

Volume recovery in epoxy glasses subjected to torsional deformations: the question of rejuvenation

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(Received 26 July 1990; accepted 21 September 1990)

Torsional dilatometry was used to examine the mechanical properties of an epoxy glass during physical ageing, i.e. after a quench from above to slightly below the glass transition temperature. Volume changes in the sample were measured simultaneously with the viscoelastic responses in stress relaxation experiments as functions of the deformation magnitude. The torque relaxation obeys time-ageing time superposition where the shift factor, a_{te} , increases with ageing time until the sample reaches mechanical equilibrium at $t^* \approx 10^4$ s, independent of the magnitude of the strain. In this epoxy, the torsional deformations induce volume expansions which relax on a time-scale similar to those of the torque relaxation. However, the volume recovery responses cannot be superposed at different ageing times by a simple shift along the time axis. Mechanical stimuli only momentarily disrupt the volume evolution following a quench. The underlying volume recovery kinetics, which are much slower than the mechanical torque or volume relaxation, remain unaltered. The facts that t^* is independent of the magnitude of the strain and that the volume recovery after a quench remains unaltered, in spite of the imposition of mechanical deformations, support the argument that mechanical stimuli neither alter the underlying (non-equilibrium) thermodynamic state of the glass nor erase physical ageing.

(Keywords: dilatometry; physical ageing; rejuvenation; stress relaxation; torsion; volume recovery)

INTRODUCTION

The physical ageing of polymeric glasses is an important topic that has been extensively studied¹⁻⁶. When quenched from a temperature above its glass transition, T_g , to a temperature below it, a glass will slowly densify towards its equilibrium specific volume. This behaviour is shown schematically in *Figures 1a* and *1b* which show volume-temperature response of a typical glass-forming substance (*Figure 1a*) and the isothermal volume recovery of the non-equilibrium glass (*Figure 1b*, curve A). Accompanying the volume decreases or changes in glassy structure are changes in the viscoelastic response of the glass which have come to be associated with the physical ageing process¹. Several non-linear phenomenological equations⁷⁻¹¹ describe the specific volume *versus* time behaviour or volume recovery response of glasses with reasonable success, but the detailed molecular description remains elusive. In any event, the change in the viscoelastic response of glasses during volume recovery has been found to be well-described by a time-ageing time superposition principle in which viscoelastic response curves (creep, relaxation or dynamic) could be superimposed by a horizontal shift along the time (frequency) axis¹⁻⁶.

Struik¹ observed that partially aged glasses subjected to large deformations respond differently from those subjected to small deformations. The ageing time shift factor required to superpose the large deformation

responses was smaller than that required to superpose the small deformation responses in spite of the fact that the thermal histories were identical. Struik referred to this phenomenon as erasure of ageing, although it was subsequently coined 'rejuvenation' by McKenna and Kovacs⁴ and this term has become accepted in the literature¹²⁻¹⁶. Struik interpreted erasure as resulting from an input of or change in the distribution of free volume due to the dissipation of mechanical energy upon loading and unloading of the glass (*Figure 1b*, curve B). Thus, the glass was pushed closer to the freshly quenched state by the large stresses, i.e. the glass was rejuvenated.

In their work with epoxy glasses near to the conventionally measured glass transition, Lee and McKenna^{5,17,18} also observed the 'signature' of rejuvenation, that the shifts required to superpose the mechanical response curves at increasing ageing times decrease with increasing stress. Because of the proximity of these experiments to T_g ageing or rejuvenation were apparent only up to moderate times after a thermal quench. At long times and as the samples approach equilibrium, the mechanical properties approach their equilibrium responses and negligible shifting is required for superposition. These authors then defined t^* as the time to reach mechanical equilibrium and observed that it is a material property dependent on temperature and crosslink density, but independent of the imposed stress. The fact that the magnitude of the mechanical stimulus (stress or strain) has no effect on t^* argues against the rejuvenation hypothesis, i.e. imposing large stresses or deformations does not retard ageing as measured from the evolution of the mechanical properties.

