

Investigation of Nonlinear Material Behavior Using Simultaneous Measurements of Volume Recovery and Physical Aging

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Abstract

At temperatures below the glass transition, amorphous polymers evolve slowly toward thermodynamic equilibrium. Some experiments have suggested that different material properties equilibrate at different rates, but such comparisons are typically made using different samples in different instruments, leading to questions about the comparability between the materials or thermal histories. Using the NIST Torsional Dilatometer, simultaneous measurements of volume (a measure of the thermodynamic state) and mechanical response (using torsional stress-relaxation experiments) can be made on the same sample. Recent experiments in this laboratory with an epoxy indicate that the volume and mechanical behavior equilibrate at the same time. The epoxy has also exhibited significant chemical aging, as manifested by increasing relaxation times, over the (3 year) course of the experiments.

Introduction

Cooling an amorphous polymer below its glass transition temperature (T_g) places it in a state that is not in thermodynamic equilibrium. If the polymer is then held at a temperature below T_g , the polymer glass evolves slowly toward equilibrium. This evolution can be observed in measurements of the volume, enthalpy, optical properties or mechanical properties of the material. One might expect that the equilibration process would be reflected in the same way through experimental measurement of the different properties, but some experiments have indicated differences in the rate of equilibration or the time required for equilibration of different properties [1-7], whereas in other cases evolution of different properties are found to coincide [8,9]. Differences in the behavior of these properties would imply that models of the evolution process would need to be fairly complex, requiring different 'clocks' to describe each property. For example, Scherer cited a number of examples for inorganic glasses in which different properties exhibit different kinetics, and he argued that the different properties could depend on different aspects of the structure of the glass, which evolve at different rates [1]. Roe and Millman found that the enthalpy equilibrated well before the creep compliance in experiments on polystyrene using only downward temperature changes, and also argued that different properties could reflect different segmental motions that have different relaxation times [2]. In experiments with poly(vinyl acetate), Delin *et al.* also found that the mechanical properties equilibrated later than the volume following downward temperature jumps, but that the opposite was true for upward temperature jumps [7]. In contrast, Struik compared volume recovery with the torsional creep compliance for polycarbonate, polystyrene and poly(vinyl chloride), and he concluded that the two properties evolve identically following a temperature change and argued that the creep time scale is uniquely determined by the polymer specific volume [8]. In aging experiments measuring creep and enthalpy

recovery for a polyetherimide, Echeverria *et al.* also concluded that the equilibration of the different properties occurred at the same time [9], and they also suggested that the differences observed by Roe and Millman [2] might be a result of differences in thermal histories for the two types of tests. Similar difficulties are possible for most such comparisons, because different properties are typically measured using different samples in different instruments, leading to questions about the comparability between the materials used as well as the thermal histories. For example, Struik was forced to correct for differences in the thermometers used in different experiments [8].

This problem is eliminated in the NIST Torsional Dilatometer [10], in which measurements of volume recovery and the evolution of the mechanical response in stress relaxation can be made simultaneously on the same sample. (The isothermal evolution of the mechanical response below T_g has been labeled physical aging [11].) Experiments with the Torsional Dilatometer have been performed using upward and downward temperature jumps, after which the sample was subjected to intermittent torsional deformations to follow the evolution of the mechanical properties. In addition to a torque response, the torsional deformation also induces a volume change (comparable to the volume change caused by the temperature jump) and a normal force along the axis of the cylindrical sample. All three of these properties are measured, and we will compare the evolution of the torque and normal force relaxations to the volume change caused by the temperature jumps.

