Non-linear viscoelastic properties of solid polymers

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A torsion pendulum has been constructed to study the dynamic mechanical properties of solid polymers at temperatures between −60°C and 250°C and at strains of up to 5%. The frequency of oscillation was ~1 Hz. The specimen consisted of a hollow cylinder of thin wall thickness. Experiments on four polymers — poly(methyl methacrylate), poly(ethyl methacrylate), poly(n-butyl methacrylate) and nylon-6,6 — are reported. The results show that with increasing strain, the in-phase shear modulus, G', decreases while the out-of-phase shear modulus, G'', generally increases. The G'' relaxation peaks broaden and intensify but there is no significant shift along the temperature axis. The magnitude of the changes in G' and G'' (with increasing strain) is greater between the α and β peaks and is greater for nylon-6,6 than for the poly(alkyl methacrylates). The results are discussed in terms of a mechanical model consisting of Hookean springs and non-linear Eyring dashpots. The best description of poly(methyl methacrylate) is obtained using a model consisting of a number of elements in parallel representing the β relaxation process together with a modified Maxwell element containing a non-linear dashpot to represent the α process.

INTRODUCTION

Most past work on the non-linear viscoelastic properties of solid polymers has been performed using creep and stress-relaxation techniques but such experiments are time consuming. Dynamic mechanical measurements provide a complementary approach. In one account of the dependence of the dynamic mechanical properties on stress or strain found in the literature, Litt and Torp[1] measured the in-phase modulus, E', and the out-of-phase modulus, E'', for polycarbonate in tension at four different strain levels between 0.9 and 3.6% and over the temperature range 141–413 K using a dynamic viscoelastometer (Rheovibron) at a frequency of 110 Hz. The present paper deals with the use of a torsion pendulum to study the strain and temperature dependence of the in-phase shear modulus, G', and the out-of-phase shear modulus, G''. A free-vibrating torsion pendulum was chosen, as opposed to forced vibration methods, because simple experiments and uncomplicated instrumentation could be used. A disadvantage is that the frequency of the test varies with the modulus of the polymer and decreases slightly with increasing temperature.

A number of approaches have been used in dealing with the representation of non-linear viscoelastic behaviour. In one approach, simple empirical relations are chosen to model experimental results. This approach has been found unsuccessful when the stress or strain history is complex. Another approach has concentrated on the mathematical modelling of non-linearity using the multiple-integral representation[2,3]. One of the main limitations of the multiple-integral representation is that it requires great quantities of very accurate data and also it offers very little physical insight into non-linear viscoelasticity. Between these two extremes of the empirical approach and the multiple-integral representation, there are a number of intermediate suggestions. Some of these lean towards the multiple-integral approach with a single-integral representation but with sophisticated arguments based on mechanics or even thermodynamics. Others lean towards the empirical approach but without accepting severe constraints on the form of the stress–strain and time functions. Examples of these intermediate suggestions are the modified superposition principle suggested by Leaderman[4], the Schapery thermodynamic theory[5] and the Bernstein–Kearsley–Zapas theory[6]. The practical use and limitations of these three single-integral theories have been considered by Smart and Williams[7].

In this paper, a semi-empirical mechanical model is used to describe the experimental results. The model consisted of elastic springs obeying Hooke's Law and non-linear dashpots obeying the Eyring viscosity equation[8]. Evidence for the usefulness of the Eyring viscosity equation is derived from both creep[9,10] and yield experiments[10–13]. The Eyring viscosity equation, expressed in its simplest form, is

$$\dot{e} = a \sinh(b\sigma) \qquad (1)$$

where $\dot{e}$ is the strain rate, σ the stress and a and b are constants. The significance of the two constants has been discussed by Haward and Thackray[14]. In terms of molecular quantities, a and b are given by the equations

$$a = Ae^{-\Delta G/kT} \quad \text{with } A = \frac{2VkT}{V_m\,h} \qquad (2)$$

$$b = \frac{V}{2kT} \qquad (3)$$

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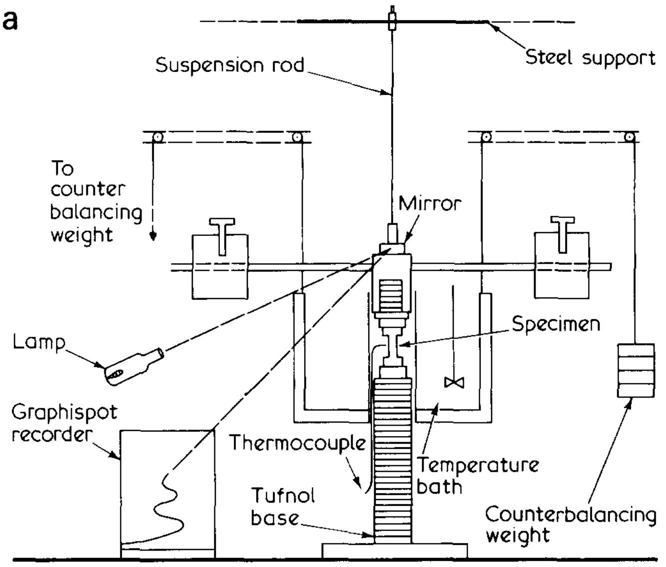

Figure 1a Torsion pendulum apparatus for studying the in-phase shear modulus, G', and the out-of-phase shear modulus, G'', for solid polymers over a temperature range -60°C to 250°C and in a strain range of 0–5%

