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Deconvolution of overlapping relaxations in dynamic mechanical spectra

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In conventional electromagnetic spectroscopy, energy changes are represented by the absorption of radiation, and the overlapping of several transitions does not usually represent a serious problem because the individual absorption bands can be obtained by a least squares deconvolution procedure taking advantage of the additivity of the component peaks. However, if transitions or relaxations overlap in dynamic mechanical spectra the deconvolution procedure is severely complicated by the fact that relaxations may be superimposed by either a series or a parallel combination of elements, or an intermediate mixture of both. Furthermore, a knowledge of the peak shape is required before any computer resolution of processes can be attempted. In this work a skewed hyperbolic function is shown to fit the experimental peak shape for the γ and β relaxations in α, ω-diamine-cured bisphenol A epoxy resins. A least squares method using this function has been applied to the overlapping relaxations in a network polymer prepared from 1,12-dodecamethylene diamine and DGEBA. Results consistent with the addition of the loss compliances, rather than the loss moduli, were obtained and an activation energy for the resolved γ process within the accepted range for the γ relaxation reported for other polymers containing polymethylene sequences was found.

1. Introduction

A review of the literature covering investigations into relaxations in the glassy region of epoxy resins has been presented [1], and several recent publications have also dealt with the topic in detail [2, 3]. The general conclusion reached by the majority of workers is that the β relaxation, which for most compositions occurs in the range -70 to $-30\,^\circ\mathrm{C}$, is due to movement of glyceryl groups, and the γ process, occurring near $-140\,^\circ\mathrm{C}$, results from the motion of four or more consecutive methylene units.

Problems have been encountered in the characterization of the mechanical relaxations in several epoxy polymers [3, 4], and other systems [5, 6], because the low temperature loss peaks are not clearly separated from each other. This is particularly evident in resins prepared from diamine or diepoxide monomers which contain a large proportion of methylene groups. In conventional electromagnetic spectroscopy, such as infrared and nuclear magnetic resonance, the overlapping of peaks does not usually represent a serious problem because the absorbance for each component can, in theory, be determined by finding the combination of the most probable individual absorbances which add together directly to give the experimental spectrum. Computer least squares analysis [7] simplifies the procedure and removes most of the subjectivity associated with the separation of curves by eye. The task is further aided by the fact that the peak shapes for these absorbances are usually either Gaussian, Lorentzian or a combination of both [8, 9].

The necessary input data for a computer least fitting procedure consists of the heights, measured at appropriate intervals, together with the corresponding wavelengths, or other x co-ordinate values, and initial estimates of the peak height, the width at half the peak height and the position of the peak maximum. These last three parameters may be fixed or allowed to vary in order to give the optimum fit.

The situation is more complex in dynamic mechanical spectra because there are a number of totally different ways in which individual processes can combine. Furthermore, if an objective method of decomposing the overlapping relaxations is to be applied, then knowledge of the band shape is also required.

The present work illustrates a method for the deconvolution of overlapping peaks in dynamic mechanical spectra, based on a modified single relaxation time model taking into account the peak skewness observed when data are measured as a function of reciprocal temperature [10].

2. Experimental procedure

Reagents and reaction conditions used in the preparation of the networks were as specified in an earlier publication [11]. The following abbreviations are used to identify the monomers employed: DGEBA

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(diglycidylether of bisphenol A), C12 diamine (1,12-dodecamethylene diamine), C3 diamine (1,3-propane diamine) and MPD (*m*-phenylene diamine).

A freely damped torsion pendulum was used, as previously specified [2], to measure the loss factor, tan δ, and period of oscillation. These were determined at intervals of 5 or 10 °C at temperatures ranging from − 180 °C up to and including the rubbery plateau region. The instrument was equipped with an air bearing which enabled frequencies covering 0.25–10 Hz to be obtained. The storage and loss moduli (G', G'') and storage and loss compliances (J', J'') were calculated using relationships given by Ferry [12].

The computer program used to define the shape of the relaxations and to resolve overlapped relaxations was essentially the same as the program LSQ described by Frazer and Suzuki [7]. This program uses the Gauss–Newton method as the basis for the least squares minimization method, and is written in Fortran IV. To enable the program to operate on skewed hyperbolic functions, several of the subroutines were rewritten.