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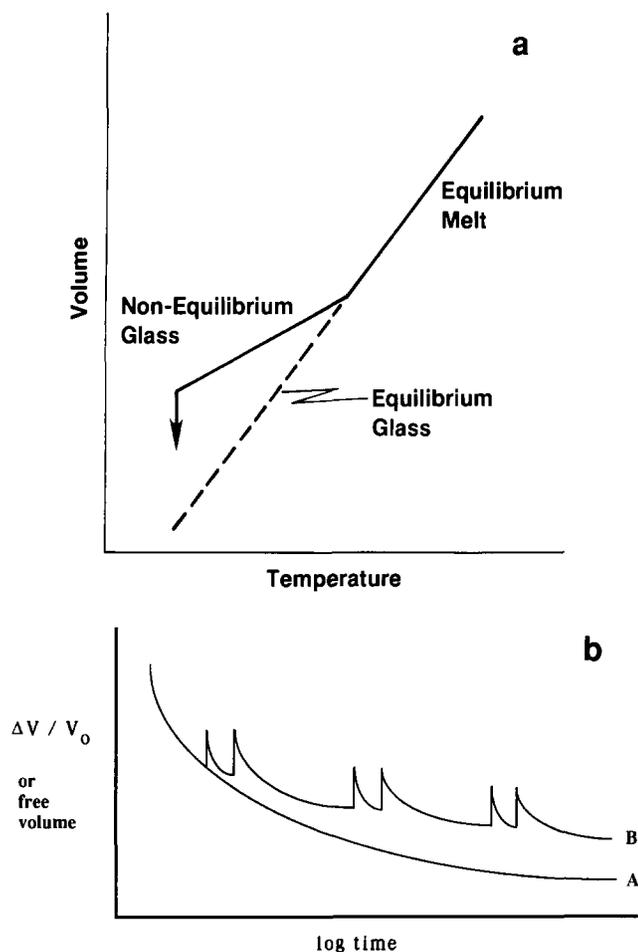


Figure 1 (a) Schematic of the volume *versus* temperature behaviour of a glass-forming material. (b) Curve A, volume recovery response of a glass after a quench from above to below T_g ; curve B, expectations of rejuvenation following a large mechanical stimulus (load followed by unload) changing the (free) volume recovery of an ageing glass

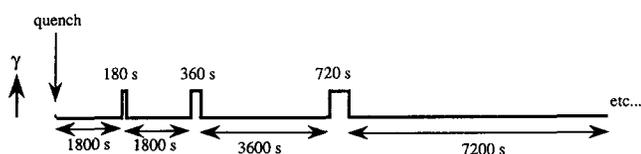


Figure 2 Schematic of loading sequence to study the effect of ageing time t_c after a quench on the mechanical response of a glass

The question then arises whether the evolution of the volume or free volume following a quench reflects the strain-independent equilibration time t^* obtained from the mechanical measurements, or is rejuvenation apparent in the volume recovery response? We can only answer this question partially as we have no way to measure free volume; however, dilatometric experiments yield the global volume of a sample, which may reflect free volume, particularly in the kinetics of the volume recovery. As a test of the rejuvenation hypothesis, in this paper we present results from a study which show the effects of torsional deformations on the evolution of the total sample volume of an epoxy glass quenched from above to below its glass transition temperature. We compare the kinetics of the volume evolution for samples subjected to sequential deformation histories and for undeformed samples. We also compare the apparent equilibration of the sample based on the mechanical

response (i.e. t^* as defined by Lee and McKenna^{5,17,18}) and the time required to reach volume equilibrium in the same experiment.

EXPERIMENTAL

Experiments were performed on an epoxy network (Jeffamine*, DGEBA/D400) which has been described previously^{5,17-21}. The volumetric measurements were made in an automated precision torsional dilatometer of our own design which is described elsewhere^{21,22}. The instrument allows simultaneous real time measurements of volume change, torque, normal force, temperature and time for arbitrary torsional deformation histories. Thermal stability was assured by using a high precision bath (stability ≈ 1 mK) to circulate fluid through the dilatometer. Generally, exposure of the hoses and dilatometer chamber itself to the atmosphere resulted in a dilatometer thermal stability of 15–20 mK which limits the typical long-term specific volume resolution to $\sim \pm 2.5 \times 10^{-5} \text{ cm}^3 \text{ cm}^{-3}$, although in this study for several week-long runs we succeeded in maintaining the temperature stability within ± 10 mK, yielding a resolution of $1.5 \times 10^{-5} \text{ cm}^3 \text{ cm}^{-3}$.