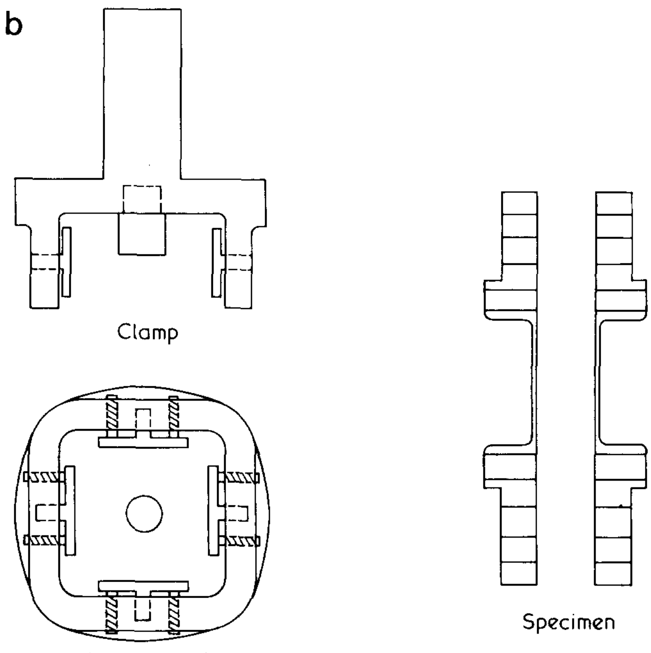

Figure 1b Specimen and clamps for use in the torsion pendulum experiments

where ΔG is the energy of activation for the process, k, Boltzmann's constant, h, Planck's constant, T, the temperature, V_m, the volume of the moving unit of the polymer chain and V, the volume swept out by the moving unit. V is usually called the Eyring volume.

EXPERIMENTAL

Apparatus

Figure 1a is a schematic diagram of the apparatus. This pendulum differs from the torsion pendulum of standard design (see Heijboer[15]) because of its size and because of the method of suspension of the inertia system. A steel rod, called the suspension rod, was used instead of a thin wire and counterbalancing weight to suspend the inertia system. The upper end of the suspension rod was rigidly clamped. The use of the steel suspension rod has two advantages. Firstly the damping of the pendulum is lowered and a larger number of oscillations is obtained in a given strain range. This helps in defining more accurately the curves of G' and G'' *versus* strain. Secondly, the oscillations are very nearly sinusoidal so that the equations for sinusoidal deformation could be used to represent the distortion of the polymer sample. Rods of different diameter (0.2–0.6 cm) but of the same length (25 cm) were made. Depending on the damping and stiffness of the polymer, a rod was chosen so that G' and G'' could be determined with reasonable accuracy. The inertia rod was ~ 1 m long and each inertia mass was ~ 6 kg.

The specimen and clamps are shown in *Figure 1b*. Hollow cylindrical specimens of 1.5 cm gauge length and 1.0 cm external diameter were machined from solid cylinders. The wall thickness of the specimens was less than 1 mm. This specimen geometry was chosen in order to achieve a moderately large uniform strain in the specimen while avoiding buckling. The specimen was held rigidly in the clamps by means of metal flats. This method of clamping proved successful even near the glass transition temperature when the glassy polymers softened. The nylon-6,6 specimens used in the experiments were made from samples of rod available commercially. The specimens of poly(methyl methacrylate), poly(ethyl methacrylate), and poly(n-butyl methacrylate) were made from samples prepared in the laboratory by free-radical polymerization.

The temperature bath was made of copper, the inner cylinder fitting smoothly around the base of the pendulum. The bath could be lowered to allow the specimen to be clamped and then raised around the specimen. For temperatures below room temperature, a freezing mixture of methanol and liquid nitrogen was used. Between room temperature and about 60°C, water was used as the thermal liquid and a thermostatted heater provided the temperature control. Above about 60°C, silicone oil was the thermal liquid. The temperature was controlled using two heating elements, a mercury contact thermometer and an electronic relay system. The temperature range available was then -60°C to 250°C.

A Graphispot recorder was used to record the damped, almost sinusoidal oscillations. It consisted essentially of an electronically controlled photoelectric follower moving on a fixed horizontal carriage. Strains in the specimen of up to about 5% could be recorded.

Experimental procedure

After the polymer specimen has been clamped in position and the temperature bath adjusted as necessary the apparatus is brought into action by displacing the inertia bar until the sample is twisted to a strain of about 4% and then releasing it. The heights of successive peaks and depths of successive troughs can subsequently be determined from the chart of the Graphispot recorder. Because of the asymmetry of the initial displacement there is a slight migration of the centre of oscillation during the course of a run. To allow for this the following procedure was adopted in determining amplitudes. If the chart readings for two successive troughs were a_{i-1} and a_{i+1} and the reading for the intervening peak was a_i it was assumed that the log decrement was constant over the oscillation so that the position of the centre of the oscillation a_o was given by

$$(a_o - a_{i-1})/(a_i - a_o) = (a_i - a_o)/(a_o - a_{i+1}).$$

The amplitude is then $A_i = (a_i - a_o)$. The corresponding log decrement is $\lambda_i = \ln(A_{i-1}/A_{i+1})$. Periods were determined from the chart by measuring the time required for five complete oscillations. As the amplitude of oscillation decreased through the course of a run each run gives a set of results for the variation of clamping and period with amplitude.

In general measurements were commenced at the lowest temperature (about −60°C) then the temperature of the bath increased in steps of five to ten degrees, runs being performed at each stage after a wait of about one hour for attainment of equilibrium. Two runs were carried out at each temperature and the results taken from the second. Preliminary checks had shown that the first and second runs differed slightly but that the second and subsequent runs were indistinguishable.

At room temperature the thermostat fluid was changed from methanol to water and the stepwise increase in temperature continued to 60° when a second change was made to silicone fluid. The same specimen was used for the whole set of runs which usually occupied two successive days. As the temperature was increased and the stiffness of the polymer specimen decreased it was often necessary also to replace the inertia rod first used (0.8 or 0.56 cm diam.) with a thinner rod. The position of the weights was adjusted so that the frequency of oscillations was always about 1 Hz.

The results obtained for λ against amplitude showed a small, approximately sinusoidal variation about a smooth curve which was more pronounced at high temperatures and which was attributed to small rocking motions of the inertia bar. These variations were eliminated and a smooth curve constructed by using a least square technique. Then replicate measurements on a single specimen give values of λ varying within a range of about $\pm 3\%$ from the mean.

CALCULATION of G', G'' AND π TAN δ

When the polymer specimen is clamped the equation for the torsional motion of the compound pendulum is of the form:

$$I\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} + C\frac{\mathrm{d}\theta}{\mathrm{d}t} + (k_s G_s + k_p G_p^*)\theta = 0 \tag{4}$$

where $C(\mathrm{d}\theta/\mathrm{d}t)$ is an air damping term, I the moment of inertia of the inertia system, G_s the shear modulus of the suspension rod and G_p^* the complex shear modulus of the polymer; k_s and k_p are the shape factors of the suspension rod and the polymer specimen, respectively, given by the equations:

$$k_s = \frac{\pi r_s^4}{2l_s}; \quad k_p = \frac{\pi(r_2^4 - r_1^4)}{2l_p} \tag{5}$$

where r_s and l_s are the radius and the length of the suspension rod, r_2 and r_1 are the outer and inner radii of the specimen and l_p the gauge length of the specimen.

