

# Simulation of Viscoelastic Behavior of Glassy Polymers

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**ABSTRACT:** The frequency master curves of thermoset and thermoplastic glassy polymers were determined by dynamic mechanical analysis, and the results were simulated by sinusoidal response of the standard viscoelastic model. The elastic and viscous elements of the model were determined and correlated with structure of glassy polymers. The advantage of this viscoelastic approach in toughening studies of polymers was discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 971–982, 1997

**Key words:** viscoelastic model; CR-39 resin; poly(methyl methacrylate); polystyrene; thermoplastic polycarbonate; frequency master curve; toughening

## INTRODUCTION

Viscoelasticity has a significant role in toughening mechanism of rubber-modified bifunctional thermoset resins.<sup>1</sup> It is postulated that in rubber-modified resins, the viscoelastic processes at crack tip control the fracture resistance of the resins. The viscoelastic dependence of fracture has been shown by correlating the fracture energy  $G_c$  with viscoelastic parameters, such as time, to fracture at crack tip.<sup>2</sup> However, in multifunctional thermoset resins, the role of viscoelasticity is yet far more crucial. In these resins, the tightly cross-linked structure must be loosened to simulate thermoplastic behavior in order to improve the ability of the network structure to react in a more viscoelastic manner.<sup>3</sup> The higher viscoelasticity enables the resin to relieve fracture energies at crack tip under loading. Therefore, it is important to assess the viscoelasticity of network polymers in toughening purposes. In this work, we introduce a viscoelastic model to provide a quantitative measure to evaluate the tightness of structure of glassy polymers. The aim is to estimate quantitatively the restriction of yielding in glassy polymers with cross-linked structures compared to the thermoplastic polymers. This approach could particu-

larly be useful in toughening studies of highly cross-linked glassy polymers, in which the viscoelasticity of these polymers plays a decisive role in fracture resistance of polymer.

## EXPERIMENTAL

### Multiple Fixed Frequency Experiments

Dynamic mechanical experiments were performed using a DuPont 983 dynamic mechanical analyzer. Samples of poly(diethylene glycol bisallyl carbonate), which is a thermoset polymer and commonly known as CR-39 resin, poly(methyl methacrylate) (PMMA), polystyrene (PS), and thermoplastic polycarbonate (PC) were tested over various temperature ranges between 25 and 120°C in steps of 5°C. Five frequencies (0.1, 0.25, 0.5, 1, and 2 Hz) were used to probe the dynamic response of the samples. The samples were tested at a constant small strain amplitude of 0.5 mm. The results of the experiments were shifted using the Du Pont Superposition version 4.1 B software package.

### Resonant Frequency Mode

This mode is particularly useful for analyzing stiff, low-loss polymers. The modulus tempera-

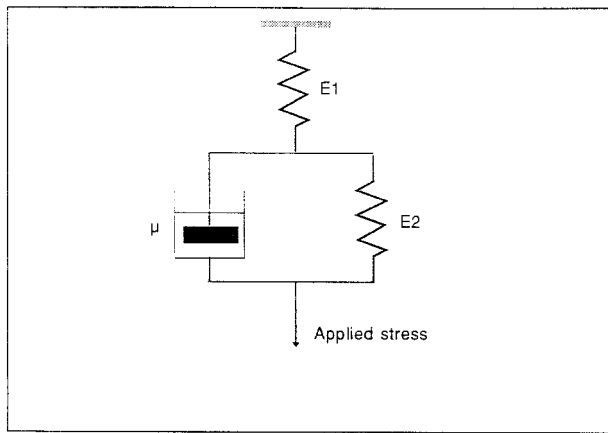


Figure 1 Standard linear solid model.

ture and  $\tan \delta$  temperature thermograms were obtained using a DuPont 983 dynamic mechanical analyzer at a heating rate of  $20^\circ\text{C}/\text{min}$  in resonant mode from room temperature to  $200^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Sinusoidal Response of Glassy Polymers and Standard Linear Solid Model

The dual concept of viscosity and elasticity behavior of polymers can be conceptualized with a combination of viscous components and elastic components. To simulate the viscoelastic behavior of a polymer, it is convenient to consider a standard linear solid model with the elastic moduli  $E_1$  and  $E_2$  and the viscosity  $\mu$  of the viscous element (Fig. 1). This model has the advantage that the differential equations of its response to a sinusoidal loading can be solved analytically and, also, the sinusoidal response of the model closely imitates those of polymers.

The response of the standard linear solid model to a sinusoidal loading is important as the dynamic mechanical behavior of polymers are determined in sinusoidal vibrating stress and strain conditions. To obtain a satisfactory understanding of the viscoelastic behavior, data are required over a wide range of frequency (time) and temperature. Many experimental techniques are used to measure dynamic mechanical properties. The main techniques are creep, stress relaxation, resonance frequency, fixed frequency, and multiple fixed frequencies. In considering time-temperature equivalence in viscoelastic study of glassy polymers, it is possible to make a master curve

by superposition method to cover the whole range of frequency.

In this study, the multiple fixed frequency of PMMA, PC, PS, and CR-39 were determined. To implement superposition, a reference temperature was chosen and horizontal shift factor applied on a logarithmic scale to join all segments as smoothly as possible to form one master curve. The modulus frequency and  $\tan \delta$ -frequency master curves of CR-39, PMMA, and PS, and associated shift factors, have been shown in Figures 2–12. The shift factors can be correlated with temperature by the Williams-Landel-Ferry (WLF) equation and also by the Arrhenius equation.<sup>4</sup> The Arrhenius equation is

$$\log a_T = -\frac{E}{R(T - T_0)} \quad (1)$$

where  $a_T$  is the shift factor,  $E$  is the activation energy,  $R$  is the gas constant;  $T$  is the temperature at which the data points were taken, and  $T_0$  is the reference temperature. The WLF equation is

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \quad (2)$$

where  $C_1$  and  $C_2$  are constants. The activation energy and  $C_1$  and  $C_2$  values for CR-39 fall in the range of those of thermoplastic polymers (Table I). In order to simulate these frequency master curves of polymers with a solid linear elastic model, it is required to determine the frequency response of this model. The differential equation for this model is

$$\frac{de}{dt} + \frac{E_2 e}{\mu} = \frac{(E_1 + E_2)\sigma}{\mu E_1} + \frac{1}{E_1} \frac{d\sigma}{dt} \quad (3)$$

