ΔG–T curve of Fig. 1 exhibits a pronounced upward curvature, which corresponds to a *decrease* in the pre-exponential with stress by about ten orders of magnitude in the experimental range. Such a large variation cannot easily be accounted for by any normal dislocation-obstacle interaction. A natural inference is that the pre-exponential must have a pronounced temperature dependence in addition to the usual τ^*/μ dependence, and that this can be attributed, for example, to a rapid increase in the density of activatable sites with temperature. This could arise, in the present instance, if the density of activatable sites depends on the concentration of point defects, particularly vacancies. For the case of dislocation-point defect interaction in MgO, the pre-exponential factor includes the defect concentration due to the presence of impurities and due to non-stoichiometry. At low temperatures the thermal vacancy concentration is too small to affect $\dot{\epsilon}_0$ to any significant extent. As a result, the ΔG–T curve will be either straight or concave in this temperature range. The thermal point defect concentration becomes larger at higher temperatures, however, and the ΔG–T curve can then be expected to exhibit progressively increasing upward curvature as the temperature increases. It is precisely at the higher temperatures (298 to 473 K) in the case of the MgO data of Fig. 1 that the curvature of the ΔG–T plot is the most pronounced.

In order to extract the temperature dependence of $\dot{\epsilon}_0$ from experimental data, the temperature dependence of ΔG *at constant effective stress* τ^* (or the ΔG–τ^* dependence *at constant* T) must be known. In addition, suitable correction terms must be added to Equation 3 to allow for the temperature dependence. As τ^*–T data for MgO are not available at different strain rates, it was not possible in the present case to determine the functional form of $\dot{\epsilon}_0$. It can nevertheless be concluded that the upward curvature of ΔG–T plots in MgO and similar materials can have a physical basis, and that this is likely to involve a rapid increase in the pre-exponential factor with temperature. The latter, in turn, is probably associated with the increase in vacancy concentration, and therefore in the density of activatable sites, that accompanies the increase in temperature.

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The relation between linear and non-linear viscoelasticity of polypropylene

At present there exists no description of non-linear viscoelastic behaviour of solids under multiaxial loading, which is of proven validity and also fruitful in suggesting physical origins of the non-linearity. In these respects the following extension of the theory of linear viscoelasticity is attractive. For a creep experiment in which the stress tensor $\boldsymbol{\sigma}$ is applied at time $t = 0$, define the mean stress σ_m and deviatoric stress tensor $\boldsymbol{\sigma}'$

$$\sigma_m \equiv \tfrac{1}{3} Tr\boldsymbol{\sigma}\,,\ \boldsymbol{\sigma}' \equiv \boldsymbol{\sigma} - \mathbf{I}\sigma_m$$

where $\mathbf{I}$ is the unit matrix. An isotropic linear viscoelastic solid with shear compliance function $J(t)$ and compressibility function $B(t)$ then deforms at $t > 0$ with strain tensor $\boldsymbol{\epsilon}(t)$ given by

$$\boldsymbol{\epsilon}(t) = \frac{J}{2}(t)\boldsymbol{\sigma}' + \frac{B}{3}(t)\sigma_m\mathbf{I}\,. \qquad (1)$$

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Now consider an initially isotropic *non-linear* viscoelastic solid whose non-linearity in creep is caused *solely* by $J(t)$ and $B(t)$ depending upon the prevailing stress state, defined by its invariants I_1, I_2, I_3. (We consider strains so small, $\epsilon_{ij} \lesssim 0.01$, that the conventional definitions of $\boldsymbol{\sigma}$ and ϵ may be employed without infringing the requirement of objectivity of stress and strain measures [1].) If this simplification could be shown to apply, it would greatly aid physical understanding of non-linearity. For such a solid multiaxial creep response would be given by

$$\boldsymbol{\epsilon}(t) = \frac{J}{2}(t, I_1, I_2, I_3)\boldsymbol{\sigma}' + \frac{B}{3}(t, I_1, I_2, I_3)\sigma_{\mathrm{m}}\mathbf{I}\,. \tag{2}$$

Equation 2 has already been suggested as applying to non-linear viscoelastic polymers [2, 3]. Quantitative evidence for its validity, however, is meagre [2].