When the specimen is removed, the equation of motion of the inertia system becomes:

$$I\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} + C\frac{\mathrm{d}\theta}{\mathrm{d}t} + k_s G_s \theta = 0 \tag{6}$$

If ω is the frequency and λ_{cp} the logarithmic decrement for the compound pendulum with the polymer specimen, and if ω_o is the frequency and λ_o the logarithmic decrement for the suspension rod alone, then the equations can be solved to give:

$$G' = \frac{I}{k_p}\left\{\omega^2 - \omega_o^2 - \frac{\omega^2\lambda_{cp}}{4\pi^2} + \frac{\omega\omega_o\lambda_{cp}\lambda_o}{2\pi^2} - \frac{\omega_o^2\lambda_o^2}{4\pi^2}\right\} \tag{7}$$

$$G'' = \frac{I}{\pi k_p}\{\omega^2\lambda_{cp} - \omega\omega_o\lambda_o\} \tag{8}$$

$$\lambda = \pi \tan\delta = \pi G''/G'$$

In equation (7) the terms

$$\frac{\omega^2\lambda_{cp}}{4\pi^2}, \quad \frac{\omega\omega_o\lambda_{cp}\lambda_o}{2\pi^2} \quad \text{and} \quad \frac{\omega_o^2\lambda_o^2}{4\pi^2}$$

are small compared with ω^2 and ω_o^2. In equation (8) $\omega\omega_o\lambda_o \ll \omega^2\lambda_{cp}$ and G'' varies approximately like λ_{cp}.

The strain in the specimen was directly proportional to the amplitude of the oscillations recorded and it was more convenient to consider the results as a function of the amplitude of oscillation rather than strain. If A_i and A_{i+1} were the heights (depths) of successive peaks (troughs) then the damping $\lambda_i = \ln(A_i/A_{i+1})$ was taken to be the damping at a mean amplitude $\bar{A}_i = (A_i + A_{i+1})/2$. The strain in the specimen was

$$\frac{(r_1 + r_2)}{2l_p} \cdot \frac{\bar{A}_i}{2L}$$

where L was the distance of the Graphispot from the pendulum. Smooth curves were fitted to the results for λ_{cp} *versus* $\bar{A}_i$ and the time period of the pendulum, T, *versus* $\bar{A}_i$ using a least squares approximation. G' and G'' were calculated from equations (7) and (8). For the glassy polymers the error in G' was estimated to be about 4% below the glass transition temperature and about 6% in the glass transition region. For nylon-6,6 the error was slightly smaller. The errors in G'' were about 5% below and about 6% in the glass transition region.

THEORY

Mechanical models, consisting of elastic springs and viscous dashpots, are often used to help visualize the deformation behaviour of polymeric materials. The springs account for the elastic, time-independent components and the dashpots the time-dependent, dissipative flow components in the behaviour of the polymer chains. In this section the behaviour of the modified Maxwell element, consisting of a Hookean spring and a non-linear Eyring dashpot, is considered in sinusoidal deformation. The results are then used in the generalization to more involved models.

Modified Maxwell element

The spring response follows Hooke's law so that

$$\sigma = Ge,$$

σ and e being the stress and strain and G a modulus. The dashpot is non-linear and the strain rate $\dot{e} \equiv \mathrm{d}e/\mathrm{d}t$ is related to the stress by a relation of the Eyring type

$$\dot{e} = a \sinh(b\sigma)$$

in which a and b are constants. Since the spring and dashpot are in series the total strain is the sum of the strains in each of these components and the constitutive relation becomes

$$\frac{\mathrm{d}e}{\mathrm{d}t} = \frac{1}{G}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + a \sinh(b\sigma) \qquad (10)$$

and when the strain varies sinusoidally with time at angular frequency ω, and with amplitude e_o,

$$\frac{1}{G}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + a \sinh(b\sigma) = -\omega e_o \sin \omega t \qquad (11)$$

The substitutions

$$\Sigma = \frac{\sigma}{Ge_o}, \quad \alpha = \frac{a}{\omega e_o}, \quad \beta = be_oG, \quad \varphi = \omega t \qquad (12)$$

give

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\varphi} + \alpha \sinh(\beta\Sigma) = -\sin \varphi \qquad (13)$$

Use is made of the torsion pendulum to determine the energy loss per complete cycle, ΔW, and the maximum energy stored during the cycle, W_{st}. Theoretically, these are given by

$$\Delta W = \int_{t=0}^{t=2\pi/\omega} \sigma \mathrm{d}e = -Ge_o^2 \int_0^{2\pi} \Sigma \sin \varphi \, \mathrm{d}\varphi \qquad (14)$$

$$-W_{st} + \tfrac{1}{4}\Delta W = \int_{t=0}^{t=\pi/2\omega} \sigma \mathrm{d}e = -Ge_o^2 \int_0^{\pi/2} \Sigma \sin \varphi \, \mathrm{d}\varphi \qquad (15)$$

In the region of linear viscoelasticity ΔW and W_{st} can be related to the in-phase and the out-of-phase components, G' and G'', of the dynamic modulus[16]

$$W_{st} = \tfrac{1}{2}G'e_o^2, \quad \Delta W = \pi e_o^2 G'' \qquad (16)$$

For non-linear materials a sinusoidally varying strain is not associated with a sinusoidally varying stress and G' and G'' cannot be defined in the same way as for linear materials. It is convenient, however, to use relations (16) to define G' and G'' for use in expressing theoretical and experimental results.