For the experiments described here, the torsional dilatometer was attached first to a 100 mK stability bath at 44°C. By use of quick disconnect fittings the dilatometer was subsequently connected to the high precision bath at 33.5°C which results in a quench of the system in which the dilatometer itself attains the testing temperature within 0.1°C in approximately 15 min. This time is short relative to the total time of the experiments of ~ 5 days.

Figure 2 shows the deformation history applied to the sample following Struik's¹ protocol for physical ageing experiments. Successive deformations were applied at ageing times which doubled with each test, i.e. $t_c = 30$ min, 60 min, 120 min, etc. The duration t' of the deformation, prior to twisting back to the undeformed state, was varied so that the ratio t'/t_c was constant and equal to 0.10 throughout the ageing experiment. Note that the finite quench time of 15 min confounds the definition of ageing time, t_c . Here we have taken t_c defined with respect to the midpoint of the quench process, i.e. $7\frac{1}{2}$ min after the temperature baths were switched. Experiments were conducted at four deformation levels, $\gamma = 0.0025, 0.01, 0.03$ and 0.05 . Torque and volume change were monitored for $5\frac{1}{3}$ days (4.6×10^5 s) for each of these.

RESULTS AND DISCUSSION

Figure 3 shows the ageing responses of the epoxy glass at each deformation level as double logarithmic plots of torsional modulus *versus* time at the different ageing times after the quench. Here the time for each twist is defined as starting at the midpoint of the twist process which occurs over a short time, $t_1 \approx 0.5$ s. *Figure 3a* illustrates

* Jeffamine is an amine-terminated poly(propylene oxide) manufactured by Texaco Chemicals. Certain commercial materials and equipment are identified in this article to specify the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the materials and equipment identified are necessarily the best available for the purpose