We have examined the accuracy of Equation 2 well into the non-linear viscoelastic region of strain, using combined tension-torsion creep experiments on isotropic polypropylene at a temperature of 65.5°C. The specimen was a thin-walled tube (of length 65 mm, radius 4 mm, wall thickness 0.4 mm, with 4 mm radius shoulders), machined from an isotropic bar of Propathene PXC 8830* and annealed at 100°C for 6 h to relieve machining stresses. It was subsequently heated in the creep apparatus to 65.5°C ± 0.1°C and maintained at this temperature for 3 weeks before initiating experiments. In each creep experiment an axial load and a torque were applied at time $t = 0$, yielding an axial tensile stress σ and shear stress τ in the wall of the tube. Several series of experiments were performed, each series characterized by a constant ratio σ/τ. Within a given series the loading programme took the form of simultaneous rectangular pulses of σ and τ of 120 sec duration separated by 1200 sec recovery periods. Successive pulses were of uniformly increasing magnitude. The longitudinal tensile strain $\epsilon(t)$ and shear strain $\gamma(t)$ were determined from the relative displacement and rotation of the end flanges of the tube. Maximum stresses were chosen to ensure that $\epsilon(t)$ and $\gamma(t)$ never exceeded 0.012. Under these conditions results were found to be entirely reproducible to within the precision of measurement. In addition, any residual strains remaining at the end of each recovery cycle were always less than the resolution with which they could be measured ($\sim 1\%$ of the preceding creep strain).

According to Equation 2 the measured responses in a combined tension-torsion creep experiment are given by

$$\left.\begin{aligned} \epsilon(t) &= \left[\frac{J}{3}(t, I_1, I_2, 0) + \frac{B}{9}(t, I_1, I_2, 0)\right]\sigma \\ \gamma(t) &= J(t, I_1, I_2, 0)\tau\,. \end{aligned}\right\} \tag{3}$$

Evidence from previous work [4] shows $B(t)$ to be independent of pressure (and hence I_1) to a high accuracy for volume strains of the order encountered in this work ($\leqslant 0.002$). We also assume $B(t)$ to be independent of I_2. These assumptions are not critical to our interpretation of results, in view of the small size of the contribution made by $B/9$ in comparison with $J/3$ in Equation 3 ($\sim 7\%$). Since Equation 3 applies exactly, without dependencies on I_1, I_2 and I_3, in the limit of small stresses (see Equation 1) $B(t)$ was obtained from Equation 3 by extrapolating the ratios $\epsilon(t)/\sigma$ and $\gamma(t)/\tau$ obtained in pure tension and pure torsion creep tests respectively to the limits $\sigma \rightarrow 0$ and $\tau \rightarrow 0$. This procedure gave $J(100\ \text{sec}) = 3.99\ \text{m}^2\ \text{GN}^{-1}$ and $B(100\ \text{sec}) = 0.765\ \text{m}^2\ \text{GN}^{-1}$. This value of $B(100\ \text{sec})$ was then used to compute independent values of $J(100\ \text{sec}, I_1, I_2, 0)$, via Equation 3, from $\epsilon(t)/\sigma$ and $\gamma(t)/\tau$ measured during combined tension-torsion creep experiments over the whole stress range covered. We shall denote the two determinations of J for a particular stress state (particular stress pulse experiment) as J_ϵ and J_γ respectively.

In Fig. 1 $J_\epsilon(100\ \text{sec}, I_1, I_2, 0)$ is plotted against $J_\gamma(100\ \text{sec}, I_1, I_2, 0)$ for five series of creep experiments conducted at different constant values of σ/τ. Equation 3 of course predicts the 45° straight lines through the origin shown. Clearly, all the data points agree with these to within the estimated limits of experimental error (given by the arms of the crosses). Similar agreement was also obtained for values of creep time other than 100 sec.