In general equation (13) is not soluble in terms of elementary mathematical functions and numerical methods must be used. However, while α and β depend on the amplitude, e_o, of the oscillation, their product $\alpha\beta = abG/\omega$ does not. As the amplitude e_o decreases to zero, equation (13) reduces to the linear equation

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\varphi} + (\alpha\beta)\Sigma = -\sin \varphi \qquad (17)$$

and then

$$G' = G/(1 + (\alpha\beta)^2); \quad G'' = (\alpha\beta)G/(1 + (\alpha\beta)^2) \qquad (18)$$

Solution of the equations

Equation (13), describing the modified Maxwell element, was integrated on an ICL 1906S computer by means of a fourth order Runge–Kutta method. For this method an initial value of Σ is required but is not known *a priori*; the actual constraint which makes the solution unique lies not in the specification of an initial condition but in the requirement of a periodic solution. However provided a reasonable initial value is chosen the computed solution becomes periodic after a few cycles of φ. In practice the initial value chosen was that given by the linear equation $\Sigma = 1/(1 + (\alpha\beta)^2)$.

Figure 2 shows the results for the modified Maxwell element for G'/G and $\pi G''/G$ as a function of β with $\alpha\beta = 0.1$. It is seen that G'/G decreases slightly with β but $\pi G''/G$ increases in an approximately parabolic manner. *Figure 3* shows the results for $\pi G''/G$ *versus* $\log(\alpha\beta)$, for $\beta = 0$ and $\beta = 3$. It is seen that as β increases the curve broadens somewhat and shifts to lower values of $\alpha\beta$. Since β is proportional to the amplitude of oscillation, e_o, this can be interpreted as a shift of the peak of lower values of $\alpha\beta$ as the strain increases. Now

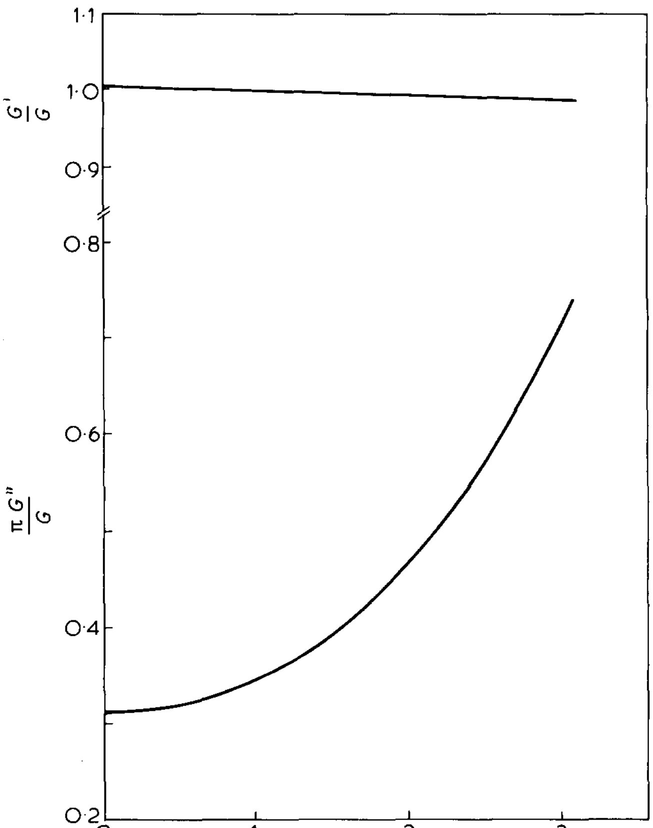

Figure 2 G'/G and $\pi G''/G$ as a function of β for the modified Maxwell element. The assumed value for the product $(\alpha\beta)$ is 0.1

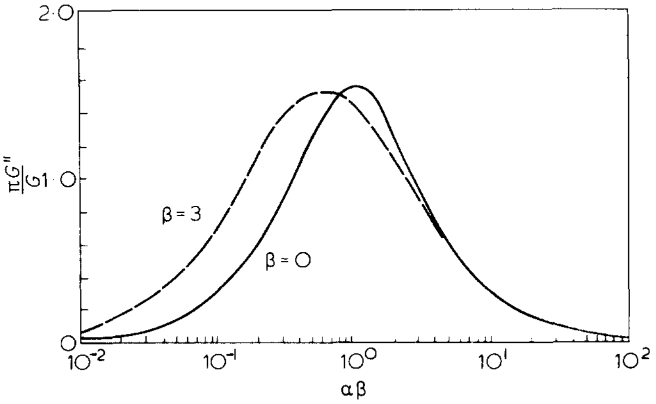

Figure 3 $\pi G''/G$ as a function of $(\alpha\beta)$ for the modified Maxwell element. The results are for $\beta = 0$ and $\beta = 3.0$

$$\alpha\beta = \frac{abG}{\omega} = \frac{V^2G}{V_m\omega}\exp\left[-\frac{\Delta G}{\mathrm{k}T}\right] \qquad (19)$$

and

$$\log(\alpha\beta) = k_1 - \log\omega \text{ where } k_1 = \log(abG)$$

or

$$\log(\alpha\beta) = k_2 - \frac{\Delta G}{\mathrm{k}T} \text{ where } k_2 = \log\left(\frac{V^2G}{V_m\omega}\right)$$

The plot against $\log(\alpha\beta)$ can be interpreted as a plot against $-\log\omega$ at constant temperature or (assuming G varies, at most, only slowly with temperature) as a plot against $-T^{-1}$ at constant frequency. The loss peak should shift with increasing strain towards higher frequencies at constant temperature or towards lower temperature (higher T^{-1}) at constant frequency.

This theory goes some way towards justifying stress–time superposition which has been found useful in extending creep data in a number of studies[17,18]. In analogy to time–temperature superposition[19] it is assumed in stress–time superposition that increased stress shortens time scales by increasing rate of molecular motion so that in non-linear viscoelasticity, increase of stress results in shift of a loss peak to lower frequency without any change of shape.

Modified Maxwell elements in parallel

It is well known[16,19] that the viscoelastic behaviour of polymeric materials cannot be matched by that of models consisting of single Maxwell elements but that, in the region of linear viscoelasticity, the behaviour is matched by that of models consisting of many parallel Maxwell elements. In particular the loss peaks of real materials cover a wider frequency range than do those for Maxwell element models and can be matched only if the model consists of multiple Maxwell elements with varying relaxation times. It is not to be expected therefore that a single modified Maxwell element would provide a satisfactory model in the non-linear region and sets of such elements in parallel need to be considered.