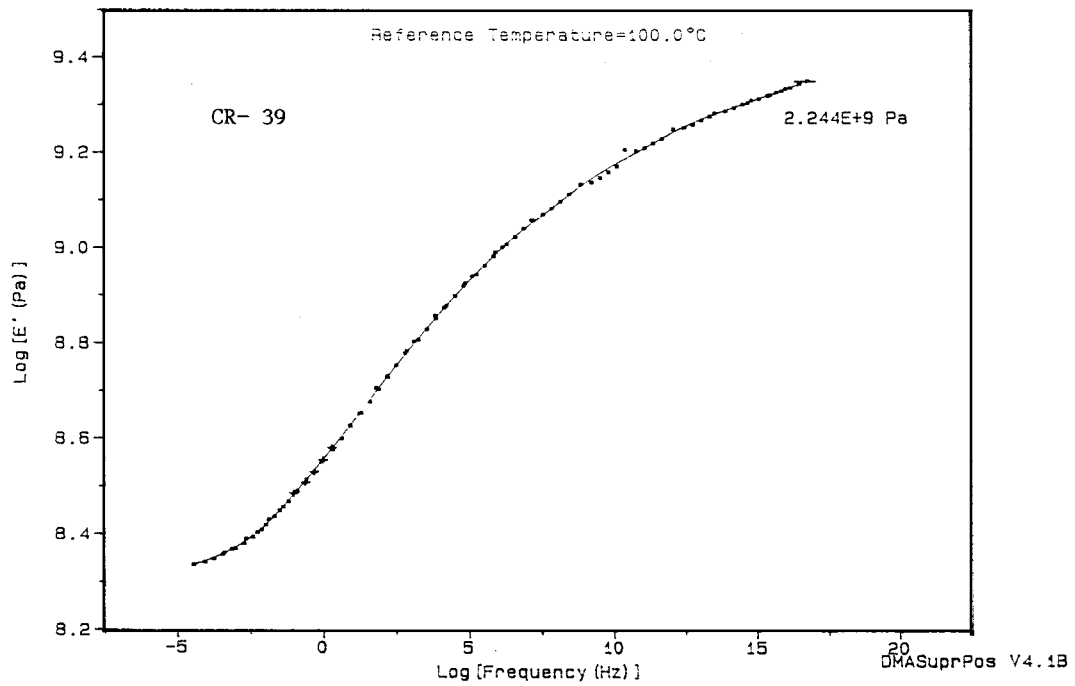
where  $e$  is the strain and  $\sigma$  is the stress.<sup>5</sup> The mathematical solution of this equation for a sinusoidal stress loading of the form

$$\sigma = \sigma_0 \sin \omega t \quad (4)$$

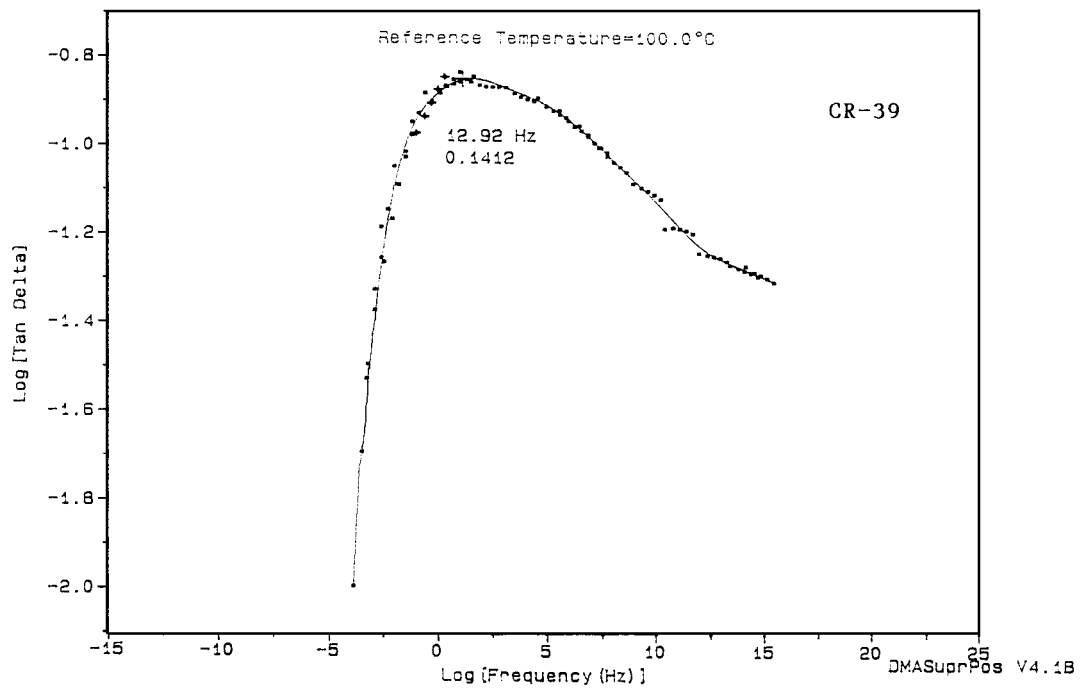
would be

$$e(t) = \frac{\sigma_0}{E'} \sin \omega t - \frac{\sigma_0}{E''} \cos \omega t \quad (5)$$

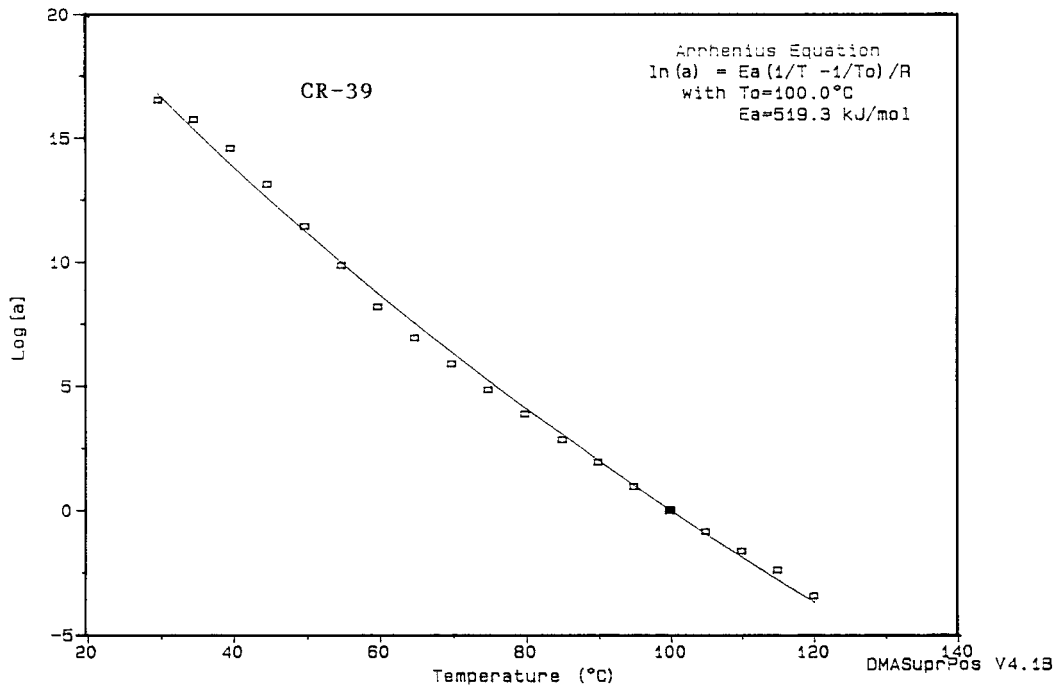
where  $\omega$  is the angular frequency,  $E'$  is the storage modulus, and  $E''$  is the loss modulus. These