Previous Torsional Dilatometer experiments with an epoxy very close to the glass transition temperature indicated that the mechanical properties equilibrated before the volume in downward temperature jumps, while the opposite was true in upward temperature jumps [4]. Experiments so close to the glass transition temperature are somewhat difficult because the mechanical response is small, and the volume and mechanical properties relax rapidly. Reanalysis of that data does not invalidate the previous interpretation, but suggests that firm conclusions are difficult once all of the experimental uncertainties have been taken into account. Subsequent experiments with the same epoxy have been undertaken at lower temperatures to improve the resolution of time and force [5], and the data acquisition system has been improved during the current series of experiments. The results of these additional experiments farther below the glass transition temperature suggest that the volume and the mechanical properties (torque and normal force) equilibrate at approximately the same time in this regime, although there are differences in the relative rates of change depending on the temperature and the direction of the jump. It is clear that the differences in the time-scales for equilibration (if any) are subtle, and may well depend on the molecular structure of the glassy material and the temperature as well as the thermal history.

There are clear differences in some of the time scales that are observed in the Torsional Dilatometer experiments, however. As mentioned above, each twist causes an axial normal force and a

volume increase in addition to the torque response. All three of these mechanically induced behaviors relax much faster than the volume change caused by the temperature jump, by several orders of magnitude [3]. What seems most interesting is that the volume increase caused by the twist is completely uncoupled from the volume change caused by the temperature jump, even though these volume changes are of similar magnitudes [3]. In addition, the rate at which the mechanical properties evolve (physically age) decreases with increasing strain [3,11,12], although the time for equilibration remains unchanged [3,12]. In contrast, the evolution of the underlying volume associated with the temperature jump is unaffected by the level of the applied strain [3].

We have also found that the epoxy used in this study has exhibited significant chemical aging, as manifested by increasing relaxation times at a given temperature, over the (3 year) course of the experiments. The increasing relaxation times indicate that the glass transition temperature of the material is increasing, possibly caused by additional curing or by changes in the moisture content of the specimen.

Experimental

The Torsional Dilatometer is described in detail in the paper by Duran and McKenna [10]. 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 [12]. 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 shear strain varies linearly with the radius, and this amount of twist leads to a shear strain of 0.0300 at the outer radius of the sample (standard uncertainty: 0.0004). 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 into 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 $2 \times 10^{-5} \text{ cm}^3$ for the volume measurement.

Temperature-jump experiments are performed by connecting the dilatometer to one constant-temperature bath and allowing the sample to equilibrate, and then switching the connection to a second constant-temperature bath using valves. Because of the large mass of the dilatometer, the temperature change actually takes about 2700 s to accomplish. The standard uncertainty in the dilatometer temperature after thermal equilibration is approximately 0.01 °C. Temperature jumps for the work reported here are typically 2 °C, and the aging time is measured from the point at which the valves are changed. Both up-jumps and down-jumps have been performed to a single final temperature to mimic Kovacs's asymmetry of approach experiments [13,14], which demonstrated that the volume recovery process depends on the temperature as well as the magnitude and sign of the deviation from equilibrium.

In order to prevent large stresses in the sample caused by thermal expansion, the connection between the grip and the motor is left free until aging time $t_c = 900 \text{ s}$. After that connection is made, the data acquisition program that measures the torque, normal force and volume recovery is started. The mechanical response of the material is probed sequentially following Struik's protocol for physical aging experiments [11]. At $t_c = 1350 \text{ s}$, a constant twist is applied for 90 s and then the twist is removed for 900 s to erase any memory of the deformation. At $t_c = 2340 \text{ s}$, the next twist is applied for 180 s and then returned to zero for 1800 s, and the length of each subsequent twist step doubles, as does the time to erase the memory of the deformation. Initially, a time offset of 450 s was subtracted to account for thermal equilibration, so that the first twist was scaled as one-tenth the aging time, but we have since concluded that the time offset should not be included; the sequence of testing was retained for comparison with earlier experiments. Typically, ten twist/untwist sequences are applied in order to capture the equilibration of the material at the new temperature.