These results show that for polypropylene at 65.5°C, Equation 2 is obeyed over a range of strain where the viscoelastic behaviour becomes highly non-linear (J increases from 4 to 6 m^2 GN^{-1} with increasing stress). The non-linearity in creep of polypropylene in a tension-torsion experiment is, therefore, to be understood merely in terms of the dependence of $J(t)$ on I_1 and I_2.

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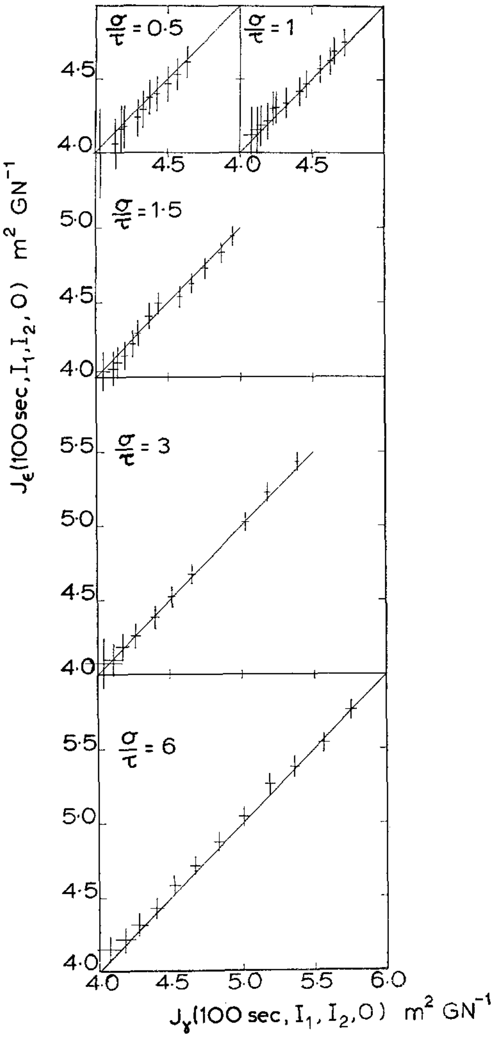

Figure 1 Comparison of measured values of $J(100\text{ sec}, I_1, I_2, 0)$ obtained from $\epsilon(100\text{ sec})$ (J_ϵ) and $\gamma(100\text{ sec})$ (J_γ) using Equation 3.Estimated error limits are indicated.

For the purpose of gaining further insight, it is helpful to consider $J(t)$ to be defined by I_1 and I_2', the second invariant of σ'. I_1 depends only on the hydrostatic component of σ, whereas I_2' depends only on the distortional component of σ. The dependence of the present results on I_1 and I_2' will be discussed elsewhere. Attempts have been made [5, 6] to treat non-linear viscoelastic behaviour of polymers using the Lévy-Von Mises equations of classical plasticity theory. Such attempts assume the material remains isotropic under stress, a concept consistent with Equation 2. In addition, however, they assume that $B(t, I_1, I_2, I_3) = 0$, for all values of its arguments, and that $J(t)$ depends only on I_2'. In the present work the assumption $B(t, I_1, I_2, I_3) = 0$ would cause J_ϵ to always exceed J_γ by $0.255\ \mathrm{m^2\,GN^{-1}}$, which is well outside the experimental error (see Fig. 1). Furthermore, measurements of the pressure dependence of shear modulus for a wide range of polymers [7] have shown that the effect of I_1 on $J(t)$ cannot be neglected if errors of several per cent are to be avoided.

The significance of the present results will not be apparent until it is shown whether knowledge of $J(t, I_1, I_2, I_3)$ and $B(t, I_1, I_2, I_3)$ is sufficient to describe the non-linear deformation of polymers other than polypropylene at 65.5° C. If this is so, advantages of a practical nature will follow. The creep testing of polymers will be reduced to determining $J(t, I_1, I_2, I_3)$ and $B(t, I_1, I_2, I_3)$. This is the only information which will be required to completely determine the strain state of a component subjected to uniform, multiaxial creep stresses.

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