

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

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SYNOPSIS

Unidirectional (UD) composite laminates based on glass fibers (GF) and high-performance polyethylene fibers (PEF) were prepared with partially polymerized methyl methacrylate (MMA) at room temperature and then heated at 55°C (well below the softening point of PEF) for 2 hrs. The viscoelastic behavior of the composite was studied through dynamic mechanical analysis at different volume fractions of fibers. Several parameters such as storage modulus (E'), loss modulus (E''), and loss factor or damping efficiency ($\tan \delta$) were determined to be between 40 and 160°C in a resonant frequency mode. All the properties were compared between the two composite laminates. It was found that the shift of the glass transition temperature (T_g) due to incorporating fibers was higher in the case of a PEF-reinforced composite than that of a GF-reinforced composite at the same volume fraction of fibers. It was also observed that the efficiency of both the composites decreases with the increase in the volume fraction of fibers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The present trend for polymer scientists is to prepare thermoplastics and thermosetting composites exhibiting high mechanical behavior, light-weight, low-cost and covering different static and dynamic fields of application. By permutating and combining various fibers and polymers, a wide range of composites that have unique properties for versatile applications, as alternatives to conventional materials like metals and wood, has been prepared.

It is worthwhile, studying the polymer composite structure, to investigate the dynamic mechanical properties, particularly of the dynamic modulus and internal friction, over a wide range of temperatures.¹⁻⁴ The dynamic mechanical properties of the UD-composites are dependent upon the volume fraction of 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 direction of fiber alignment at different volume fractions of fibers.

The 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 GF.¹⁰ Due to these unique properties, PEF have a high potential for applications in composite structures, notably if good damping properties are required.¹⁰⁻¹⁵ A few workers have used PEF as reinforcing fibers, but these works are mainly based upon the thermoset matrix. Composites based upon thermoplastic polymeric matrices potentially offer several advantages compared to those based upon thermosetting resins.^{16,17} Thus, one could expect a unique composite structural material based on poly(methyl methacrylate) (PMMA), that is, a thermoplastic polymer as matrix. GF, a well-known reinforcing fiber-reinforced PMMA, was also prepared at the same range of fiber volume fractions.

The purpose of this work is to obtain fundamental information concerning the viscoelastic proper-

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ties in dynamic condition of UD-PEF-reinforced PMMA laminates (PEFRC) and GF-reinforced PMMA laminates (GFRC) at different volume fractions of fibers. Theoretically reduced $\tan \delta$ values are compared with experimental values of the same. All the viscoelastic properties are also compared between PEFRC and GFRC at the same volume fractions of fibers range.

THEORETICAL ASPECT

If the mechanical damping of a filled polymer results only from the inherent damping of constituents, then the damping of a UD-composite can be approximated by:¹⁸

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

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 fibers.

GF can be considered as a pure elastic material; hence, the damping efficiency of GF is effectively zero² and eq. (1) can be rewritten as

$$\frac{\tan \delta_c}{\tan \delta_m} = (1 - V_f) = V_m \quad (2)$$

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 Corporation, Petersburg, USA.
2. GF (433 BF-225) supplied by Owens Corning Fiberglas Corporation, Ohio, USA.
3. MMA supplied by Western Chemical Corporation, Calcutta, India.
4. Benzoyl Peroxide (BZ_2O_2) supplied by Loba-Chemie Indoaustranal Corporation, Bombay, India.
5. N,N dimethyl aniline (NDA) supplied by E. Merck Limited, Bombay, India.

MMA was purified by the standard technique^{19,20} and BZ_2O_2 was recrystallized 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 composites were treated with chromic acid, following Peijs et al.¹⁰ and Ladizesky and Ward.²² The surface of GF were already treated with the standard treatment, used directly for making composites. The wetting characteristics of PMMA on treated and untreated GF and PEF have been 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

The UD-plyies were made in a dustfree chamber on a glass sheet using partially polymerized MMA as the resin with an amine-peroxide (NDA- BZ_2O_2) initiator system in bulk at room temperature.²⁸ Laminated structures were prepared by stacking these plyies 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, and shrinkage was controlled using extra resin in the mold. Finally the composite was heated to a temperature of 55°C for 2 hrs to ensure the completion of MMA Polymerization. UD-laminates were prepared up to four plyies for PEF (designated as S_1 to S_4 , respectively) and GF (designated as G_1 to G_4 , respectively). A detailed description of the preparation of laminates is given elsewhere.²⁷

The dynamic mechanical properties were measured by using the 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 nitrogen at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Figure 1 displays the sample's resonant frequency (related to Young's or elastic modulus) as a function of temperature. For both the composites (GFRC and PEFRC) and matrix PMMA, the modulus decreases with an increase in temperature over the whole range of the experiment. The variation of E' with temperatures at different V_f is shown in Figure 2. It is seen that E' increases with an increase in V_f at all temperatures due to the fact that the inherent stiffness imparted by the fibers that allows efficient stress transfer. Comparing GFRC and PEFRC, E' of PEFRC is higher than that of GFRC in glassy regions at the same V_f . This is due to the fact that the modulus of elasticity (E) of PEF is higher than that of GF [E is 103 GPa (PEF) and 70 GPa (GF)].

