The time dependent strain potential function for a polymeric glass

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Torsion and normal force measurements were made during single step stress relaxation experiments on a polymeric glass (PMMA). Isochronal data were analysed using an approach adapted from that developed by Penn and Kearsley[1] (for incompressible elastic materials) to determine the derivatives $\partial W/\partial I_1$ and $\partial W/\partial I_2$ of the time dependent strain potential function. $\partial W/\partial I_1$ and $\partial W/\partial I_2$ are determined from existing solution to the torsion of an incompressible cylinder. A special solution to the torsion of a compressible cylinder is presented and it is shown that the values of $\partial W/\partial I_1$ and $\partial W/\partial I_2$ obtained using this solution to analyse the data do not differ greatly from those obtained using the incompressible solution. It is found from both solutions that $\partial W/\partial I_1$ is negative and increases towards zero with increasing time and deformation while $\partial W/\partial I_2$ is positive, greater in magnitude than $\partial W/\partial I_1$ and decreases towards zero with increasing time and deformation. These results were unexpected and a full understanding of their meaning has yet to be reached.

(Keywords: compressible material; non-linear viscoelasticity; poly(methyl methacrylate); polymer glass; strain potential function; torsion)

INTRODUCTION

Several years ago, Penn and Kearsley[1] showed that data obtained from torque and normal force measurements on an elastic cylinder subjected to a twist with the length held constant can be used to determine the derivatives of the elastic strain energy function for an incompressible material. In addition, Rivlin[2] has shown that for single step stress relaxation type deformation histories on viscoelastic materials isochronal data can be treated in the same fashion as equilibrium data for an elastic material. Using these results, we subsequently reported[3,4], in brief, on relaxation experiments in torsion of poly(methyl methacrylate) in which values of the strain potential function derivatives were obtained assuming that the torsion applied to the material is an isochoric motion, i.e. no volume change occurred. The salient results of this prior work were that $\partial W/\partial I_1$ was found to be negative and to increase (towards zero) with both time and deformation. At the same time $\partial W/\partial I_2$ was positive, greater in magnitude than $\partial W/\partial I_1$, and decreased with both increasing time and deformation.

Although these results were unexpected, they did permit us to explain, qualitatively at least, some unusual results reported first by Sternstein and Ho[5], and observed at somewhat larger deformations by us[4], i.e., the rate of stress relaxation in torsion can be greater than it is in extension, even at relatively small deformations, without invoking a time dependent Poisson's ratio for the material. See ref. 3 for a discussion of this.

Although we were able to use our results from the incompressible material analysis quite successfully, we had to acknowledge upon questioning[6] that it was merely an approximation. Furthermore, results obtained by one of us[7] and recent data reported in the literature[8] have shown that torsion of cylinders of polymer glasses results in measurable, albeit small, volume changes.* Therefore, we have reanalysed our results in light of a more exact solution for torsion of a compressible material. In this paper we report in detail the experimental results and show that the compressible material analysis of the torsion problem gives (qualitatively) the same important results as the incompressible material analysis; i.e. that for PMMA $\partial W/\partial I_1$ is negative and $\partial W/\partial I_2$ is positive and greater in magnitude than $\partial W/\partial I_1$.

EXPERIMENTAL

The poly(methyl methacrylate) used in this study was a commercial grade material. It was obtained as solid rods which were annealed† at 100°C for 24 h, oven cooled at ≈ 3°C min^{-1}, machined to a diameter of 2.52 cm and then tested. Examination of the cylinders between crossed polarizers indicated no residual orientation in the cylinders.

Single step stress relaxation experiments were performed in torsion maintaining the cylinder length constant. Both torque and normal force were measured at times which increased in powers of two from 0.05 to 1678 s. The time required to apply the step in deformation varied with the magnitude of the deformation, but never exceeded 0.10 s. Overshoot in the deformation was less than 2%.

Two specimens were used for all of the tests. The deformations were applied to each specimen starting with

*Interestingly in Poynting's[9] original experiments he was able to measure the dilatation of steel wires subjected to twisting moments. On the other hand Matsuoka[8] and we[7] have found that polymer glasses decrease in volume on twisting whether with free[8] or fixed[7] ends.

†The samples were 'annealed' at 100°C which is near the glass transition for PMMA ($T_g \approx 105$°C) and oven cooled to closely match the thermal history used by Sternstein and Ho[5]. It is recognized that thermal history significantly affects the mechanical properties of glasses[20].

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the lowest and increasing to the highest as follows: (1) deformation γ_i applied to the sample for 1678 s, (2) deformation returned to zero and sample held at zero deformation for a minimum of 18 000 s (5 h) to reduce effects of previous deformation history, (3) deformation $\gamma_{i+1} > \gamma_i$ applied to sample for 1678 s, (4) deformation returned to zero and sample held at zero deformation 18 000 s, (5) steps 3 and 4 repeated until the highest deformation was reached.

The mechanical testing was performed using in Instron* servocontrolled tension–torsion hydraulic test machine. The machine was interfaced with a Hewlett–Packard 2100 mini-computer* for control and data acquisition. All tests were carried out at 296 ± 1 K (23°C + 1°C) in laboratory air.

THEORETICAL CONSIDERATIONS

Incompressible material

For simple visocelastic materials Rivlin[2] has shown that for certain deformation histories, such as those obtained in single step stress relaxation experiments, one can treat isochronal data in the same manner as equilibrium data for elastic materials. For incrompressible materials, he showed that the stress in any deformation can be described using two material functions which are functions of time, t, and the invariants in the principal stretches, I_1 and I_2. Though one need not assume the existence of a strain potential (or energy) function to describe single step stress relaxation histories, we shall use the BKZ[10]-type notation consistent with our prior work[3,10,12].