A modified Maxwell element is characterized by three parameters, the spring modulus, G, and the two parameters, a and b, associated with the Eyring dashpot. At low strains these elements behave as ordinary Maxwell elements with relaxation times $\tau = 1/(abG)$ and conventional methods of investigating relaxation spectra will suffice to relate the moduli values, G, to relaxation times in a multi-element model. However, a full description of the model with modified Maxwell elements capable of prediction of the effect of strain amplitude would require the separate specification of the dependence of the constants a and b as functions of τ. The achievement of such separate specifications appears an extremely difficult task. In the present investigation multi-element models will only be discussed qualitatively. It is worth noting here that for a parallel model the components of the complex modulus are the sums of those for the elements as in the linear case.

EXPERIMENTAL RESULTS AND PRELIMINARY DISCUSSION

To test the accuracy of the apparatus, experiments were first performed at low strain (<0.5%).

Results at low strain

The experimental results for poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(n-butyl methacrylate) (Pn-BMA) are shown in *Figure 4* where G' and G'' are plotted *versus* temperature. The results are in good agreement with those of Heijboer[20]. Two damping maxima are observed in the temperature range of the experiment. In the notation of Deutsch, Hoff and Reddish[21] they are referred to (from higher to lower temperature) as the α- and β-maximum. For these polymers the α-relaxation corresponds to the glass–rubber transition[22]; the main effect of lengthening the side chain is a shift of the glass transition temperature, T_g, to lower temperatures. This can be understood as resulting from an increase in free volume.

The β-maximum of G'' for the three polymers occurs at about 10°C. Studies using mechanical, nuclear magnetic

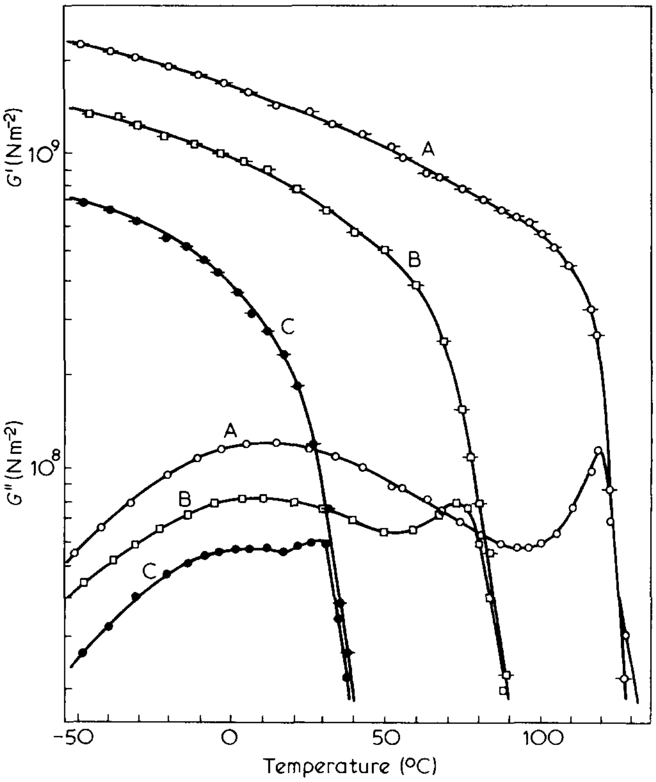

Figure 4 Temperature dependence of the in-phase shear modulus, G', and of the out-of-phase shear modulus, G'', for (a) poly(methyl methacrylate), (b) poly(ethyl methacrylate) and (c) poly(n-butyl methacrylate) at low strain

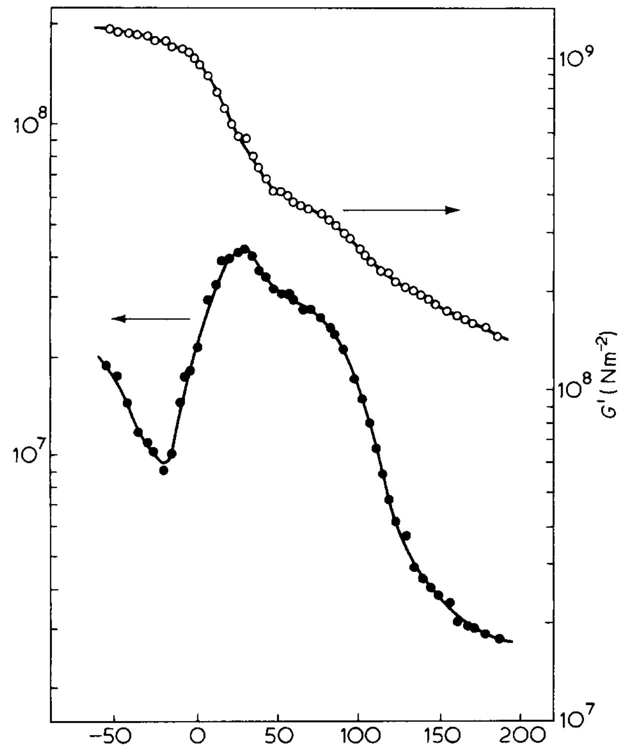

Figure 5 Temperature dependence of the in-phase shear modulus, G', and of the out-of-phase shear modulus, G'', for nylon-6,6 at low strain