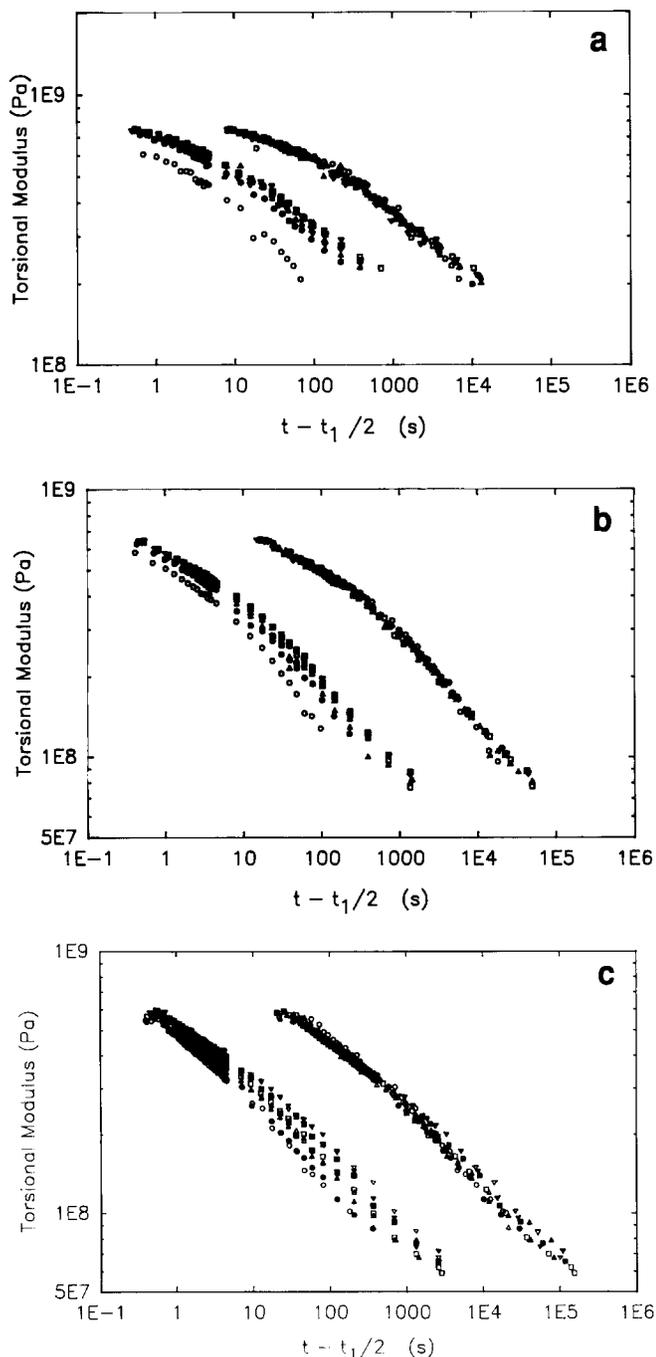


Figure 3 Torque response for DGEBA/D400 glass in single step stress relaxation experiment at strains of (a) $\gamma = 0.01$, (b) $\gamma = 0.003$ and (c) $\gamma = 0.05$ and at different ageing times after a quench from 44 to 33.5°C: $t_e = 1350$ s (\circ); 3150 s (\bullet); 6750 s (Δ); 13950 s (\blacktriangle); 28350 s (\square); 57150 s (\blacksquare); 114750 s (∇); 229950 s (\blacktriangledown). Points at the far right are shifted by a factor of 100 along the time axis and show the time-ageing time superposition of the data

that the torque response at a deformation of 0.010 follows the typical ageing behaviour, i.e. the viscoelastic curves move towards longer times as the ageing time increases and a time-ageing time superposition can be used to create a single reduced curve. Here, for better visibility, the master curve is shifted to longer times by a factor of 100. At a strain of 0.030 the viscoelastic curves do not shift as much with increased ageing time, as shown in Figure 3b. At a strain of 0.05 the shifts are smaller still, as seen in Figure 3c. (Again the master curve is shifted by a factor of 100.) This latter response is the signature of erasure of ageing or rejuvenation of the glass, in

concurrence with Struik's observations that $d \log a_{te} / d \log t_e$ decreases as stress or deformation increases. In the following discussion, however, we arrive at an interpretation that differs from Struik's.

Although a comparison of the results from Figure 3a-3c suggests that large strains slow the evolution of the mechanical properties after a quench, Figure 4, a double logarithmic plot of the shift factor a_{te} versus ageing time t_e , suggests that mechanical properties cease evolving at approximately the same equilibration time, $t^* = 10^4$ s, regardless of the strain (up to 5%) used in determining the torque relaxation. The fact that t^* is independent of the strain, within the experimental error, is in general agreement with the work of Lee and McKenna^{5,17,18}, and we also obtain a value of t^* similar to theirs for this D400 epoxy at this temperature. Note that after t^* , mechanical properties continue to evolve very slowly, also in agreement with Lee and McKenna. As they observed, before t^* the mechanical relaxation after small strains evolves further and more rapidly than those resulting from large strains; however, the mechanical properties always 'equilibrate' at the same ageing time t^* for a given temperature. This suggests that large strains do not move the sample back towards the newly quenched state, since we would then expect t^* to increase as the strain increases. This is true even though we have both the signature of rejuvenation, i.e. that $d \log a_{te} / d \log t_e$ decreases with increasing strain, and we are well into the non-linear viscoelastic range as evidenced by the fact that the relaxation moduli depicted in Figure 3a-3c either shift to shorter times or decrease as the strain increases.

As demonstrated previously^{21,22}, torsional deformations on this epoxy, equilibrated and tested near to the conventionally defined T_g , induce expansions that recover to zero on a time-scale of minutes. Struik's rejuvenation hypothesis suggests that the volume evolution following a quench, such as that illustrated in Figure 1b curve B, should be delayed, shifted up or to the right, by the large torsional deformations. Since deformations of 1, 3 and 5% were sufficient to display the signature of rejuvenation, i.e. smaller shift factors at larger strains prior to t^* , we expect the same magnitudes of strain to be sufficient to display the change in the volume recovery response, if such a change occurs.