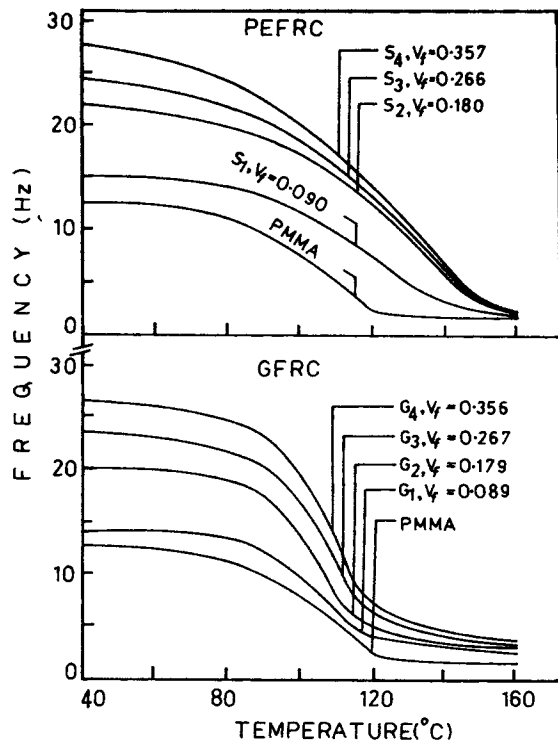


Figure 1 Variation of resonant frequency with temperature.

But at the rubbery region, E' of GFRC shows higher values than that of PEFRC at the same V_f . At this region of the viscoelastic fiber, PEF become rubbery, resulting in a decrease of E' .

Table I shows the variation of the modulus retention term²⁹ of the composites with V_f . From the table it is clear that there is no appreciable change in modulus up to 105°C (T_g of PMMA). The change is quite appreciable up to 160°C. At the same V_f , it is also found that the drop in modulus of PEFRC is higher than that of GFRC for the higher temperature region.

The modulus enhancement of composites is also demonstrated by the reduced storage modulus (E'_c/E'_m , where E'_c and E'_m are the E' 's of the composite and matrix, respectively) values. The non-linear variation of the reduced modulus with V_f is observed at higher V_f (Figure 3). At higher V_f , the fiber interaction takes place, and either they tend to bundle up among themselves or touch each other physically, due to the fact that the hand lay-up technique produces a more-or-less random nature of fiber distribution in the matrix. Due to the above facts, the proper and uniform penetration of the matrix does not take place throughout the fiber surfaces, causing inefficient stress transfer at the interface.^{30,31} These facts are reflected in

the experiment on 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.³² It has been observed that by incorporating fibers the T_g is shifted to a higher region. In the case of GFRC the T_g is shifted from 105°C (PMMA) to about 112°C (G_4), whereas for PEFRC it is shifted to about 128°C (S_4). Composites with intermediate V_f had values between these two extremes. At the same V_f , the shift is much higher for PEFRC than that of GFRC. Incorporating fibers inhibits the molecular segmental motion of chains at the transition region, yielding a higher value of T_g . The coefficient of thermal expansion of PEF¹⁰ is much higher than that of GF.³³ Hence, the PEF [approaches its melting point (147°C)] occupies a much higher volume with respect to GF and puts more constraints on the molecular segmental motion of the PMMA matrix at the transition region. Probably due to this fact, the shift of T_g of the PEFRC is higher than for GFRC. The situation of

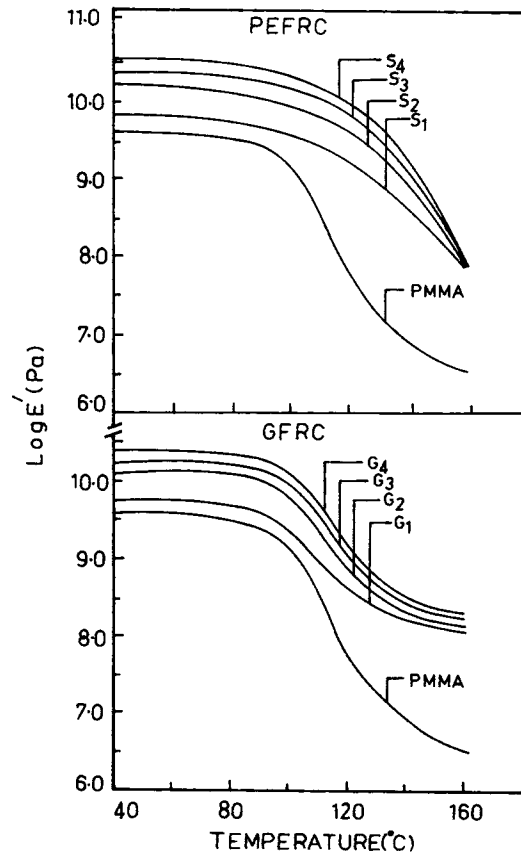


Figure 2 Variation of storage modulus with temperature.