3. Results and discussion

The single relaxation time expressions normally used to describe mechanical relaxations have been empirically modified by Fuoss and Kirkwood [13, 14] to take into account the distribution of relaxation times encountered in real systems. These workers have derived the following equations

$$\begin{aligned} G'' &= G''(\max)\,\mathrm{sech}\,(m \ln \omega\tau) \\ &= G''(\max)\,\mathrm{sech}\left(m\Delta H\left|\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right|\right) \qquad (1) \end{aligned}$$

where

$$\begin{aligned} m &= 2G''(\max)/(G'_{\mathrm{u}} - G'_{\mathrm{r}}) \\ &= 2R\ln(2 + 3^{1/2})/(\Delta H\,\delta 1/T) \qquad (2) \end{aligned}$$

and $G''(\max)$ is the value of the shear loss modulus at the peak maximum, ω is the measuring frequency, τ is the relaxation time, ΔH is the activation enthalpy for the relaxation, T_{m} is the temperature at the peak maximum, G'_{u} and G'_{r} are the unrelaxed and relaxed shear storage moduli, respectively, and δ/T is the half-width of a plot of the loss factor against $1/T$. Similar relationships hold for J'' also [12]. For the C3 diamine/DGEBA system, ΔH determined by frequency scanning is 73 kJ mol^{-1} [3], and from Equation 2, m has a calculated value of 0.16. Substituting these values into Equation 1, together with the temperature of the maximum loss, results in the curve shown in Fig. 1. The experimental data are also included in Fig. 1, and from the comparison it is apparent that the Fuoss–Kirkwood relationship does not fit the data adequately over the entire temperature range. The experimental data for the β relaxation in this system, and also for all the other diepoxide–diamine networks which were examined, shows a pronounced