Figure 5 illustrates the effects of sequentially imposed

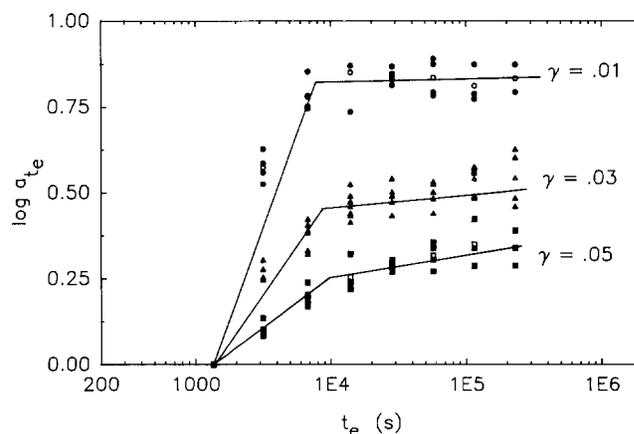


Figure 4 $\log a_{te}$ versus t_e for DGEBA/D400 glass aged at 33.5°C at the strains indicated. Open symbols represent averages from the data represented by the filled symbols

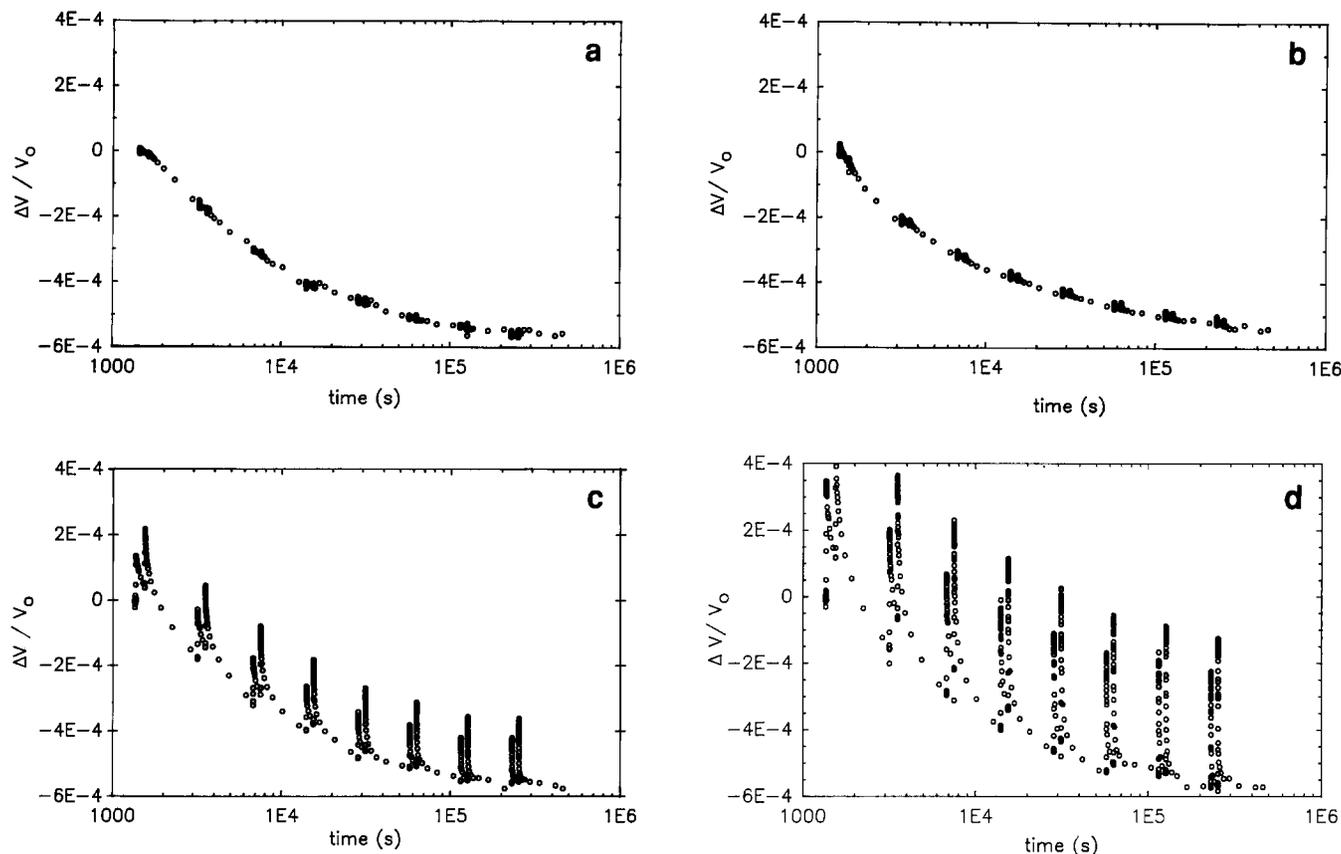


Figure 5 Volume recovery for DGEBA/D400 glass after a quench from 44.5 to 33.5°C. (a) $\gamma = 0.0025$; (b) $\gamma = 0.01$; (c) $\gamma = 0.03$; (d) $\gamma = 0.05$

(see Figure 2) strains on the volume evolution following a quench from 44 to 33.5°C. Figure 5a, with 0.25% strain, shows the baseline kinetics for the volume recovery, as torsions of this small magnitude have negligible effects on volume. At higher strains, in Figure 5b–5d, the curves consist of two components: the slow volume recovery from the quench and the expansions from each twist and untwist which appear as spikes in the baseline, since the volume recovers from the torsion much more rapidly than from the quench. At 3 and 5% strains, the momentary expansions become quite large, and their magnitudes attain a significant fraction of the total volume change from the recovery after the quench. The rapid expansions, however, do not measurably alter the underlying contraction or volume recovery due to the thermal history, in direct contradiction to rejuvenation. The fact that the kinetics of volume recovery from torsionally induced volume changes is more rapid than those from the thermal quench suggests that different mechanisms are involved in the two processes.