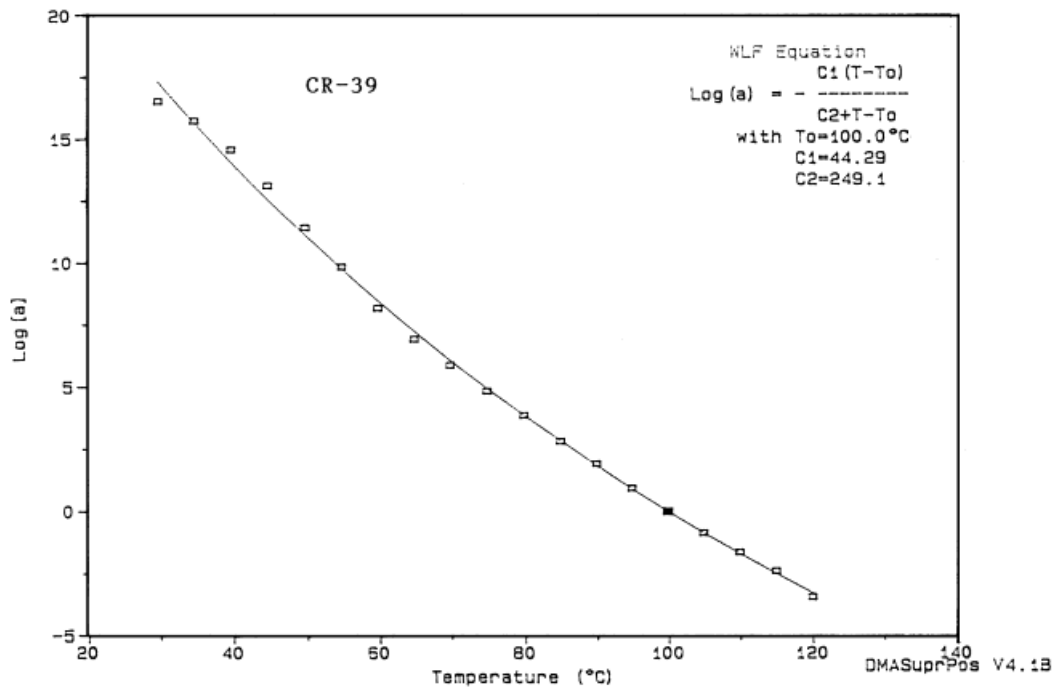
**Figure 2** Master curve from modulus data gathered around the  $\alpha$  relaxation peak of CR-39.



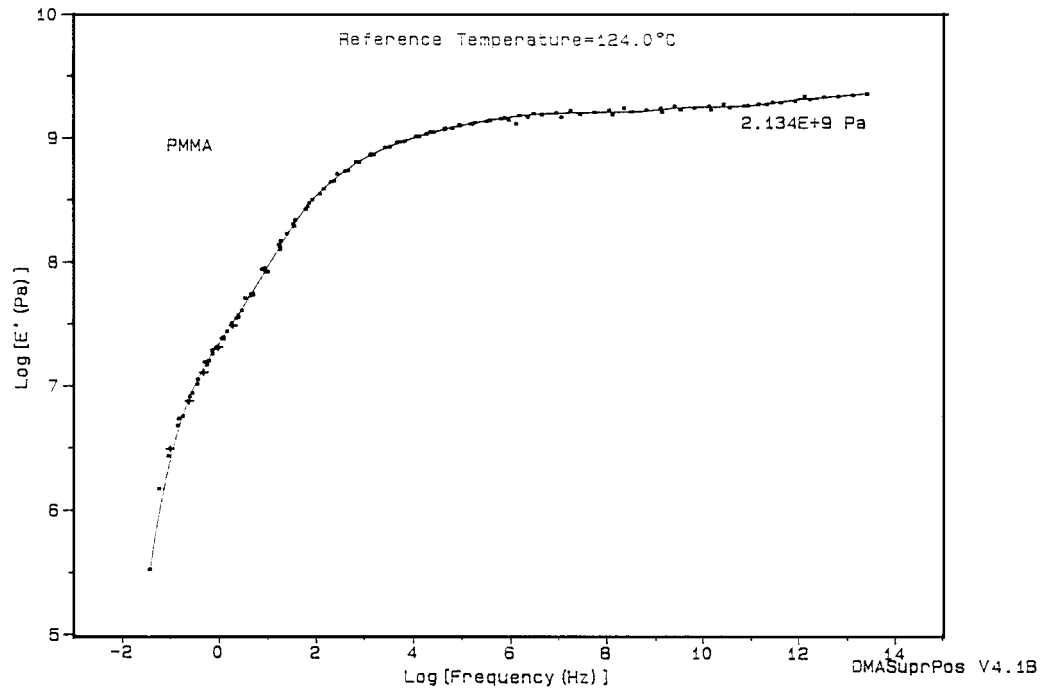
**Figure 3** Master curve from  $\tan \delta$  data gathered around the  $\alpha$  relaxation peak of CR-39.



