A Dynamic Mechanical Study on Unidirectional Carbon Fiber-Reinforced Polypropylene Composites

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SYNOPSIS

Fiber-reinforced polymer composites show high specific strength and stiffness. The alignment of reinforcing fibers results in anisotropy of the material. This anisotropic behavior has been studied through dynamic mechanical analysis of unidirectional carbon fiber-reinforced polypropylene (CFRPP) composites measured in both parallel and transverse directions to fiber arrangement. Several parameters such as storage modulus (E'), loss modulus (E''), loss factor or damping factor ($\tan \delta$), and complex viscosity (MU*) have been determined over a wide range of frequencies and at a fixed temperature. Relaxation and retardation spectra have been constructed for these composites. Modulus enhancement occurs due to stiffness imparted by the fiber and efficient stress transfer at the interface. Relaxation of the polymer matrix ceases with increase in the volume fraction of the fibers. α'-relaxation is observed for the composite having a 13% volume fraction of fibers and is ascribed to relaxation in the crystalline phase where the additional crystallinity arises out of the transcrystalline growth at the fiber–matrix interface. There exists a good correlation between theoretical curves with the experimental ones. Relaxation and retardation spectra and the dynamic parameters determined for these composites show a good correlation with the volume fraction of fibers as well as the direction of the applied load. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Relaxation processes play an important role in understanding the mechanical behavior of polymers. Both the morphology and the crystallinity influence the relaxation maps. In composite materials, the interfacial effect that allows high toughness of the composites is also quite important in addition to the individual phases of the fibers and the matrix and their arrangement/distribution.

Investigation on dynamic mechanical properties, particularly on dynamic modulus and internal friction, over a wide range of frequencies is quite useful in studying the composite structure of polymers in relation to performance.[1-4] Unidirectional fiber-reinforced composites are anisotropic and show high strength and modulus in the direction of the fiber orientation. Accordingly, the dynamic properties of these composites are greatly influenced by fiber orientation.[5,6] Hence, in the study of anisotropic behavior of composites by dynamic mechanical analysis, it is important to characterize the dynamic properties of composites both in parallel and in transverse directions with respect to the fibers. The dynamic mechanical properties of the composites are also dependent on the volume fraction of fibers in the composites.[7,8] The dynamic parameters characterizing the relaxation and retardation spectra indicate the long-term response of the polymer matrix over time. Thus, for unidirectional fiber-reinforced composites, generation of these spectra in both parallel and transverse directions helps in characterizing their anisotropic behaviors.

Isotactic polypropylene (i-PP) is a semicrystalline polymer. Various mechanical relaxations in i-PP have been thoroughly investigated.[9] Both short and long (unidirectional) glass fiber-reinforced i-PP have also been subjected to dynamic mechanical analysis. The effect of a coupling agent on glass fiber reinforcement is also reported. Unfortunately, the

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Journal of Applied Polymer Science, Vol. 51, 831–840 (1994)
 CCC 0021-8995/94/050831-10

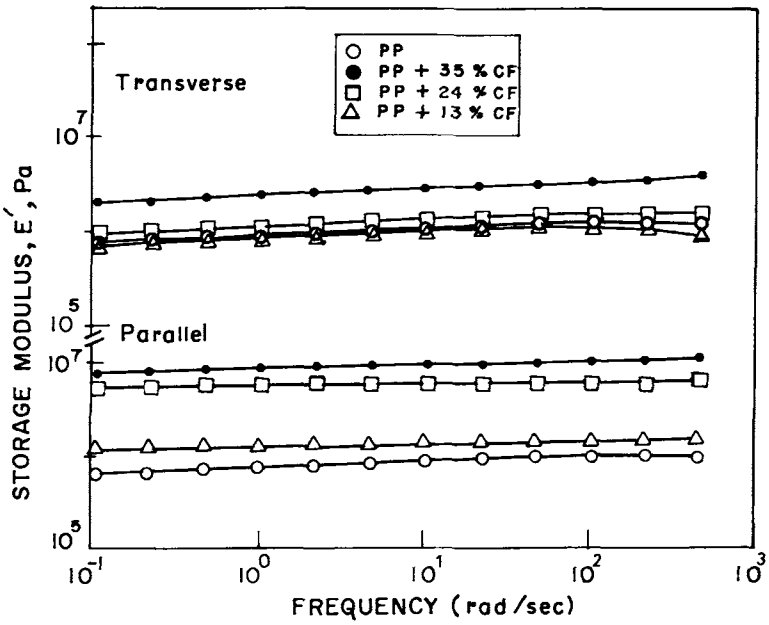


Figure 1 Storage modulus as a function of frequency for different volume fractions of fibers.