Figure 6 shows the mechanical volume recovery data at different ageing times. Unlike the torque relaxation responses, the mechanical volume recovery response taken at different ageing times cannot be superposed by horizontal shifts along the time axis. In fact, as ageing proceeds, the magnitude of the volume change induced by the torque decreases at short times and increases at longer times which results in the curves for different ageing times crossing over one another. It is readily seen from these data that the mechanical volume recovery time is much shorter than that due to the quench, since zero is recovered within much less than the $> 4.5 \times 10^5$ s required for the thermal volume recovery (compare

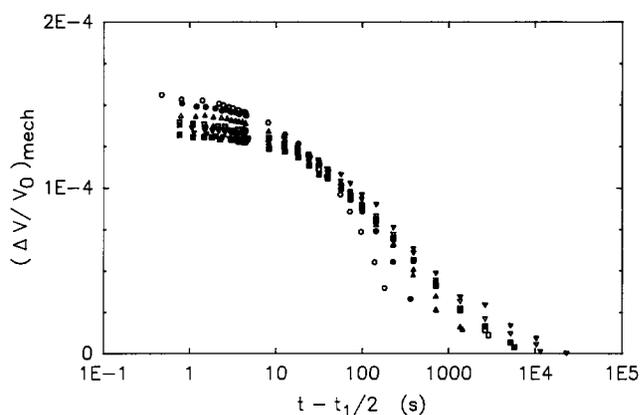


Figure 6 Volume recovery after each twist step at $\gamma = 0.03$ at different times after a quench from 44 to 33.5°C. Symbols as in Figure 3

Figure 6 with Figure 5a–5d). Additionally, where the torque relaxation responses have virtually ceased to evolve beyond $t^* \approx 10^4$ s (Figure 3a–3c, Figure 4), the mechanical volume recovery curves appear to continue to change for the duration of the experiments. This may be related to the extremely gradual evolution of the torque response after t^* and to the fact that the thermal volume recovery continues to proceed for times which are ~ 15 times longer than t^* .