In the BKZ theory of an elastic fluid[10], the existence of a time dependent strain potential function is postulated. If we consider single step stress relaxation deformations, then we can define isochronal values for the derivatives of the strain potential function as follows:

$$W_i(t) = \frac{\partial W}{\partial I_i}(I_1,I_2,t) = \int_{-\infty}^{t} \frac{\partial U}{\partial I_i}(I_1,I_2.t-\tau)\mathrm{d}\tau \qquad (1)$$

where U is the potential function of the BKZ theory, and now the I_i's are the i^{th} invariants of the left relative Cauchy deformation tensor, t is the present time, and τ is the past time.

For torsion of an elastic rod with fixed ends, Penn and Kearsley[1] have shown that the derivatives of the strain energy function can be determined from torque and normal force measurements at varying angles of twist. The relevant equations are[1]:

$$T = 4\pi\psi \int_0^R [W_1 + W_2] r^3 \mathrm{d}r \qquad (2)$$

and the normal force, N, by:

$$N = -2\pi\psi^2 \int_0^R [W_1 + 2W_2] r^3 \mathrm{d}r \qquad (3)$$

where the W_i are the derivatives of the strain energy function, ψ is the angle of twist per unit length, R is the outer radius of the cylinder and r is the radial position coordinate. By making a variable change and differentiating the torque with respect to ψ and the normal force with respect to ψ^2, Penn and Kearsley were able to derive two algebraic equations for W_1 and W_2 in terms of the experimental variables. By a similar analysis for a material with a time dependent strain potential function we arrive at similar equations:

$$W_1(t) + W_2(t) = \frac{1}{4\pi\psi R^4}(3T + \psi T_\psi) \qquad (4)$$

$$W_1(t) + 2W_2(t) = \frac{1}{\pi\psi^2 R^4}(N + \psi^2 N_{\psi^2}) \qquad (5)$$

where $T_\psi = \partial T/\partial\psi$ and $N_{\psi^2} = \partial N/\partial(\psi^2)$. These equations can then be solved simultaneously for W_1 and W_2 for any value of time, t.

Torsion of a compressible cylinder

The approach we take in the solution of the problem of torsion of a compressible material is similar to that used for the incompressible one in that we postulate the existence of a time dependent strain potential function $W(I_1,I_2,I_3,t)$ where we note that now the strain potential function depends also on the third invariant of the deformation, I_3. The solution to the problem of torsion of a compressible cylinder has been treated in various fashions by Odgen[13,14], Blackburn and Green[15], Wack[16], Levinson[17], and Green and Zerna[18] to mention just a few. Because the general solution of an inhomogeneous deformation of a compressible material requires explicit knowledge of the strain energy function most analyses have focussed on almost incompressible materials[13,14,16], perturbation methods[17] or assumed forms of the strain energy function coupled with numerical solutions[16,17]. In this work, we assume a deformation in which the volume change depends only on radial position in the cylinder and then solve the problem exactly for the torque and normal force responses. These results can be used to show that the $W_1(t)$ and $W_2(t)$ values obtained from the compressible material analysis are not greatly different from those obtained using the incompressible analysis and, therefore, the major conclusions from ref. 3 remain unchanged. Furthermore, we evaluate $W_1(t)$ and $W_2(t)$ from our data if it is further assumed that the strain potential function is of such a form that volume change is associated only with the hydrostatic pressure and the bulk modulus. The details of our solution are presented in Appendix A, the important results follow here.

The equations for the torque and normal force of a compressible cylinder subjected to a twist with constant length and for which the volume ratio, μ, is a function of radial position only, i.e. $\mu = \mu(r)$ are given by:

$$T = 4\pi\psi \int_0^R \mu(r)[W_1 + W_2] r^3 \mathrm{d}r \qquad (6)$$

$$N = -2\pi\psi^2 \int_0^R \mu(r)[W_1 + 2W_2] r^3 \mathrm{d}r + 2\pi \int_0^R [W_1 + W_2]\left(\mu(r) - \frac{1}{\mu(r)}\right) r\,\mathrm{d}r \qquad (7)$$

* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

where the variables are defined as in the previous section except that R is now the radius of the cylinder in the deformed configuration and the volume ratio $\mu(r)$ is defined below.

Equations (6) and (7) were derived without making any assumptions about the form of the strain potential function. Before going further in the analysis, it is possible to compare equations (6) and (7) with their counterparts for the incompressible cylinder, equations (2) and (3). First we note that equation (6) differs from equation (2) only in that R has now changed and by the presence of the volume function $\mu(r)=1/\sqrt{I_3}$ inside the integral, multiplying (W_1+W_2). The equation (7) for the normal force, however, is quite different. Not only has R changed and $\mu(r)$ multiplies (W_1+2W_2), but there is an additional term which includes W_1, W_2 and $\mu(r)$. Note that this term is a function of r rather than r^3 and that its dependence on ψ comes only through the functional dependence of W_1, W_2 and μ on the strain invariants I_1, I_2 and I_3. At this point these are unknown. However, we can say one thing about this term. If the volume change is negative, i.e. $\mu(r)>1$, then since $(W_1+W_2)>0$, the magnitude of N is decreased relative to the incompressible solution (for the same values of W_1 and W_2). The inverse is true if the volume change is dilational, i.e. $\mu(r)<1$. Thus, because it is experimentally observed that polymer glasses decrease in volume[7,8] when subjected to a torsion, our previous analysis using incompressible theory would actually be 'conservative' because the large normal force in equations (4) and (5) is responsible for the result that W_1 is negative. Thus simply from examination of the equations, one can see that our prior results, while perhaps quantitatively incorrect, were qualitatively correct. In what follows, we will show that with the not unreasonable assumption that volume changes associated with the twisting of the cylinder are due to the hydrostatic pressure alone, the quantitative differences between the results from the compressible and incompressible analysis are not very large. The analysis is given in detail in Appendix B.