low specific elastic modulus of glass fiber-reinforced composites warrants its application in major spacecraft applications. On the other hand, Kevlar (Aramid)-reinforced composites show extreme anisotropy, being very weak in the transverse direction. Carbon fiber (CF)-reinforced composites, however, exhibit high values in both axial directions, as does glass fiber. Although CF-reinforced PP (CFRPP)

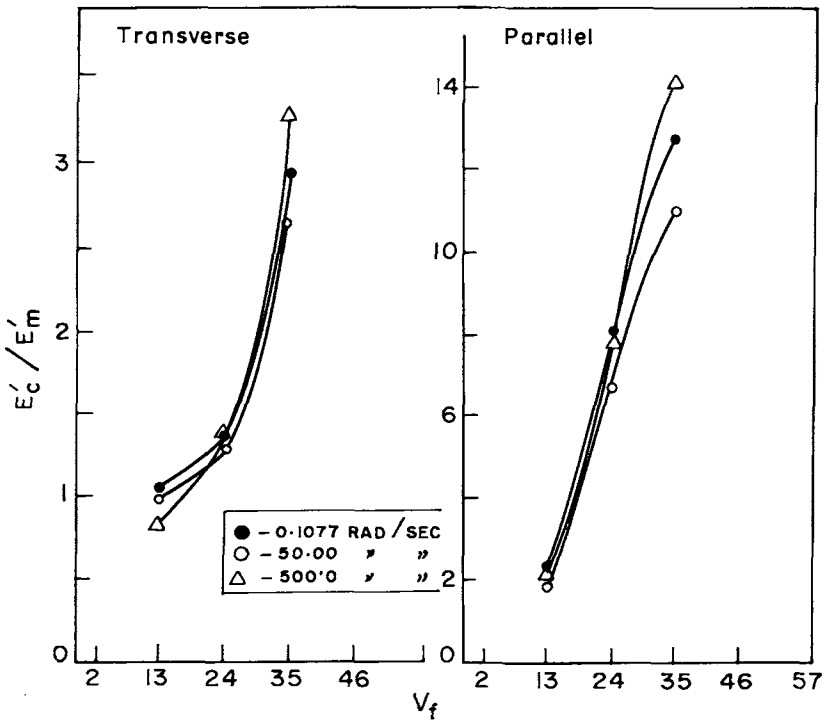


Figure 2 Reduced storage modulus vs. volume fraction of fibers.

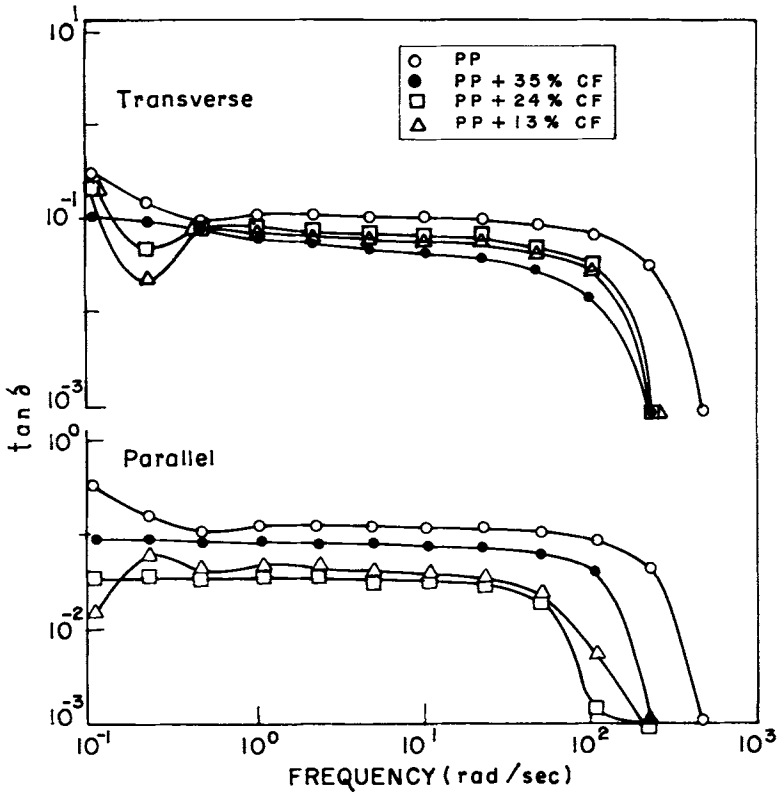


Figure 3 Damping factor response against frequency.

would be rarely used as an engineering material, a systematic study on CFRPP composites seems to be highly desirable as composites based on engineering plastics and a PP blend reinforced with CF show great promise for many practical applications.

In this article, we report the frequency spectrum of dynamic properties of unidirectional CFRPP composites at different volume fractions under isothermal conditions. These experimental curves have also been compared with the theoretical one, the latter being constructed using the Halpin–Tsai equation.[10] The dynamic parameters have also been used to construct relaxation and retardation spectra of the composites.

