

SIMULTANEOUS MEASUREMENT OF TORQUE, AXIAL NORMAL FORCE AND VOLUME CHANGE IN THE NIST TORSIONAL DILATOMETER - EXPERIMENTS AND ANALYSIS

Carl R. Schultheisz, *Polymers Division, National Institute of Standards and Technology*
Gregory B. McKenna, *Department of Chemical Engineering, Texas Tech University*

Abstract

The NIST Torsional Dilatometer measures simultaneously the torque, axial normal force and volume change in response to a torsional deformation. While the torque is a linear function of the angle of twist per unit of length, the normal force and volume change are effects of geometrical nonlinearities. In stress-relaxation experiments with an epoxy cylinder near its glass transition temperature, the torque and normal force decay monotonically, but the volume change associated with the torsion shows a significant non-monotonic decay at lower temperatures. The measurements are investigated with a series solution for torsion of an elastic, compressible material [Murnaghan, F.D. (1951) *Finite Deformation of an Elastic Solid*. Wiley, New York.].

Introduction

The NIST Torsional Dilatometer has been used to study the evolution of the properties of an amorphous polymer following temperature jumps in the regime below the glass transition temperature [1-3]. The evolution of the sample volume (a measure of the thermodynamic state of the material) was compared with the evolution of the mechanical response in torsional stress-relaxation experiments in order to compare the rate of equilibration of different material properties. Simultaneous measurements on a single sample eliminate any questions of differences between samples or thermal histories.

In this paper, we focus on an interesting behavior observed in measurements made in the equilibrium stages of three experiments performed with the same sample at different temperatures. In addition to the torque (or moment), the response of the material to the torsional deformation includes the nonlinear effects of a compressive normal force along the axis of the cylindrical sample, and an increase in the volume of the sample. The torque and normal force behave as expected, relaxing monotonically, and the torque response demonstrates time-temperature superposition. However, the volume change associated with the twist is radically different from the torque or normal force, and it varies considerably with temperature; at the lowest temperature investigated, the volume change demonstrates behavior that is not monotonic.

Penn and Kearsley [4] showed that, for an incompressible material, measurements of the torque and normal force as a function of angle of twist were sufficient to

determine the derivatives of the strain energy function with respect to the first two strain invariants (the third invariant being a constant for incompressible materials). It was hoped that measurements of the torque, normal force and volume change (radial expansion) in the NIST Torsional Dilatometer would be sufficient to determine the derivatives of the strain energy function with respect to all three of the strain invariants for the case of elastic compressible materials. However, Wineman and McKenna [5] have recently concluded that since the deformed geometry depends on the material properties, the measurements of the torque, normal force and volume change are insufficient to determine directly the derivatives of the strain energy function with respect to the strain invariants. Instead, the torque, normal force and volume change are briefly investigated using a viscoelastic adaptation of the truncated series expansion for the torsion of an elastic, compressible cylinder of Murnaghan [6]. In this analysis, the volume change and normal force are associated with higher-order, nonlinear terms in the strain energy density function.

While the experiments with epoxy in the NIST Torsional Dilatometer [1-3] have consistently shown an increase in the sample volume in response to a twist, other researchers have obtained different results on other materials. Wang, *et al.* [7] report data for poly(methyl methacrylate), polycarbonate, poly(tetrafluoroethylene), and an acetal copolymer, tested at room temperature under torsion at a constant angular rate. Unlike our experiments, the specimen length was not constrained, and all four polymers showed an increase in length and a decrease in radius (as measured by dial gauge and an extensometer, respectively). The net volume increased for the acetal copolymer, but decreased for the other three materials. Pixa, *et al.* [8] studied unplasticized poly(vinyl chloride) apparently at room temperature using an apparatus similar to the one used for our experiments, except that the specimen was free to extend along its length. They also found that the volume decreased upon imposition of a small torsional deformation, but as the level of deformation increased, the volume would also begin to increase back toward its initial value.