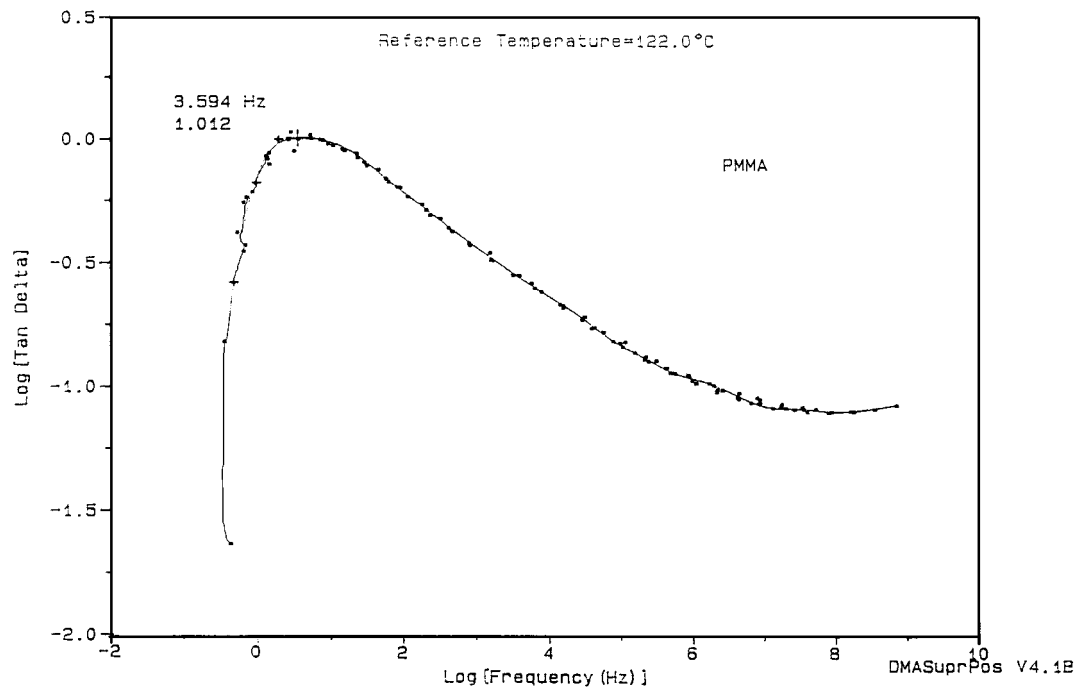
**Figure 4** Plot of shift factor versus temperature for the shifted data gathered around the  $\alpha$  relaxation peak of CR-39 fitted with Arrhenius equation.



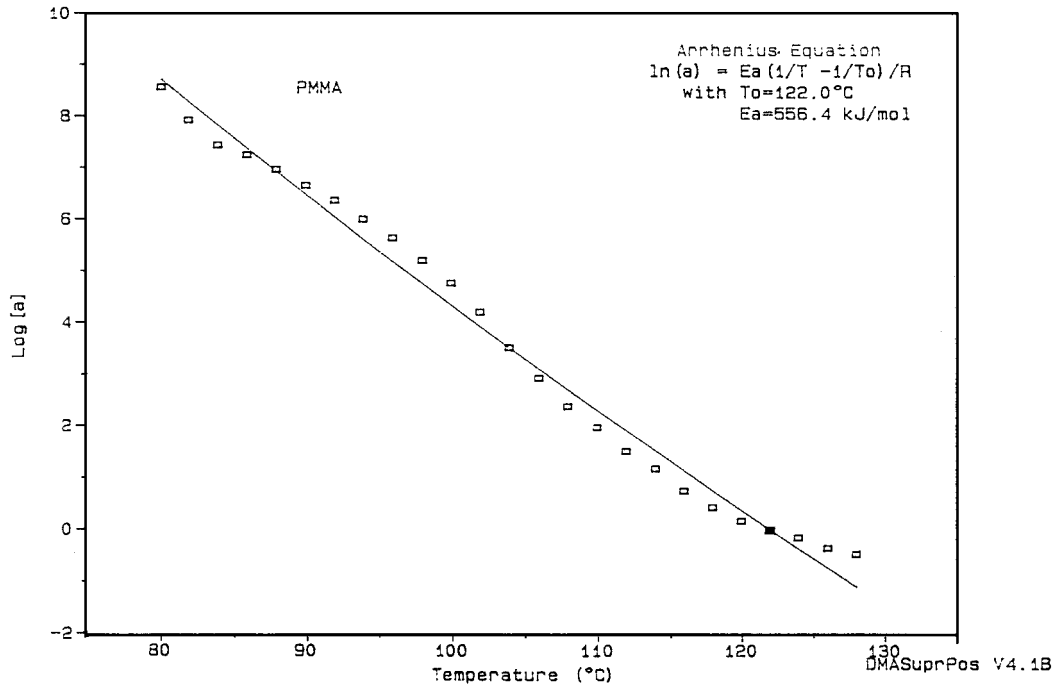
**Figure 5** Plot of shift factor versus temperature for the shifted data gathered around the  $\alpha$  relaxation peak of CR-39 fitted with WLF equation.



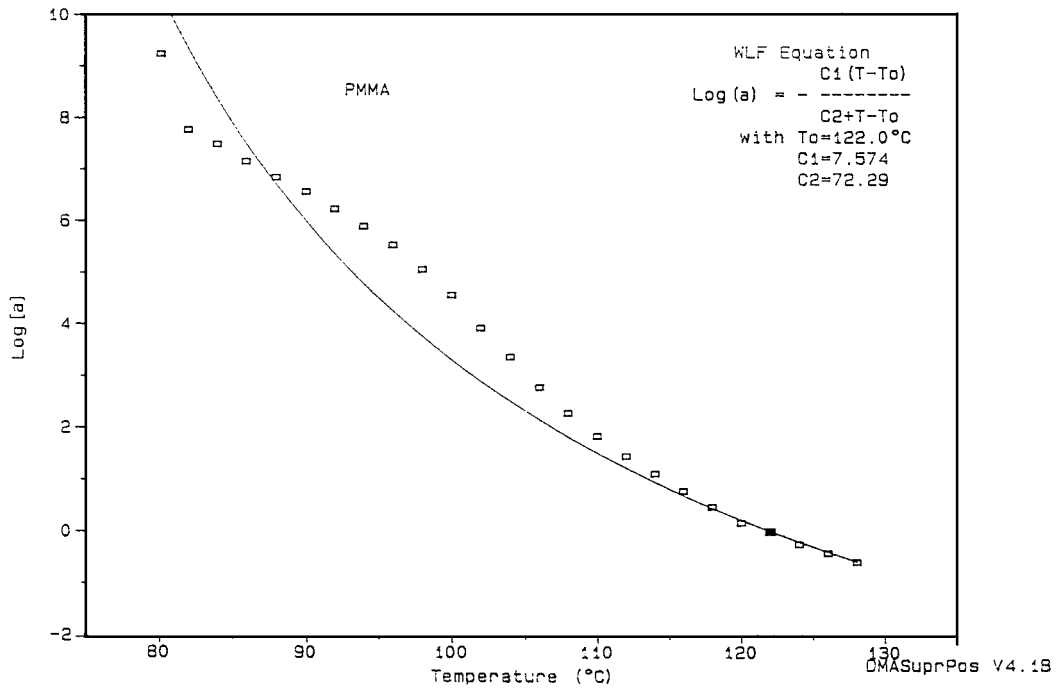
**Figure 6** Master curve from modulus data gathered around the  $\alpha$  relaxation peak of PMMA.