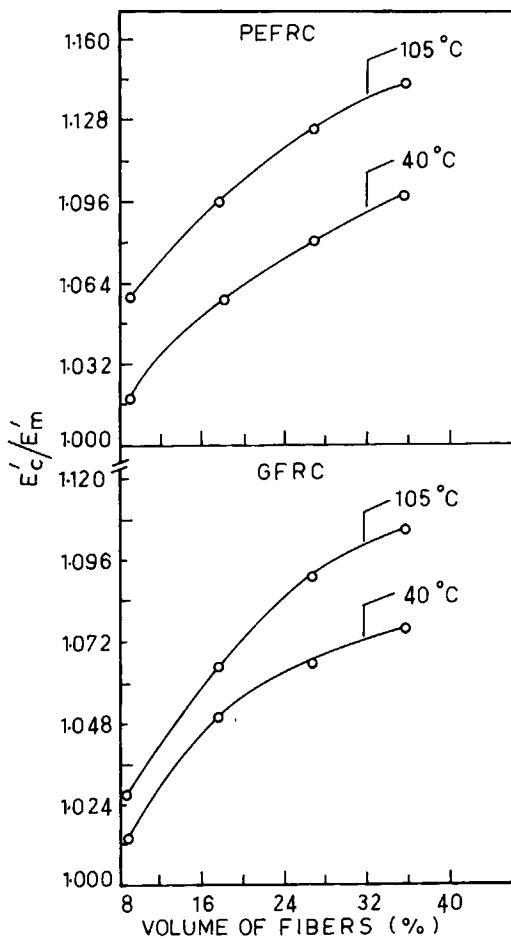
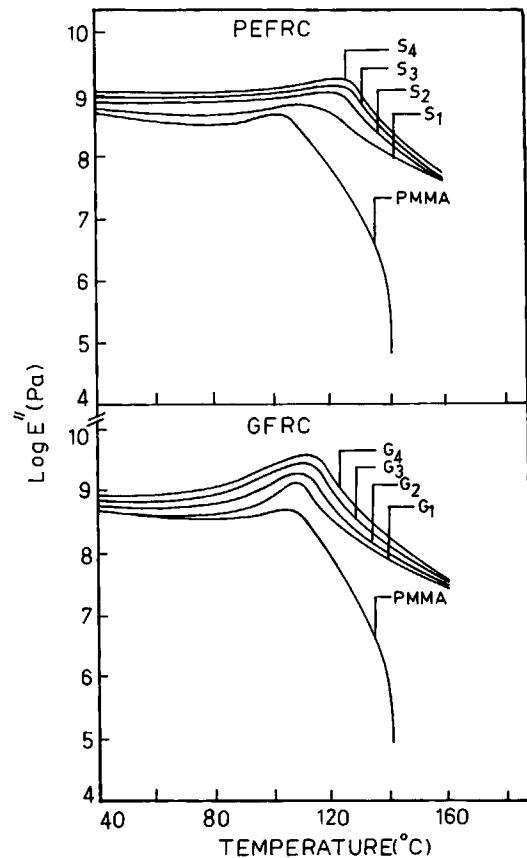
Table I Variation of Modulus Retention Term with Volume Fraction of Fibers

Volume of Fibers (%)	Modulus Retention	
	$E'_{105^\circ}/E'_{40^\circ} \times 100$	$E'_{160^\circ}/E'_{40^\circ} \times 100$
GFRC		
8.9 (G ₁)	96.5	84.4
17.9 (G ₂)	95.4	81.4
26.7 (G ₃)	95.9	81.0
35.6 (G ₄)	96.2	80.8
PEFRC		
9.0 (S ₁)	97.4	79.6
18.0 (S ₂)	97.0	77.3
26.6 (S ₃)	97.3	75.7
35.7 (S ₄)	97.4	74.7

simultaneous segmental motion of both the PEF and PMMA is more pronounced as the V_f increases from single ply to four plies; as a result the peak (where

E'' is at a maximum) becomes less prominent at higher V_f .

