Connection between dielectric and mechanical properties of phenyl and chlorophenyl esters of poly(acrylic acid)

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Cole–Cole dielectric plots were determined for poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCPA), poly(*m*-chlorophenyl acrylate) (PMCPA) and poly(*o*-chlorophenyl acrylate) (POCPA) at temperatures above their respective glass transition temperatures. Master curves for the real $E'(\omega)$ and loss components $E''(\omega)$ of the complex relaxation modulus $E^*(\omega)$ were also obtained using the time–temperature superposition principle. By relating the complex dielectric permittivity $\varepsilon^*(\omega)$ with the complex shear viscosity $\eta^*(\omega)$ semiquantitative values for the radii of the relaxing species were obtained. These quantities are remarkably close to the lengths of the carbonyl and C–Cl bonds.

(Keywords: dielectric properties; mechanical properties; polyacrylic acid)

INTRODUCTION

The relaxation times associated with segmental motions in the glass–rubber relaxation are dependent on the probe used[1–6]. Thus it has long been observed that the mechanical relaxation times are larger than the dielectric times and even the relaxation times corresponding to dynamic variables which are conjugated to each other, such as the electric field E and the dielectric displacement D (τ_E is the relaxation time at constant E and τ_D the relaxation time at constant D) can be vastly different[7]. An important and still unsolved problem for a quantitative interpretation of relaxation experiments is the availability of reliable models relating the measured time correlation functions to the local structural complexity of the chains. Both the complex permittivity and the complex relaxation modulus are related to their corresponding time correlation functions by the equations[8]:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\int_0^\infty\left[-\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}\right]\exp(-i\omega t)\mathrm{d}t \qquad (1)$$

$$\frac{G^*(\omega)-G_\infty}{G_0-G_\infty}=\int_0^\infty\left[-\frac{\mathrm{d}g(t)}{\mathrm{d}t}\right]\exp(-i\omega t)\mathrm{d}t \qquad (2)$$

where $\phi(t)$ and $g(t)$ are the dielectric and mechanical correlation functions respectively, which are given by the Kohlrausch–Williams–Watts (KWW) function[9–11]:

$$\phi(t)=\exp(-t/\tau_E)^{1-n_E} \qquad (3)$$

$$g(t)=\exp(t/\tau_M)^{1-n_M} \qquad (4)$$

The subscripts 0 and ∞ in equations (1) and (2) refer to the values of the physical magnitudes at the extreme frequencies indicated, while $(1-n_E)$ and $(1-n_M)$ represent the fractional exponents in the KWW function. The larger n_E and n_M, the larger are the interchain interactions that take place in the dielectric and mechanical glass–rubber processes, respectively.

In spite of the fact that the decay function is different for dielectric and mechanical relaxations, DiMarzio and Bishop[12] proposed a method by which it is possible to obtain information about the size of the dipolar relaxing entities by relating the complex permittivity and the complex relaxation modulus of a material. These authors generalized the Debye[13] theory on dielectric relaxations so that it is applicable to cases where the friction coefficient is a function of frequency or time. This procedure is used in the present work to interpret the glass–rubber relaxations of phenyl and chlorophenyl esters of poly(acrylic acid).

EXPERIMENTAL

Poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCA), poly(*m*-chlorophenyl acrylate) (PMCPA) and poly(*o*-chlorophenyl acrylate) (POCPA) of number-average molecular weights 240 000, 600 000, 350 000 and 150 000, respectively, were obtained by radical polymerization at low conversion of benzene solutions of the corresponding phenyl and chlorophenyl acrylates using methods outlined elsewhere[14]. The glass transition temperatures, measured with a Perkin DSC-4 calorimeter, were found to be 50, 57, 39 and 45°C for PPA, PPCPA, PMCPA and POCPA, respectively.

Dynamic mechanical experiments were performed by flexion dual cantilever deformation of moulded samples, 1 mm thick and 10 mm in width, in a DMTA (PL) Mark II apparatus. Values of the complex relaxation modulus were obtained at 0.3, 1, 3, 10 and 30 Hz in the vicinity of the glass transition temperatures of the polymers. Dielectric experiments were carried out on samples 1 mm thick coated with gold to ensure good contact of the sample with the electrodes. The experiments were made with a capacitance bridge (General Radio, type 1620 A) at frequencies in the range 0.1–100 kHz. The complex

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permittivity for PPA, PPCA, PMCPA and POCPA was measured as a function of frequency at 71.8, 92.2, 64.8 and 83.6°C, respectively.