This latter point may be important in the following sense. We observe, as did Lee and McKenna^{5,17,18}, that after a quench the mechanical properties virtually cease to change at a characteristic time t^* . In this study, however, we have been able to show that well beyond the mechanically (torque) determined t^* , the thermal volume recovery is continuing to evolve and the

Table 1 Time scales relevant to physical ageing (DGEBA/D400 glass at 33.5°C)

Response	Time scale (s)
Mechanical	
Torque relaxation	10^2 – 10^3
Mechanical volume recovery	10^2 – 10^3
Physical ageing	
Thermal volume recovery	$> 10^5$
Torque response evolution	$\sim 10^4$
Mechanical volume recovery evolution	$> 10^5$

mechanically (torsionally) induced volume recovery response is also continuing to change. *Table 1* compares five different time scales which are relevant to the processes being studied. The apparent differences in kinetics for the torque relaxation, mechanical volume recovery and thermal volume recovery are surprising and suggest areas for future research.

It is clear from these experiments that the mechanical volume recovery occurs over a time-scale which is considerably shorter than that for the thermal volume recovery. Furthermore, it is obvious that the time-scales associated with the evolution of the torque and mechanical volume responses are different, the latter apparently following the thermal volume recovery while the former undergoes a dramatic change in rate of evolution at t^* which is a much shorter time-scale. These results are new. We have also stated that the torque relaxation time-scale appears to be much shorter than the thermal volume recovery time-scale. This result contradicts the interpretation given by Bero and Plazek²³ for a different epoxy system and based upon a large vertical shift in the volumetric retardation spectrum when it was superimposed on the torsionally determined retardation spectrum. This is an area which requires further analysis.

CONCLUSIONS

Several important points emerge from our torsional dilatometry study, especially in light of the rejuvenation question. First, the time t^* for mechanical properties to equilibrate is independent of the magnitude of the strain and remains constant for a given temperature, in agreement with Lee and McKenna's^{17,18} creep tests. However, in agreement with Struik¹, we do observe greater and more rapid evolution of the torque relaxation response at small strains. Though the signature of rejuvenation is apparent in the mechanical response immediately after a quench, we observe that t^* , the equilibration time, does not change. Further, the thermally-induced volume recovery kinetics do not change when the glass is subjected to large mechanical stimuli (strains), as evidenced by the fact that the baseline underlying the volume recovery is independent of the magnitude of the applied intermittent strain. We emphasize that since the change in total volume is a direct measure of the global thermodynamics, our studies also refute a redistribution of free volume which should be reflected in the volume recovery kinetics. The fact that both t^* and the baseline volume recovery response are invariant with deformation magnitude strongly supports the contention that mechanical stimuli do not change the underlying thermodynamic state (structure) of the glass, i.e. rejuvenation does not occur. Other reasons for the differences in ageing time shift factors between large and

small deformations need to be provided. Phenomenologically, Lee and McKenna^{17,18} simply noted that the large deformation response of the glass is influenced less by the volume recovery than is the small deformation response. There is currently no microscopic theory to explain this result.

In addition to the major point of this paper, i.e. that direct volumetric measurements do not support the concept that large mechanical stimuli erase prior ageing or rejuvenate the glass, we also have discovered that there are several distinct time-scales which characterize the physical ageing phenomenon. First, there are mechanical response time-scales, i.e. the torque and volume recovery behaviour after a mechanical deformation. These occurred on a time-scale of 10^2 – 10^3 s at the testing temperature of 33.5°C with this glass. Second, there is a thermal volume recovery time-scale which is greater than 10^5 s at the temperature studied here. Third, there are the mechanical response evolution time-scales for both the torque and mechanical volume recovery responses after the quench. We found that an apparent t^* at which the torque relaxation had virtually ceased to evolve was of the order of 10^4 s while the mechanical volume recovery response was still evolving at the longest ageing times studied, i.e. $> 10^5$ s. Understanding the basis for the differences among these time-scales requires further research.

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Note added in proof

In recent work, G'Sell and McKenna²⁴ have found that the t^* determined from yield stress measurements during ageing of the same epoxy glass is greater than that obtained from the viscoelastic measurements reported here or by Lee and McKenna⁵.