Experimental

The Torsional Dilatometer is described in detail in the paper by Duran and McKenna [1]. The material is a diglycidal ether of bisphenol-A epoxy, cured with a flexible poly(propylene oxide) diamine with a molar mass of 400 g/mol, giving a nominal glass transition temperature of 42.4

°C [9]. Use of a thermoset is intended to allow repeated experiments on the same sample. The epoxy sample is bonded between two stainless-steel end grips and machined to form a cylindrical test section 115.1 mm long (with a standard uncertainty of 0.5 mm) and 15.22 mm in diameter (standard uncertainty of 0.05 mm). One grip is attached to a torque and normal force transducer, and the other grip is attached to a servo motor, which is used to apply a constant angle of twist for stress relaxation experiments. The angle of twist per unit length applied in these experiments was 3.94 rad/m with a standard uncertainty of 0.05 rad/m. The specimen is sealed into a stainless-steel chamber, and the remainder of the chamber is filled with mercury, which is free to flow up through a vertical precision capillary. The core of an LVDT is floated on top of the mercury in the capillary to measure the mercury level and thus determine the change in the volume of the specimen in the dilatometer. The temperature in the instrument is controlled to a standard uncertainty of 0.01 °C by circulating fluid from a constant-temperature bath through copper coils wrapped around the chamber containing the sample and the mercury.

Results and Discussion

Torque, normal force and volume relaxations are shown in Figure 1, for experiments in which the sample was equilibrated at 38.0 °C, 35.5 °C and 32.8 °C. These data have been normalized so as to lie between 0 and 1. The time origin is taken as the point at which the twist is applied. In all three experiments, the normal force relaxation is similar to the torque relaxation, but the volume behavior is very different from the other two. The volume change is in the form of the relative deviation from equilibrium (or volumetric strain) $\epsilon(t)$, with $\epsilon(t) = [V(t) - V_0]/V_0$, where $V(t)$ is the current volume at time t , and V_0 is the equilibrium volume (at the current temperature). In this case, the equilibrium volume is also the volume in the initial, undeformed configuration. The change in the volume behavior with temperature in the experiments is clear. In magnitude, the torque is on the order of 20 Nm, the normal force is on the order of 100 N, and $\epsilon(t)$ is on the order of 2×10^{-4} .

Although the volume recovery behavior looks odd compared to the torque and normal force, it can be modeled to some extent using a viscoelastic adaptation of the truncated series expansion for the torsion of an elastic, compressible material of Murnaghan [6]. Murnaghan's analysis leads to solutions for the moment, normal force and volume as functions of the Lamé constants λ and μ , as well as two higher-order elastic constants m and n . For a single step experiment, time-dependent viscoelastic functions can be substituted for the elastic constants, giving $\epsilon(t)$, $\mu(t)$, $m(t)$ and $n(t)$ [10]. In each experiment, we measure three quantities: the torque (or moment) $M(t)$, normal force $N(t)$ and relative volume deviation from equilibrium $\epsilon(t)$. First,

we define $d(t) = 2[(1 + \epsilon(t))^{1/2} - 1] = 2 R(t)/R_0$ as twice the change in the cylinder radius from its initial value of R_0 (to first order and very good approximation, $d(t) = \epsilon(t)$). Murnaghan's result is then

$$\mu(t) = \frac{2M(t)}{R_0^4} \quad (1)$$

$$n(t) = \frac{16}{2R_0^2} \left[\frac{N(t)}{R_0^2} \mu(t)d(t) \right] \quad (2)$$

$$m(t) = \frac{4}{2R_0^2} \left[\frac{N(t)}{R_0^2} \epsilon(t)d(t) \right] - \epsilon(t) - 2\mu(t) \quad (3)$$

where $\epsilon(t)$ is the angle of twist per unit length. Equations (1) and (2) show that $\mu(t)$ and $n(t)$ can be evaluated directly from the measured quantities, but the equation (3) shows that $\epsilon(t)$ and $m(t)$ can only be expressed in terms of one another. The moment $M(t)$ follows a stretched exponential function, so $\mu(t)$ would also be well-described by that type of function.

The shear modulus (and the moment itself) is well-described by a single stretched exponential function, and adheres to time temperature superposition, with

$$\mu(t, T) = b(T) \left\{ \mu_1 \exp \left[- \left(\frac{t}{a(T)} \right) \right] + \mu_2 \right\} \quad (4)$$

where μ_1 , μ_2 , and $a(T)$ govern the relaxation at a reference temperature where $a(T) = 1$ and $b(T) = 1$. We use 35.5 °C as the reference temperature. The fit of equation (4) to the shear modulus is shown in Figure 2. The standard uncertainty in μ is calculated using the propagation of uncertainties to be $0.002 \text{ GPa} + (0.03)\mu$. We also constrain the shift factors to have the same temperature dependence, with $\log [b(T)] = C \log [a(T)]$, where C is a constant determined in the fitting procedure.