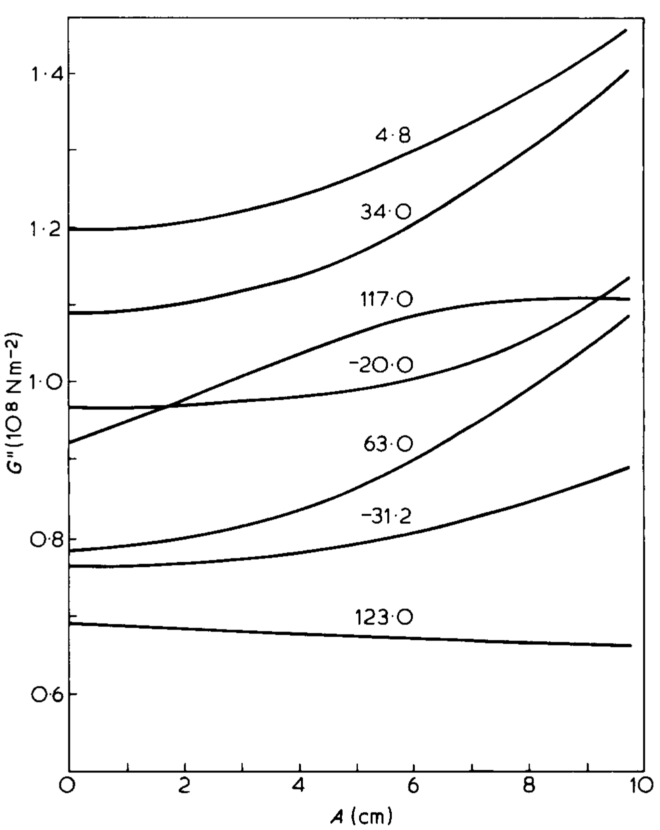

Figure 6 The out-of-phase shear modulus, G'', *versus* the amplitude of oscillation, A, for poly(methyl methacrylate) at temperatures between −50° C and T_g

resonance and dielectric techniques support a mechanism involving motion of the ester side group[16]. However it is not clear whether the motion is rotational or to what extent the main chain participates in the motion.

Figure 5 shows the experimental results for nylon-6,6. In the temperature range of the experiment the α relaxation is clearly defined together with part of the β region. It has been suggested that the α-relaxation in nylon-6,6 and other polyamides is related to the amorphous glass transition (see McCrum, Read and Williams[16]). The drop in G' as the region is traversed is distinct but is not nearly as marked as that for an amorphous polymer at its glass transition because of the semi-crystalline nature of nylon-6,6. There is evidence of a further relaxation region, indicated by the shoulder at about 80°C on the high temperature side of the α peak.

The height of the β peak is affected by the water content of the samples. Illers[23] found that the mechanical β peak for nylon-6,12 increased in height with increasing water content and the dielectric results of Curtis[24] showed that the β peak was almost eliminated by drying. Illers suggested that the β relaxation was due to the motion of carbonyl groups to which water molecules were attached by hydrogen bonds.

Results at moderately high strain

Figure 6 shows the smoothed curves for G'' *versus* the amplitude of oscillation, A, for poly(methyl methacrylate) at some temperatures between $-40°\mathrm{C}$ and 120°C. An amplitude of 1 cm is equivalent to a strain in the specimen of 0.35%. At temperatures below T_g, G'' increases approximately parabolically with amplitude. As T_g is approached the curves level off at high amplitude. Above T_g, G'' is almost independent of amplitude. *Figure 7* shows that the in-phase modulus, G', decreases slightly with

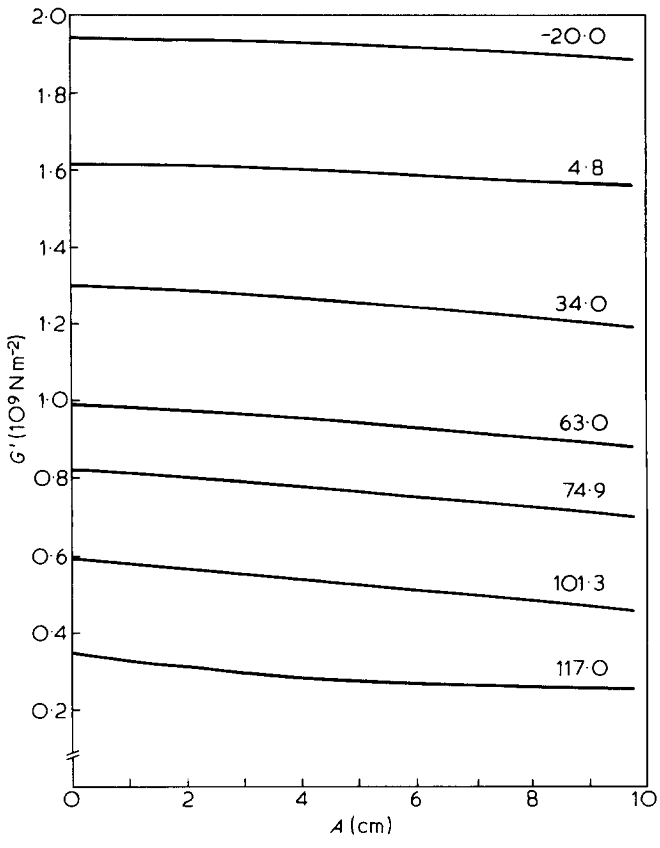

Figure 7 The in-phase shear modulus, G', *versus* the amplitude of oscillation, A, for poly(methyl methacrylate) at temperatures between −50° C and T_g