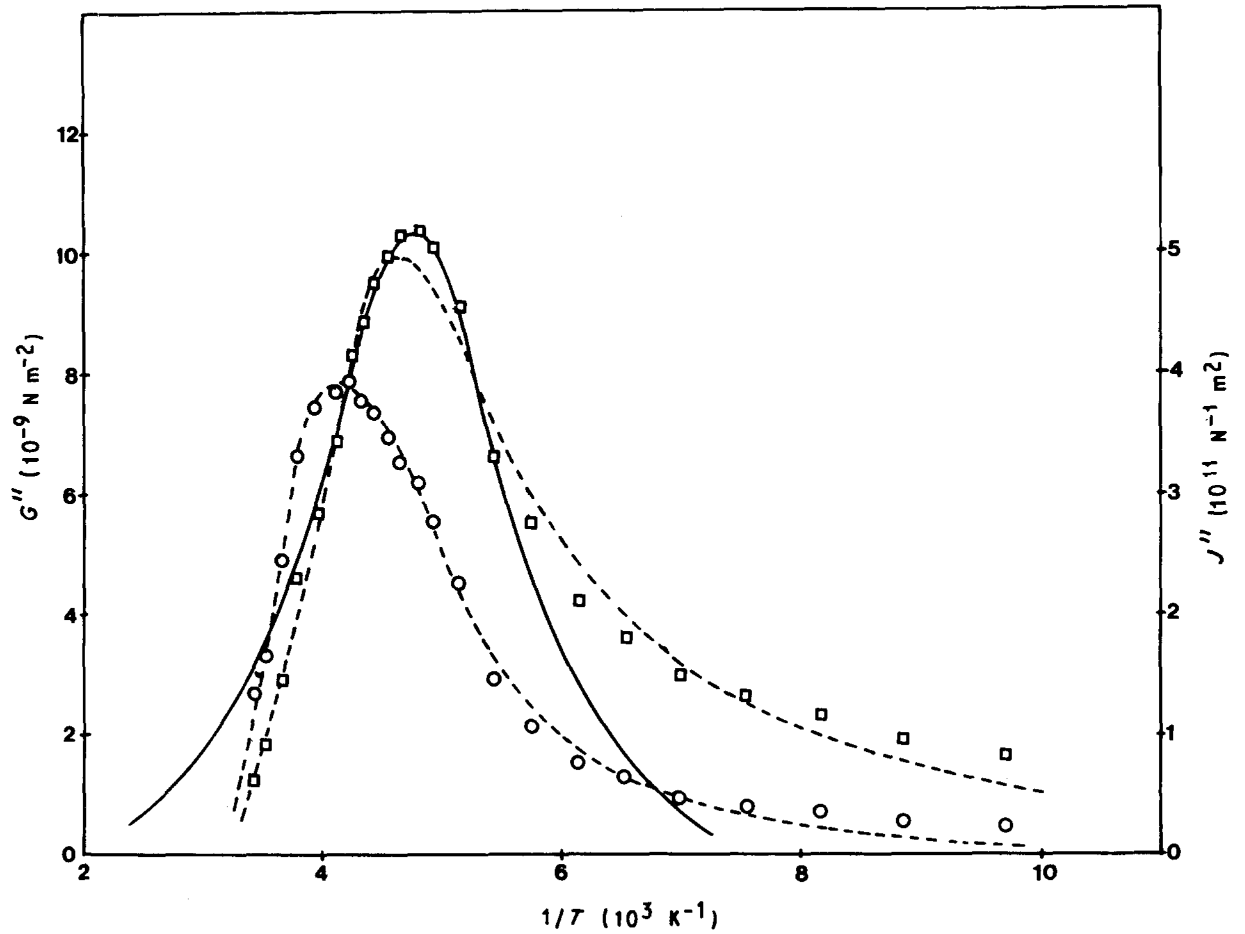

Figure 1 Experimental (○) J'' and (□) G'' data for the β relaxation in the C3 diamine/DGEBA system plotted against reciprocal temperature. (———) The symmetrical Fuoss–Kirkwood relationship, (– – –) computer least squares fits according to Equation 3.

skewness towards low temperature. One empirical method of allowing for this asymmetry, whilst still retaining the basic hyperbolic shape, is to replace the term, $m \ln \omega\tau$ in Equation 1 by the term $1/b$ $(1 + mb \ln \omega\tau)$, where b is an adjustable parameter determining the degree of skewness [8, 9]. When this substitution is made and the resulting expression is rearranged in terms of quantities derivable directly from the data, the following expressions result:

for $$1/T > \left[\left((1/T_m) - \frac{\Delta 1}{T/2b}\right)\right]$$

$$G'' = G''(\max) \operatorname{sech} [\cosh^{-1}(2/b) \ln [1 + 2b[(1/T) - (1/T_m)]/(\Delta 1/T)]\} \quad (3)$$

and for

$$1/T < \left[(1/T_m) - \left(\frac{\Delta 1}{T/2b}\right)\right], \quad G'' = 0 \quad (4)$$

where

$$b = \sinh^{-1}(\Delta_1^2 - \Delta_2^2)/2\Delta_1\Delta_2 \quad (5)$$

$$\Delta 1/T = (\Delta_2 - \Delta_1)b/\sinh b, \quad b \neq 0 \quad (6)$$

$$\Delta_1 = \frac{1}{T_l} - \frac{1}{T_m} \quad (7)$$

$$\Delta_2 = \frac{1}{T_u} - \frac{1}{T_m} \quad (8)$$

$1/T_u$ and $1/T_l$ are the upper and lower values of reciprocal temperature, respectively, at which the loss parameter becomes half its maximum value. Similar equations can be shown to relate J'' to reciprocal temperature.

Equation 3 is illustrated in Fig. 2 for several values of b. It can be seen from these plots that the original symmetry of the Fuoss–Kirkwood relationship is restored as b becomes vanishingly small, and the curves become more asymmetrical as b increases. A comparison between this function and the experimentally determined β relaxation in C3 diamine/DGEBA is shown in Fig. 1. The function was calculated from a multiple non-linear regression analysis of the experimental data, allowing the four parameters characterizing the peak (i.e. $G''(\max)$, δ_1/T, $1/T_m$ and b) to vary. For this purpose the computer program written by Frazer and Suzuki [7] was adapted to operate on the function represented by Equation 3. The function was found to fit reasonably closely all systems examined (for a further example see Fig. 3), including the polymethylene-induced γ relaxation in polyethylene. Because similar polymethylene sequences have been shown to be responsible for the γ relaxation in epoxide resins [3], it was assumed that the γ relaxation in these systems could also be described by Equation 3.