RESULTS AND DISCUSSION

DiMarzio and Bishop[12] developed a model to correlate the dielectric and mechanical relaxations for dipoles embedded in rigid beads which are in turn embedded in the viscous medium. An important hypothesis of the model is that the friction coefficient ξ between the bead and the medium is not constant, but is dependent on the frequency of the alternating field. According to this approach, the relaxation time τ^* associated with a dipolar entity is related to the macroscopic relaxation time τ_E by the expression:

$$\tau_E(\omega)=\tau_E^*(\omega)\,\frac{\varepsilon_0+2}{\varepsilon_\infty+2} \tag{5}$$

where ε_0 and ε_∞ represent the relaxed and unrelaxed dielectric constants, respectively. The dependence of the τ_E^* term on the frequency implies a non-exponential decay of the relaxing electric dipoles. The theory predicts that the complex permittivity is related to $\tau(\omega)$ by a single Debye-like term:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\frac{1}{1-\omega\tau_E(\omega)} \tag{6}$$

The distinction between this theory and other theories[15,16] is that in DiMarzio and Bishop's theory one Debye term is enough to explain a skewed arc, whereas in other theories one assumes many Debye-like terms:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\sum\frac{A_j}{1-i\omega\tau_j} \tag{7}$$

to obtain the same result. The relaxation time τ_j in equation (7) is of course independent of frequency. By assuming a spherical geometry for the relaxing dipole species, $\tau^*(\omega)$ can be written as:

$$\tau_E^*=\frac{\xi^*(\omega)}{2\kappa T}=\frac{4\pi R^3\eta^*(\omega)}{\kappa T} \tag{8}$$

where κ is the Boltzmann constant. The generalized Navier–Stokes equation:

$$\xi^*(\omega)=8\pi R^3\eta^*(\omega) \tag{9}$$

is used to relate $\xi^*(\omega)$ to the radius of the sphere R and the viscosity of the medium $\eta^*(\omega)$.

The phenomenological theory of linear viscoelasticity predicts that the dynamic viscosity $\eta^*(\omega)$ is given by:

$$\eta^*(\omega)=-\frac{iG^*(\omega)}{\omega} \tag{10}$$

where $G^*(\omega)$ is the complex shear stress relaxation modulus. From equations (5), (6), (8) and (10) it is deduced that $\varepsilon^*(\omega)$ and $G^*(\omega)$ are related by:

$$\frac{\varepsilon^*(\omega)-\varepsilon_0}{\varepsilon_0-\varepsilon_\infty}=\frac{1}{1+KG^*(\omega)} \tag{11}$$

where the factor K can be written as:

$$K=\frac{4\pi R^3}{\kappa T}\,\frac{(\varepsilon_0+2)}{(\varepsilon_\infty+2)} \tag{12}$$

Cole–Cole plots at the temperatures of interest are shown for phenyl and chlorophenyl esters of acrylic acid in *Figure 1*. An inspection of the plots reveals striking differences between the dielectric behaviour of phenyl and chlorophenyl esters of poly(acrylic acid), strongly related to the symmetry of the side group. Thus whereas the plots for PPA and PPCPA are skewed arcs which approach the abscissa at high frequency along a straight line, the plots corresponding to PMCPA and POCPA suggest that overlapping between the α and β relaxations occurs at the high frequency region. The shape of the arcs in this zone was obtained by adjusting the experimental results to the Havriliak–Negami[17] equation:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\frac{1}{(1+(i\omega\tau_0)^{1-\bar{\alpha}})^{\bar{\beta}}} \tag{13}$$

Values of the $\bar{\alpha}$, $\bar{\beta}$ and τ_0 that describe the dielectric glass–rubber relaxation of the polymers in the whole frequency range are given in *Table 1*.