If we perform the same type of analysis as Penn and Kearsley[1] carried out for the incompressible cylinder we find two equations in the experimental variables, but three unknowns, W_1, W_2 and μ (see Appendix B).

$$\mu[W_1+W_2](1+\varepsilon)^4\left[\frac{1+3\varepsilon}{1+\varepsilon}\right]=\frac{\psi M_\psi+3M}{4\pi\psi R^4} \tag{8}$$

$$-(1+\varepsilon)^4\left\{\mu(W_1+2W_2)\left[\frac{1+2\varepsilon}{1+\varepsilon}\right]-\frac{(W_1+W_2)\left(\mu-\frac{1}{\mu}\right)(1+2\varepsilon)}{R^2(1-\varepsilon)^3\psi^2}\right\}=\frac{\psi^2N_{\psi^2}+N}{\pi\psi^2R^4} \tag{9}$$

where the variables are as defined previously and ε is a small number which reflects the change in the radius R relative to the radius in the undeformed configuration. As noted in Appendix B it does not significantly affect the results.

With just equations (8) and (9) we cannot determine W_1, W_2 and μ. If, however, we make the assumption that the volume change depends only on the hydrostatic pressure, we arrive at a third equation (see Appendix B):

$$\left(\frac{1}{\mu^2}-1\right)K=\frac{2\mu}{3}\left[\left(1+\psi^2+\frac{1}{R^2(1+\varepsilon)^2}\left(\frac{1}{\mu^2}-1\right)\right)W_1+\left(1+\frac{1}{\mu^2}+\frac{1}{R^2(1+\varepsilon)^2}\left(\frac{1}{\mu^2}-1\right)\right)W_2\right] \tag{10}$$

Thus, equations (8), (9) and (10) form a system of nonlinear equations in terms of the experimental variables. This system of equations is readily solved using a Newton–Raphson numerical technique[19]. The results show that there is not a great difference between the solution given by the compressible material analysis and the incompressible material analysis. In the following section we present the data and compare the results for $W_i(I_1,I_2,t)$ with those for $W_i(I_1,I_2,I_3,t)$.

RESULTS

In *Figure 1* are presented the torque data for PMMA as a function of angle of twist and at the 0.41, 1.64, 13.1, 105 and 1678 second isochrones. In *Figure 2* the results for the normal force are presented. While the normal force data show more scatter, the fact that replicate tests and a large number of deformations were used gives us a confidence in these data of $\pm10\%$ above $\psi=1.187$ ($\psi R=\gamma=0.015$). Below this deformation the results are based on an extrapolation using a slope of 2 (i.e. $N\alpha\psi^2$). We note from the nonconstancy of the slopes for the torque (and the normal force) data that the PMMA exhibits nonlinear (non-second order) behaviour at relatively small deformations and we observe that the onset of the nonlinear behaviour moves to smaller deformations as the time increases.

These torque and normal force data were used to obtain values for $W_1(t)$ and $W_2(t)$ from the incompressible material analysis for torsion of a cylinder (c.f. equations (4) and (5)). The results are presented in *Figures 3* and *4* as

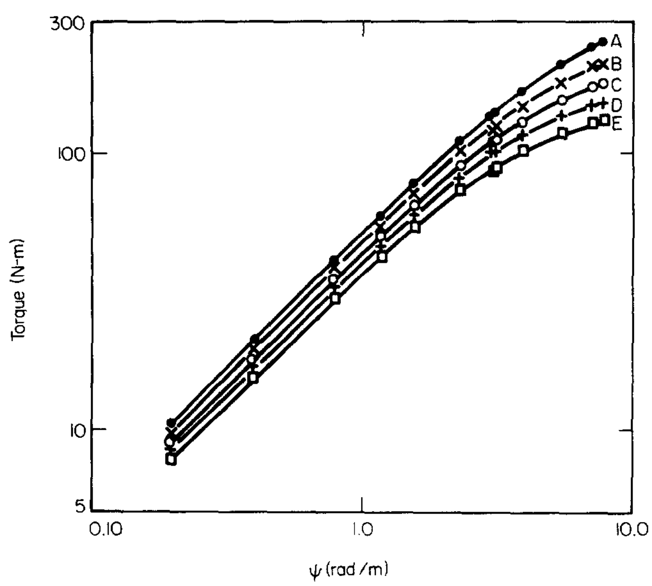

Figure 1 Torque vs. ψ isochrones from single step stress relaxation experiments on PMMA solid cylinders (annealed at 296 K). Curve A: 0.41s; curve B: 1.64s; curve C: 13.1s; curve D: 105s; curve E: 1678s