From first principles it is not possible to predict the way in which these two types of relaxing species might combine to produce a composite peak, because a number of equally likely combinations can occur. For example, consider the two most elementary configurations consisting of a series combination of elements (I), and a parallel combination of elements (II).

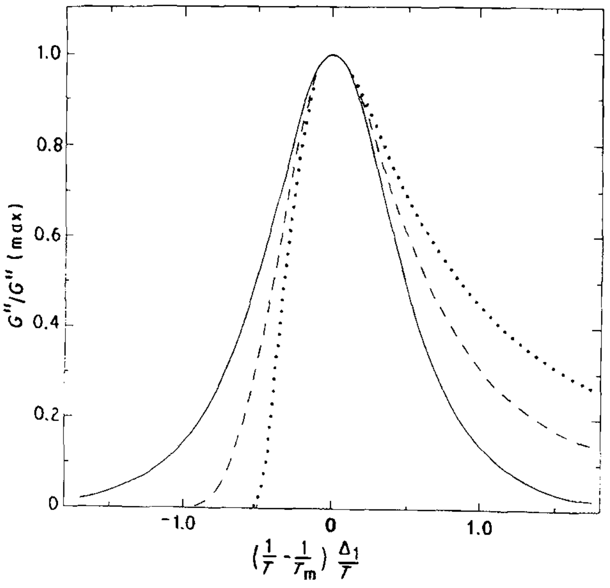

Figure 2 A plot of Equation 3 for a range of values of b: (· · · · ·) 1.0, (– – – –) 0.5, (———) 10^{-4}.

In a type I combination, the total complex compliance, J_T^*, is the series combination of the two complex compliances, J_γ^* and J_β^*, characterizing the polymethylene and glyceryl relaxing units, respectively

$$J_T^* = J_\gamma^* + J_\beta^* \quad (9)$$

In simple terms this represents a combination in which the stress experienced by both units is the same but their strain response is different. In a type II combination, the total complex compliance is the parallel addition of the two individual complex compliances

$$1/J_T^* = 1/J_\gamma^* + 1/J_\beta^* \quad (10)$$

Written in the terms of the complex moduli, this becomes

$$G_T^* = G_\gamma^* + G_\beta^* \quad (11)$$

This model implies that the stress experienced by the two units is different but their strain response is the same.

Equating the imaginary parts of these two expressions enables the following relationships to be written

$$G_T'' = G_\gamma'' + G_\beta'' \quad (12)$$

$$J_T''^* = J_\gamma'' + J_\beta'' \quad (13)$$

The most probable γ and β relaxations for the C12 diamine/DGEBA system which result from the application of the least squares resolution method to the experimental J'' and G'' versus reciprocal temperature plots are shown in Fig. 4. The sums of the two calculated relaxations in both cases are very close to the experimental curves and it appears impossible to state on the basis of goodness of fit alone, which is the more correct combination. However, it is possible to distinguish between the two combinations by utilizing the fact that the γ relaxation has a smaller activation enthalpy than the β relaxation [3]. This difference must cause the γ relaxation to shift its position by a greater amount than the β relaxation for a given