THEORETICAL ASPECT

The dynamic properties of a material are specified mainly by two basic quantities: dynamic storage modulus, which provides a measure of the effective stiffness of the material, and the loss factor or damping factor, characterized by the heat energy dissipated per cycle. In addition, complex viscosity, MU*, is also an important parameter for characterizing composite materials. Two additional viscoelastic functions may also be introduced, viz., the relaxation (H) and retardation (L) spectra. The significance of these spectra is best understood by considering the model of Maxwell and Voigt.[1] H and L as a function of τ, the relaxation or retardation time, may be represented in a number of ways[1,11]:

$$E(t) = E_e + \int_{-\alpha}^{\alpha} He^{-t/\tau}\, d \ln \tau \qquad (1)$$

$$D(t) = D_g + \int_{-\alpha}^{\alpha} L(1 - e^{-t/\tau})\, d \ln \tau \qquad (2)$$

where $E(t)$ is the time-dependent modulus; $D(t)$, the time-dependent compliance; E_e, the value of the modulus at $\tau = \alpha$; and D_g, the value of compliance at $\tau = 0$.[1] It is thus possible to calculate H and L from the storage modulus and loss modulus and by using the interrelationship between the spectra. H may be calculated from the storage modulus by using the relation[1]

$$H(\tau) = AE'd \log E'/d \log \omega|_{1/\omega} = \tau \qquad (3)$$

where ω is the measurement or experimental frequency; m, the negative slope of H in a doubly logarithmic plot of H and τ; and A, a function of m, expressed by

$$A = (2-m)/2\Gamma(2-m/2)\Gamma(1+m/2) \text{ and } m < 1$$

Using this calculated value of H and the values of storage and loss moduli, L may be calculated using the following expression[1]:

$$L(\tau) = \frac{H(\tau)}{\left[E'\left(\frac{1}{\tau}\right) - E''\left(\frac{1}{\tau}\right) + 1.37H(\tau)\right]^2 + \pi^2 H^2(\tau)} \qquad (4)$$

EXPERIMENTAL

Materials

Polypropylene (PP) of MFI 10 (grade M0030) and MFI 3 (M3030), IPCL, Baroda, India, was used as the matrix. Carbon fiber (CF) (7.5 μm diameter, modulus in the parallel direction, 230 GPa, and in the transverse direction, 36.5 GPa; grade RK 30/12) of R.K. Carbon Fibres, U.K., was used for making the composites.

Sample Preparation

Unidirectional CF-reinforced composites with different fiber volume fractions were prepared using a film-stacking technique.[12] These composites were cut both in parallel and transverse directions. The dimensions of the specimens are as follows:

Length	0.0650 ± 0.0005 m
Width	0.0126 ± 0.0006 m
Thickness	0.0020 ± 0.0006 m.

Measurements

The samples were subjected to testing in a dynamic spectrometer (Rheometrics, USA) in a three-point bending mode. The following conditions were set for all the samples:

Strain	$3.000E-01$
Temperature	25°C
Frequency	$1.000E-01$ to $5.000E+02$ rad/s.

Dynamic parameters, viz., E', E'', tan δ, and MU* were measured over this frequency range at constant temperature.

RESULTS AND DISCUSSION

Storage Modulus and Reduced Storage Modulus

The variation of storage modulus with frequency at different volume fractions of fibers is shown in Figure 1. The increase in modulus is quite appreciable when measurements are made in a parallel mode. However, a significant increase in modulus occurs only at a high volume fraction of fibers (cf. 35% V_f) in transverse mode measurements. In the former case, modulus enhancement occurs due to stiffness imparted by the fiber that allows efficient stress transfer, whereas this property is controlled mainly by the matrix/fiber–matrix interface rather than by the reinforcing fibers in the latter.

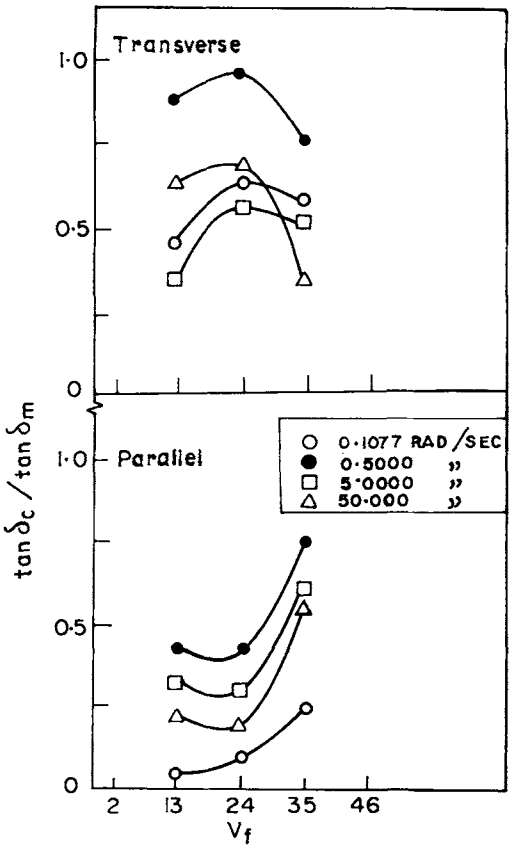


Figure 4 Reduced tan δ against volume fraction of fibers.