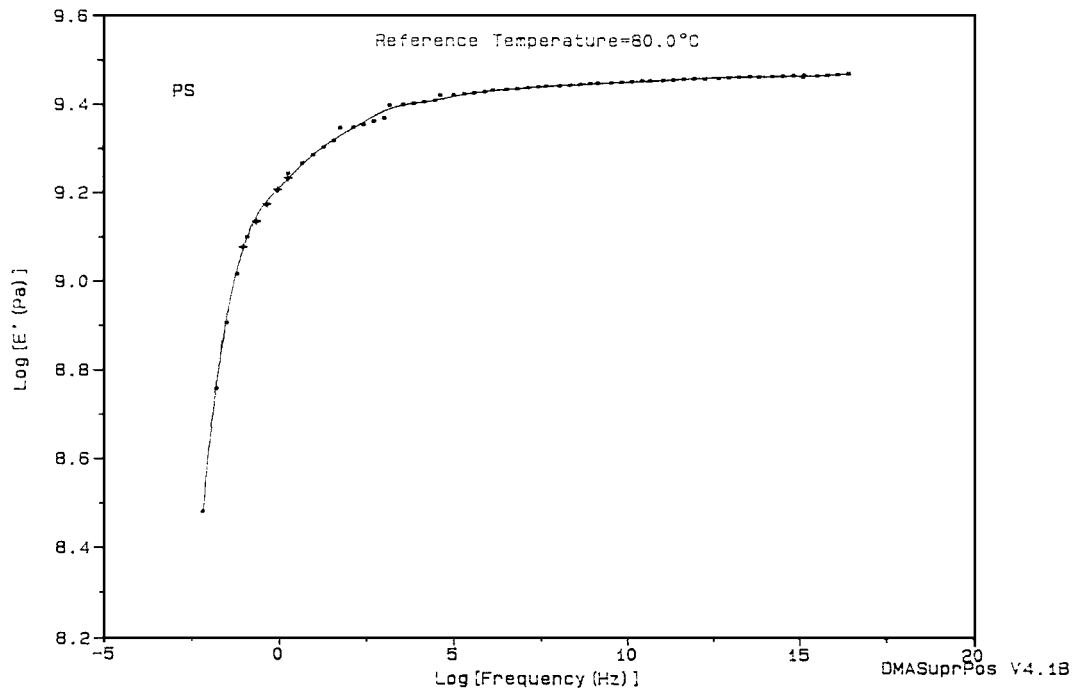
**Figure 7** Master curve from  $\tan \delta$  data gathered around the  $\alpha$  relaxation peak of PMMA.



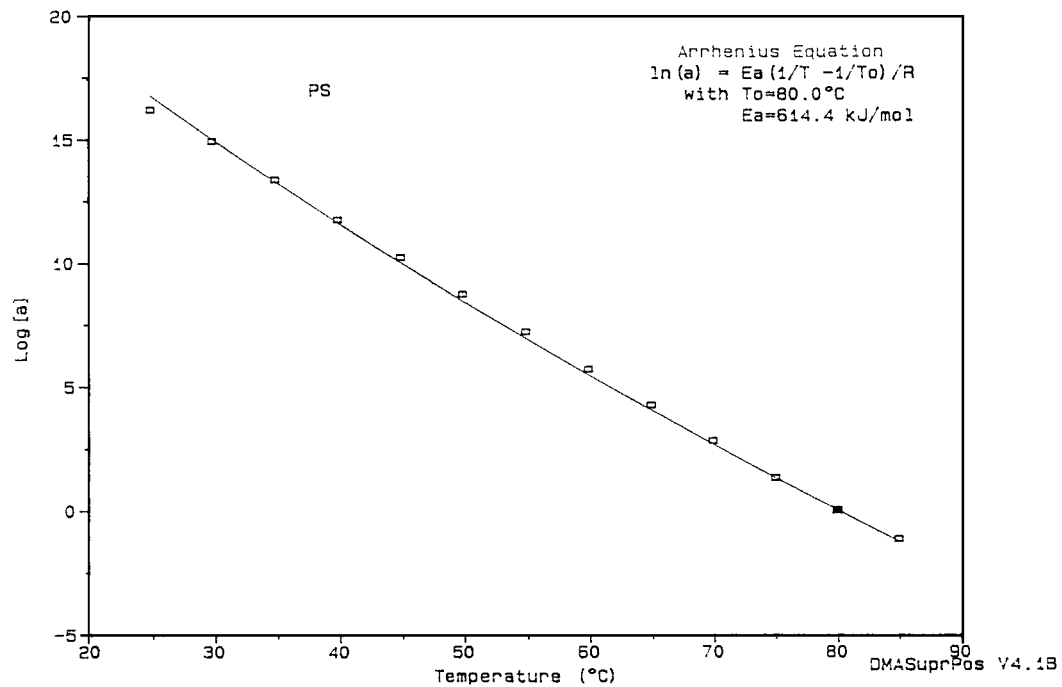
**Figure 8** Plot of shift factor versus temperature for the shifted data gathered around the  $\alpha$  relaxation peak of PMMA fitted with Arrhenius equation.



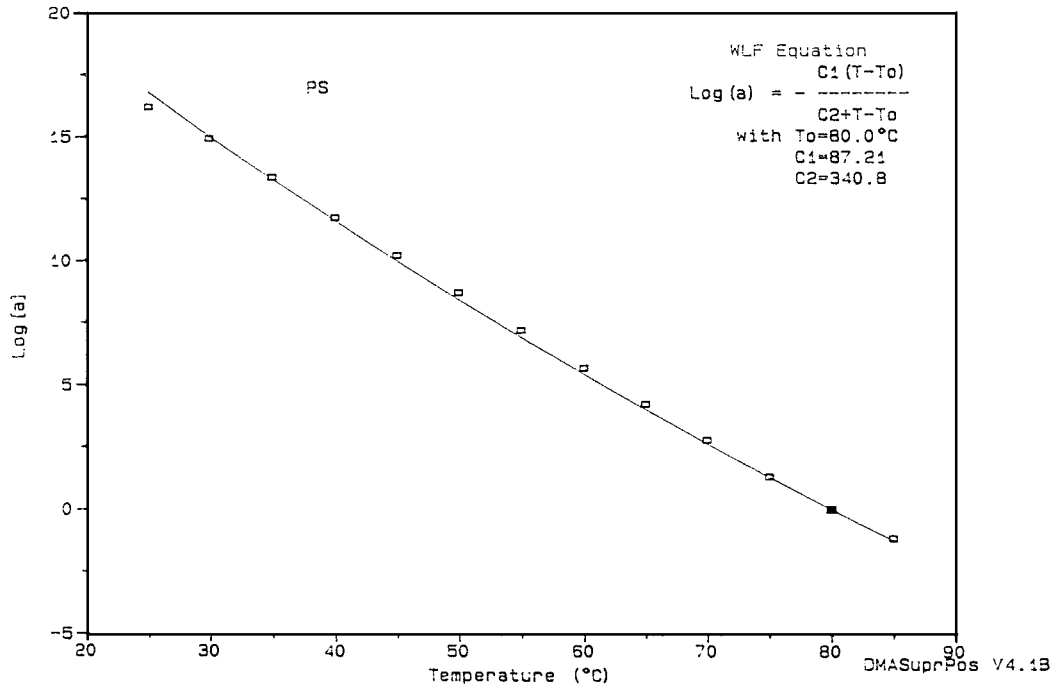
**Figure 9** Plot of shift factor versus temperature for the shifted data gathered around the  $\alpha$  relaxation peak of PMMA fitted with WLF equation.