Analysis

For a down-jump in temperature, the torque and normal force relaxations shift to longer times, while for an up-jump the relaxations shift to shorter times. The sequential relaxation curves can be shifted to superimpose using an aging-time shift factor [11] (an approach similar to time-temperature superposition [15]). The evolution of the mechanical response after a temperature jump will therefore be characterized using the aging-time shift factor for comparison with the volume recovery. The torque relaxation or moment $M_n(t)$ at the n th twist step is fit to a stretched exponential

$$M_n(t) = M_1 \exp[-(t/\tau_{Mn})^\beta] + M_0 \quad (1)$$

where the parameters M_1 , M_0 and β are held constant over the sequence of twists for a given experiment, and τ_{Mn} is a separate characteristic time for the torque relaxation for each twist. For a given experiment, all of the torque relaxation data for the sequence of twists are combined into a single large data set to fit the parameters. An aging time shift factor a_e can then be calculated as $\log(a_e) = \log(\tau_{Mn}/\tau_{ref})$, where τ_{ref} is some reference time (typically taken from one particular relaxation curve). For comparison between experiments jumping to different temperatures, it is interesting to take $\tau_{ref} = 1 \text{ s}$, in which case $\log(a_e)$ is equivalent to $\log(\tau_{Mn})$. Taking $\tau_{ref} = 1 \text{ s}$, we then look at the evolution of the characteristic relaxation times directly.

A similar procedure is used to fit the normal force response $N_n(t)$ to a stretched exponential

$$N_n(t) = N_1 \exp[-(t/\tau_{Nn})^\beta] + N_{0n} \quad (2)$$

Again, all of the normal force relaxation data from a given experimental sequence are combined to fit the parameters. In this case N_1 and β are held constant for all the curves, but both N_{0n} and τ_{Nn} are allowed to vary for each normal force relaxation. Unlike the torque, the baseline of the normal force is affected by the thermal expansion and volume recovery in response to the temperature jump (and to any subsequent thermal fluctuations). It is therefore necessary to allow the baseline (parameter N_{0n}) to vary for each twist step.

Results and Discussion

Figure 1 shows a typical plot of the volume as a function of time for a jump from 37.5 °C to 35.5 °C, with ten twist/untwist steps. Following Kovacs [13,14], the volume is put into the form of the relative deviation of the volume from its equilibrium value, $\delta(t,T)$, with

$$\delta(t,T) = [V(t,T) - V_{\infty}(T)] / V_{\infty}(T) \quad (3)$$

where $V(t,T)$ is the current volume at time t and temperature T , and $V_{\infty}(T)$ is the equilibrium volume at temperature T . As time progresses, $\delta(t,T)$ tends toward zero. There is also an increase in volume associated with each twist, which relaxes much more quickly than the volume change associated with the temperature jump. Each subsequent untwist also leads to a brief volume increase, because the volume change is an even function of the angle of twist. Experiments demonstrate that the volume recovery associated with the temperature jump is unaffected by the changes in volume associated with the twists and untwists [3]. The symbols represent the points at the end of each untwist step, and the dashed line is a stretched exponential fit through the symbols in order to calculate the volume at equilibrium. The standard uncertainty in $\delta(t,T)$ is 10^{-6} . The dilatometer temperature is also shown in Figure 1, and it can be seen that at the time of the first twist step, the temperature is still approximately 0.1 °C from its final value.

Figure 2 compares the evolution of the torsional response of the material (represented by τ_{Mn} for each sequential torque relaxation) against the volume (represented by $\delta(t,T)$) for both up-jumps and down-jumps to several different final temperatures. The solid lines are linear regressions fit to each sequence of twists. Each sequence moves toward $\delta = 0$, and it can be seen that the characteristic time for the torque relaxation moves in concert with the volume recovery. The standard uncertainty in the characteristic time for the relaxation of the torque, τ_{Mn} , is less than $0.021\tau_{Mn}$ for all the data shown. The dashed line in Figure 2 suggests that the aging time shift factor a_{δ} is similar to the volumetric shift factor a_{δ} in the KAHR model of volume recovery [14], which is calculated as $\log(a_{\delta}) = -650\delta$ using the 'universal' values suggested by those authors [14]. The vertical position of the dashed line is arbitrary (effectively, an arbitrary choice of temperature with an associated shift). Although the slopes of the experimental data vary somewhat with temperature and direction of jump, the experimental results are similar to the slope of the dashed line.