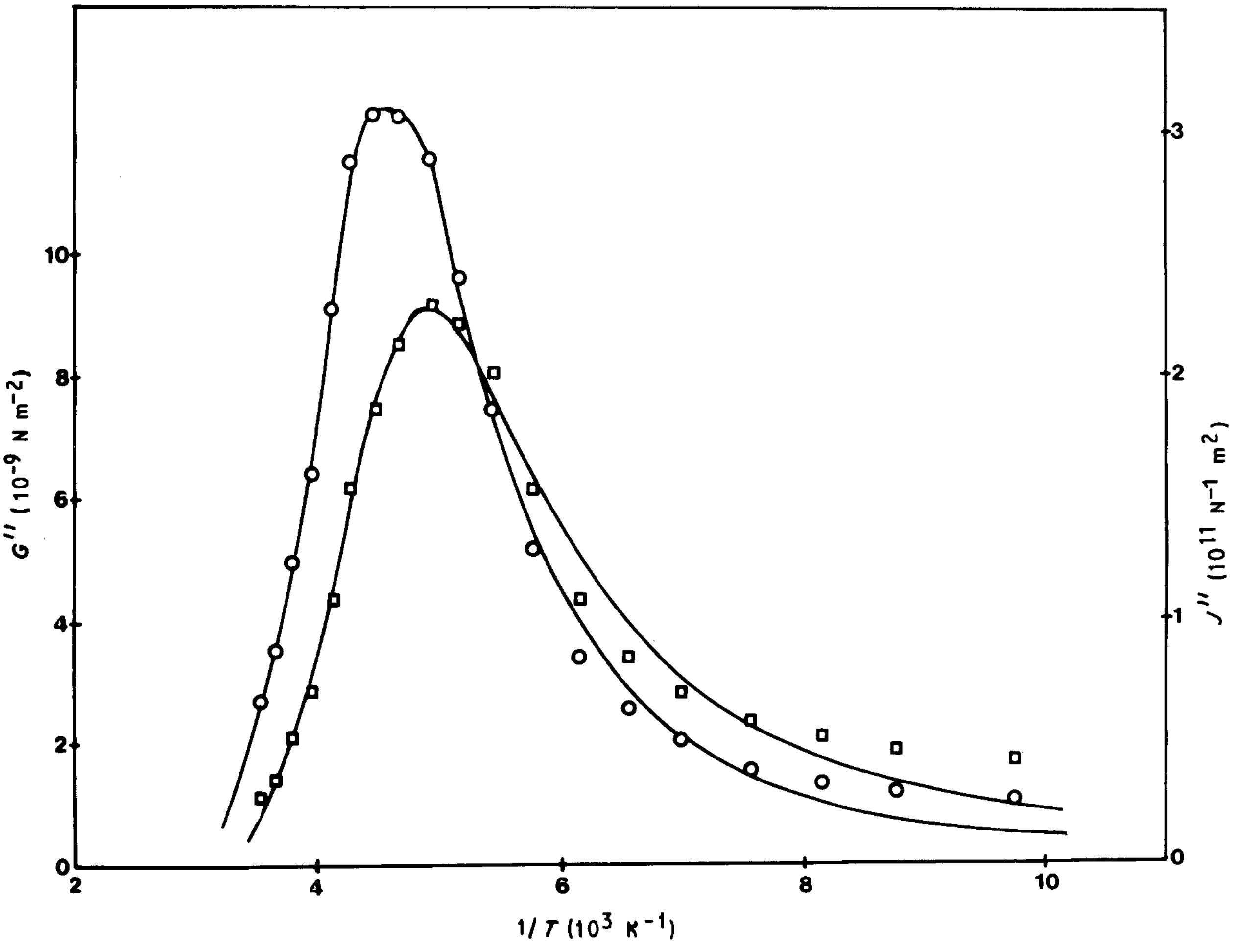

Figure 3 Computer generated least squares fits using Equation 3, to plots of (○) J'' and (□) G'' as a function of reciprocal temperature for the MPD/DGEBA system.