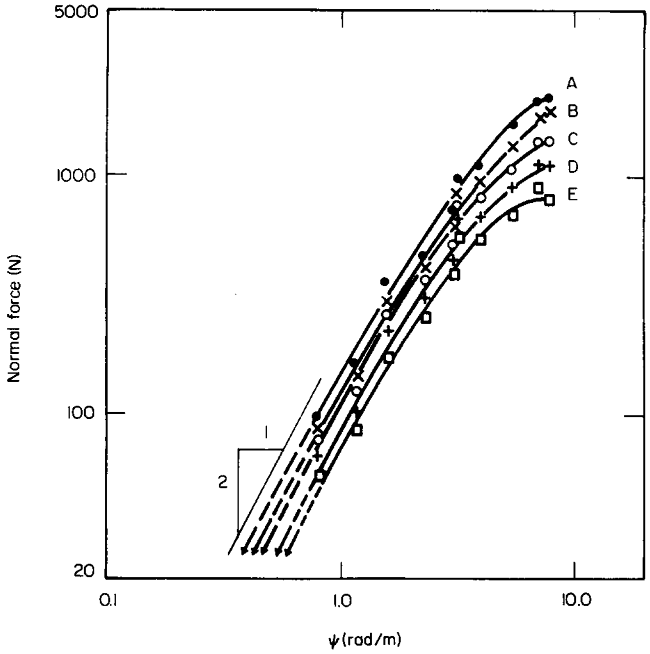

Figure 2 Normal force vs. ψ isochrones from single step relaxation experiments on PMMA solid cylinders (annealed at 296 K). (See *Figure 1*)

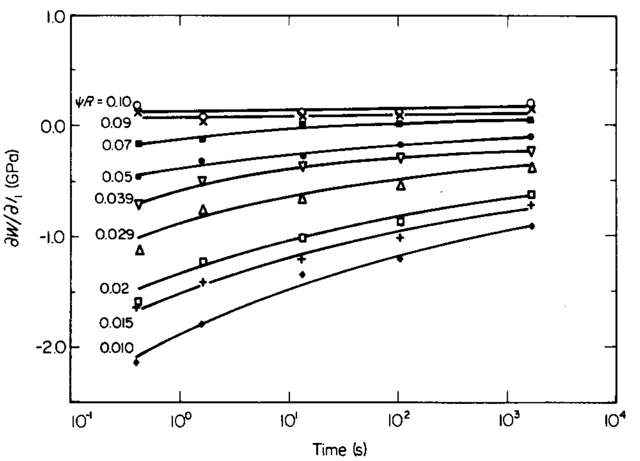

Figure 3 Incompressible analysis of annealed PMMA. $\partial W/\partial I_1$ vs. time at various values of strain (ψR) as indicated. Calculated from data of *Figures 1* and *2* using the incompressible material analysis

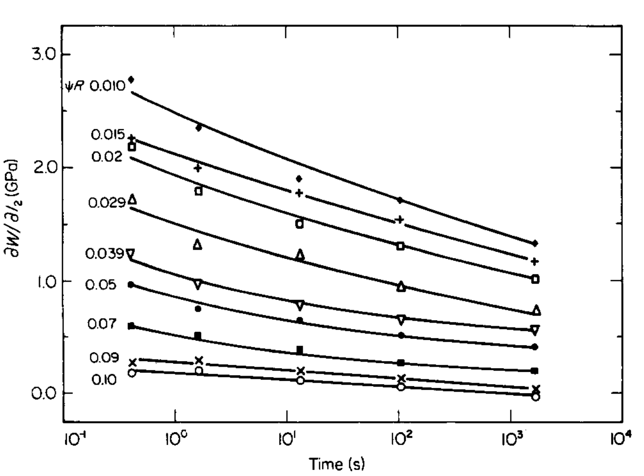

Figure 4 Incompressible analysis of annealed PMMA. $\partial W/\partial I_2$ vs. time at various values of strain (ψR) as indicated. Calculated from data of *Figures 1* and *2* using the incompressible material analysis

plots of $W_1 = \partial W/\partial I_1$ and $W_2 = \partial W/\partial I_2$ vs. $\log(t)$ at different values of maximum strain in the cylinder $\gamma = \Psi R$. As can be seen, W_1 is negative and increases towards zero with increasing time and deformation. At the largest deformations and at the longest times W_1 becomes positive. W_2, on the other hand is positive and decreases towards zero as both time and deformation decreases. In all cases where W_1 is negative W_2 is larger in magnitude then W_2, as expected since $2(W_1 + W_2)$ is the shear modulus and must be positive.

In order to compare the results from the compressible material analysis with those for the incompressible material, we carried out a numerical solution to equations (8), (9) and (10) using a value for the bulk modulus, K, for PMMA of 2.11 GPa which was determined from the small strain torque and compression data on the same cylinders of PMMA as used in this study. K was found to be time independent in these experiments. The results for $W_1 = \partial W/\partial I_1$ and $W_2 = \partial W/\partial I_2$ are presented in *Figures 5* and *6* as plots of W_1 and W_2 vs. $\log(t)$ at different values of maximum strain in the cylinder, ψR. The results are quite similar to those obtained from the incompressible analysis. W_1 is negative and increases towards zero with increasing time and deformation. At large deformations and long times it becomes positive. W_2 is positive and decreases with increasing time and deformation. In all