Figure 3 indicates the effect of chemical aging of the specimen during a series of up-jumps and down-jumps to 35.5 °C. The characteristic time for the torque relaxation at equilibrium is plotted as a function of the lifetime of the specimen, and the characteristic time shows a steady increase that suggests additional curing or a decrease in the moisture content of the specimen, which shifts the T_g of the material. Assuming that the material follows the typical 3 °C per decade change in the relaxation spectrum [15], the T_g of the material has increased by less than 1.4 °C, indicating the sensitivity of the mechanical measurements.

Figure 4 compares the characteristic time for the relaxation of the torque to the characteristic time for the relaxation of the normal force (the parameters τ_{Mn} and τ_{Nn} from equations 1 and 2). The normal force relaxation generally seems to lag the torque relaxation slightly, but the two parameters are highly correlated. There is more noise in the normal force measurements than in the torque measurements, for two reasons. First, the magnitude of the normal force is relatively small compared to the capacity of the transducer, and second, the normal force is directly affected by temperature changes through

thermal expansion and volume recovery. The standard uncertainty in τ_{Nn} is less than $0.19\tau_{Nn}$ for all the data shown, and is typically closer to $0.1\tau_{Nn}$. The standard uncertainty in τ_{Nn} is indicated in Figure 4 by uncertainty bars in those cases where the bars are larger than the symbols.

Conclusion

The NIST Torsional Dilatometer has been used to measure simultaneously the evolution of the sample volume (structural recovery) and mechanical response to torsion (physical aging) for an epoxy cylinder following upward and downward temperature jumps. In the current experiments well below the glass transition temperature, the volume, the torque and the normal force equilibrate at approximately the same time, but the rate of approach to equilibrium depends to some extent on the temperature and the direction of the jump. While these results exhibit a similarity in the evolution of the volume and mechanical properties, the variety of results found in the literature [1-9] suggests that the question is still unresolved, and that the differences, if any, are subtle. Differences can certainly occur if separate properties reflect different aspects of the underlying microstructure of the glass, if those different aspects rearrange themselves at different rates.

Of course, there are some obvious differences in time scales in the torsional dilatometer experiments. The mechanically induced torque, normal force and volume increase all relax much faster than the volume change caused by the temperature jump, by several orders of magnitude, and the volume increase caused by the twist is apparently completely uncoupled from the volume change caused by the temperature jump, even though these volume changes are of similar magnitudes [3].

The epoxy has also exhibited significant chemical aging, as shown by increasing relaxation times at a given temperature, over the course of the experiments. These changes suggest the epoxy is continuing to cure, or that the moisture content is changing.

References

1. Scherer, G.W., **Relaxation in Glass and Composites**, Wiley, New York, 1986.
2. Roe, R.-J. and Millman, G.M., "Physical Aging in Polystyrene: Comparison of the Changes in Creep Behavior with the Enthalpy Relaxation," *Polym. Eng. Sci.*, Vol. 23, 318-322, 1983.
3. Santore, M.M., Duran, R.S. and McKenna, G.B., "Volume recovery in epoxy glasses subjected to torsional deformations: the question of rejuvenation," *Polymer*, Vol. 32, 2377-2381, 1991.
4. McKenna, G.B., Leterrier, Y. and Schultheisz, C.R., "The Evolution of Material Properties During Physical Aging," *Polym. Eng. Sci.*, Vol. 35, 403-410, 1995.
5. McKenna, G.B., Schultheisz, C.R. and Leterrier, Y., "Volume Recovery and Physical Aging: Dilatometric Evidence for Different Kinetics," *Deformation, Yield and Fracture of Polymers*, Proceedings of the 9th International Conference, Cambridge, UK, paper 31/1, (1994).
6. Schultheisz, C.R., Colucci, D.M., McKenna, G.B. and Caruthers, J.M., "Modeling the Differing Time Scales of Structural Recovery and Mechanical Relaxation Observed in Aging Experiments," *Mechanics of Plastics and Plastic Composites MD-68/AMD-215*, M.C. Boyce, ed, American Society of Mechanical Engineers, New York, 251-282, 1995.
7. Delin, M., Rychwalski, R.W., Kubat, J., Klason, C. and Hutchinson, J.M., "Physical Aging Time Scales and Rates for Poly(Vinyl Acetate) Stimulated Mechanically in the T_g -Region," *Polym. Eng. Sci.*, Vol. 36, 2955-2967, 1996.