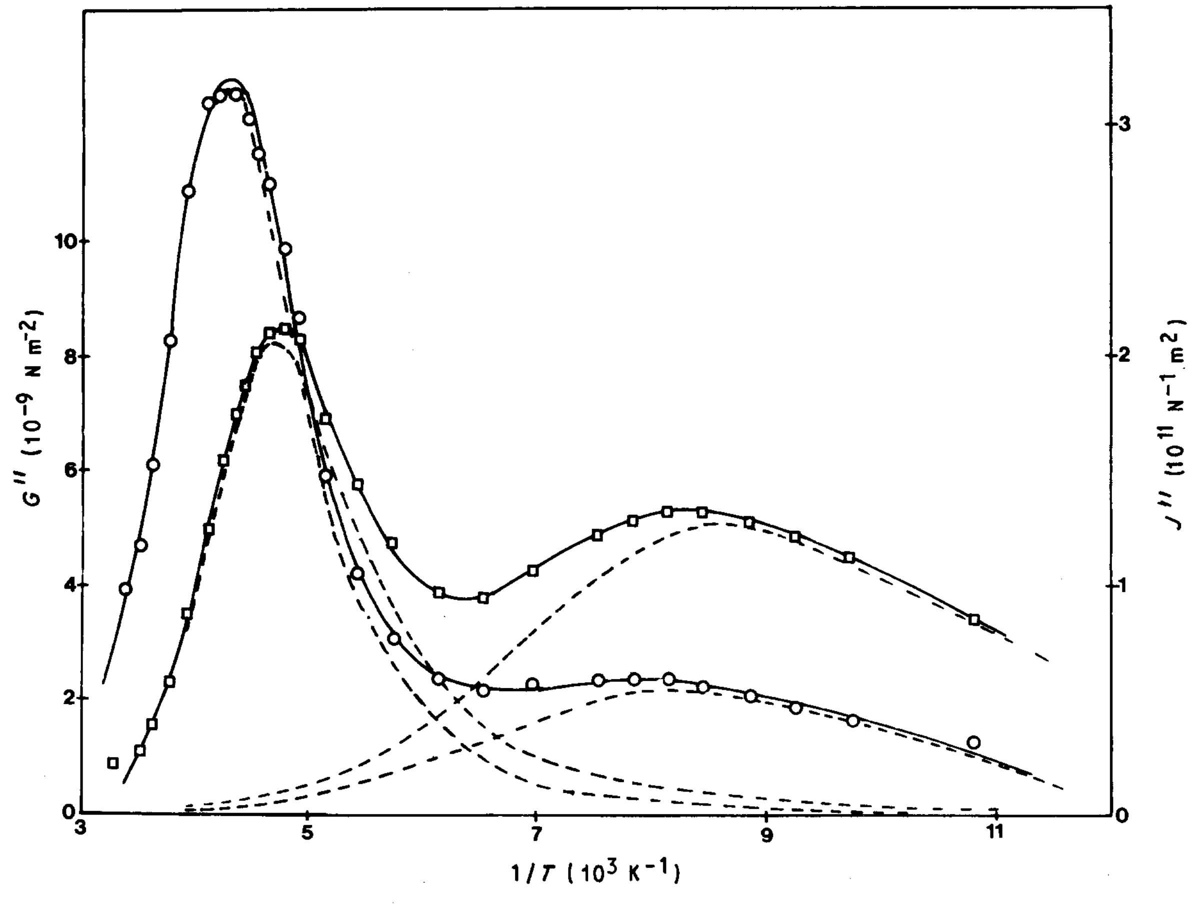

Figure 4 Computer-resolved (○) J'' and (□) G'' γ and β relaxations for the C12 diamine/DGEBA system (– – –). The resolved curves, and (———) the respective sums of the resolved curves.

TABLE I Computer-refined parameters for the β and γ relaxations in the composite G'' and J'' spectra for the C12 diamine/DGEBA system

G''					J''				
ω	β relaxation		γ relaxation			β relaxation		δ relaxation	
(Hz)	G''(max) (S.D.) (10^{-9} N m^{-2})	$1/T_M$ (S.D.) (10^3 K^{-1})	G''(max) (S.D.) (10^{-9} N m^{-2})	$1/T_M$ (S.D.) (10^3 K^{-1})	ω (Hz)	J''(max) (S.D.) (10^{11} N^{-1} m^2)	$1/T_M$ (S.D.) (10^3 K^{-1})	J''(max) (S.D.) (10^{11} N^{-1} m^2)	$1/T_M$ (S.D.) (10^3 K^{-1})
0.46	8.81 (0.09)	4.77 (0.03)	4.78 (0.10)	8.64 (0.11)	0.46	6.63 (0.06)	4.37 (0.03)	1.07 (0.04)	8.29 (0.25)
0.92	8.44 (0.10)	4.72 (0.03)	4.97 (0.06)	8.52 (0.06)	0.92	6.46 (0.14)	4.30 (0.03)	1.09 (0.05)	8.20 (0.37)
3.50	8.30 (0.17)	4.59 (0.02)	5.74 (0.06)	8.16 (0.07)	3.50	6.71 (0.14)	4.18 (0.04)	1.25 (0.07)	7.88 (0.36)
8.35	8.69 (0.35)	4.44 (0.03)	5.59 (0.09)	7.81 (0.15)	8.35	6.90 (0.15)	4.10 (0.04)	1.05 (0.10)	7.61 (0.60)