**Figure 10** Master curve from modulus data gathered around the  $\alpha$  relaxation peak of PS.



**Figure 11** Plot of shift factor versus temperature for the shifted data gathered around the  $\alpha$  relaxation peak of PS fitted with Arrhenius equation.



**Figure 12** Plot of shift factor versus temperature for the shifted data gathered around the  $\alpha$  relaxation peak of PS fitted with WLF equation.

moduli are correlated with the model parameters as follows:

$$\tan \delta = \frac{E'}{E''} \tag{8}$$

$$\frac{1}{E'} = \frac{1}{E_1} + \frac{1}{E_2} \frac{E_2^2}{E_2^2 + \omega^2 \mu^2} \tag{6}$$

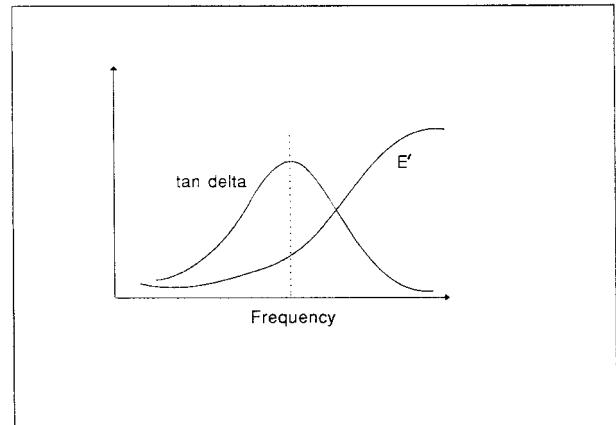
$$\frac{1}{E''} = \frac{1}{E_2} \frac{\omega \mu E_2}{E_2^2 + \omega^2 \mu^2} \tag{7}$$

For high frequencies,  $E'$  approaches  $E_1$ . A further parameter of practical importance is the loss factor written as

The plots of  $E'$  and  $\tan \delta$  versus frequency for a standard linear solid model have been shown schematically in Figure 13. The forms of the curves closely resemble the frequency response of glassy polymers. The curve of  $\tan \delta$  shows a maximum at

**Table I** The Arrhenius and WLF Equations's Parameters Obtained for Thermoset and Thermoplastic Polymers by Multiple Fixed Frequency Experiments

Polymer	Activation Energy (kJ/mol)	C1	C2
CR-39	519.3	44.29	249.1
PMMA	556.4	7.57	72.29
PS	614	87.21	340.8



**Figure 13** Sinusoidal loading response of standard linear solid.



**Table II Viscoelastic Parameters of Glassy Polymers Simulated by a Standard Linear Solid Model**

Polymer	$E_1$ (GPa)	$E_2$ (GPa)	$\mu$ (GPa sec)
CR-39	2.45	7.53	0.116
PC	2.35	0.37	0.026
PMMA	2.2	0.295	0.033
PS	2.6	0.003	0.007

$$\omega = \frac{\mu}{E_1 + E_2} \sqrt{\frac{E_2}{E_1 + E_2}} \quad (9)$$

with a magnitude of

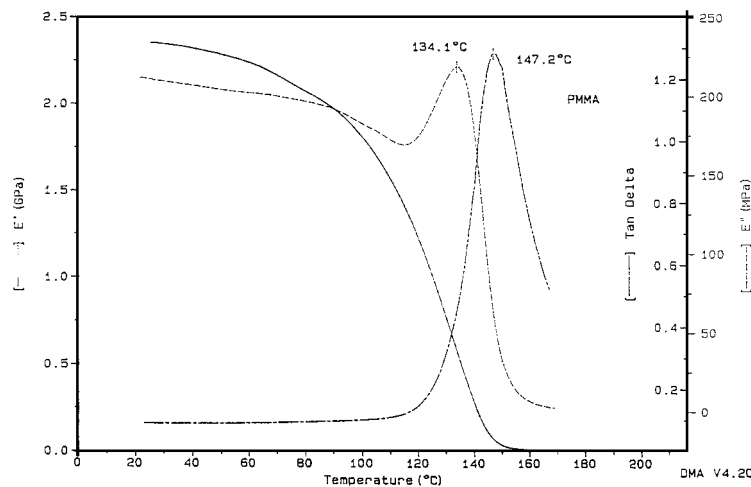
$$(\tan \delta)_{\max} = \frac{1}{2} \frac{E_1}{E_2} \sqrt{\frac{E_2}{E_1 + E_2}} \quad (10)$$

From the frequency master curves of CR-39 and thermoplastic glassy polymers such as PMMA and PC measured by a dynamic mechanical spectrometer around the  $\alpha$  relaxation peak, the values of  $\tan \delta$  and frequency at maximum and also the value of  $E'$  at highest frequency can be determined. These values are used in eqs. (9) and (10) to determine the values of  $E_1$ ,  $E_2$ , and  $\mu$  ( $E_1$  is approximately equal to storage modulus at very high frequencies). The results are presented in Table II. Now the importance of this viscoelastic model approach becomes clear. The values of  $E_2$  and viscosity  $\mu$  manifest that in thermoplastic glassy polymers, the resistance to plastic flow are

remarkably higher than a crosslinked glassy polymer. The values of  $E_1$  are approximately equal to flexure modulus of each polymer at room temperature. The higher viscosity and  $E_2$  imply more solid elastic response and restriction of viscous flow in crosslinked structures, whereas the lower viscosity and  $E_2$  in thermoplastics evidence more liquid-like response and ease of viscous flow.