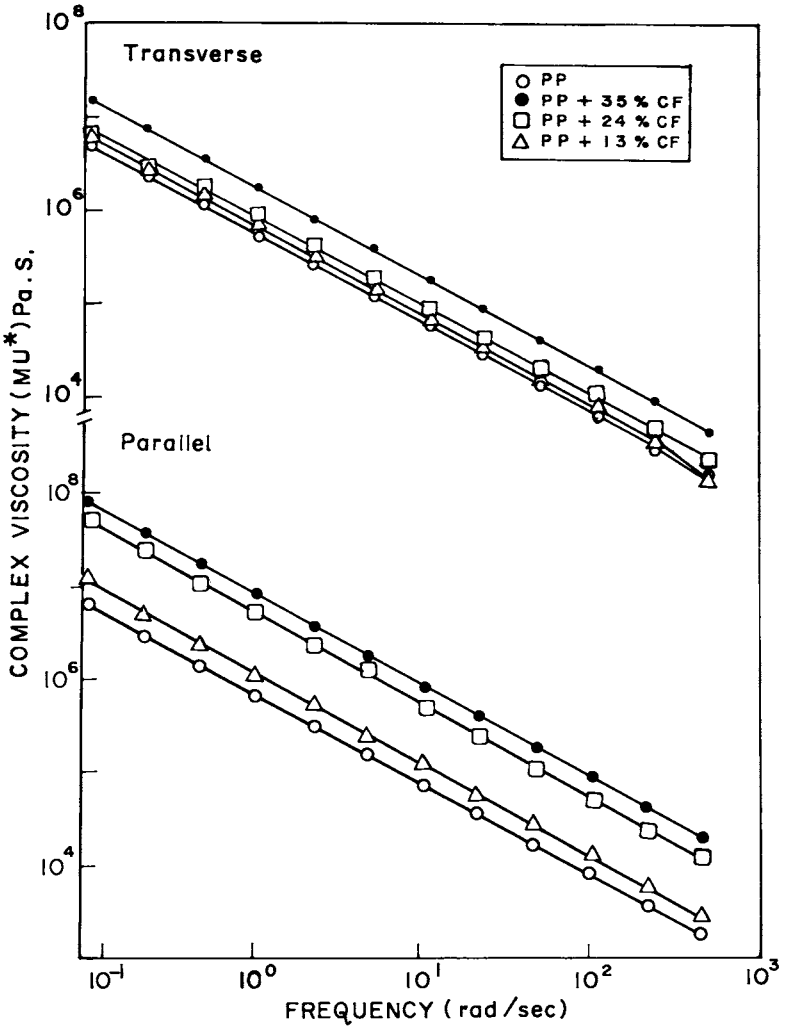
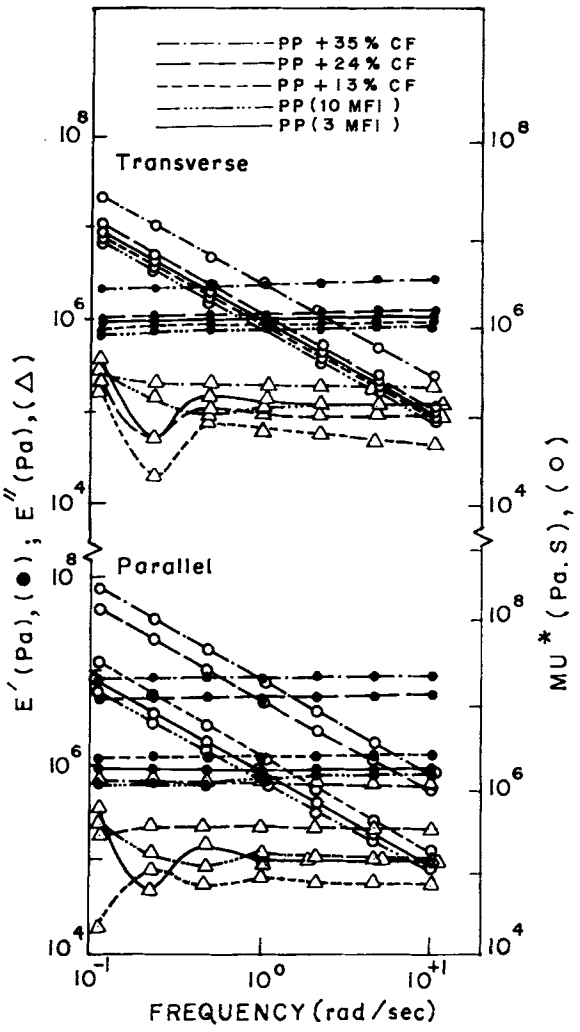


Figure 5 Plot of complex viscosity against frequency.

