Characterization of Engineering Polymers by Dynamic Mechanical Analysis

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CHARACTERIZATION OF ENGINEERING POLYMERS BY DYNAMIC MECHANICAL ANALYSIS

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INTRODUCTION

There is a growing need for the use of polymers in high-strength and engineering applications, and many new materials and composites have been developed to satisfy this need. Traditionally, thermosetting polymers have been employed as high-strength materials, with the incorporation of various fillers or additives to improve shortcomings in strength and temperature performance. Although these materials are largely unrivaled in high-temperature performance, some of the newer engineering thermoplastics, such as poly(ether ether ketone) (PEEK), poly(ether sulfone) (PES), poly(phenylene sulfide) (PPS), and the new backbone liquid-crystal polymers are becoming much more widely used. With this widespread use and with the increasing complexity of polymer blends and composites, there is a strong requirement for a universal means of characterizing such materials in terms of mechanical properties and high-temperature performance. A powerful and versatile analytical technique which is capable of application to a very wide range of materials is that of dynamic mechanical spectrometry. This technique can be used to establish basic material relaxation temperatures and frequencies, the modulus and loss behavior, as well as factors such as degree of cure, filler/matrix bonding, and phase separation.

This paper examines the application of dynamic mechanical spectrometry

to engineering polymers, including rubber-toughened epoxies, composites, and engineering thermoplastics, and discusses some specific examples of the use of the technique.

DYNAMIC MECHANICAL SPECTROMETRY: THEORY AND PRACTICE

Dynamic mechanical spectrometry is a technique which has evolved over a number of years and there are a number of excellent texts reviewing its development [1-5]. It can be implemented via a range of slightly differing techniques. Essentially, all the methods measure the response of a material to periodic forces, and thus the vibrational parameters such as amplitude, frequency, and type of oscillation and wave propagation need to be monitored. Generally, measurements are carried out by using (i) free vibrations (e.g., torsion pendulum), (ii) resonance vibrations (e.g., Du Pont DMA), and (iii) forced sinusoidal excitation and response.

It is the third method of forced vibration that is the major subject of this paper, with particular reference to the use of a Rheometrics Dynamic Spectrometer, RDS 7700 Mark 2 [6] (Fig. 1). This determines the dynamic mechanical properties of a material by measuring the response to a forced sinusoidal shearing action applied from a servomotor. The response is measured by a torque transducer, permitting computation of the elastic modulus, G', the loss modulus, G'', and the loss tangent, tan δ. G' represents the amount of energy stored elastically upon deformation and recovered per cycle, and G'' represents the energy lost to viscous dissipation, such as heat.

The applied force and resulting response vary sinusoidally with time at a constant frequency. At small strains, in the linear viscoelastic region, the strain alternates sinusoidally, but is out of phase with the stress (Fig. 2).

The phase lag results from the time scale of molecular rearrangements within the material and is related to the relaxation behavior. The two sinusoidal motions of stress and strain can be expressed by

$$\text{strain } \epsilon = \epsilon_0 \sin(\omega t), \tag{1}$$

$$\text{stress } \sigma = \sigma_0 \sin(\omega t + \delta), \tag{2}$$

where ω is the angular frequency, δ is the phase angle, and t is the time.

Equation (2) can be expanded to give

$$\sigma = \sigma_0 \sin(\omega t) \cos \delta + \sigma_0 \cos(\omega t) \sin \delta \tag{3}$$
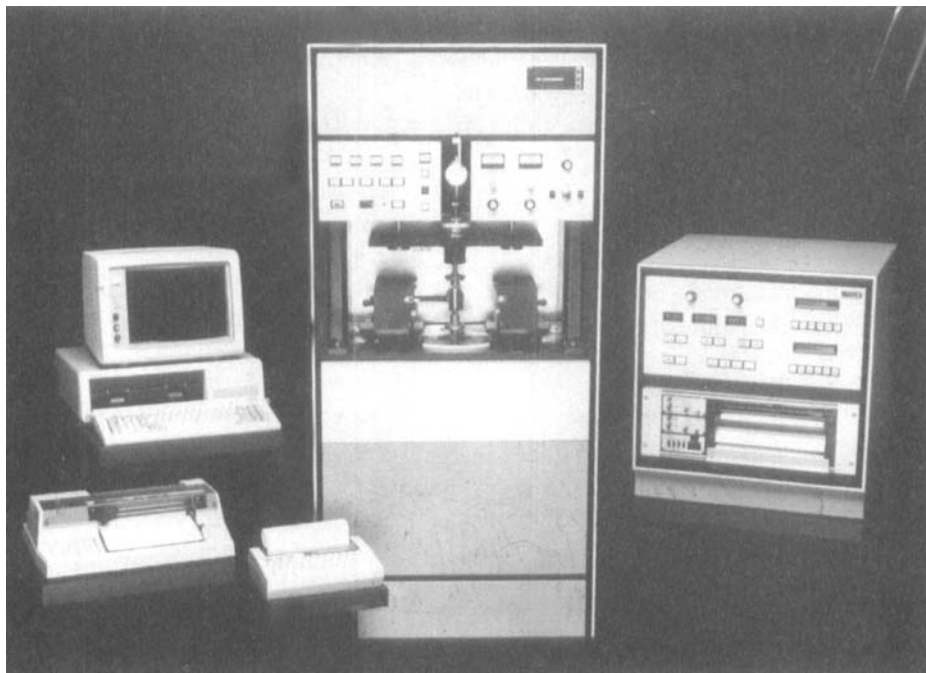
FIG. 1. Rheometrics dynamic spectrometer, RDS 7700 Mark 2. (Courtesy Rheometrics Europe GmbH.)

$$\text{Modulus } G^* = \frac{\hat{t}}{\hat{8}} \qquad \text{Loss } \delta = \tan^{-1}\frac{G''}{G'}$$
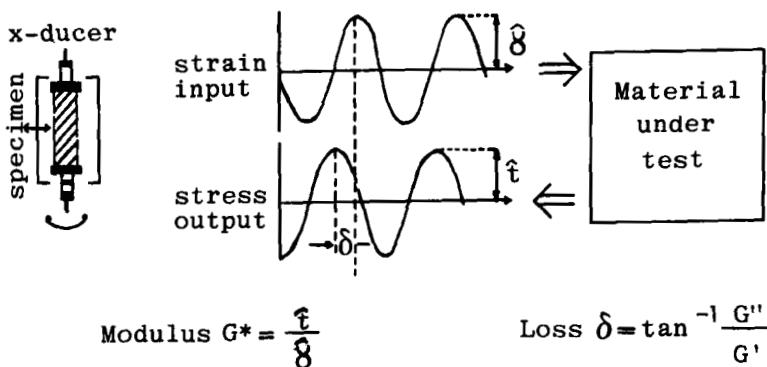
FIG. 2. Stress and strain response in the linear viscoelastic region. (Courtesy Rheometrics Europe GmbH.)