8. Struik, L.C.E., "Dependence of relaxation times of glassy polymers on their specific volume," *Polymer*, Vol. 29, 1347-1353, 1988.
9. Echeverria, I., Su, P.C., Simon, S.L. and Plazek, D.J., "Physical Aging of a Polyetherimide: Creep and DSC Measurements," *J. Polym. Sci.: Part B: Polym. Phys.*, Vol. 33, 2457-2468, 1995.
10. Duran, R.S. and McKenna, G.B., "A torsional dilatometer for volume change measurements on deformed glasses: Instrument description and measurements on equilibrated glasses," *J. Rheology*, Vol. 34, 813-839, 1990.
11. Struik, L.C.E., **Physical Aging in Amorphous Polymers and Other Materials**, Elsevier, Amsterdam, 1978.
12. Lee, A. and McKenna, G.B., "Effect of crosslink density on physical ageing of epoxy networks," *Polymer*, Vol. 29, 1812-1817, 1988.
13. Kovacs, A.J., "Transition vitreuse dans les polymeres amorphes. Etude Phenomenologique," *Fortschritte der Hochpolymeren-Forschung*, Vol. 3, 394-507, 1963.
14. Kovacs, A.J., Aklonis, J.J., Hutchinson, J.M., Ramos, A.R., "Isobaric Volume and Enthalpy Recovery of Glasses. II. A Transparent Multiparameter Theory," *J. Polym. Sci.: Polym. Phys. Ed.*, Vol. 17, 1097-1162, 1979.
15. Ferry, J.D., **Viscoelastic Properties of Polymers**, Third Edition, Wiley, New York, 1980.

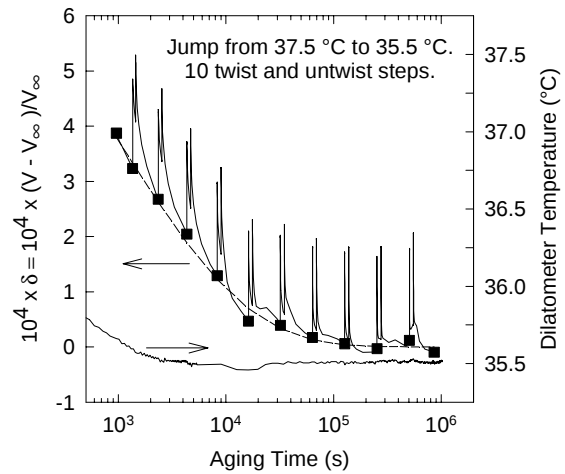


Figure 1. Volume recovery in a jump from 37.5 °C to 35.5 °C, with a sequence of ten twist/untwist steps. Squares indicate the end of each untwist step, and the dashed curve fit through the squares shows the baseline volume change caused by the temperature change. Also shown is the dilatometer temperature, indicating the time for thermal equilibration.

