M. Ward, *J. Mater. Sci.*, **24**, 3763 (1989).
23. J. I. Yamaki and Y. Katayama, *J. Appl. Polym. Sci.*, **19**, 2897 (1975).
24. C. Sellitti, S. Vargiu, E. Martuscelli, and D. Fabbra, *J. Mater. Sci.*, **22**, 3477 (1987).
25. B. Tissington, G. Pollard, and I. M. Ward, *J. Mater. Sci.*, **26**, 82 (1991).
26. N. Saha, A. N. Banerjee, and B. C. Mitra, *Polym. Adv. Technol.*, **6**, 637 (1995).
27. P. Ghosh and N. Mukherjee, *Eur. Polym. J.*, **15**, 797 (1979).
28. J. U. Otaigbe, *Polym. Eng. Sci.*, **31**, 104 (1991).
29. A. R. Bunsell, *Fiber Reinforcements for Composite Materials*, Vol. 2, *Composite Materials Series*, Elsevier, Amsterdam, 1988, p. 15.