It is now clear that there are two components of the stress, one in phase with the strain and one 90° out of phase. The two moduli G' and G'' are determined by resolving the stress and strain components:

$$G'(\omega) = \frac{\sigma_0}{\epsilon_0} \cos \delta, \tag{4}$$

$$G''(\omega) = \frac{\sigma_0}{\epsilon_0} \sin \delta. \tag{5}$$

The complex modulus is defined as

$$G^* = G' = iG''. \tag{6}$$

In a cyclic deformation the ratio of energy lost to energy stored yields the loss tangent, or damping factor, tan δ:

$$\tan \delta = G'/G'' \tag{7}$$

The loss modulus G'' and the loss tangent are particularly sensitive to molecular motions within a material and also to various transitions, relaxation processes, structural heterogeneities, and the structure and morphology of multiphase systems. In particular, the dynamic mechanical spectrum of a material as a function of temperature will "fingerprint" that material in terms of its α and lower-order transitions. In the α-transition region, damping is high due to the onset of micro-Brownian motion within the molecular structure of the main chain.

Some chain segments are free to move while others are not. Much energy is stored by frozen-in chain segments during the sinusoidal cycle, and this is released as heat as soon as the frozen-in segments become free to move. Such a transition is characterized by an inflection point in the elastic modulus G' and a corresponding peak in the loss modulus G'', and the tan δ (Fig. 3). The G'' peak occurs at a slightly lower temperature than that of the tan δ peak.

Lower-order transitions, β- and γ-dispersions, etc., involve motions of molecular segments smaller than those of the main chain [7-9] and, as such, their activation energies are generally smaller than those of the primary or α dispersions.

Tan δ is often the parameter that is employed as a measure of primary and lower-order transitions. It can provide a sensitive indication of structural changes occurring within homopolymers, copolymers, blends, and composites.
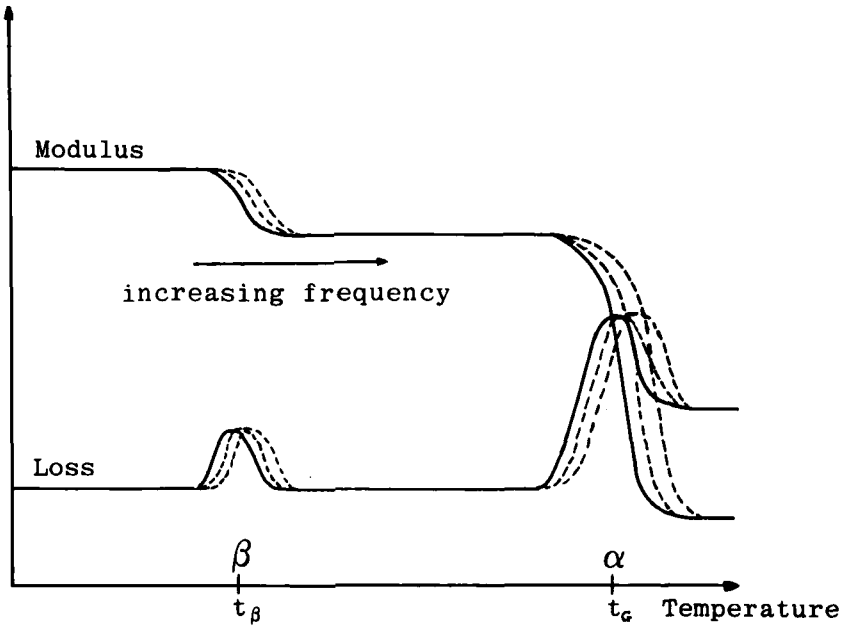
FIG. 3. Dynamic mechanical behavior in a transition region. Upper curve G', lower curve G''. (Courtesy Rheometrics Europe GmbH.)

In semicrystalline homopolymers, for example, the magnitude, shape, and position of the α-peak is directly affected by the proportion of the amorphous phase, and this is also the case in filled semicrystalline materials, where crystallinity can be disrupted by added filler [10, 11].

Glassy or rubbery crosslinked systems can also be usefully characterized by dynamic mechanical spectrometry as the dynamic mechanical properties and loss behavior of crosslinked materials are strongly dependent upon crosslink density and architecture [12-16]. In rubbers, the glass-transition temperature or α-transition shifts to higher temperatures with increasing crosslink density, and, in fact, this shift can be utilized to assess the molecular weight between crosslinks, M_c [1].

$$M_c \simeq 3.9 \times 10^4 / (T_g - T_{g_0}) \qquad (8)$$

where T_{g_0} is the transition temperature of the uncrosslinked polymer. Similar relationships have also been employed for glassy crosslinked systems [17],

as well as the function relating modulus to molecules to molecular weight between crosslinks:

$$M_c = \rho RT/G \qquad (9)$$

where ρ is the density of the rubber and R is the gas constant.

A similar criterion can be used for glassy crosslinked polymers, such as epoxides, that possess higher crosslink densities than rubbers. Here, the dynamic mechanical behavior can be significantly affected by the stoichiometric balance of reactants and the cure conditions.

ENGINEERING POLYMERS

Many engineering polymers are systems of two or more components. These may either make use of blends of different homopolymers to develop specific properties or employ solid particulate fillers to increase the modulus and enhance mechanical properties. In the case of polymer blends, one of the largest engineering applications is in the toughening of brittle glassy matrices, such as polystyrene (Fig. 4) to form a "high-performance" blend. The toughness of these materials is improved by the incorporation of small, generally elastomeric inclusions as a second phase. This area of research is particularly active in structural adhesives [18-23] and is continuing to develop new materials with enhanced temperature and toughening performance.

The basis of the rubber toughening process is to provide an *immiscible* blend of a glassy polymer matrix with discrete elastomer particles. The particles then act as energy absorbers by a range of mechanisms, such as multiple craze formation, depending on their distribution and concentration. Rubber-modified thermosets are prepared from a homogeneous solution of rubber in the resin, which precipitates a discrete elastomeric phase during the course of the curing reaction. The solubility parameters of the component materials are selected to give the highest degree of incompatibility in the reacted state while maintaining a good particle-matrix bond. One system currently widely used is a carboxyl-terminated butadiene-acrylonitrile random copolymer (CTBN) as the toughening rubber, a resin based on the diglycidyl ether of Bisphenol A (DGEBA), and an amine-based curing agent [18, 21, 22].