Application of equation (11) to the experimental results requires the determination of the complex relaxation modulus at temperatures and frequencies similar to those used in the measurements of the complex permittivities of the polymers. However, owing to experimental difficulties, dynamic mechanical experiments could only be performed

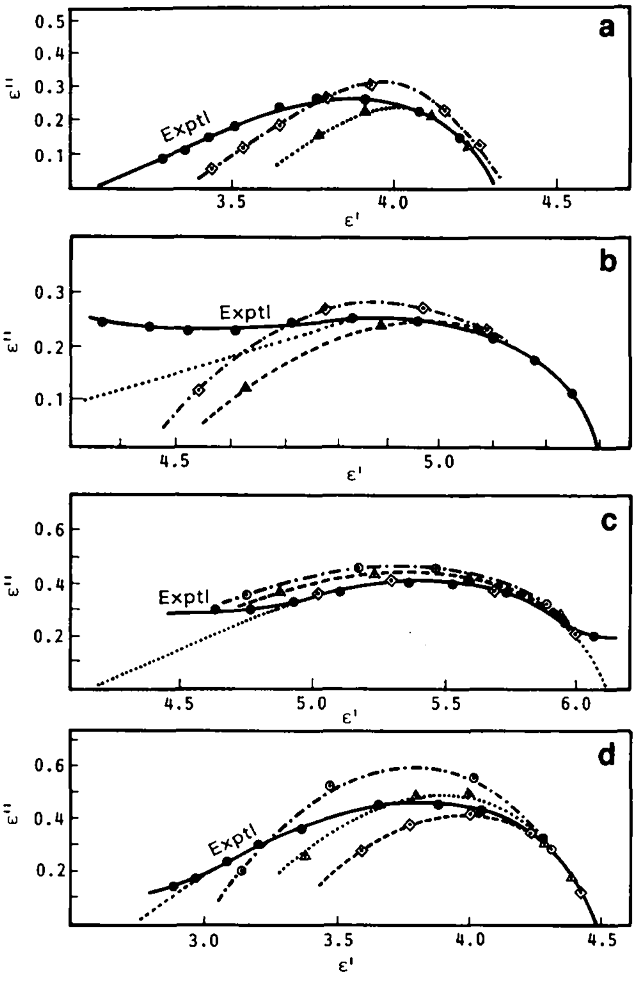

Figure 1 Cole–Cole plots obtained by means of equation (11) for different values of the radius of the relaxing species and temperatures. (a) PPA, $T=71.8$°C, $R=1.2$ Å (△), 1.5 Å (◇); (b) POCPA, $T=83.6$°C, $R=1.5$ Å (△), 1.7 Å (◇); (c) PMCPA, $T=64.8$°C, $R=1.3$ Å (◇), 1.4 Å (△), 1.5 Å (○); (d) PPCPA, $T=92.2$°C, $R=1.2$ Å (◇), 1.4 Å (△), 1.7 Å (○). ——, Experimental values of ε'' *versus* ε'

Table 1 Parameters of the Havriliak-Negami equation for poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCPA), poly(*m*-chlorophenyl acrylate) (PMCPA) and poly(*o*-chlorophenyl acrylate) (POCPA)

Polymer	T (°C)	$\bar{\alpha}$	$\bar{\beta}$	$\tau_0 \times 10^4$ (s)
PPA	71.8	0.245	0.294	8.38
PPCPA	92.2	0.140	0.418	4.08
PMCPA	64.8	0.240	0.246	14.90
POCPA	83.6	0.355	0.496	5.49