The modulus enhancement of composites is also demonstrated by the reduced storage modulus (E'_c/E'_m) values. The change in the reduced modulus of the composites with the volume fraction is linear up to 24% V_f, after which it is nonlinear (Fig. 2). At a high fiber/resin ratio, improper wetting of the fiber by the matrix resin occurs, thereby causing inefficient stress transfer at the interface. These affect the composite response to the dynamic condition at higher frequency and ultimately reduce the modulus enhancement ability of the fiber.

Damping Factor and Reduced tan δ

In a composite system, damping is improved through the incorporation of fibers. This is due mainly to shear stress concentrations at the fiber ends in association with the additional viscoelastic energy dissipation in the matrix material. In the CF–PP system, the nature of the relaxation processes and energy-dissipative mechanism have been ascertained from the plot of tan δ against frequency. Relaxation of the polymer matrix is concentrated mainly in the low-frequency region. With an increase in the volume fraction of the fibers, the tan δ curve becomes flat as the fiber restricts the relaxation of the polymer when measurements are made in a parallel mode (Fig. 3). The polymer behaves as a rigid material. Some relaxations are found to occur in virgin PP and in composites (13% V_f). α′-relaxation is observed for this composite and is due to relaxation in the crystalline phase. This additional crystallinity may result from the transcrystallinity development



at the fiber–matrix interface.[13] There is, however, no such relaxation observed in virgin PP. The heat-dissipating efficiency of the polymer in composites that is dictated by the value of tan δ increases as the volume fraction of fiber in the composites increases.[14]

The extent of interfacial adhesion in composites is manifested by the tan δ value observed in transverse-mode measurements. Improvement in interfacial bonding in composites (13 and 24% V_f) occurs as observed by the lowering in tan δ value. A high volume fraction of fibers (viz., 35% V_f) leads to fiber–fiber friction due to improper wetting of the fibers by the matrix resin (Fig. 3). This increases the tan δ value of the composites to a significant extent.

A normalized tan δ value, however, gives a better picture of the relaxation process and energy-dissipative mechanism. Thus, initial low values of the reduced tan δ ($=$ tan δ_c/tan δ_m) for a low volume fraction of fibers in the composites indicate good interfacial bonding (up to 24% V_f) (Fig. 4). However, in transverse-mode measurements, the response of tan δ_c is found to be frequency-dependent.

Complex Viscosity (MU*) and E'–MU* Plot

Dynamic mechanical properties are also expressed in terms of complex viscosities. The real part of the complex viscosity is an energy-dissipation term similar to the imaginary part of the complex modulus.

The variation of complex viscosity (MU*) with frequency is shown in Figure 5. A monotonic de-

Table I Derived Value of Frequency at E' and MU* Inflection Point

Mode	Sample	E''/MU* (s^{-1})	$(E''/MU^*)^2$	Frequency (ω)* (rad/s)
	PP	0.131	0.017	1.008
Parallel	PP + CF			
	13%	0.083	0.006	1.003
	24%	0.039	0.001	1.000
	35%	0.050	0.002	1.001
Transverse	PP + CF			
	13%	0.084	0.007	1.003
	24%	0.088	0.007	1.003
	35%	0.077	0.005	1.002

* Calculated from the expressions MU* $= \sqrt{(E'^2 + E''^2)}/\omega$ and $\omega = \sqrt{1 + (E''/MU^*)^2}$ when the magnitude of E' and MU* becomes equal.

crease of MU* with increase in frequency is observed in both parallel- and transverse-mode measurements. This reflects the inverse relationship between MU* and the frequency. The effect of the volume fraction of fibers in MU* is similar to that observed in E' vs. frequency plot, as MU* is directly related to E'.

The presence of an inflection point at a particular frequency for all the specimens is quite interesting when E' and MU* are superimposed on the same graph (Fig. 6). The point is found to be the characteristics of the matrix irrespective of the modes and melt flow index of the matrix material used. The corresponding data are tabulated in Table I. It is observed that the parameter $(E''/\text{MU}^*)^2$ is responsible for keeping the inflection at the same frequency. The dimension of the parameter (E''/MU^*) is s^{-1} and it implies that response of the composites in the dynamic condition is very much strain-dependent.