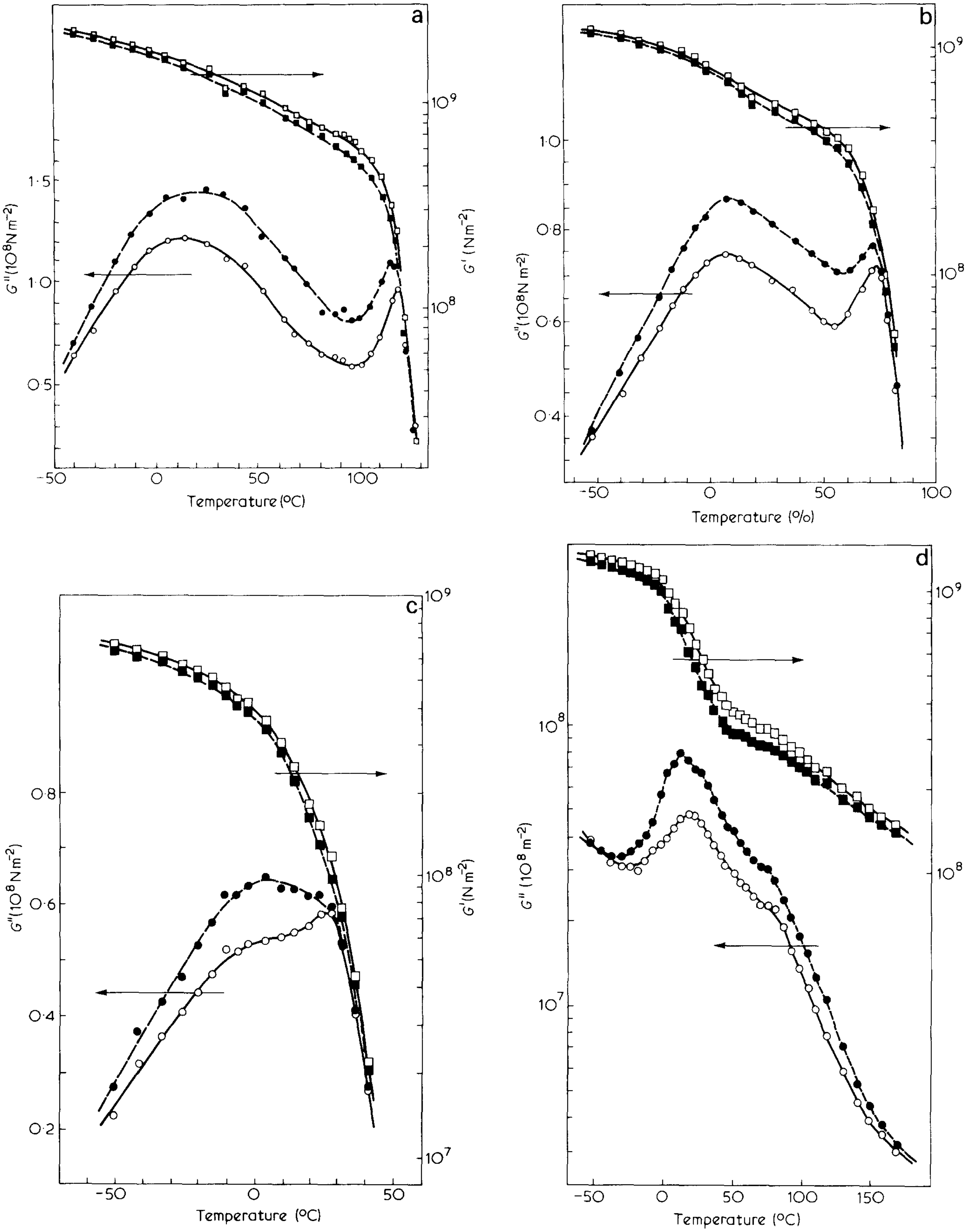

Figure 8 The in-phase shear modulus, G', and the out-of-phase shear modulus, G'', *versus* temperature for strains of (——) 0.3 and (– – – –) 3.0% for (a) poly(methyl methacrylate), (b) poly(ethyl methacrylate), (c) poly(n-butyl methacrylate) and (d) nylon-6,6

increasing amplitude, the magnitude of the decrease becoming greater as T_g is approached.

The effect of strain can also be seen in plots of G' and G'' *versus* temperature. *Figure 8a* shows the results of G' and G'' for poly(methyl methacrylate) at two different strains, 0.3 and 3.0%. *Figures 8b–d* similarly show the results for poly(ethyl methacrylate), poly(n-butyl methacrylate) and nylon-6,6. For the three glassy polymers the results at 0.3% are in good agreement with those obtained previously at low initial strain (see *Figure 4*). However, for

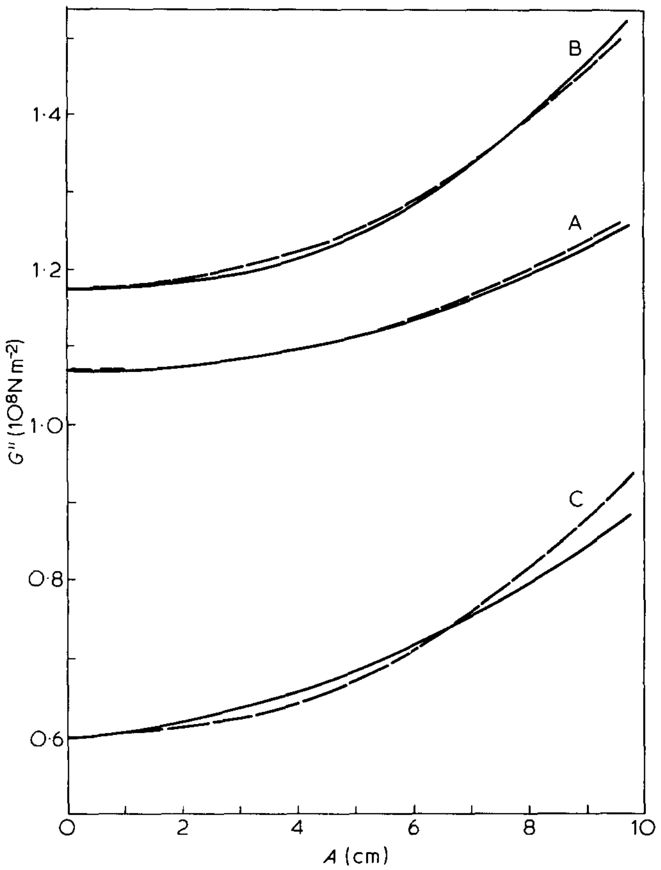

Figure 9 Comparison of the experimental results (——) for the out-of-phase shear modulus, G'', *versus* the amplitude of oscillation, A, with the predictions of the modified Maxwell element (— — —). The results are for temperatures of (a) −11.2°C, (b) 25.4°C and (c) 85.1°C

nylon-6,6 below the α peak, the results for G'' at 0.3% strain are significantly greater than those obtained with a low initial strain; above the α peak the two sets of results are in good agreement. It seems that increasing initial strain produces changes in the internal structure of semicrystalline nylon-6,6 although above the α peak the polymer recovers quickly to its original state. This type of behaviour appears to be similar in nature to that observed by Ward and Onat[25] in conditioning experiments on polypropylene.

DISCUSSION

The experimental results for poly(methyl methacrylate) on the variation of G'' with amplitude of oscillation, A, were first compared with predictions from the single Maxwell element model. By means of equation (18) the parameters G and $\alpha\beta = abG$ can be calculated from the low-strain data. The parameter b is then chosen to fit most accurately the variation of G'' with strain amplitude, e_o. In *Figure 9* the results obtained at three temperatures for PMMA are compared with the predictions for the modified Maxwell element. The fit is satisfactory at the lower temperatures but deteriorates near T_g.

