# Simultaneous Measurement of Torque, Axial Force and Volume Change in the Torsional Dilatometer and the Implications for Constitutive Modeling

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## Abstract

The NIST Torsional Dilatometer measures simultaneously the torque, axial normal force and volume change in response to a torsional deformation. 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 is used to study the evolution of the properties of an amorphous polymer following temperature jumps in the regime below the glass transition temperature. The evolution of the sample volume (a measure of the thermodynamic state of the material) is 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 differences in thermal histories.

In this paper, we focus on an interesting behavior observed in measurements made in the equilibrium stages of two 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 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, as it varies considerably with temperature, and at the lower temperature demonstrates behavior that is not monotonic. The torque, normal force and volume change are briefly investigated using the truncated series expansion for the torsion of an elastic, compressible cylinder of Murnaghan [1951]. In his analysis, the volume change and normal force are associated with higher-order, nonlinear terms in the strain energy density function.

## Experimental

The Torsional Dilatometer is described in detail in the paper by Duran and McKenna [1990]. The material is a diglycidal ether of bisphenol-A epoxy, cured with a flexible poly(propylene oxide) diamine with a molecular mass of 400 g/mol, giving a nominal glass transition temperature of 42.4 °C [Lee and McKenna, 1988]. Use of a thermoset is intended to allow repeated experiments on the same sample. The sample is bonded between two stainless-steel end grips and shaped into a cylinder 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 is 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; the mercury 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 by circulating fluid from a constant-temperature bath through copper coils wrapped around the chamber containing the sample and the mercury. The standard uncertainties are 0.2 Nm for the torque measurement; 2 N for the normal force measurement; and 2 x $10^{-5}$ $cm^3$ for the volume measurement.

## Results and Discussion

Torque, normal force and volume relaxation functions are shown in Figures 1 and 2, for experiments in which the sample was equilibrated at 35.5 °C and 32.8 °C, respectively. 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 both figures, the normal force relaxation is similar to the torque relaxation, but the volume behavior is very different from the other two. In both experiments, the torque (or moment) M(t) is very well represented by a stretched exponential of the form

$$M(t) = M_1 \exp[-(t/\tau)^\beta] + M_\infty \qquad \textbf{(1)}$$

where τ is a characteristic time constant. The value of β is nearly identical for the torque data at the two temperatures in Figures 1 and 2, so the two curves can be superposed. However, both a horizontal shift and a vertical (multiplicative) shift are necessary to superpose the two curves. While a stretched exponential fits the normal force data in Figure 1 quite well, at the lower temperature in Figure 2 there is some deviation suggesting the presence of an additional relaxation mechanism. The volume change is in the form of the relative deviation from equilibrium δ(t), with $\delta(t) = [V(t)-V_\infty]/V_\infty$, where V(t) is the current volume at time t, and $V_\infty$ is the equilibrium volume (at the current temperature). The change in the volume behavior between the two 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 δ(t) is on the order of 2 x $10^{-4}$.

Although the volume recovery behavior looks odd compared to the torque and normal force, it can be modeled using the truncated series expansion for the torsion of an elastic, compressible material of Murnaghan [1951]. 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 λ(t), μ(t), m(t) and n(t) [Rivlin, 1956]. In each experiment, we measure three quantities: the torque (or moment) M(t), normal force N(t) and relative volume deviation from equilibrium δ(t). First, we define $d(t) = 2[(1+\delta(t))^{1/2} - 1] = 2\Delta R(t)/R_0$ as twice the change in the cylinder radius from its initial value of $R_0$ (to first order, d(t) = δ(t)). Murnaghan's result is then

$$\mu(t) = \frac{2M(t)}{\pi\psi R_0^4} \qquad \textbf{(2)}$$

$$n(t) = \frac{16}{\psi^2 R_0^2}\left[\frac{N(t)}{\pi R_0^2} + \mu(t)d(t)\right] \tag{3}$$

$$m(t) = \frac{4}{\psi^2 R_0^2}\left[\frac{N(t)}{\pi R_0^2} - \lambda(t)d(t)\right] - (\lambda(t) + 2\mu(t)) \tag{4}$$

where ψ is the angle of twist per unit length. Equations (2) and (3) show that μ(t) and n(t) can be evaluated directly from the measured quantities, but the equation (4) shows that λ(t) and m(t) can only be expressed in terms of one another. The moment M(t) follows a stretched exponential function, so μ(t) would also be well-described by that type of function. By inverting the above equations to write the normal force and volume change in terms of the moduli, it can be shown that the normal force and volume change are functions of all four modulus functions, so that a single stretched exponential might only fit the normal force in certain regimes, depending on the time dependence of each function.

At this point, we make some assumptions about the modulus functions, and determine if the experimental results are consistent with our expectations. First, we assume that the modulus functions are all monotonic, so that the behavior of the volume is a result of different time dependencies. The moduli λ(t) and μ(t) also appear in combinations such as Poisson's ratio ν(t) = λ(t)/[2(λ(t) + μ(t))] and the bulk modulus K(t) = (3λ(t) + 2μ(t))/3. We anticipate that ν(t) remains nearly constant [Ferry, 1961] and that the relative decrease of the bulk modulus with time is much less than that of the shear modulus μ(t) [Ferry, 1980]. Choosing Poisson's ratio at time t = 0 as ν(0) = 0.35, we examine two cases that represent approximate limits of physically reasonable behavior. Case 1: Assume λ(t) is a constant, in which case Poisson's ratio is a slightly increasing function in time and the relative change in the bulk modulus with time is minimized. This assumption is also equivalent to assuming that the time dependence of λ(t) is outside the time scale of the experiment. Case 2: Assume that λ(t) is a multiple of μ(t), in which case Poisson's ratio is constant and the bulk modulus is also a multiple of μ(t).