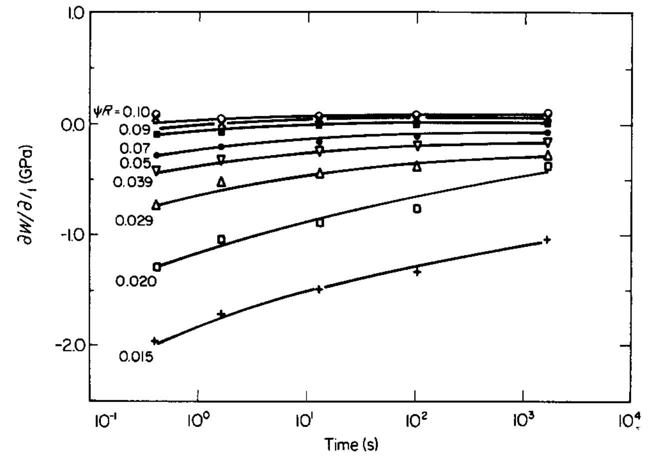

Figure 5 Compressible analysis of annealed PMMA. $\partial W/\partial I_1$ vs. time at various values of strain (ψR) as indicated. Calculated from data of *Figures 1* and *2* using the compressible material analysis

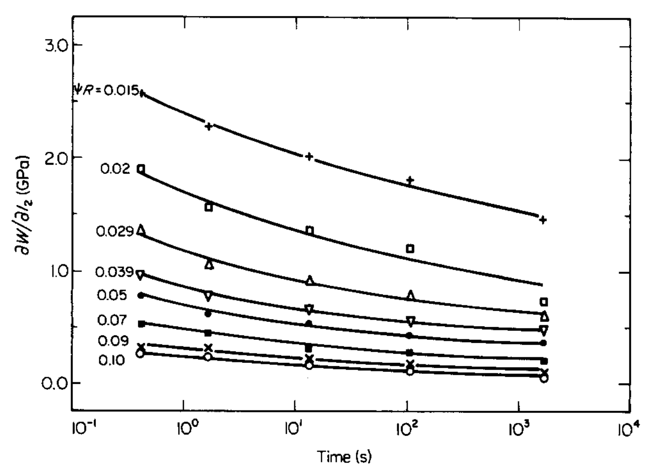

Figure 6 Incompressible analysis of annealed PMMA. $\partial W/\partial I_2$ vs. time at various values of strain (ψR) as indicated. Calculated from data of *Figures 1* and *2* using the compressible material analysis

cases in which W_1 is negative, W_2 is greater in magnitude. Therefore $2\mu(W_1+W_2)$ (the shear modulus) is always positive, as expected. In fact, the differences in W_1 and W_2 determined from the compressible and incompressible analyses is at most only about 25%, except near zero where some sign changes occur in W_1.

SUMMARY

In the past, we presented results for the strain potential function of a polymer glass (PMMA) based upon an incompressible material analysis for a viscoelastic rod subjected to single step stress relaxation histories in torsion at fixed length[3]. In this paper we have shown that the analysis of the same data using a solution to the torsion of a compressible cylinder does not significantly alter the results reported previously, i.e., that $\partial W/\partial I_1$ is negative and increases (towards zero) with increasing time and deformation. On the other hand, $\partial W/\partial I_2$ is positive, greater in magnitude than $\partial W/\partial I_1$, and increases towards zero with increasing time and deformation.

A general solution to the torsion of a rod of compressible material is presented for the case in which volume changes are dependent on only the radial position, r. This analysis shows that, in materials for which the volume change upon torsion is negative (compressive), the normal force measured is lower than it would be for the incompressible cylinder with the same $\partial W/\partial I_1$ and $\partial W/\partial I_2$. This suggests that the results which we presented previously were qualitatively correct, because the negative $\partial W/\partial I_1$ occurred because of the high normal forces actually measured.

Reanalysis of the torque and normal force data obtained on PMMA assuming that the volume change was due totally to the pressure times the bulk modulus, gave quantitative results for the derivatives of the strain potential function of a compressible material. The results from the compressible material analysis and the incompressible material analysis were compared and found to differ by only about 25% except where $\partial W/\partial I_1$ crossed through zero. Thus, we have shown that the derivatives of the strain potential function for PMMA can be determined within a fair accuracy from torque and normal force measurements on rods subjected to twist at constant length.

We have shown nearly unequivocally the existence of a negative $\partial W/\partial I_1$ for PMMA. This result also supports the observation[3,5] and approximate calculations that at relatively small deformations the rate of relaxation in torsion and in simple extension can be different even without a time varying Poisson's ratio.

Although we assumed that the strain potential function is of a form in which the volume change is dependent only on the hydrostatic pressure and the bulk modulus, further work is required to verify this. Simultaneous and accurate measurement of volume changes, torque and normal forces as functions of twist could be used to more accurately determine the material functions of compressible materials.

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APPENDIX A. TORSION OF A CYLINDER OF COMPRESSIBLE MATERIAL

In this appendix we follow the approach of Green and Zerna[18] in the solution of problems in finite elasticity.

Defining the deformation

We consider a cylinder which in the undeformed state has a radius R_0 and a length l, and we consider a torsional deformation of the cylinder in which planes normal to the axis remain plane and undergo only a pure rotation proportional to their distance from one end of the cylinder. The body remains cylindrical in form and in the strained state will have a length l and a radius R.