Theoretical Curves

Theoretical curves of dynamic properties like E', tan δ, and MU* are constructed using the Halpin–Tsai equation with some modification and have been compared with the experimental curves (Figs. 7–9). There exists a good correlation between the two curves. However, some deviation is observed in case of tan δ at a high volume fraction of fibers (35% V_f), particularly in parallel-mode measurements. At this high volume fraction of the fiber, the frictional energy caused by fiber–fiber friction contributes to the energy dissipation by the polymer matrix, thereby leading to a high tan δ value.

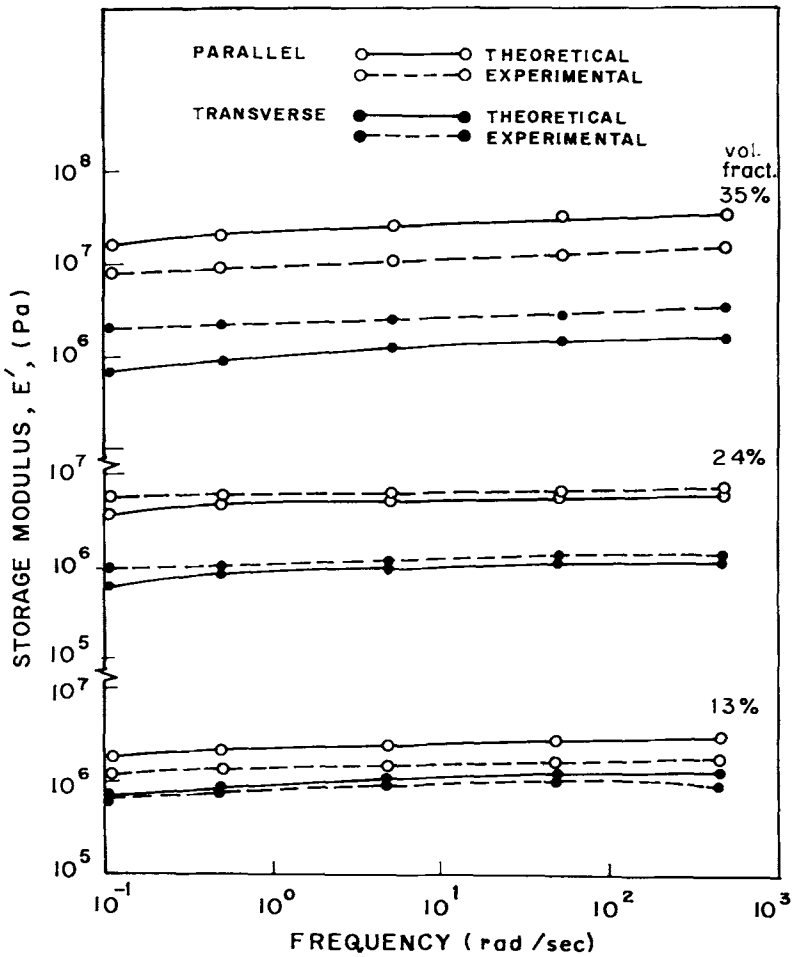


Figure 7 Plot of E' against frequency.

Relaxation and Retardation Time Spectra

Relaxation and retardation time spectra reflect the dimensional stability of the composites under loads over a prolonged period. This also reveals the spectral strength and spectral compliance of the composites in relation to the inherent structure, e.g., the anisotropy of the composites over the continuous time scale. Fibers used as reinforcement in composites also play a critical role in the relaxation and retardation processes of the polymer matrix as it imparts a high modulus to the composite. A spectral strength increment with respect to virgin PP is higher for composites with 13% V_f of fibers compared to others (Fig. 10).

In both parallel- and transverse-mode measurements, the region of maximum relaxation, H_{max}, differs well over a continuous time scale with increase in volume fraction of the fibers. It is also observed that relaxation of the polymer ceases to a great extent with increase in volume fraction of the fibers (35% V_f) when the measurements are made in the parallel mode, mainly because of hindrance in the mobility of polymer chain by the fibers. However, relaxation of the polymer exists even at a high volume fraction of fibers in the transverse mode. This is, however, distributed over the entire time scale rather than in a shorter time domain in a parallel mode.

Spectral compliance that manifests the creep behavior of composites with a change in frequency is improved with increase in the volume fraction of the fibers, particularly in the parallel mode (Fig.