Dynamic mechanical analysis is an invaluable tool in these systems to assess the degree of compatibility of the material in its final form. For completely phase-separated, incompatible materials, each phase will exhibit its characteristic molecular relaxations, and the dynamic mechanical spectrum will appear

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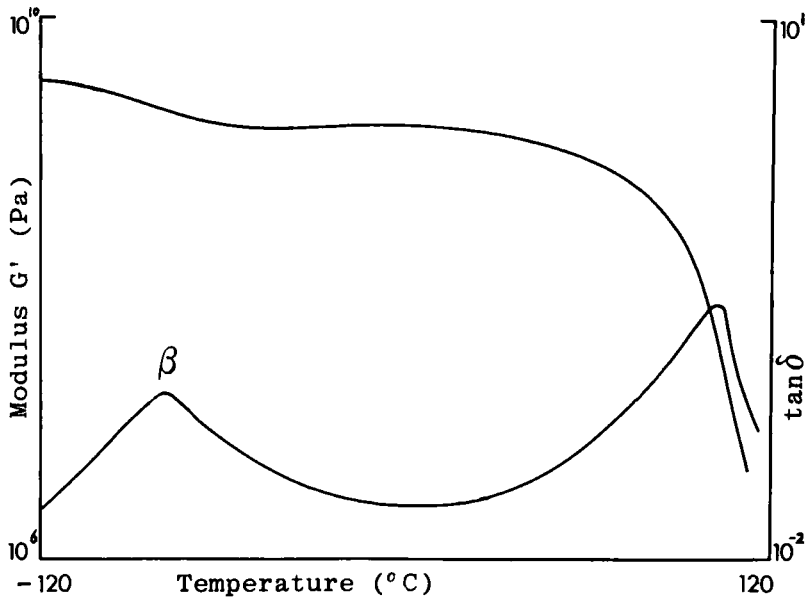
Impact correlates with
the low temperature (β)
transition

The loss peak at -80°C
is achieved by incorporating
poly-butadiene

FIG. 4. Dynamic mechanical behavior of toughened polystyrene. (Courtesy Rheometrics Europe GmbH.)

as the superposition of the two or more individual components. For rubber-modified epoxies, the value of the modulus will indicate whether the epoxy remains the continuous phase. If phase inversion occurs, causing the rubber to assume the continuous phase, then a low-modulus material results.

In a very few circumstances, for example in electrical applications [24],

it is desirable to achieve complete miscibility between components, leading to a single-phase homogeneous solid state. In this case, the tan δ loss peak maximum (T_{max}) for the blend has been predicted to move monotonically, in line with the Flory-Fox equation for T_g [2], which can be expressed by

$$T_{max,blend} = V_1 T_{max,1} + V_2 T_{max,2} \tag{10}$$

where V_1 and V_2 are the volume fractions of the two components and $T_{max,1}$ and $T_{max,2}$ are the tan δ loss peak maxima for the two components.

For phase-separated systems with some degree of miscibility, an intermediate situation exists. A shift will be observed in the transition temperature of each component if a proportion of the second component is present in that phase. Similar analysis can be applied to continuous multilayer laminate composites to determine layer interactions [25].

Polymer composites employing solid particulate fillers have enormously varied applications. Historically used to cheapen polymer products, they are now increasingly making use of sophisticated high-strength fillers, such as carbon fibers and polyaramid fibers (Kevlar), to generate highly specific engineering properties, such as in light-weight aerospace materials. For isotropic rigid fillers, the most pronounced effect in tan δ is a broadening of the transition region by a high concentration of filler. A secondary effect that can occur is a decrease in the magnitude of tan δ, which can be approximated by [1]

$$\tan \delta_{comp} = \tan \delta_1 V_1 + \tan \delta_2 V_2 \tag{11}$$

where $\tan \delta_1$ and $\tan \delta_2$ are the tan δ values for the filler and the matrix respectively, and V_1 and V_2 are the volume fractions of the filler and matrix.

The dynamic modulus and tan δ in fiber-reinforced composites are strongly influenced by fiber orientation. It is much more difficult to predict the dynamic moduli of the composite under these conditions, but a general empirical approach utilizing fairly simple models has been developed [2]. For a unidirectional composite, with rigid fibers oriented parallel to each other, an approximation for the tensile modulus is given by

$$E_c = V_f + (1 - V)E_m \tag{12}$$

where E_c = the modulus of the composite
$\quad\quad\quad E_f$ = the modulus of the fiber
$\quad\quad\quad E_m$ = the modulus of the matrix
$\quad\quad\quad V$ = the volume fraction of fiber

EPOXY RESIN

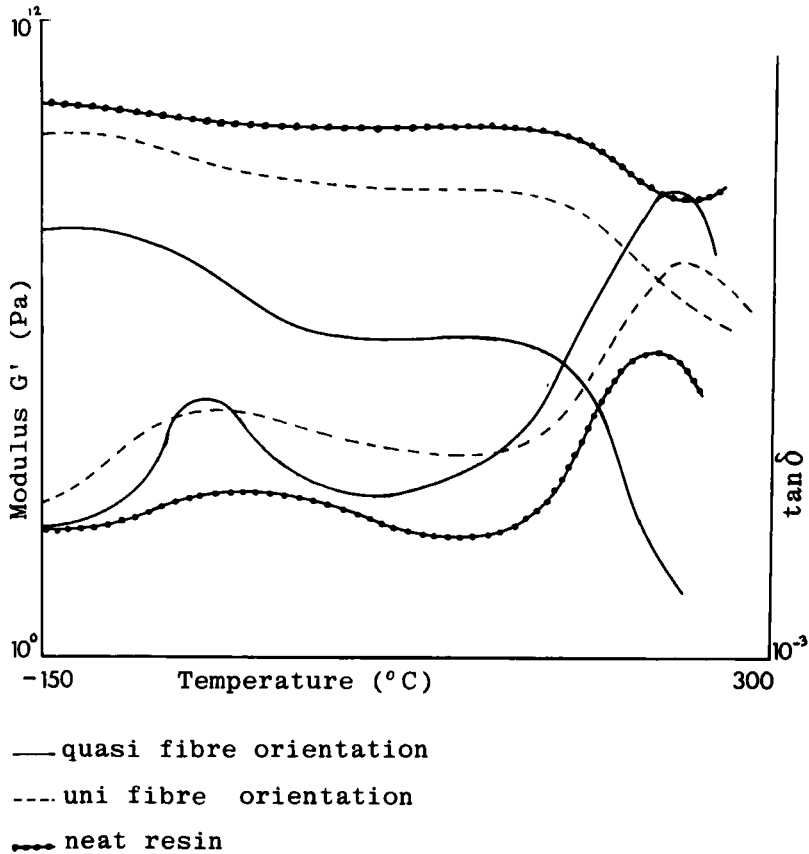——— quasi fibre orientation

----- uni fibre   orientation

●●●● neat resin

FIG. 5. Effect of fiber orientation on the dynamic mechanical performance of a filled epoxy resin. (Courtesy Rheometrics Europe GmbH.)

Figure 5 shows how fiber orientation in a filled epoxy can influence the dynamic storage modulus G' and tan δ [26], particularly at the low-temperature transition. Dynamic mechanical spectrometry can also determine the effect of aging on composite systems, such as the effect of absorbed water on epoxy-carbon fiber composites, which can account for a shift in T_g of around 80°C for 5% moisture content [27] in some materials.

High-performance composites based on an elastomeric matrix are also employed in special applications, such as composite propellants [28, 29] and shock and vibration isolators [30]. Here a comprehensive knowledge of the mechanical behavior of the composite as a function of filler loading is necessary for successful materials and product design and in prediction of fracture behavior and fatigue life. Qualitatively, the elastic modulus G' increases with filler loading, and the loss factor, tan δ, decreases in magnitude. Hsieh et al. [30] developed a model to predict the dynamic mechanical performance of filled elastomers quantitively over a range of filler loadings.