The curvilinear coordinate system θ_i in the strained state of the cylinder is taken to be a system of cylindrical polar coordinates (r,θ,Z) so that

$$\begin{aligned} \theta_1 = r; \quad \theta_2 = \theta; \quad \theta_3 = Z \\ y_1 = r\cos\theta; \quad y_2 = r\sin\theta; \quad y_3 = Z \end{aligned} \tag{A.1}$$

The y_i axes are taken to coincide with the χ_i axes and, with the above assumptions about the deformation, the point (r,θ,Z) in the deformed state was originally at $(\mu(r)r, \theta-\Psi Z, Z)$ in the underformed state. Ψ is the angle of twist per unit length and $\mu(r)$ is a function which describes the change of radial position due to the volume change. We do not allow changes in volume to be functions of θ or Z. Then

$$\chi_1 = \mu(r)r\cos(\theta-\Psi Z); \; \chi_2 = \mu(r)r\sin(\theta-\Psi Z); \; \chi_3 = Z \tag{A.2}$$

The components of the metric tensors are found from (A.1) and (A.2) to be:

In the deformed state:

$$G_{ik}=\begin{bmatrix}1&0&0\\0&r^2&0\\0&0&1\end{bmatrix}\qquad G^{ik}=\begin{bmatrix}1&0&0\\0&1/r^2&\\0&0&1\end{bmatrix}\qquad\text{(A.3)}$$

and in the undeformed state:

$$g_{ik}=\begin{bmatrix}1&0&0\\0&\mu^2(r)r^2&-\psi\mu^2(r)r^2\\0&-\psi\mu^2(r)r^2&1+\psi^2\mu^2(r)r^2\end{bmatrix}$$
$$g^{ik}=\begin{bmatrix}1&0&0\\0&\psi^2+\dfrac{1}{\mu^2(r)r^2}&\psi\\0&\Psi&1\end{bmatrix}\qquad\text{(A.4)}$$

The strain invariants are given by:

$$I_1=g^{ij}G_{ij}=2+\frac{1}{\mu^2(r)}+\psi^2r^2$$
$$I_2=g_{rs}G^{rs}I_3=\frac{2}{\mu^2(r)}+1+\psi^2r^2\qquad\text{(A.5)}$$
$$I_3=|G|/|g|=\frac{1}{\mu^2(r)}$$

where we note that for the incompressible case the invariants would have been $I_1=I_2=3+\psi^2r^2$.

Constitutive equation

For an elastic body the constitutive equation relating stress to strain is:

$$\tau^{ij}=\frac{2}{\sqrt{I_3}}\frac{\partial W}{\partial I_1}g^{ij}+\frac{2}{\sqrt{I_3}}\frac{\partial W}{\partial I_2}B^{ij}+2\sqrt{I_3}\frac{\partial W}{\partial I_3}G^{ij}\qquad\text{(A.6)}$$

where τ^{ij} is the contravariant stress tensor, the I_i's are the strain invariants defined by equation (A.5), W is the strain energy function and $W=W(I_1,I_2,I_3)$, g^{ij} and G^{ij} are the metric tensors and B^{ij} is defined by

$$B^{ij}=I_1g^{ij}-g^{ir}g^{js}G_{rs}\qquad\text{(A.7)}$$

and

$$B^{ij}=\begin{bmatrix}1+\dfrac{1}{\mu^2(r)}+\psi^2r^2&0&0\\0&\psi^2+\dfrac{2}{\mu^2(r)r^2}&\psi\\0&\psi&0\end{bmatrix}\qquad\text{(A.8)}$$

Hence from (A.3) through (A.8) we find:

$$\tau^{11}=2\mu(r)\frac{\partial W}{\partial I_1}+2\mu(r)\left[1+\frac{1}{\mu^2(r)}+\psi^2r^2\right]\frac{\partial W}{\partial I_2}+\frac{2}{\mu(r)}\frac{\partial W}{\partial I_3}$$

$$\tau^{22}=2\mu(r)\left[\psi^2+\frac{1}{\mu^2(r)r^2}\right]\frac{\partial W}{\partial I_1}$$
$$+2\mu(r)\left[\psi^2+\frac{2}{\mu^2(r)r^2}\right]\frac{\partial W}{\partial I_2}+\frac{2}{\mu(r)r^2}\frac{\partial W}{\partial I_3}\qquad\text{(A.9)}$$

$$\tau^{33}=2\mu(r)\frac{\partial W}{\partial I_1}+2\mu(r)\left[1+\frac{1}{\mu^2(r)}\right]\frac{\partial W}{\partial I_2}+\frac{2}{\mu(r)}\frac{\partial W}{\partial I_3}$$

$$\tau^{23}=2\mu(r)\psi\left[\frac{\partial W}{\partial I_1}+\frac{\partial W}{\partial I_2}\right]$$

$$\tau^{31}=\tau^{12}=\tau^{13}=\tau^{21}=0$$

When the strained cylinder is in equilibrium, and the body forces are zero, the equations of equilibrium become:

$$\tau^{ik}_{,i}+\Gamma^i_{ir}\tau^{rk}+\Gamma^k_{ir}\tau^{ir}=0\qquad\text{(A.10)}$$

where the comma denotes partial differentiation and the Γ^k_{ij} denotes the Christoffel symbols of the second kind. The only Christoffel symbols, derived from the metric tensor of the strained body, which are non-zero are

$$\Gamma^1_{22}=-r\quad\text{and}\quad\Gamma^2_{12}=\Gamma^2_{21}=\frac{1}{r}\qquad\text{(A.11)}$$

Then from (A.9)–(A.11) we obtain

$$\frac{\partial\tau^{11}}{\partial r}+\frac{\tau^{11}-r^2\tau^{22}}{r}=0$$
$$\frac{\partial p}{\partial\theta}=\frac{\partial p}{\partial Z}=0\qquad\text{(A.12)}$$

where $p=2\sqrt{I_3}\frac{\partial W}{\partial I_3}=\frac{2}{\mu(r)}\frac{\partial W}{\partial I_3}$ and can be determined, apart from a constant of integration by the equation.

$$\frac{2W_3}{\mu(r)}=-2\mu(r)W_1-2\mu(r)\left[1+\frac{1}{\mu^2(r)}+\psi^2r^2\right]W_2$$
$$+\int_R^r\frac{\mu(r)}{r}\left[\left(1-\frac{1}{\mu^2(r)}-r^2\psi^2\right)W_1+\left(1-\frac{1}{\mu^2(r)}\right)W_2\right]dr\qquad\text{(A.13)}$$

where now $W_i=\frac{\partial W}{\partial I_i}$.