Since the measurements do not allow us to determine both $m(t)$ and $\epsilon(t)$ uniquely, we will assume a form for $\epsilon(t)$ based on results in the literature. First, we assume that $\epsilon(t)$ at the reference temperature is linearly related to $\mu(t)$, with

$$\epsilon(t, T) = b(T) \left\{ k_1 \mu_1 \exp \left[- \left(\frac{t}{a(T)} \right) \right] + k_2 \mu_2 + k_3 \right\} \quad (5)$$

Constants k_1 and k_2 are evaluated by choosing Poisson's ratio at zero time to be $\nu(0) = 0.35$ [11], and by matching the relaxation of the bulk modulus to the data of McKinney and Belcher [12,13]. Poisson's ratio is given by $\nu(t) = \epsilon(t)/[2(\epsilon(t) + \mu(t))]$ and the bulk modulus is $K(t) = (3 + \nu(t))$

$2\mu(t)/3$. With these choices, the constants are therefore taken as $k_1 = 0.696$ and $k_2 = 1.29$ GPa. Poisson's ratio (ν) remains nearly constant at 0.35, as expected [11], and the relative decrease of the bulk modulus with time is much less than that of the shear modulus $\mu(t)$ [13]. The standard uncertainty in ν is assumed to be k_1 times the standard uncertainty in μ .

A similar function is fit to $n(t)$, with

$$n(t,T) = b_n(T) \left\{ n_1 \exp \left[\left(\frac{t}{a(T)} \right)^{n_2} \right] - n_2 \right\} \quad (6)$$

where $a(T)$ is the same function used in equation (4), to enforce the same time-temperature superposition for each modulus function. Again, the shift factors are related by $\log [b_n(T)] = C_n \log [a(T)]$. The parameters, n_1 , n_2 , n_3 , n_4 , and C_n are calculated in the fitting procedure. The fit is compared to the data in Figure 3. The function $n(t)$ is negative, monotonic with time, and about an order of magnitude larger than $\mu(t)$. The figure actually shows $-n(t)$ as a function of the time after the application of each twist. The standard uncertainty in n is calculated to be approximately $0.1 \text{ GPa} - (0.04)n$.

Given our choice for $\mu(t)$, we can calculate $m(t)$, which is shown by the symbols in Figure 4. The function $m(t)$ is also negative, monotonic with time, and about an order of magnitude larger than $\mu(t)$. Like Figure 3, this figure shows $-m(t)$ as a function of the time after the application of each twist. The standard uncertainty in m is calculated to be $0.1 \text{ GPa} - (0.02)m$. The function $m(t)$ has also been fit to a stretched exponential:

$$m(t,T) = b_m(T) \left\{ m_1 \exp \left[\left(\frac{t}{a(T)} \right)^{m_2} \right] - m_2 \right\} \quad (7)$$

where $a(T)$ is again the same function used in equation (4) and $\log [b_m(T)] = C_m \log [a(T)]$. Parameters m_1 , m_2 , m_3 , m_4 , and C_m are calculated in the fitting procedure. The magnitude and monotonic relaxation behavior of $m(t)$ is not very sensitive to the choice of $\mu(t)$ within expected material behavior [11-13]; choosing $m(t)$ to calculate $\mu(t)$ can lead to unphysical results.

The parameters calculated in fitting the functions in equations (4), (6) and (7) are given in Tables 1 - 3. The shear modulus and the moment are directly related through equation (1). By inverting equations (2) and (3), we can calculate the axial normal force and the volume change. Using the functions given in equations (4) - (7) to represent our model of the material behavior, we can compare the model directly to the measured data. This comparison is made in Figures 5 and 6 where the model prediction is plotted along the experimentally measured normal force and ν , the volumetric strain.