Another important class of engineering polymers comprises the engineering or speciality plastics [31, 32] which are employed in engineering applications either as the pure resins or in a filled state, such as the high-performance carbon fiber-reinforced PEEK [33, 34], for aerospace applications. The "self-reinforcing" liquid-crystal polymers [35-37] are rapidly finding new applications, both in the pure and filled states and in blends. All these speciality plastics are characterized by their high moduli and high processing and service temperatures. Table 1 gives a summary of some of the more typical engineering thermoplastics with their α-transition temperatures and melting temperatures, where appropriate. Dynamic mechanical spectrometry has an important role to play with these materials, not least as a simple means of characterization of the resins in terms of their modulus and relaxation behavior, as well as their composite properties.

TABLE 1. Speciality Engineering Plastics

| Polymer	Melting temperature (where applicable), °C	Glass-transition temperature, T_g, °C
Poly(phenylene sulfide) (PPS)	285	185
Poly(ether ether ketone) (PEEK)	339	193
Liquid-crystal polymer (LCP)	Wide range	
Poly(amide imide) (PAI)	—	Greater than 290
Poly(ether sulfone) (PES)	—	190

EXPERIMENT AND MATERIALS

The basis of the experimental work described here is to illustrate the application of dynamic mechanical spectrometry to some engineering thermosets and thermoplastics.

The toughened thermosets employed are epoxy resins based on the diglycidyl ether of Bisphenol A (DGEBA) [18]. This may be described by the structural formula
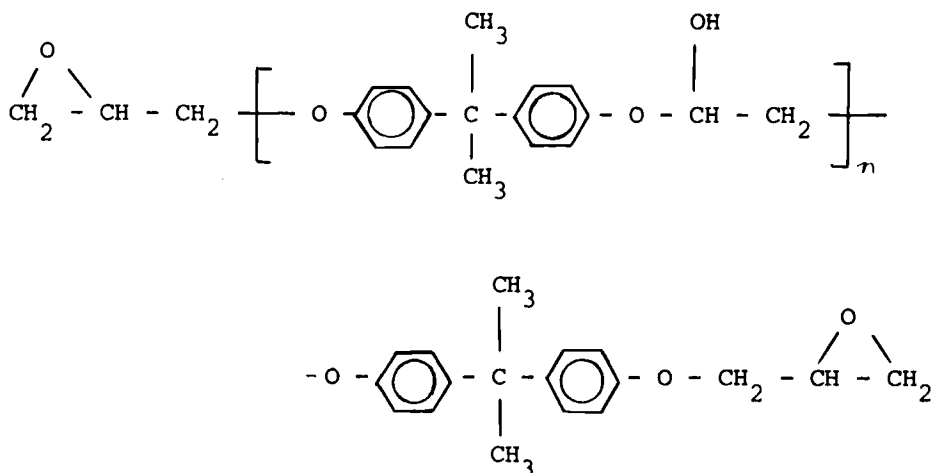
The curing agent employed was piperidine. Two types of rubber were used for toughening the epoxy. The first was a carboxyl-terminated random copolymer of butadiene and acrylonitrile (CTBN), represented by

$$HOOC-\!\left[(CH_2-CH\!=\!CH-CH_2)_x-(CH_2-\underset{\underset{CN}{|}}{CH})_y-\right]_m\!\!COOH$$
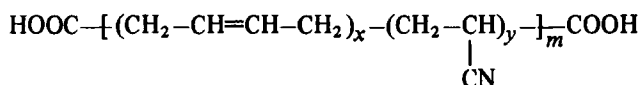
Three ratios of acrylonitrile to butadiene were employed: CTBN X 31 10 wt% acrylonitrile, CTBN X 8 17 wt% acrylonitrile, and CTBN X 13 26 wt% acrylonitrile.

To prepare the rubber-modified epoxy, the CTBN liquid rubber was added to the epoxy resin and hand mixed for 5-10 min. This mixture was then heated to 65 ± 5°C in a water bath and mixed for 5 min with an electric stirrer, followed by degassing in a vacuum oven at 60°C. When cool, the piperidine curing agent was mixed in at a ratio of 5 parts per hundred resin

(phr). This mixture was poured into a preheated mold and cured at 120°C, unless otherwise indicated. Unmodified epoxy- and glass-loaded epoxy were prepared in the same way, but without the addition of rubber.

The second rubber used in toughening was a partly epoxidized natural rubber supplied by the Malaysian Rubber Producers' Research Association, modified by 50% epoxidation, resulting in a random copolymer of *cis*-polyisoprene and epoxidized *cis*-polyisoprene. The epoxidized rubber was dissolved in DGEBA resin at 150°C for 3 h with constant stirring. Upon cooling, the curing agent was incorporated as described above and curing was effected in the same way.

Formulations were prepared in such a way as to examine how the following variables affect the dynamic mechanical performance of the cured toughened resin: (i) acrylonitrile content in the CTBN; (ii) CTBN content in the DGEBA resin at constant acrylonitrile content; (iii) epoxidized rubber content of DGEBA; and (iv) glass and rubber loading in the DGEBA.

The thermoplastics and composites were all prepared or obtained in sheet form, and measurements were carried out to illustrate the effect of fiber loading on PEEK and PTFE and to compare the properties of a range of speciality thermoplastics in the unfilled state.

Testing

All dynamic mechanical measurements were carried out by means of a Rheometrics RDS7700 Mark 2 [6] spectrometer. Samples were prepared as rectangular bars, generally of cross section 6 X 10 mm. Tests were carried out over a range of temperatures in a nitrogen atmosphere at a frequency of 1 rad/s.

RESULTS AND DISCUSSION

Rubber-Toughened Epoxies

Figures 6 to 9 show the effect of acrylonitrile level and overall rubber content of dynamic mechanical properties of the toughened epoxy. Some features are immediately obvious from Fig. 6. First, there is a slight downward shift in the α-transition of the epoxy, reducing to around 95°C in the 26 wt% acrylonitrile CTBN. Second, there is a gradual increase in the loss factor or tan δ of the material across the temperature range as the acrylonitrile level is increased. Third, the α-transition of the rubber shifts quite markedly to higher temperatures with increasing acrylonitrile content. Finally, the magnitude of the rubber α-transition decreases with increasing acrylonitrile content. All these
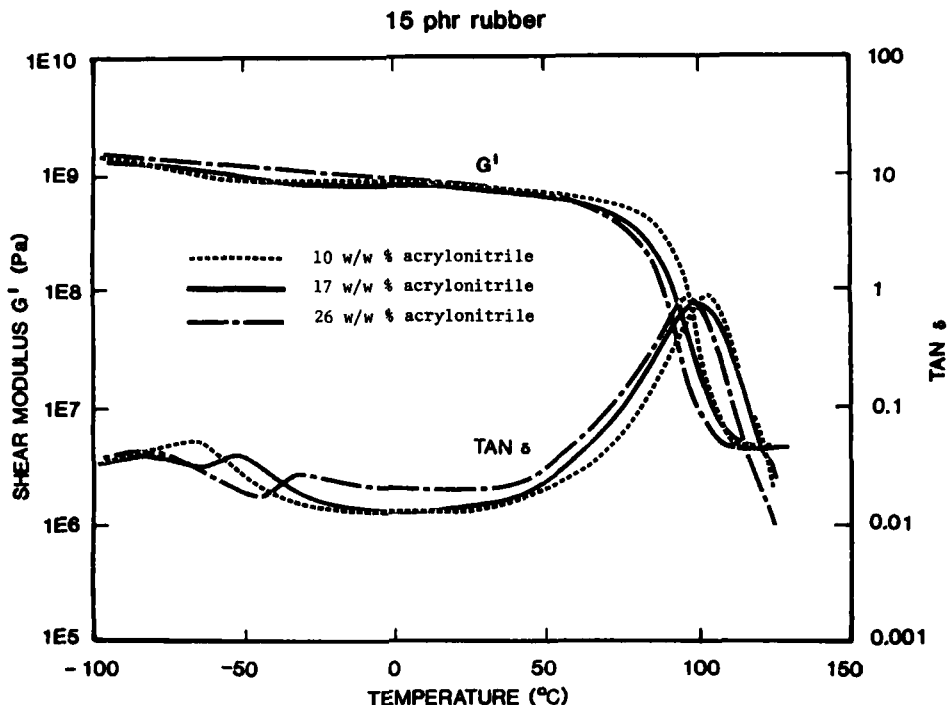
15 phr rubber