Boundary conditions

The unit normal to the curved surface of the cylinder is directed along the vector $\hat{G}^1$ so that

$$\hat{n}=\frac{\hat{G}^1}{\sqrt{G^{11}}}=\hat{G}^1,\ n_1=1,\ n_2=n_3=0\qquad\text{(A.14)}$$

Since the curved surface at $r=R$ of the cylinder is free from applied stresses, the boundary condition is

$$\tau^{11}=\tau^{12}=\tau^{13}\ \text{at}\ r=R\qquad\text{(A.15)}$$

This condition is satisfied identically for $\tau^{12}=\tau^{13}=0$ everywhere. Then from (A.9)

$$\tau^{11}_{r=R}=0=2\mu(R)W_1+2\mu(R)\left[1+\frac{1}{\mu^2(R)}+\psi^2R^2\right]W_2+\frac{2}{\mu(R)}W_3\qquad\text{(A.16)}$$

and the constant of integration in equation (A.13) is evaluated to be zero. We can then write

$$\frac{W_3}{\mu(r)} = W_1 - \left[1 + \frac{1}{\mu^2(r)} + \psi^2 r^2\right] W_2$$

$$+ \int_R^r \frac{\mu(r)}{r}\left[\left(1 - \frac{1}{\mu r(r)} - r^2\psi^2\right) W_1 + \left(1 - \frac{1}{\mu^2(r)}\right) W_2\right] dr \quad (A.17)$$

At the end $Z = l$ of the cylinder the unit normal is parallel to $\hat{G}^3$ and, therefore,

$$\hat{n} = \frac{\hat{G}^3}{\sqrt{G^{33}}}, \quad n_3 = 1, n_1 = n_2 = 0 \quad (A.18)$$

where $\hat{G}^3$ is the contravariant base vector in the deformed system. And the components of the forces acting on the plane defined by the unit normal are obtained from:

$$\hat{P} = \tau^{ij} n_i \hat{G}_j \quad (A.19)$$

where $\hat{P}$ defines the surface force vector and $\hat{G}_j$ defines the covariant base vector of the deformed body. Then the tangential force in the r direction is given as:

$$P^1 = (\tau^{11} n_1 + \tau^{21} n_2 + \tau^{31} n_3) \cdot \frac{\hat{G}^3}{\sqrt{G^{33}}} = 0 \quad (A.20)$$

the tangential force acting in the θ direction is given as

$$P^2 = (\tau^{12} n_1 + \tau^{22} n_2 + \tau^{23} n_3) \cdot \frac{\hat{G}_2}{\sqrt{G_2{}^2}} = \tau^{23} \quad (A.21)$$

and the normal force acting in the Z direction is given as

$$P^3 = (\tau^{13} n_1 + \tau^{23} n_2 + \tau^{33} n_3) \cdot \frac{\hat{G}_3}{\sqrt{G_{33}}} = \tau^{33} \quad (A.22)$$

Similar forces, only in opposite directions must be applied over the end $Z = 0$.

Now the couple, T, acting on the cylinder end can readily be calculated as

$$T = 2\pi \int_0^R r^3 P^2 dr = 2\pi \int_0^R r^3 \tau^{23} dr$$
$$T = 4\pi\psi \int_0^R \mu(r)[W_1 + W_2] r^3 dr \quad (A.23)$$

and the total normal force acting at the ends of the cylinder is given by

$$N = 2\pi \int_0^R r P^3 dr = 2\pi \int_0^R r\tau^{33} dr \quad (A.24)$$

but from equation (A.9) we can determine that

$$\tau^{33} = -2\mu(r)\psi^2 r^2 W_2 + \tau^{11} \quad (A.25)$$

and then it follows from (A.12) that

$$N = -4\pi\psi^2 \int_0^R \mu(r) W_2 r^3 dr + -4\pi \int_0^R r dr \int_R^r \frac{\mu(r)}{r}$$
$$\left[\left(1 - \frac{1}{\mu^2(r)} - r^2\psi^2\right) W_1 + \left(1 - \frac{1}{\mu^2(r)}\right) W_2\right] dr \quad (A.26)$$

Integrating the second term by parts and combining terms we find that

$$N = -2\pi\psi^2 \int_0^R \mu(r)[W_1 + 2W_2] r^3 dr + 2\pi$$
$$\int_0^R (W_1 + W_2)\left(\mu(r) - \frac{1}{\mu(r)}\right) r\, dr \quad (A.27)$$

Equations (A.23) and (A.27) are readily compared with equations (3) and (4) for the torque and normal force in an imcompressible body.

From Rivlin[2] similar equations can be written to describe the torque and normal force responses of a viscoelastic material in single step stress relaxation histories. Now, however, $W = W(I_1, I_2, I_3, t)$ is a function of time.