In thermoset polymers, the chemical cross-links prevent irreversible molecular flow at high temperatures and thereby produce the rubbery plateau region of modulus. The value of the modulus in the plateau region is directly related to the number of effective cross-links per unit volume. The influence of molecular entanglements are illustrated by Figures 14–17, which show the dynamic mechanical spectra for PMMA, PS, PC, and CR-39. It is seen that only CR-39 shows a plateau region of modulus, while thermoplastic glassy polymers flow sharply at high temperatures. It should be noted that the glass transition region is broadened in CR-39; while in thermoplastic glassy polymers, the slope of modulus is sharp, and the glass transition region is very narrow (Fig. 18). Similarly, the broadening of glass transition in CR-39 results in a broad  $\tan \delta$  curve; while in thermoplastics, it appears very narrow (Fig. 19). The pronounced liquid like features of PS are consistent with its very low values of  $E_2$  and  $\mu$ .

It is also possible to assess the cross-link density of network polymers by the creep test method using rubber elasticity. However, in thermoplastic glassy polymers, there is no rubber plateau



**Figure 14** DMA spectra for PMMA.

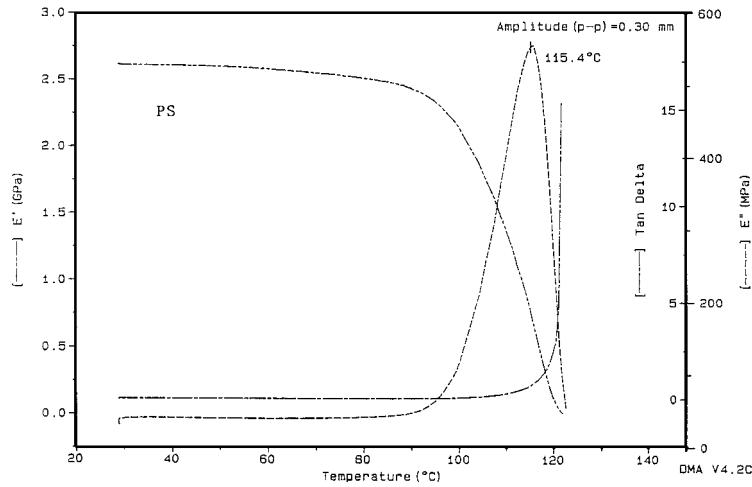


Figure 15 DMA spectra for PS.

region; therefore, the molecular between cross-links  $M_c$  approaches infinity. Hence, it is not possible to compare the thermoplastics molecular tightness with crosslinked glassy polymers. Furthermore, this present model allows to conceptualize the viscoelasticity of polymer in a quantitative basis.

Another conclusion may be drawn from com-

parison of viscoelastic parameters of glassy polymers. The dominant role of viscous flow in thermoplastics may be the main factor for amenability of these polymers to crazing process, in which the polymer structure undergoes a volume change due to formation of voids. It has been shown that the craze growth in these polymers is controlled by relaxation processes.<sup>6,7</sup> On the other hand,

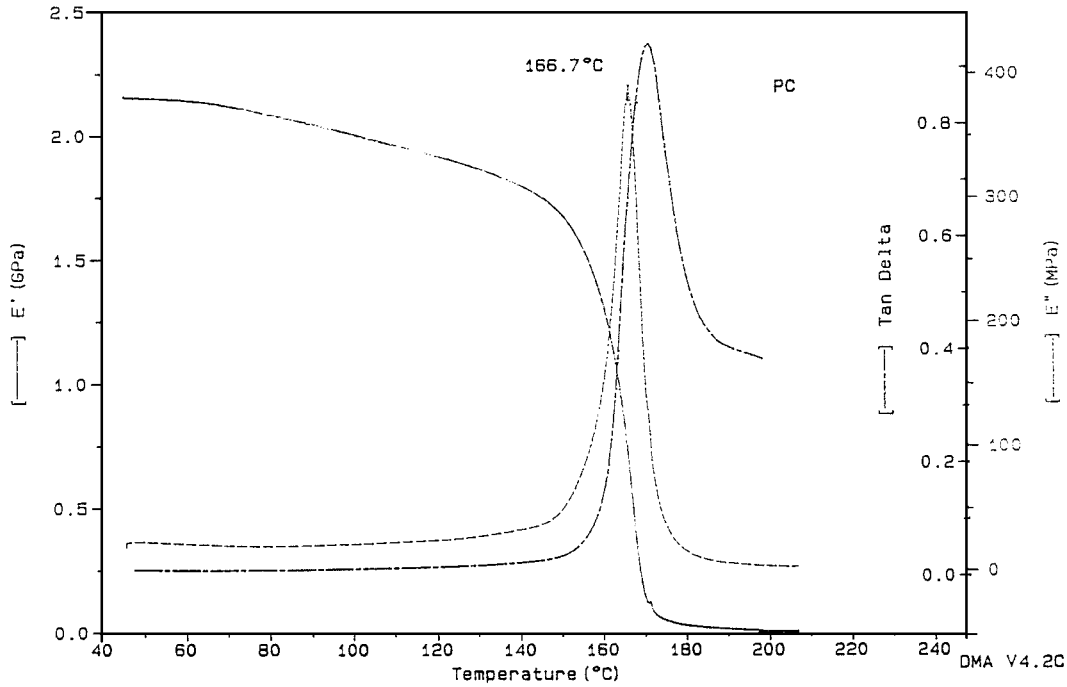


Figure 16 DMA spectra for PC.

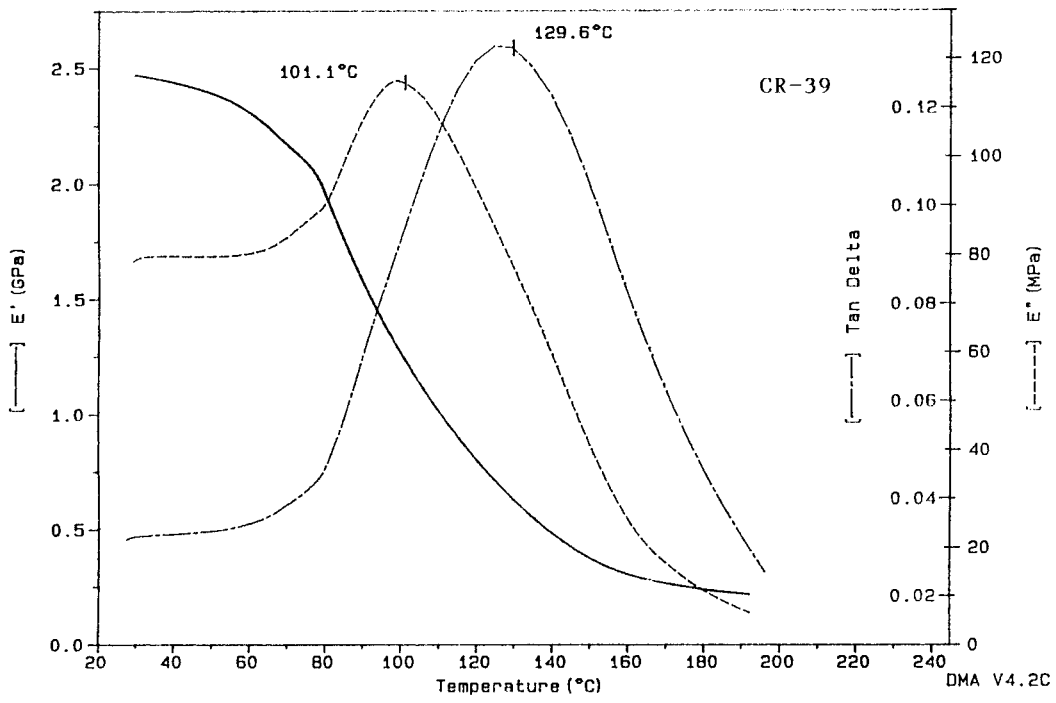


Figure 17 DMA spectra for CR-39.