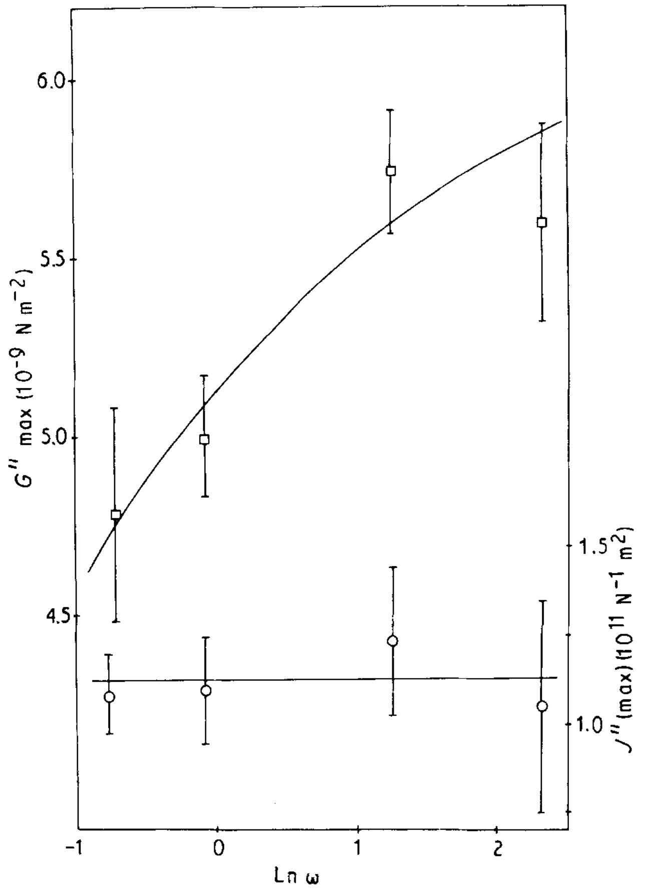

Figure 5. Plots of the computer resolved values of (○) J''_γ (max) and (□) G''_γ (max) for the γ relaxation in the C12 diamine/DGEBA system as a function of the measuring frequency.

change in the measuring frequency. Because the number of relaxing species is not a function of frequency, the size of each resolved relaxation should not change and hence the method of resolution which produces the least variation in the resolved peak heights will correspond most closely to the correct combination. Bearing this in mind, the overlapped γ and β relaxation for the C12 diamine/DGEBA system were measured at four frequencies ranging from 9.8–0.4 Hz and the composite J'' and G'' versus reciprocal temperature curves were deconvoluted into individual peaks. The information obtained in this way is shown in Table I. From these data it is apparent that both methods produce resolved β relaxations with frequency-independent peak heights (within three standard deviations). This result is not surprising in view of the fact that the γ relaxation does not have a "tail" which extends well past the position of the maximum of the β peak. However, in the case of the γ relaxation the addition of only the loss compliances produces an approximately constant peak height (see Fig. 5) and this implies that of the two methods, Equation 13 represents the combination closest to the true situation. This result is supported by the conclusions of Child and Ferry [6] who have shown that the overlapping α and β relaxations in *n*-butyl methacrylate polymers can also be resolved into component peaks by treating the loss compliances as additive.

Also included in Table I are the reciprocal temperatures of the loss peak maxima for the resolved relaxations at each of the four measuring frequencies. The data for the γ relaxation, unresolved from the composite J'' and G'' data, gives an activation enthalpy of 22 kJ mol^{-1} according to a least squares fit to a plot of reciprocal temperature against log ω. However, the resolved γ relaxation gives an activation enthalpy of 30 kJ mol^{-1}, which is just below the range of activation enthalpies for the γ relaxation reported for a variety of polyesters containing polymethylene sequences (33–42 kJ mol^{-1} [15]) and well within the range of values for the same relaxation in polyurethanes (17–38 kJ mol^{-1} [16]).

4. Conclusions

A method for resolving overlapping relaxations has been developed and applied to the γ and β relaxations in a system prepared from C12 diamine and DGEBA. Results consistent with the addition of the loss compliances rather than the loss moduli have been obtained.

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