FIG. 6. Effect of acrylonitrile content in CTBN on dynamic mechanical behavior of cured toughened epoxy resin.

factors paint a very clear picture of what is occurring at the microstructural and molecular level within the material. The downward shift in the epoxy α-transition and in part the upward shift in the CTBN transition is due to an increase in compatibility and, consequently, the miscibility of the epoxy and CTBN with increasing acrylonitrile content. However, the α-transition of the CTBN would be expected to shift to higher temperatures with increasing acryl-onitrile content even in the pure state, so that an upward shift in this transi-tion alone is not sufficient to assume an increased miscibility of the epoxy resin in the rubber phase. The observed reduction in the CTBN peak magni-tude with acrylonitrile content would indicate a reduction in the proportion of a discrete rubbery phase, which reinforces the implications of the down-ward shift of the α-transition of the epoxy. Finally, the increased loss as a function of acrylonitrile content would again reinforce the assumption of
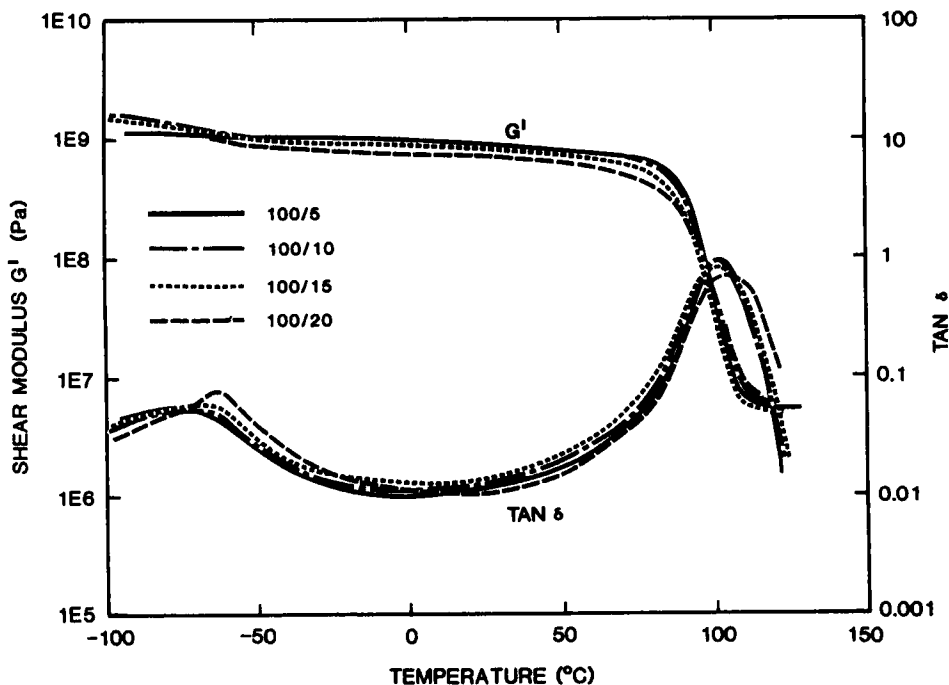
FIG. 7. Effect of increasing CTBN content (10 wt% acrylonitrile) on dynamic mechanical behavior of cured toughened epoxy resin.

a greater degree of miscibility between the CTBN and epoxy with increasing acrylonitrile content.

Figures 7, 8, and 9 show the effect of increasing CTBN content in DGEBA resin at three constant acrylonitrile levels. Figure 7 shows little change in the α-transition of the epoxy with increasing CTBN content, and the α-transition of the CTBN is fairly constant at around -62°C. The major trend with increasing CTBN level is the increase in magnitude of the α-transition of the CTBN, coupled with a slight decrease in the modulus of the epoxy. This indicates a low degree of compatibility between the CTBN and epoxy. Figure 8 shows that for 17 wt% acrylonitrile in CTBN, the CTBN α-transition at 5 phr CTBN is very difficult to distinguish, but very little change is observed generally in the CTBN α-transition with increasing CTBN content: it remains fairly constant at around -46°C. There is a slight reduction in the magnitude of the α-transition of the epoxy with CTBN content, indicating limited miscibility,
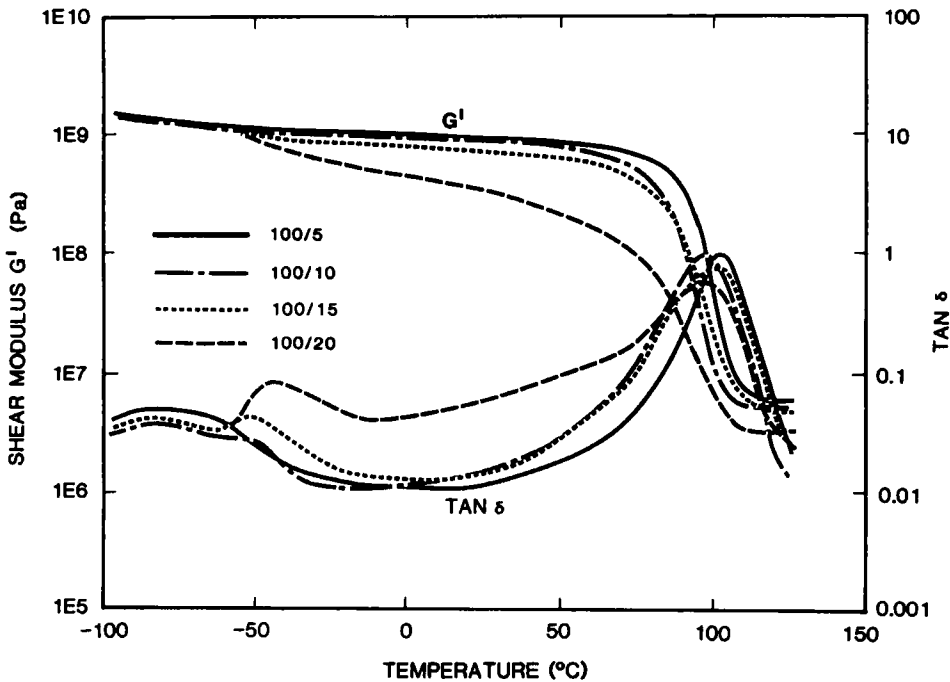
FIG. 8. Effect of increasing CTBN content (17 wt% acrylonitrile) on dynamic mechanical behavior of cured toughened epoxy resin.

coupled with a slight decrease in the magnitude of the α-transition of the epoxy, simply due to the increased proportion of CTBN.