The modulus functions have been restricted to have the same time-temperature superposition behavior, and to a single stretched exponential relaxation function. Given those restrictions, the model describes the data reasonably well, and shows that the non-monotonic volume relaxation is permissible within the theory, even though the modulus functions are all monotonic functions of time. The non-monotonic volume relaxation is a consequence of the much longer relaxation time for $m(t)$ than for the other modulus functions. The higher-order modulus functions $m(t)$ and $n(t)$ do seem to show evidence of an additional relaxation mechanism at $32.8 \text{ }^\circ\text{C}$ that affects the second-order responses to the twist of the normal force and volume change; no additional mechanism is observed in the first-order torque response, as shown by the excellent time-temperature superposition of the shear modulus in Figure 2.

Murnaghan's series could be extended to higher order terms that would capture nonlinearity in the torque response as a function of ν . Earlier work [1] suggests that the strain level in this report is still in the regime where the torque is a linear function of the strain, so the single shear modulus function is sufficient to describe the torque response.

Conclusion

The NIST Torsional Dilatometer has been used to measure simultaneously the torque, normal force and volume change resulting from the torsional deformation of an epoxy cylinder near its glass transition temperature. Whereas the torque and normal force decay monotonically, the form of the volume change associated with the torsion varies with temperature, and shows a significant non-monotonic decay at lower temperatures. The measurements have been investigated using the truncated series solution for torsion of an elastic, compressible material of Murnaghan [6]. The three measurements allow direct determination of two of the four modulus functions ($\mu(t)$ and $n(t)$), both of which exhibit time-temperature superposition. Assumptions about $\mu(t)$ lead to results for $m(t)$ that seem reasonable in that $m(t)$ is of the same sign and similar in magnitude to $n(t)$, and decays monotonically. The model has been restricted so that the same time-temperature superposition is enforced for all modulus functions, and only a single stretched exponential is used to characterize the time-dependence of each modulus function. Given the restrictions on the model, it is fairly successful and does capture many of the features observed in the experiments.

References

1. Duran, R.S. and G.B. McKenna, *Journal of Rheology*, 34, 813-839, (1990).
2. Santore, M.M., R.S. Duran and G.B. McKenna, *Polymer*, 32, 2377-2381, (1991).
3. McKenna, G.B., Y. Leterrier and C.R. Schultheisz,

- Polymer Engineering and Science*, 35, 403-410, (1995).
4. Penn, R.W. and E.A. Kearsley, *Transactions of the Society of Rheology*, 20, 227-238, (1976).
 5. Wineman, A.S. and G.B. McKenna, *Nonlinear Effects in Fluids and Solids*, M.M. Carroll and M. Hayes, Eds., Plenum Press, New York, 339-353, (1996).
 6. Murnaghan, F.D., *Finite Deformation of an Elastic Solid*, John Wiley and Sons, Inc., London, (1951).
 7. Wang, T.T., H.M. Zupko, L.A. Wyndon and S. Matsuoka, *Polymer*, 23, 1407-1409, (1982).
 8. Pixa, R., V. Le Dû and C. Wippler, *Colloid and Polymer Science*, 266, 913-920, (1988).
 9. Lee, A. and G.B. McKenna, *Polymer*, 29, 1812-1817, (1988).
 10. Rivlin, R.S., *Quarterly of Applied Mathematics*, 14, 83-89, (1956).
 11. Ferry, J.D., *Viscoelastic Properties of Polymers*, Wiley, New York, (1961).
 12. McKinney, J.E. and H.V. Belcher, *Journal of Research of the National Bureau of Standards - A. Physics and Chemistry*, 67A, 43-53, (1963).
 13. Ferry, J.D., *Viscoelastic Properties of Polymers*, Third Edition, Wiley, New York, (1980).