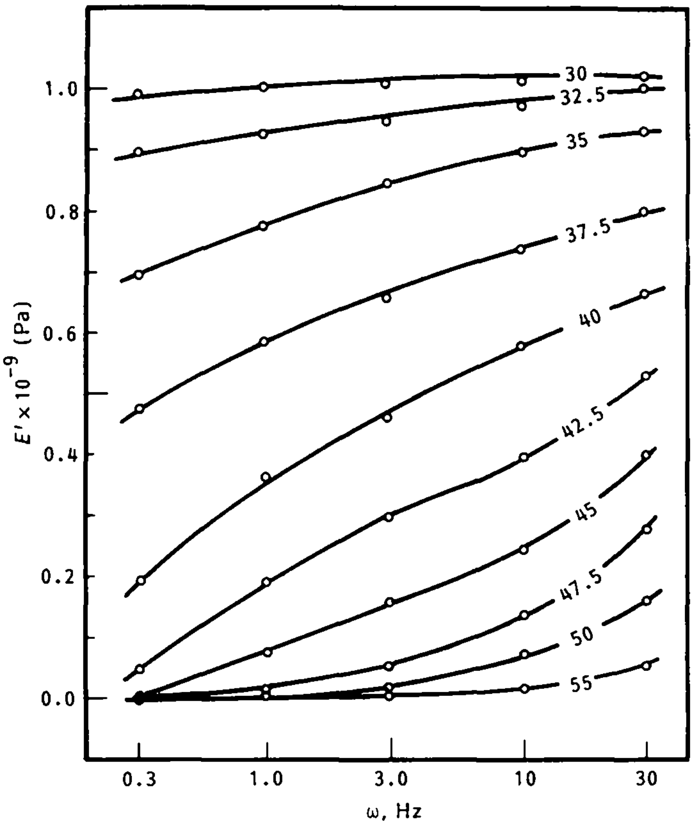

Figure 2 Values of the storage relaxation modulus E' for PMCPA as a function of frequency at different temperatures

at frequencies (<30 Hz) well below the values used to determine ε^* (>100 Hz). Since the temperature dependence of the viscoelastic response shows Williams–Landel–Ferry (WLF) behaviour[18], values of both the real E' and loss E'' components of E^* were measured at several temperatures and the master curves at the temperatures of interest were obtained using the time–temperature superposition principle. As an example, values of both E' and E'' for PMCPA, at different temperatures, are shown as a function of frequency in *Figures 2* and *3*. The master curves for E' and E'' corresponding to PPA, PPCPA, PMCPA and POCPA, at the temperatures used in the dielectric experiments, are shown in *Figures 4–7*. As usual, the shift factors a_T obey the Vogel equation[18,19].

Assuming that the Poisson ratio is independent of frequency and that its value is 0.45, G^* in equation (11) can be obtained from E^* by means of the following expression:

$$G^*(\omega) = E^*(\omega)/2.9 \qquad (14)$$

In *Figure 1* the predictions of equation (11) are compared with the experimental results for phenyl and chlorophenyl esters of poly(acrylic acid). In all cases skewed arc behaviour is predicted by the experimental values of G^*, and reasonable agreement between theory and experiment is obtained for some of the values of R given in *Figure 1*. For example, the relaxing entity in PPA is the side ester group whose dipole moment has an orientation nearly parallel to the carbonyl bond. Since the dipole moment of the side group[20] is 1.70D, the charge distribution in electronic units will be $q_{C^*} = -q_{O^*} = 0.28$, $q_C = -q_O \simeq 0$, where the asterisk refers to the carbonyl group. Therefore the relaxing group in PPA will be the carbonyl group whose length is 1.25 Å. The closeness of the value R to the length of the carbonyl group is remarkable if we consider the shortcomings of the theory. Thus the theory allows neither electric interactions between dipoles nor mechanical couplings between dipoles. In this context the theory should only be applied to dilute solutions. Moreover, the calculation was developed assuming spherical geometry for the relaxing group, an approach which could be suitable for the side groups of PPA and PPCPA, but not for asymmetric relaxing species such as the side groups of PMCPA and POCPA. In the latter two cases dielectric activity arises from rotations about $C^\alpha - C^*$ and O–PhCl bonds, in addition to the dielectric activity produced by rotations of the backbone. Comparison of the orientation of the Ph–Cl bond for POCPA and PMCPA suggests that the sweeping volume by rotation about the O–PhCl bonds should be higher in the former polymer than in the latter, as the theoretical results indicate. It should be stressed that in this case the value of R is remarkably close to the length (1.77 Å) of the C–Cl bond.