In Fig. 9, for 26 wt% acrylonitrile in CTBN, the most marked feature is that, at 5 phr CTBN content, there is no observable α-transition for the CTBN, i.e., the rubber is completely miscible in the epoxy. These transitions remain small even at 20 phr CTBN, indicating a relatively high degree of miscibility between CTBN and epoxy.

Figure 10 shows the effect of increasing cure time on G' and tan δ. By 2 h at 160°C, the CTBN rubber (17 wt% acrylonitrile, 15 phr) is fully precipitated, as seen by the CTBN peak at approximately -46°C. A slightly anomalous tan δ peak is apparent after 4 h cure, but at longer cure times this is no longer observable. With increasing cure time, the α-transition of the epoxy shifts to higher temperatures, stabilizing by 10 h cure when the crosslink architecture of the matrix is fully formed. Even by 2 h cure, however, G' is effec-
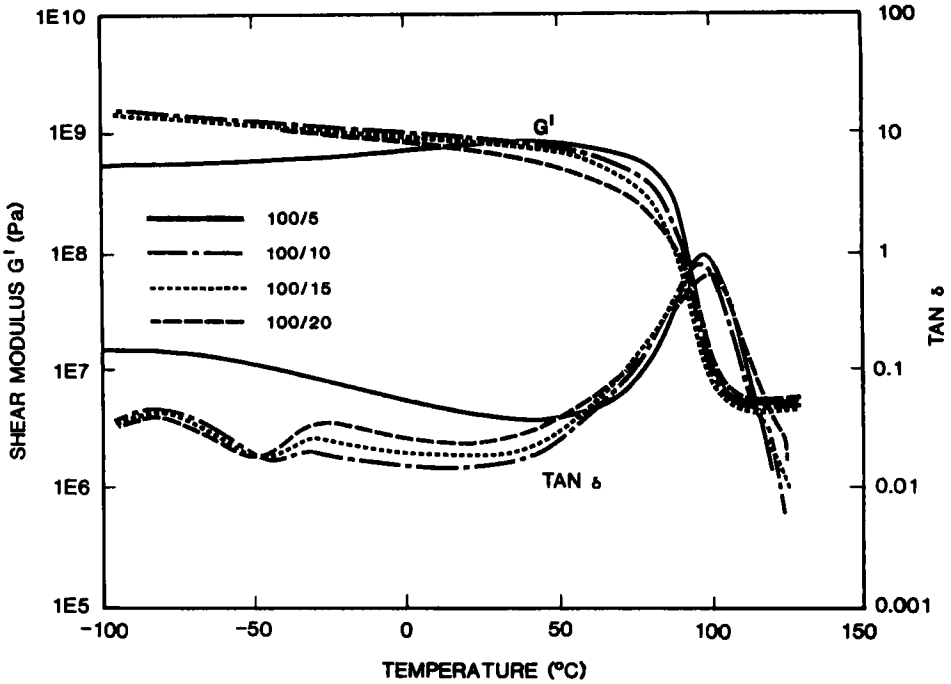
FIG. 9. Effect of increasing CTBN content (26 wt% acrylonitrile) on dynamic mechanical behavior of cured toughened epoxy resin.

tively fully stabilized, indicating that only relatively minor structural changes to the crosslinked network are taking place at longer times.

Figure 11 shows a small shift in the α-transition of the modified epoxy. At the low level of epoxidized natural rubber (ENR), this shift is accomplished by a small ENR α-peak at around -20°C, but no shift in the general tan δ or G' level. This indicates a fairly good degree of phase separation between ENR and epoxy. At higher levels of ENR, however, tan δ begins to increase significantly, accompanied by a large decrease in the G' as well as an increase in the α-transition of the ENR. This indicates an increasing degree of ENR incorporation into the epoxy matrix and epoxy into the ENR at levels of incorporation significantly above 5 phr ENR.

Figure 12 shows now, with the incorporation of 100 phr glass fiber isotropically distributed, the α-transition of the epoxy is slightly reduced in mag-
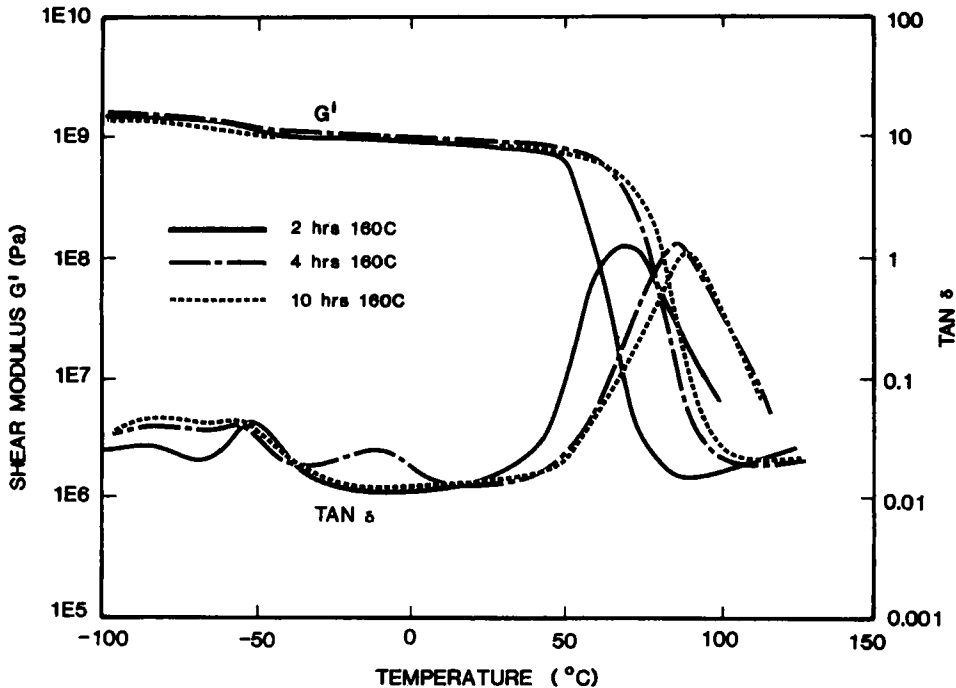
FIG. 10. Effect of cure time at 160°C on dynamic mechanical behavior of cured toughened epoxy resin (17 wt% acrylonitrile, 15 phr).

nitude, as is the tan δ over most of the temperature range, compared with the rubber-modified epoxy. Similarly, there is an increase in G' over most of the temperature range. Incorporation of *both* 15 phr CTBN and 100 phr glass fiber results in a toughened epoxy exhibiting only a small CTBN α-peak, and tan δ and G' profiles very similar to those of the material modified by CTBN alone.