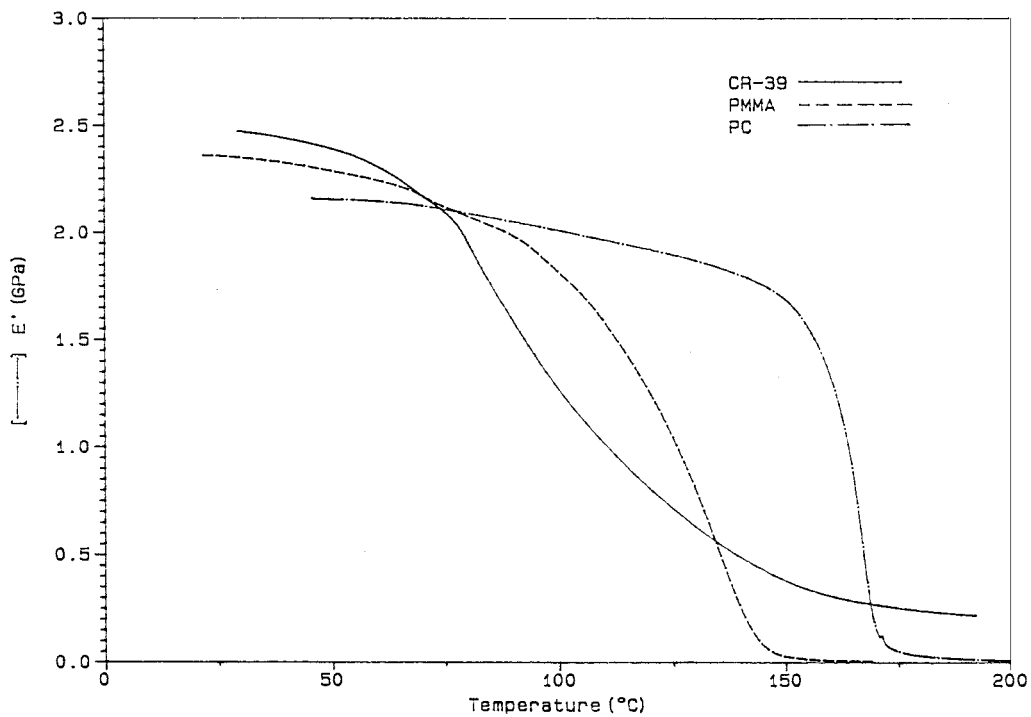


Figure 18 Variation of modulus for PMMA, PC, and CR-39.

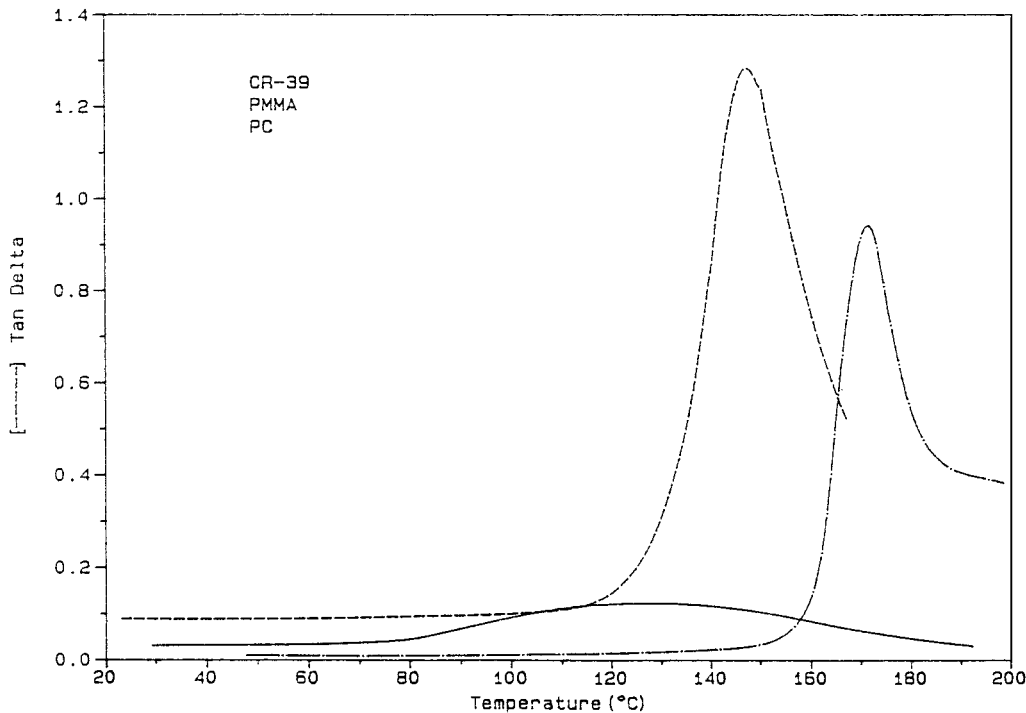


Figure 19 Variation of  $\tan \delta$  for PMMA, PC, and CR-39.

crazing has not been confirmed in CR-39<sup>8</sup> and in other thermosets, such as polyesters and epoxies,<sup>9-10</sup> where viscous flow is suppressed by cross-links between polymer chains, which reduce free volume in polymer structure.

## CONCLUSIONS

The frequency master curves of CR-39 and some thermoplastic polymers were determined by dynamic mechanical analysis. The results were used in a sinusoidal response of standard viscoelastic model. Then, it was possible to determine the viscous and elastic components of the model. These results reveal that cross-links in glassy polymers such as CR-39 render a structure that is more elastic than viscous, while thermoplastic glassy polymers show a considerable liquid viscous behavior. This approach can be used to assess the ability of modified polymer to plastic deformation in toughening purposes.

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