Another model for the interpretation of the glass–rubber relaxation processes was developed by Ngai and coworkers[7,11]. The model assumes that coupling between

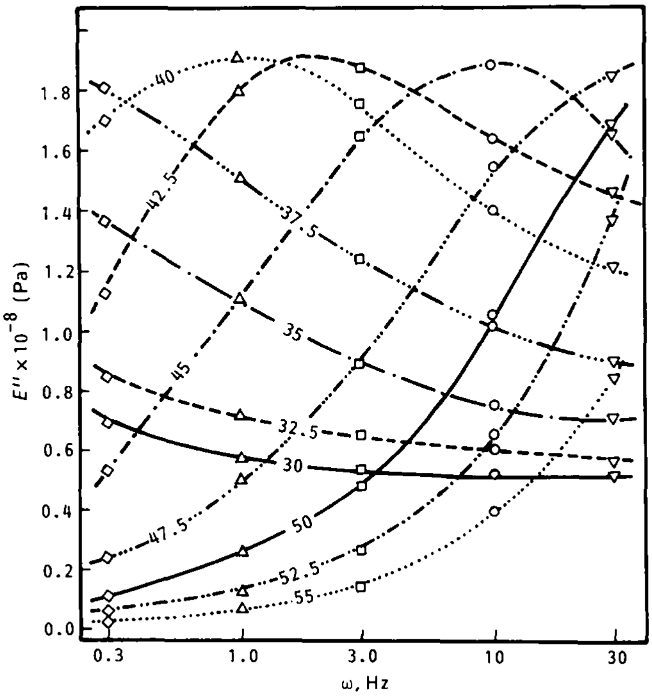

Figure 3 Variation of the loss modulus E'' for PMCPA with frequency at different temperatures