Thermoplastic Resins and Composites

The remaining data relate to the dynamic mechanical performance of engineering thermoplastic resins and composites.

Figure 13 shows the effect of glass and carbon fiber loading. Pure poly-(ether ether ketone) (PEEK) resin is compared with 20 and 30% isotropic
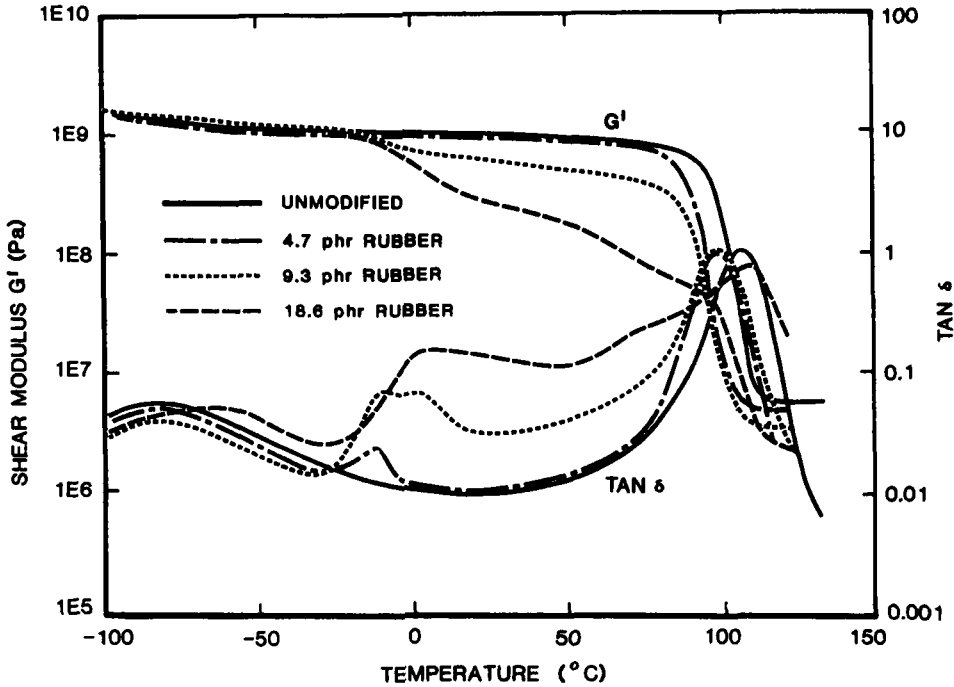
FIG. 11. Effect of epoxidized natural rubber as a toughening agent on dynamic mechanical properties of cured toughened epoxy resin.

glass loadings, and with Aromatic Polymer Composite 2 (APC-2), a quasi-isotropic composite with a 68% carbon fiber content. The α-transition temperature of the PEEK matrix is largely unaffected by filler, even in APC-2, and occurs at approximately 150°C. The dynamic elastic modulus is increased significantly even by the addition of 20% glass fiber with a corresponding depression in the magnitude of the α-transition. Loading with 30% glass fiber marginally increases the effect. In APC-2 the tan δ peak at the α-transition is considerably broadened and depressed, and G' is increased by almost an order of magnitude compared to the pure resin, with a slight increase in tan δ across the entire temperature range.

Figure 14 shows a similar effect for poly(tetrafluoroethylene) (PTFE) as the pure resin and with 25% glass loading. Although PTFE is a high-temperature polymer, its engineering applications may be limited by its relatively low
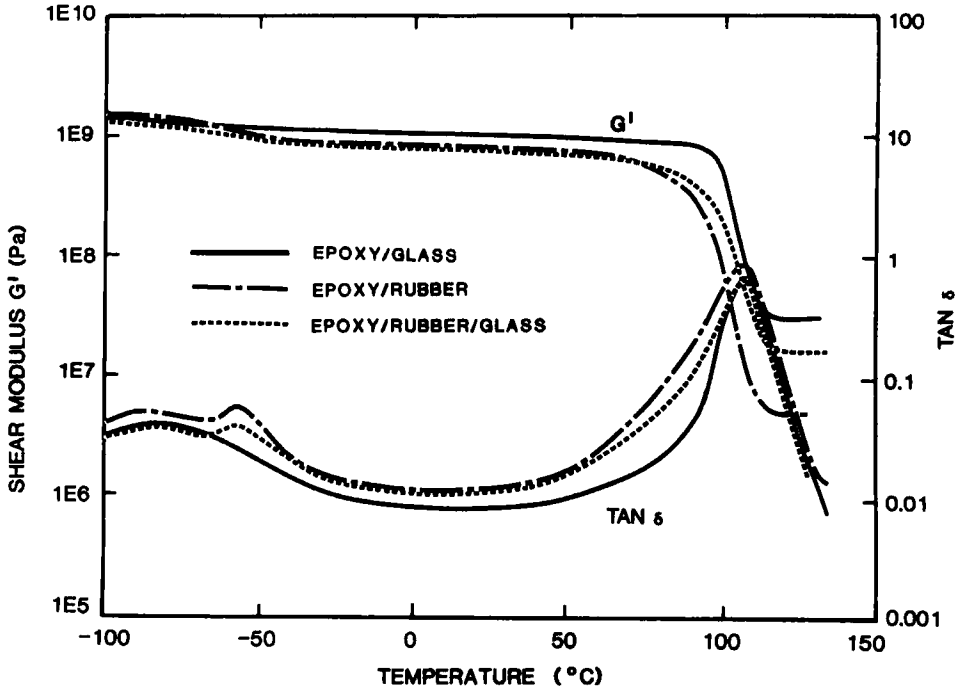
FIG. 12. Effect of incorporation of glass and CTBN rubber on dynamic mechanical properties of cured resin.

transition temperatures and corresponding low modulus. The low-temperature transition occurs at around −100°C. As expected, the effect of the glass loading is to depress tan δ slightly but without increasing G' sufficiently to make the material comparable to unfilled engineering plastics such as PEEK in a reasonable temperature range.