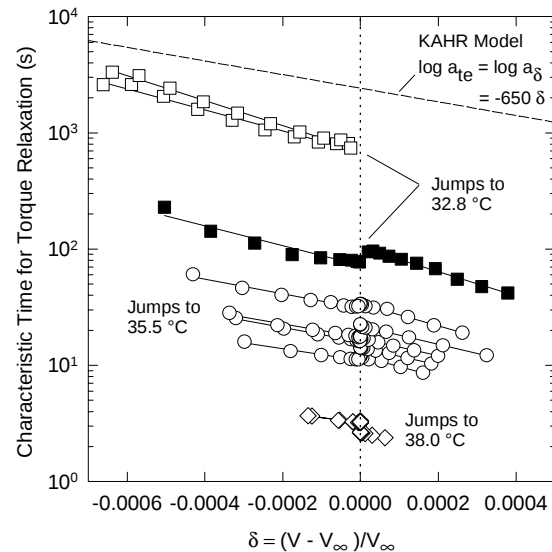


Figure 2. Comparison of the characteristic time for torque relaxation (τ_{Mn}) and the volume recovery. Solid symbols: Specimen 1[5]; open symbols: Specimen 2. Squares: jumps to 32.8 °C; circles: jumps to 35.5 °C; diamonds: jumps to 38.0 °C. Solid lines are regressions through the data for each separate experiment. Dashed line is the prediction of the KAHR model for volume recovery [14], if $a_{te} = a_{\delta}$.

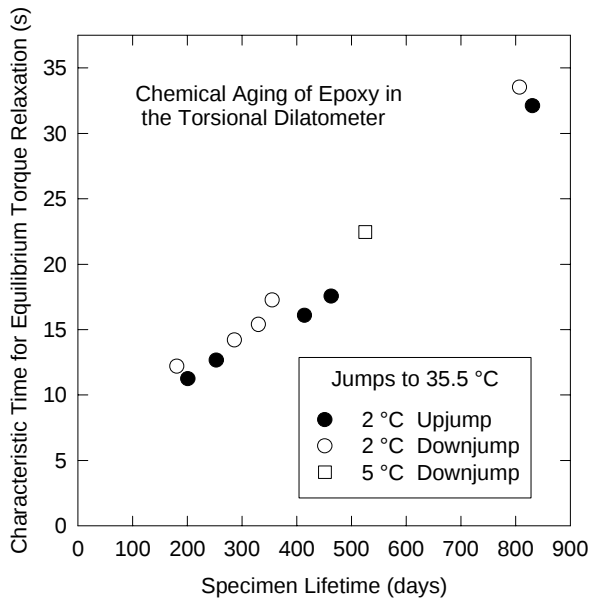


Figure 3. Increase in the characteristic time for torque relaxation at equilibrium as a function of specimen lifetime, for a series of jumps to 35.5 °C. The trend suggests T_g is also increasing as a result of chemical aging, such as additional curing of the epoxy, or a change in moisture content.

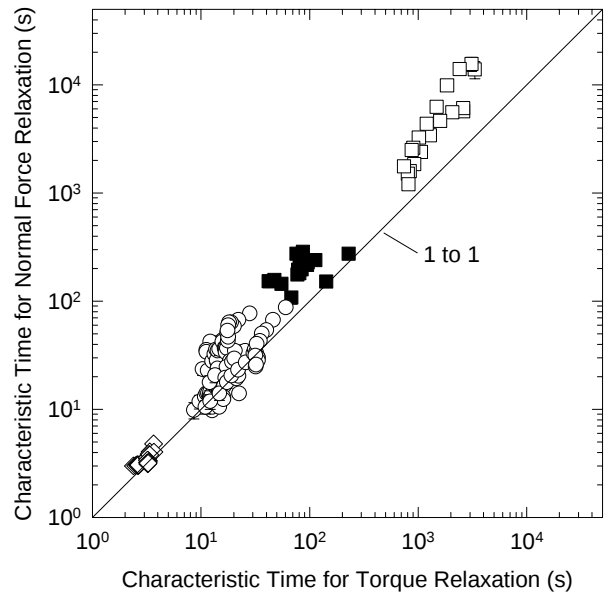


Figure 4. Comparison between the characteristic times for torque and normal force relaxation. Symbols are the same as in Figure 2.