Figure 5 shows the variation of $\tan \delta$ with temperature for various composites compared to the matrix. It is seen that the introduction of fibers has reduced the peak height; that is, $\tan \delta$ is lowered

**Figure 3** Variation of reduced modulus with volume fraction of fibers.**Figure 4** Variation of loss modulus with temperature.

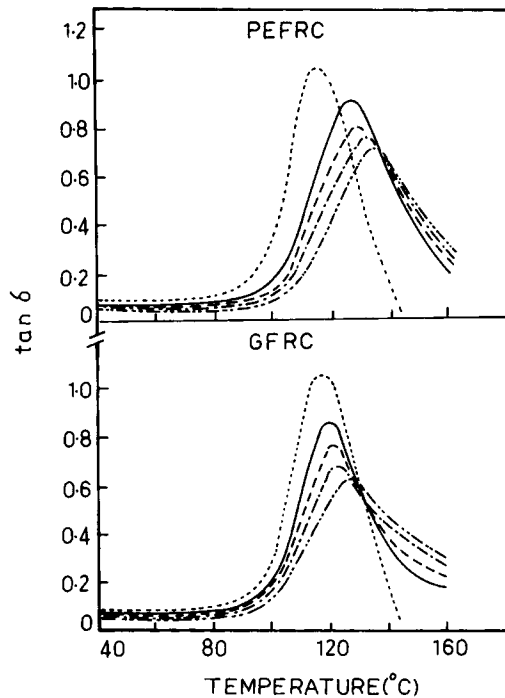


Figure 5 Variation of $\tan \delta$ with temperature. (-----) PMMA; (—) S_1, G_1 ; (- - - - -) S_2, G_2 ; (- · - · - · -) S_3, G_3 ; (- · · · · - ·) S_4, G_4 .

with an increase in fiber content. It is also found from the figure that the temperature location of peaks with respect to the matrix has shifted more in the case of PEFRC compared to GFRC. This is due to the simultaneous segmental motion of PEF and PMMA 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 inhibition of the relaxation process within the composites up 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. 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 GFRC). All the experimental points lie below the theoretical points, indicating that the presence of reinforcement has led to a greater reduction in 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-fibers interface as explained in earlier literature.^{32,34} It is also observed that the experimental curves tend

to flatten with an increase in V_f . This is due to the fact that at higher V_f , the fiber-fiber friction takes place and the fiber surfaces are not properly wetted by the matrix.

CONCLUSIONS

From the above studies the following conclusions may be drawn

1. The composite laminates as a whole have been made at room temperature, casting the required minimum amount of energy, which may be regarded as the advantage of the system.²⁷
2. Comparing same V_f , E' is higher in the case

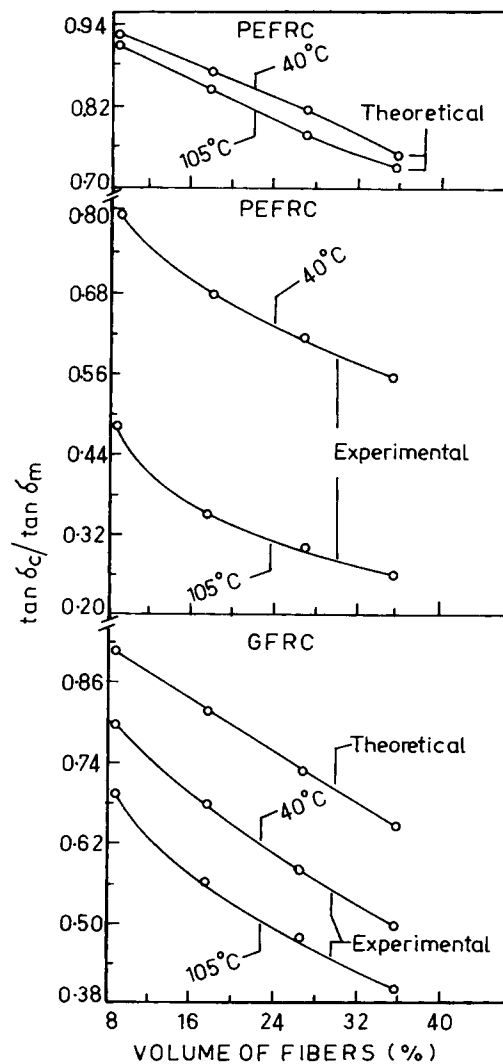


Figure 6 Variation of reduced $\tan \delta$ with volume fraction of fibers.

of the PEFRC than that of GFRC at the glassy region, but at the rubbery region the GFRC shows higher values compared to PEFRC.

3. The T_g of the composite is greater than that of the pure matrix. The shift of T_g is higher in the case of PEFRC than that of GFRC at the same V_f .
4. The efficiency of the composite reduces with an 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 .

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