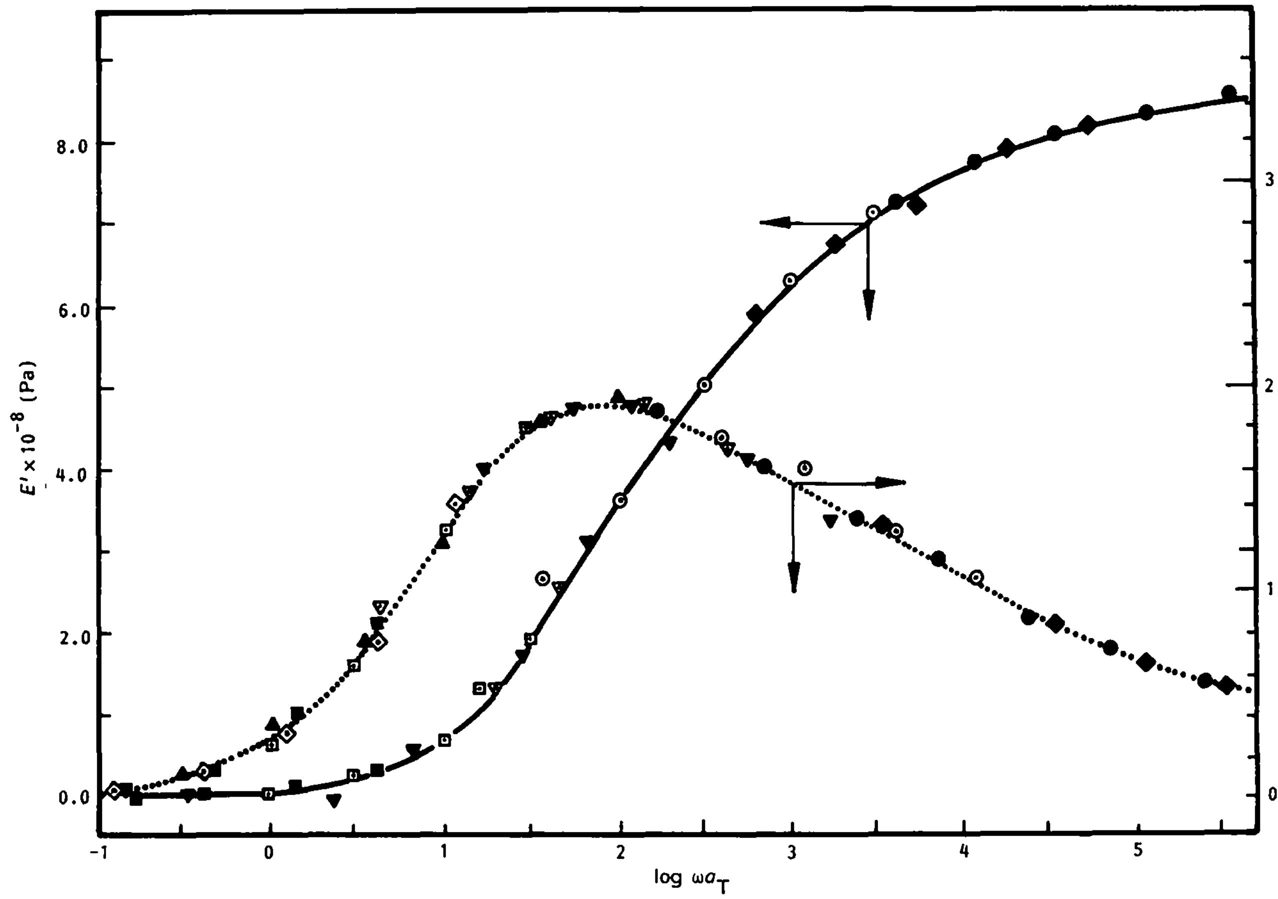

Figure 4 Composite curves for the storage and loss moduli of PPA at 71.8°C

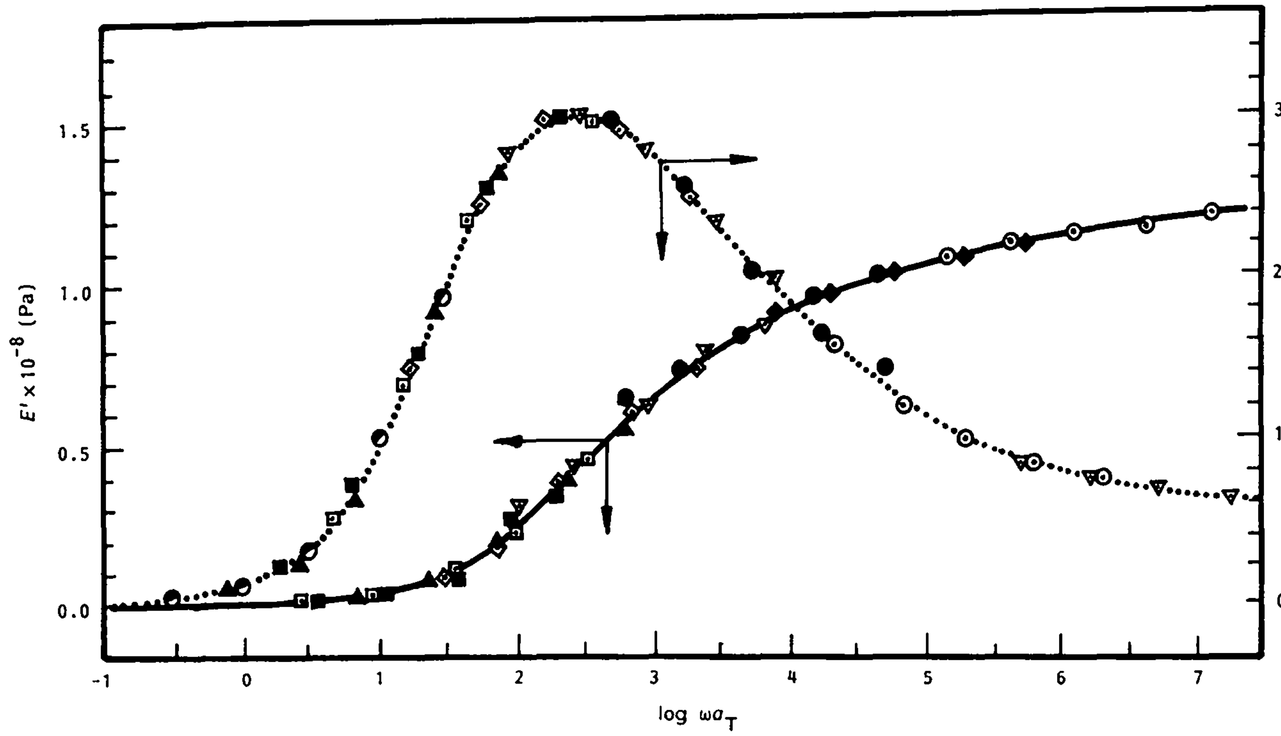

Figure 5 Composite curves for the storage and loss moduli of PPCPA at 92.2°C

the relaxing species produces a slow-down in the relaxation, and hence the decay function is not a single exponential, but is affected by an exponent, as indicated in equations (3) and (4). The higher the interactions, the higher are the values of n_E and n_M in these equations and, in general, $n_E < n_M$. The effective relaxation times that appear in the decay functions are given by[7]:

$$\tau_E \propto [B_0/(1-n_E)]/(T-T_\infty) \qquad (15)$$

$$\tau_M \propto [B_0/(1-n_M)]/(T-T_\infty) \qquad (16)$$

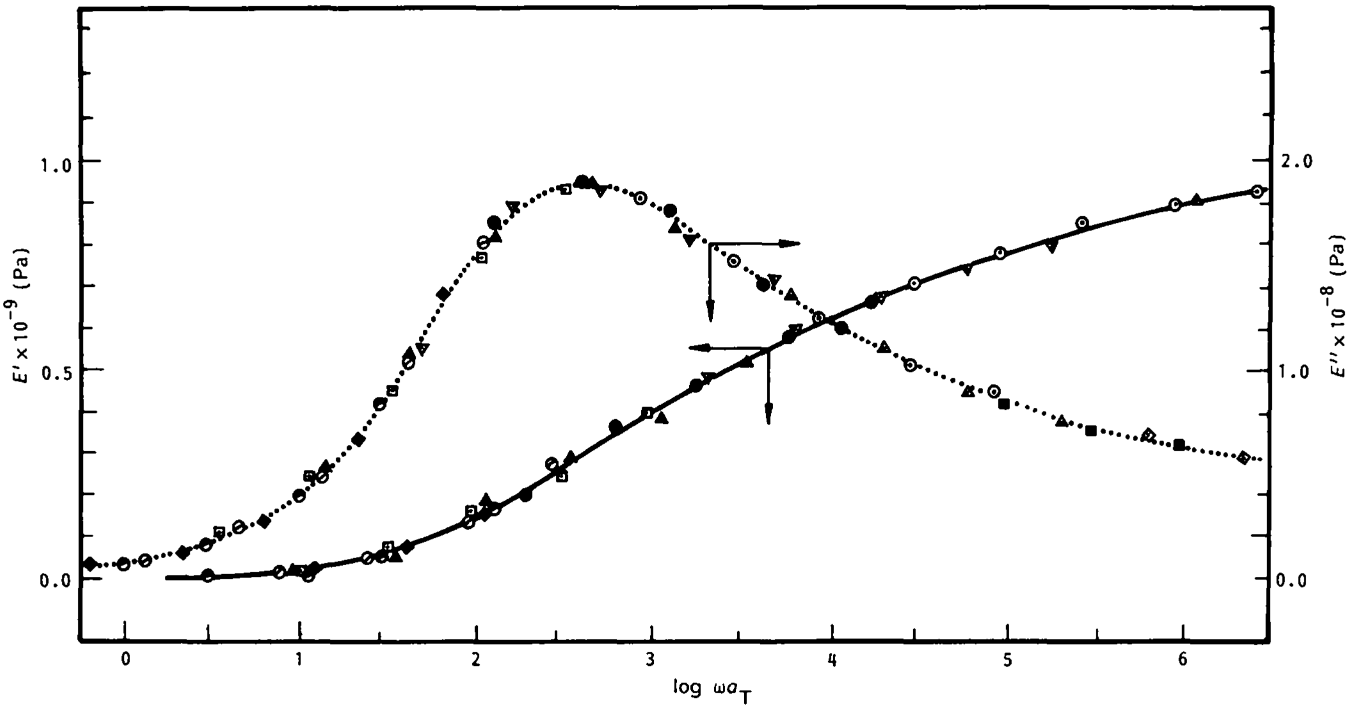

Figure 6 Composite curves for the storage and loss moduli of PMCPA at 64.8°C

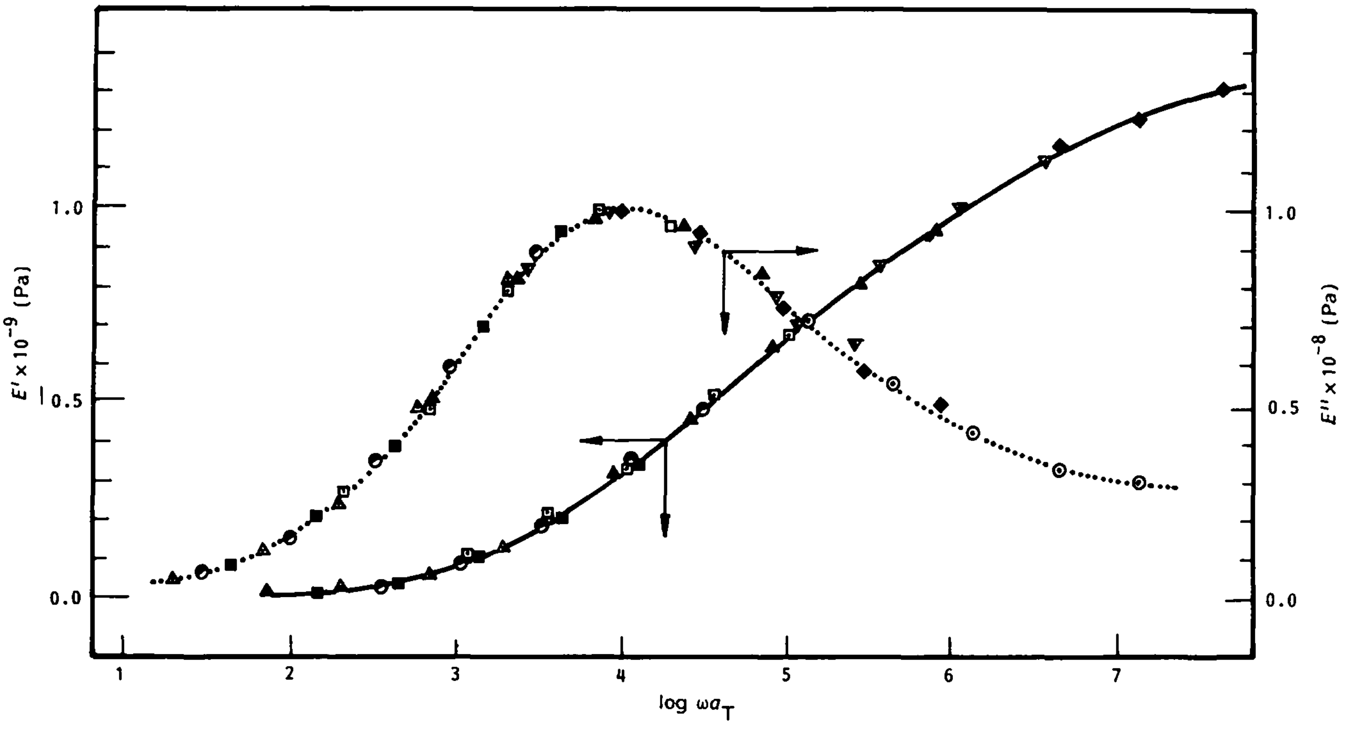

Figure 7 Composite curves for the storage and loss moduli of POCPA at 83.6°C

The coupling model predicts that B_0 is invariant for each system in the relations:

$$B_E = B_0/(1 - n_E) \qquad (17)$$

$$B_M = B_0/(1 - n_M) \qquad (18)$$

and hence:

$$(1 - n_E)B_E = (1 - n_M)B_M = B_0 \qquad (19)$$

These predictions hold reasonably well for the systems studied[21] here where the values of 856 ± 75 and 828 ± 128 are determined for B_0 from dielectric and mechanical results, respectively. Therefore equation (19) is the link between mechanical and dielectric results in the coupling model. However, the model does not give any information about the size of the relaxing species. From this point of view the information obtained by the coupling model and the DiMarzio and Bishop[12] model is complementary so that both models should be used in parallel to obtain a better knowledge about the relations between the mechanical and dielectric relaxations in the glass–rubber process.

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