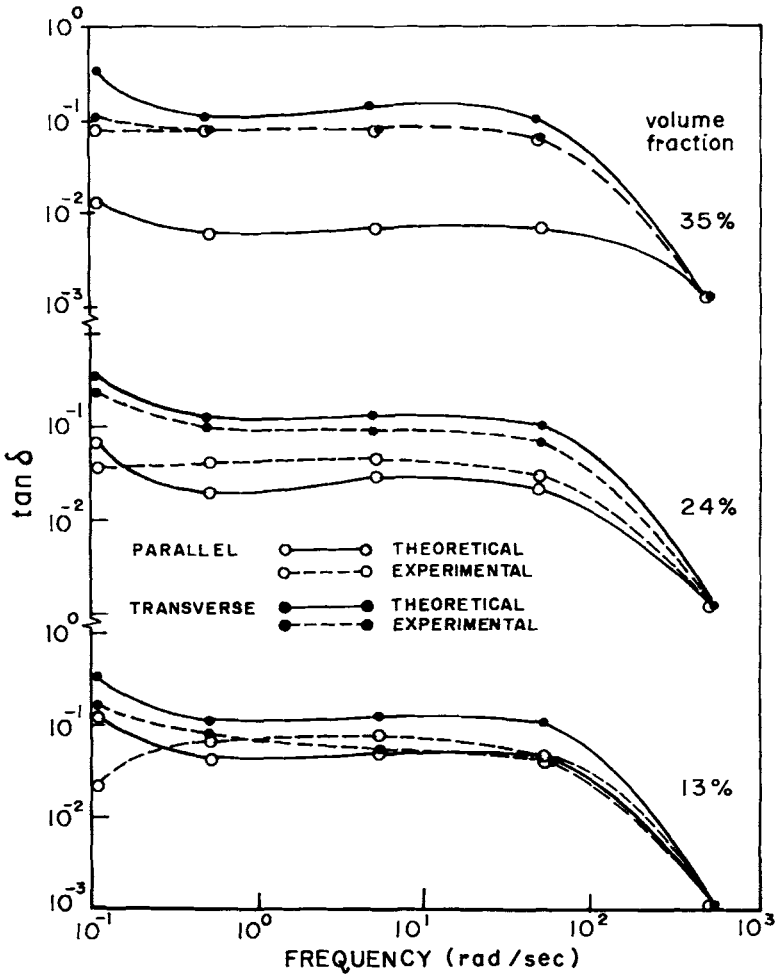


Figure 8 Plot of tan δ against frequency.

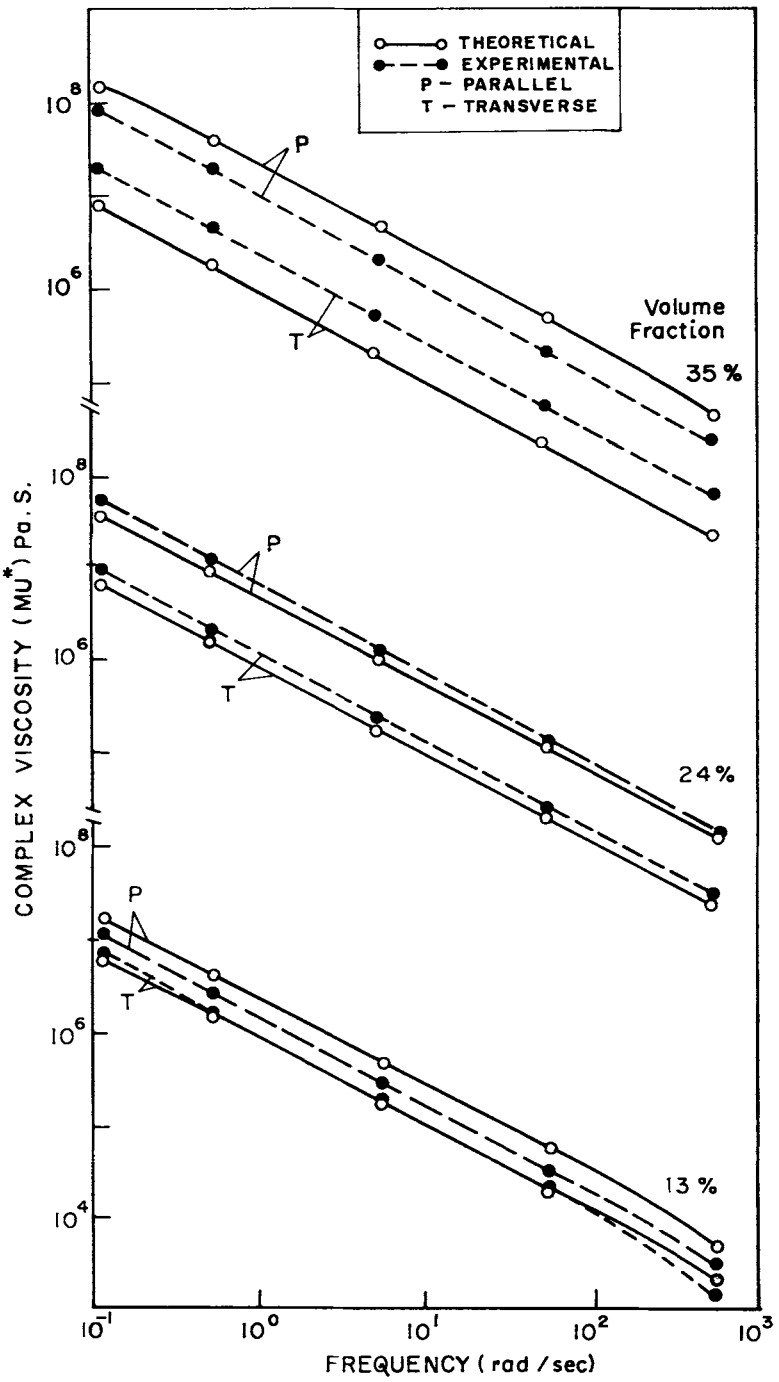


Figure 9 Plot of MU* against frequency.