As seen in Figures 3 and 4, the assumptions for the form of λ(t) do give reasonable results for the calculated m(t). Both m(t) and n(t) are negative, with magnitudes that are approximately ten times larger than μ(t). As mentioned, μ(t) at the two different temperatures can be superposed, and the choices for λ(t) guarantee that superposability holds. The function n(t) can also be superposed, but requires only a horizontal shift, which is similar in magnitude to the horizontal shift for μ(t). The shapes of the calculated m(t) curves are sufficiently different to make superposition impossible. One might be able to iterate on the functional forms for λ(t) and m(t) to enforce superposition for both curves.

Murnaghan's series can be extended to higher order terms that would capture nonlinearity in the torque response as a function of ψ. Earlier work [Duran and McKenna, 1990] 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 [1951]. The three measurements allow direct determination of two of the four modulus functions (μ(t) and n(t)), both of which exhibit time-temperature superposition. Assumptions about λ(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. It may be possible to determine λ(t) and m(t) unambiguously by enforcing time-temperature superposition or by mapping out the variations in the measurements as functions of strain level and/or cylinder radius.

## Bibliography


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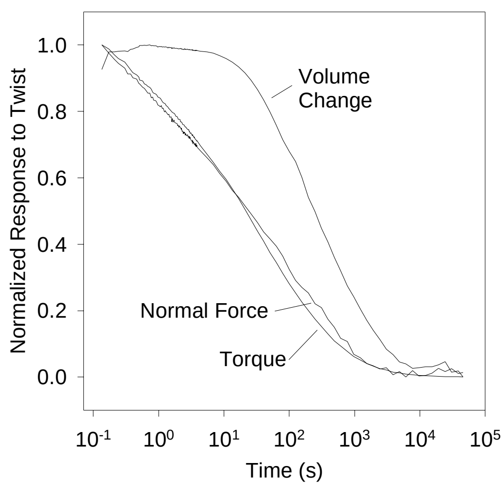


Figure 1. Normalized torque, normal force and volume change for a twist at 35.5 °C.

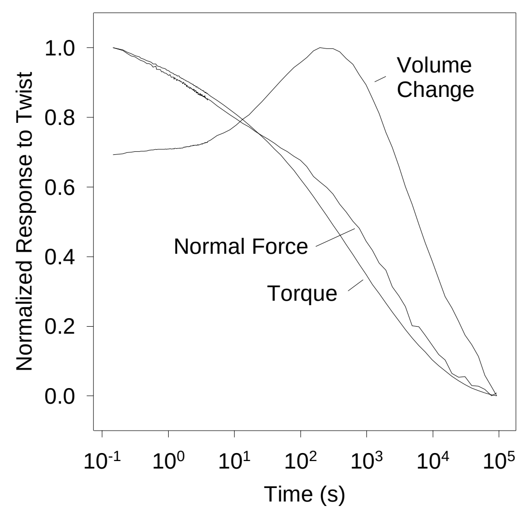


Figure 2. Normalized torque, normal force and volume change for a twist at 32.8 °C

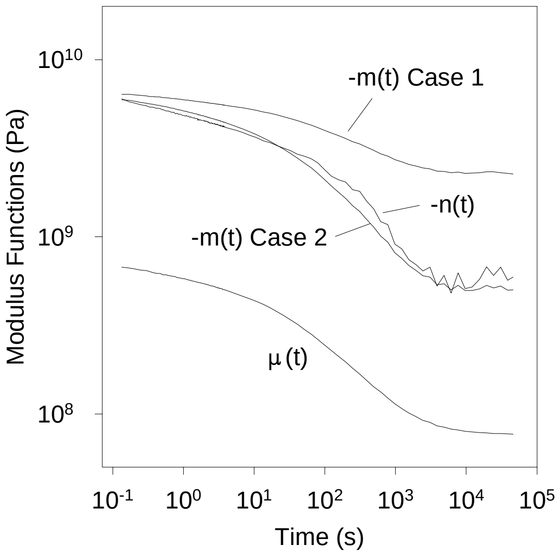


Figure 3. Modulus functions μ(t), −n(t) and −m(t) for two cases assuming λ(t) at 35.5 °C.

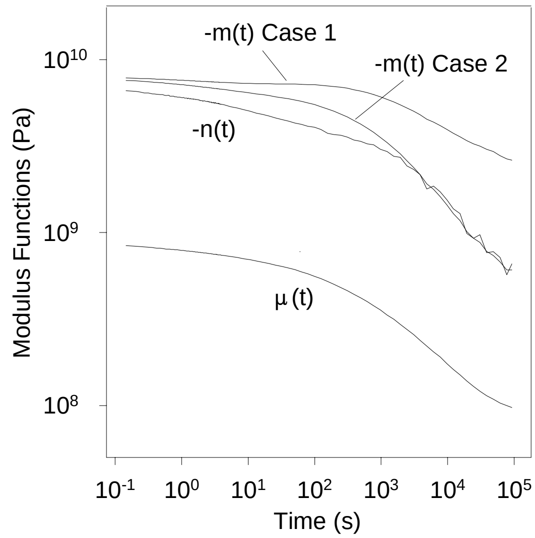


Figure 4. Modulus functions μ(t), −n(t) and −m(t) for two cases assuming λ(t) at 32.8 °C.