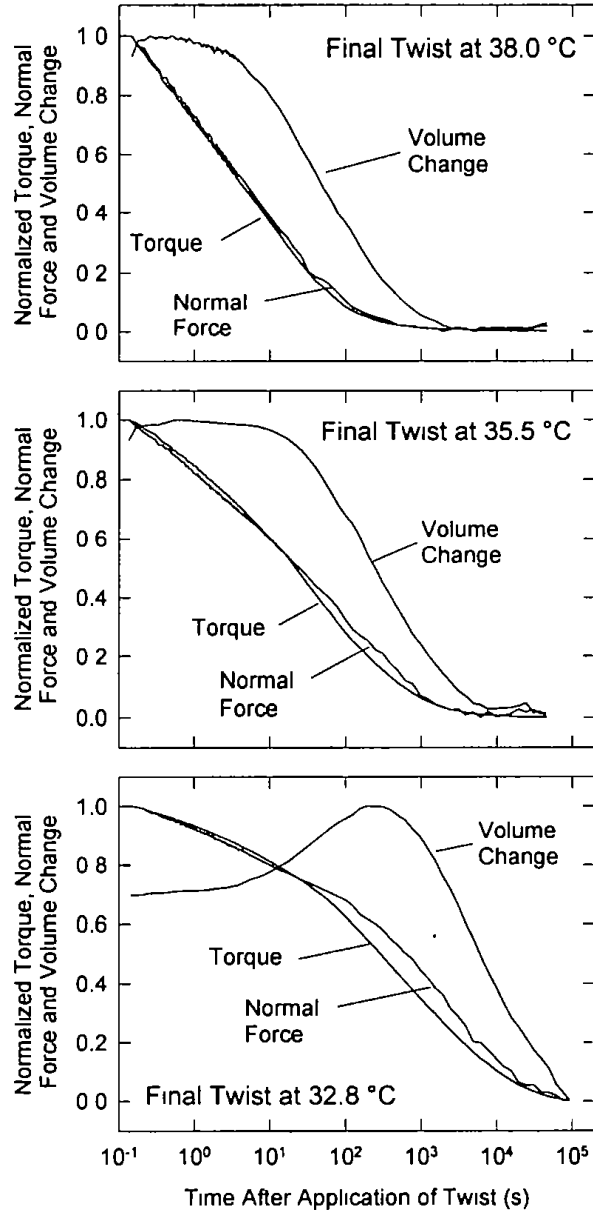


Figure 1. Normalized torque, normal force and volume relaxations caused by torsional deformations. Each experiment was the last twist in a sequence demonstrating equilibration following 2°C up-jumps to the temperatures indicated. The angle of twist per unit length applied in each case was 3.94 rad/m with standard uncertainty of 0.05 rad/m .

Table 1. Parameters for μ in equation (4).		
Parameter	Value	Standard Uncertainty
μ_1 (GPa)	0.7120	0.0021
μ_2 (GPa)	0.0768	0.0005
	0.3067	0.0013
(s)	32.39	0.36
$a(32.8^\circ\text{C})$	23.00	0.28
$a(32.8^\circ\text{C})$	1.0	
$a(32.8^\circ\text{C})$	0.1030	0.0006
C	0.0376	0.0004
RMS difference between data and model		2.56×10^{-3}

Table 2. Parameters for n in equation (6).		
Parameter	Value	Standard Uncertainty
n_1 (GPa)	-6.714	0.082
n_2 (GPa)	-0.843	0.020
n	0.2446	0.0043
n (s)	32.52	1.59
C_n	0.0113	0.0010
RMS difference between data and model		9.64×10^{-2}

Table 3. Parameters for m in equation (7).		
Parameter	Value	Standard Uncertainty
m_1 (GPa)	-4.518	0.034
m_2 (GPa)	-1.867	0.018
m	0.4094	0.0066
m (s)	134.2	3.7
C_m	0.0626	0.0007
RMS difference between data and model		9.51×10^{-2}

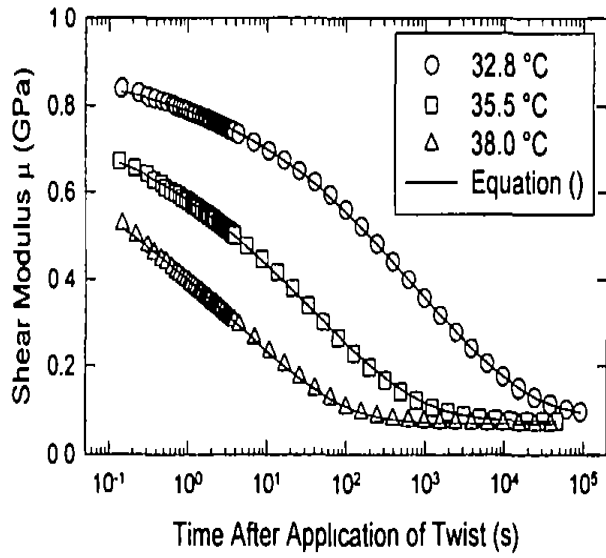


Figure 2. The shear modulus for the three experiments calculated from equation (1), and the model of equation (4).

Key Phrases

Nonlinear viscoelasticity, torsion, volume change, normal force