The last figure, Fig. 15, compares G' of a range of thermoplastic engineering resins: poly(phenylene sulfide) (PPS), poly(ether sulfone) (PES), poly(ether ether ketone) (PEEK), poly(amideimide) (PAI), and a polyester-based liquid-crystal-backbone polymer (LCP). This plot illustrates how dynamic mechanical analysis represents a quick and simple research tool for "fingerprinting" the relative properties of different materials, particularly in terms of their moduli and high-temperature performance. By using this technique, it is possible to compare materials of widely varying structures, from rubber-
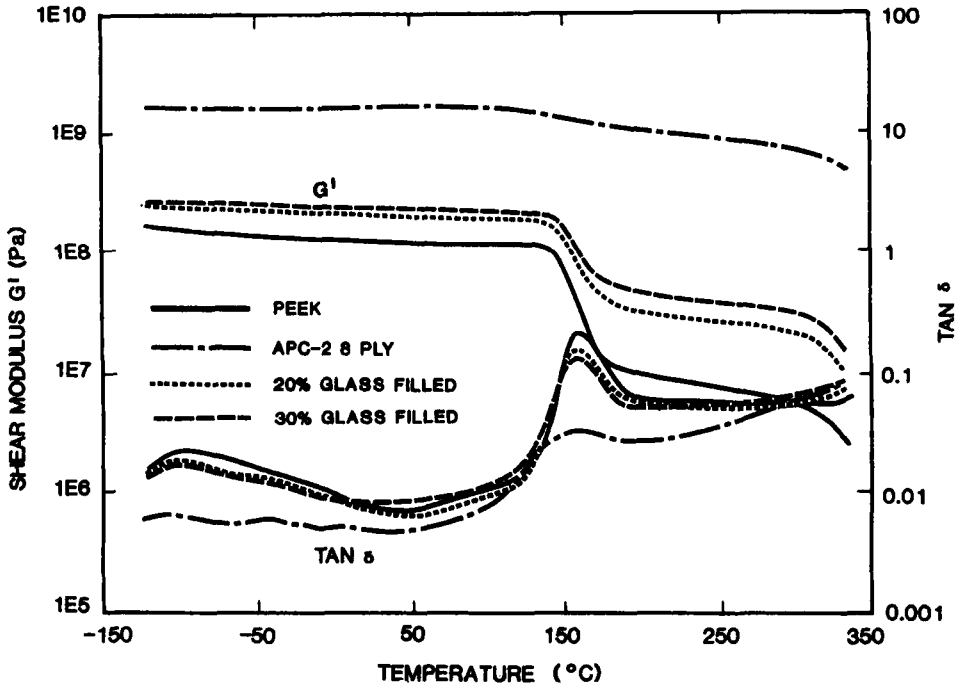
FIG. 13. Effect of glass and carbon fiber loading on dynamic mechanical performance of PEEK.

toughened thermosets to thermoplastic engineering resins, for potential application in the same engineering product.

CONCLUSIONS

Dynamic mechanical analysis is an enormously versatile technique for determining the mechanical properties and performance of a whole range of engineering polymers. Its use in characterizing the properties of pure resins, of engineering high-performance blends and alloys, and in fiber- or mineral-
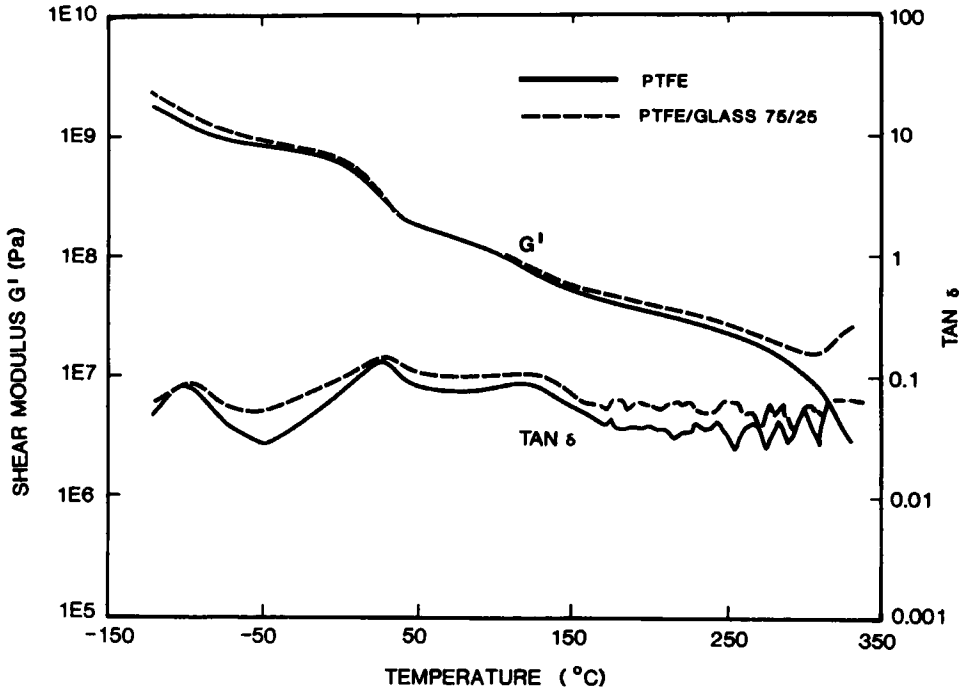
FIG. 14. Effect of glass loading on dynamic mechanical performance of PTFE.

filled composites has been reviewed briefly. Some specific examples have illustrated the application of the technique in more detail, in particular the dynamic mechanical behavior of rubber-toughened epoxy systems and, as a comparison, the dynamic mechanical performance of some engineering thermoplastics and composites. It has been shown how the technique can easily establish much of the microstructural detail of these materials and as a "fingerprinting" technique for comparing material performance over a range of conditions.
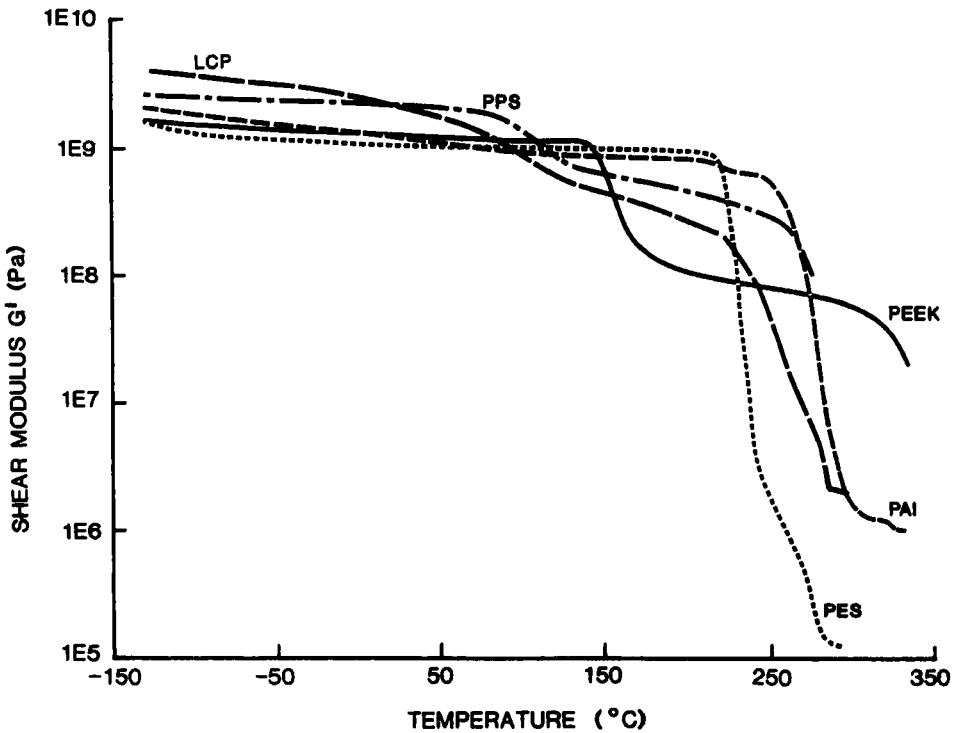
FIG. 15. Comparison of dynamic mechanical performance of thermoplastic engineering resins.

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