APPENDIX B

The determination of the strain potential function from torsion of a compressible cylinder

In this appendix we follow the approach of Penn and Kearsley[1], who developed equations which permit the calculation of $W_1 = \partial W/\partial I_1$ and $W_2 = \partial W/\partial I_2$ from torque and normal force measurements of an incompressible elastic cylinder. Because, however, we now have a term $W_3 = \partial W/\partial I_3$ and an unknown volume change, $\mu(r)$, in the material we must make an assumption concerning the form of the strain energy function. Here we will assume that, the volume change is dependent only upon the product of the hydrostatic pressure and the compressibility, as shown later.

First, we follow Penn and Kearsley and make a variable change in equations (A.23) and (A.27). Let $x = \psi^2 r^2$, then (A.23) and (A.27) become:

$$T = \frac{2\pi}{\psi} \int_0^X \mu(x)[W_1 + W_2] x dx \quad (B.1)$$

$$N = \frac{-\pi}{\psi^2} \int_0^X \mu(x)[W_1 + 2W_2] x dx$$
$$+ \frac{\pi}{\psi^2} \int_0^X \left[\mu(x) - \frac{1}{\mu(x)}\right][W_1 + W_2] dx \quad (B.2)$$

Now we wish to differentiate T with respect to ψ and N with respect to ψ^2. However, the radius, R, varies with ψ^2. Since the changes in R are small we can expand R and so the limit of the integral $X = \psi^2 R_0^2$ becomes $X = \psi^2 R_0^2(1 + \varepsilon)$ where $\varepsilon = \varepsilon' \psi^2 / R_0$. Then differentiating (B.1) with respect to ψ and grouping terms we get

$$\frac{\psi T_\psi + 3T]}{4\pi\psi R_0^4} = \mu(R)[W_1 + W_2](1+\varepsilon)^4\left[\frac{1+3\varepsilon}{1+\varepsilon}\right] \quad \text{(B.3)}$$

where $T_\psi = \partial T/\partial\psi$. Similarly differentiating (B.2) with respect to ψ^2 we obtain

$$\frac{\psi^2 N_{\psi^2} + N}{\pi\psi^2 R_0^4} = -(1+\varepsilon)^4\left\{\mu(R)(W_1 + 2W_2)\left[\frac{1+2\varepsilon}{1+\varepsilon}\right]\right. \quad \text{(B.4)}$$

$$\left. - \frac{(W_1 + W_2)\left(\mu(R) - \frac{1}{\mu(R)}\right)(1+2\varepsilon)}{R_0^2(1+\varepsilon)^3\psi^2}\right\} \quad \text{(B.4)}$$

where $N_{\psi^2} = \frac{\partial N}{\partial \psi^2}$.

These equations are similar to those derived by Penn and Kearsley for the incompressible cylinder. The experimental variables which are easily obtained are R, T, T_ψ, N *and* N_{ψ^2}. In principle R (or ε) can be obtained, although this is more difficult. However, the experimental results which have been obtained[7,8] indicate that $\varepsilon \approx 10^{-4}$ to 10^{-3} and the errors introduced by ignoring this correction are negligible relative to the experimental errors involved in measuring T, N, T_ψ and N_{ψ^2}.

However, we still have only two equations [(B.3) and (B.4)] and three unknowns [W_1, W_2 and $\mu(R)$]. In order to resolve this problem we need to make some assumption about the strain energy function. Here we have decided to make the volume change a function of the pressure times the compressibility (inverse of the bulk modulus). Then we can write

$$I_3 = 1 + pK^{-1} \quad \text{(B.5)}$$

where $p = \frac{\tau^{11} + \tau^{22} + \tau^{33}}{3}$ is the hydrostatic pressure and K is the bulk modulus. Then since $\mu(r) = I_3^{-1/2}$ we can solve (B.5) for p

$$p = \left[\frac{1}{\mu^2(r)} - 1\right]K \quad \text{(B.6)}$$

Then from the definition of $p = \frac{\tau^{11} + \tau^{22} + \tau^{33}}{3}$ equations (B.6), (A.16) and (A.9) we can write

$$p = \left[\frac{1}{\mu^2(R)} - 1\right]K = \frac{2\mu(R)}{3}\left[\left(1 + \psi^2 + \frac{1}{\mu^2(R)R^2} - \frac{1}{R^2}\right)W_1\right.$$

$$\left. + \left(1 + \frac{1}{\mu^2(R)} + \frac{1}{\mu^2(R)R^2} - \frac{1}{R^2}\right)W_2\right] \quad \text{(B.7)}$$

Because equations (B.3) and (B.4) refer to $\mu(R)$, $W_1(R)$ and $W_2(R)$ we need to evaluate (B.7) at R. In doing this we keep in mind that $R = R_0(1+\varepsilon)$ where R_0 is the original radius of the cylinder.

We then have three equations [(B.3), (B.4) and (B.7)] in three unknowns. These equations can be solved numerically for $W_1(R)$, $W_2(R)$ and $\mu(R)$ using the experimental data for T, N, T_ψ and N_{ψ^2}.

We also note that W_3 is then given by (A.16) as

$$W_3 = \mu^2(R)W_1 - \mu^2(R)\left[1 + \frac{1}{\mu^2(R)} + \psi^2 R^2\right]W_2 \quad \text{(B.8)}$$

Here we note that the values of the deformation invariants, I_1, I_2 and I_3 at R are no longer the same as in pure torsion but rather are given by equations (A.5).