The Eyring volume, V, was calculated from the parameter b according to equation (3) and is plotted against temperature in *Figure 10*. The values calculated increase slowly over the temperature range covered by the β relaxation (up to about 80°C) and increase more rapidly as T_g is approached. This is a plausible result as T_g represents a temperature at which large scale movements become possible in a polymer.

A number of estimates of the Eyring volume of polymers have been made previously, mostly from the slopes of plots of log(strain rate) against yield stress. These estimates have been reviewed and discussed by Haward and Thackray[14]. For poly(methyl methacrylate) values of 3900 and 4660 Å^3 were obtained by Lazurkin and Fegelson[11] and of 3100 Å^3 (at 30°C) and 4100 Å^3 (at 50°C) by Crowet and Homès[13]. These values are of similar magnitude but rather larger than those found at the higher temperatures in the present investigation.

Turning to the effect of temperature variation as illustrated for poly(methyl methacrylate) in *Figure 8a*, it is seen that the single modified Maxwell element model is unsatisfactory. This model predicts a movement of the loss peak to lower temperatures as the amplitude is increased with a small decrease in the maximum value of G'' while experimentally it is found that the loss peak remains at approximately the same temperature but that the height is increased. Nor is it apparent that a more complicated model with many Maxwell elements would fit the experimental results for as the loss peak for each element moves to a lower temperature it would at first be anticipated that the whole complex peak behaves in the same way.

In order to reconcile the model with the experimental observations the following proposals are made:

(1) The β relaxation processes can be represented by a model consisting of many modified Maxwell elements in parallel, the parameter b having, for all elements, a value so low that non-linearity is not apparent at the strain levels in these experiments.

(2) The α relaxation process can be represented at constant temperature, at least to a first approximation, by a single modified Maxwell element with a much larger value for the parameter b.

The first proposal seems reasonable since the volume of the ester side group whose motion is considered responsible for the β peak has a volume of only about 50 Å^3. This proposal accounts for the lack of effect of strain amplitude on the temperature of the G'' maximum.

The measurements of Lethersich[26] indicate that at low strains the α relaxation process becomes apparent at times longer than ~100 s in the creep of poly(methyl methac-

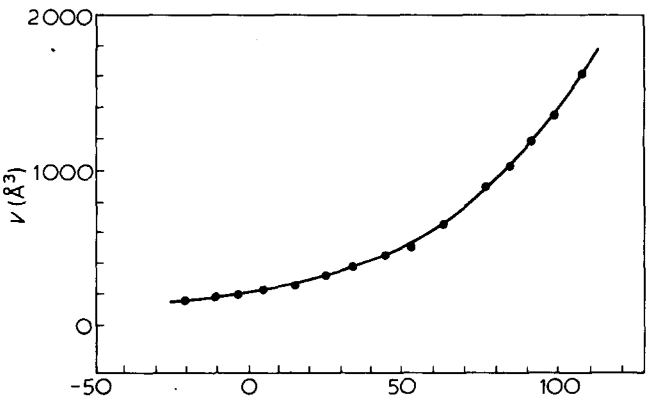

Figure 10 The Eyring volume, V, *versus* temperature for poly(methyl methacrylate). The results were obtained from the comparison of the experimental results for G'' *versus* amplitude of oscillation with the predictions of the modified Maxwell element

rylate) at a temperature of 30°C. If the Eyring volume is much greater for this process than for the β process the α process will become more important as the stress is increased and it is not unreasonable to conclude that this α process accounts for the non-linear dependence of creep rate on stress observed. This would be the case at the very high stresses required for yield. Furthermore deduction of Eyring volumes from plots of log(strain rate) against stress implies the acceptance of a modified Maxwell model as adequately accurate in representing this process over some limited range of experimental conditions. This view of the importance of the α process implies that the α peak is extremely asymmetrical when plotted on a temperature scale. This is not surprising as above T_g the viscoelasticity depends upon temperature through changes in free volume and calculations of apparent activation energy give very high values. Below T_g only normal activation energies are expected.

The compound model proposed explains many features of the results. In the first place the increasing value of the Eyring volume with temperature towards the value obtained from the rate dependence of the yield stress when this quantity is calculated from the single Maxwell element model is to be expected. With increasing temperature the importance of the β process decreases (above the β peak maximum) and the importance of the α process increases so that the Eyring parameter b should increase from a low value to a value appropriate to the α process and this process is the one active at yield.

The model explains why G'' falls slowly with increasing strain amplitude at 123°C, this temperature being just above the maximum for the α peak. Moreover the model explains the complex variation of G'' with amplitude at 117°C; the initial increase is followed, after a maximum has been reached, by a slow fall. This is the behaviour expected at a temperature just below the maximum G''. G'' at first increases as the peak moves to lower temperatures but at sufficiently high strains the maximum moves below the temperature of the experiment and G'' then begins to decrease again.

The results for the other methacrylate polymers seem similar to those for poly(methyl methacrylate) allowing for the lower T_g. Any interpretation for nylon-6,6 must be complicated by the change in microstructure which occurs on stretching and the results for this polymer will not be discussed further.

CONCLUSIONS

The results show that with the apparatus constructed it is possible to measure the in-phase shear modulus, G', and the out-of-phase shear modulus, G'', over a wide temperature range and over a strain range of up to 5%. The apparatus has been used to study the behaviour of three glassy polymers; poly(methyl methacrylate), poly(ethyl methacrylate) and poly(n-butyl methacrylate) and one semi-crystalline polymer — nylon-6,6. G' decreases with strain at all temperatures. For the poly(alkyl methacrylate), G'' increases with strain at temperatures up to the α peak; above the α peak G'' is almost constant in the strain range used. In the case of nylon-6,6, G'' increases with strain at all temperatures. The curves of G'' *versus* temperature show that with increasing strain the relaxation peaks broaden and intensify somewhat but there is no significant shift along the temperature axis.

The best description of the results for poly(methyl methacrylate) is obtained using a mechanical model consisting of a number of Maxwell elements in parallel representing the β relaxation process together with a modified Maxwell element containing a non-linear dashpot to represent the α process. The results for the other methacrylate polymers seem similar to those for poly(methyl methacrylate) allowing for the lower T_g.

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