verse mode, presumably due to a change in the interfacial property at a high fiber/resin ratio. The retardation process in the polymer matrix is found to be broadly distributed over the continuous time scale in multiple regions that impart resistance to strain decay in dynamic conditions and make the composite more creep-resistant.

CONCLUSION

Dynamic mechanical properties of unidirectional carbon fiber-reinforced polypropylene composites are greatly affected by the direction of the applied load and the volume fraction of the fibers. Thus, both of these variables play an important role in

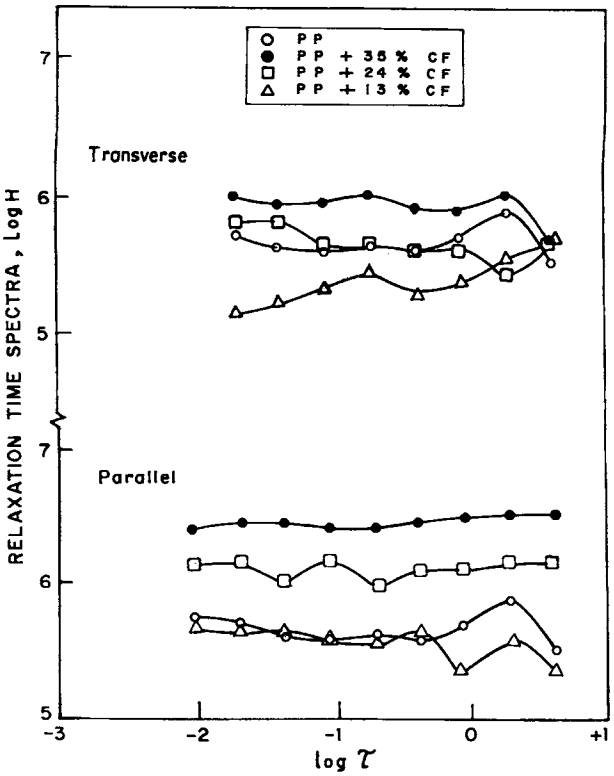


Figure 10 Relaxation time spectra of composites for different volume fractions of fibers.

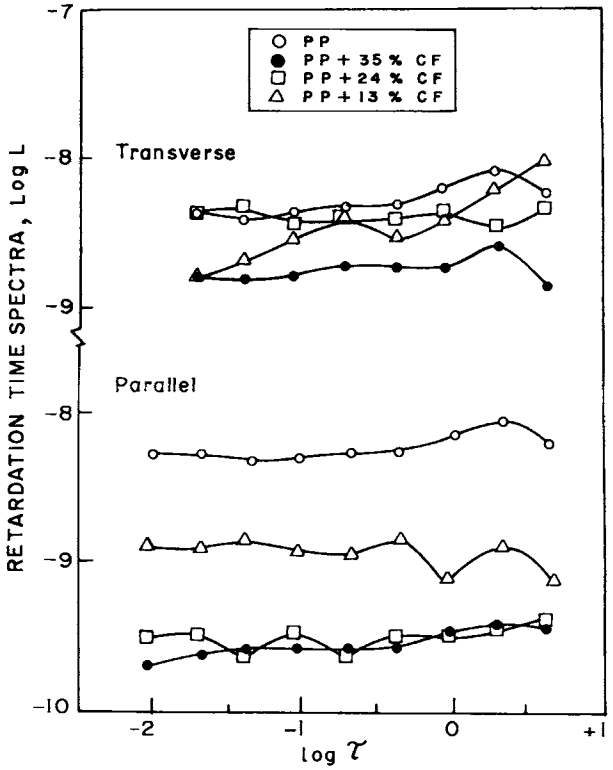


Figure 11 Retardation time spectra of composites for different volume fractions of fibers.

determining the ultimate performance of the composites under dynamic conditions. Generation of relaxation and retardation spectra of the composites is found to be useful in understanding the relaxation and retardation processes of the polymer over a continuous time scale. It also relates the spectral strength and spectral compliance, which are useful in predicting the performance of composites under dynamic conditions.

One of the authors (D.M.) is thankful to the Council of Scientific & Industrial Research (C.S.I.R.), Govt. of India, for providing a Senior Research Fellowship.

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Received May 5, 1993
Accepted July 2, 1993