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The τ-effective paradox: new measurements towards a resolution

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Abstract

New volume recovery measurements have been made on an epoxy glass for temperature down- and up-jumps from 1.0 to 4.0 K to investigate the τ-effective paradox. Due to the sensitivity of the measurements and to the fact that data points are obtained linearly in time, we are able to accurately measure the effective relaxation time at much smaller departures from equilibrium than those examined originally by Kovacs and subsequently by other researchers. The paradox is observed for the largest (2.0 and 4.0 K) up-jumps performed at the highest aging temperature. The magnitude of the expansion gap disappears as the departure from equilibrium approaches zero indicating a resolution of the paradox.

Keywords: Structural recovery; Volume recovery; Glass

1. Introduction

Kovacs wrote a seminal paper in 1963 reporting volume recovery after temperature up- and down-jumps from equilibrium density into the glassy state [1]. The experimental results show that the volume recovery response is non-exponential indicating a breadth of relaxation times. In addition, comparison of the up- and down-jumps to the same aging temperature show that the response is asymmetric, with the volume changes autoaccelarating with the logarithm of time for up-jumps as the material approaches equilibrium due to the increasing volume which results in increased mobility, whereas an autoretarded response is observed after down-jumps due to the fact that volume is decreasing with time.

Kovacs [1] analyzed the so-called asymmetry of approach data by evaluating an effective relaxation time, τ-effective or τ_{eff}:

$$\tau_{\mathrm{eff}}^{-1} = -\frac{1}{\delta}\left(\frac{\mathrm{d}\delta}{\mathrm{d}t}\right) \tag{1}$$

where δ denotes the relative departure from equilibrium,

$$\delta = \frac{v(t) - v_\infty}{v_\infty} \tag{2}$$

and $v(t)$ is the instantaneous volume and v_∞ is the volume at equilibrium. For a hypothetical exponential linear relaxation process in which $\delta = \delta_0 \exp(-t/\tau)$, τ_{eff} equals the relaxation time τ and is a constant which depends on the aging temperature. For Kovacs' volume recovery data, on the other hand, τ_{eff} evolves as the material approaches equilibrium due to both the relaxation time distribution and its evolution with volume (i.e. due to the non-exponentiality and non-linearity of the process). Kovacs' original τ-effective plot is shown in Fig. 1 in which the negative logarithm of τ_{eff} is plotted versus the departure from equilibrium δ for poly(vinyl acetate), PVAc. The responses for different down-jumps and up-jumps made to the same final temperature are plotted with down-jump responses at positive δ on the right hand side of the plot and up-jump responses at negative δ on the left. It is clear that the down-jump or contraction curves converge to the same point for a given aging temperature as δ approaches zero, i.e. near the equilibrium state. However, the effective relaxation time for up-jumps depends on the initial temperature T_0 even near equilibrium for a given aging temperature such that the up-jump or expansion curves neither converge nor do they approach the same limit at

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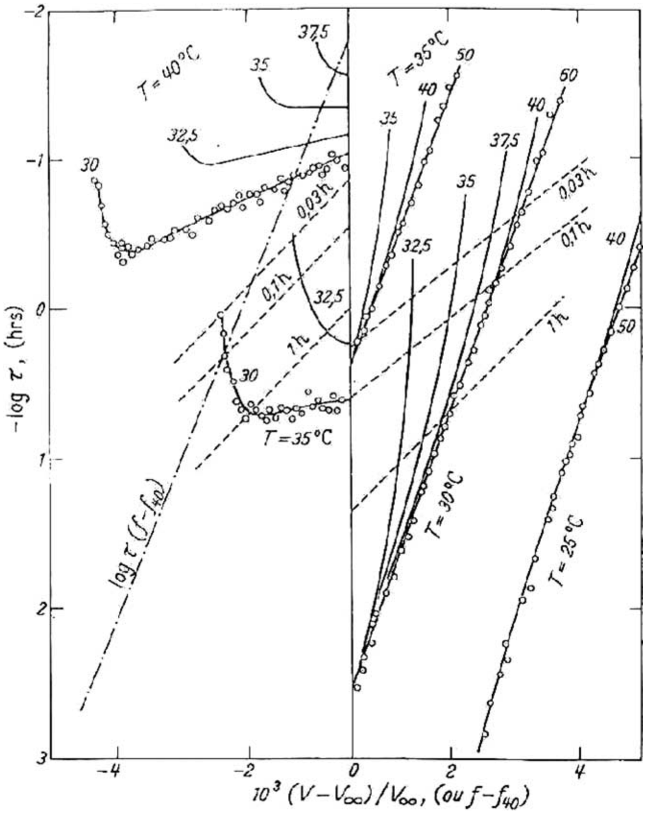

Fig. 1. Original τ-effective plot from Kovacs [1] for poly(vinyl acetate). The values of the final aging temperature T and initial temperature from which temperature jumps are made are indicated.

equilibrium as do the down-jumps. These results, known as the expansion gap and τ-effective paradox, respectively, are anomalous because, at equilibrium, the prior history of the sample should have no effect on the response and, therefore, τ_{eff} at $\delta=0$ is expected to be independent of thermal history.

Several authors have discussed this paradox in reviews concerning structural relaxation and the glass transition [2–4]. In addition, Struik [5] and McKenna et al. [6] individually reanalyzed the original volume recovery data of Kovacs. According to Struik [5], the existence of the τ_{eff} paradox is uncertain due to the noise in Kovacs' data, which Struik claims lead to errors in τ_{eff} of 20–30% at a δ of 5×10^{-4} increasing with decreasing δ, such that the error in τ_{eff} becomes infinite at $\delta=0$. The problem with Struik's analysis, as pointed out by McKenna et al. [6], is that Struik assumed that the errors were uncorrelated; i.e. that the error in the rate $\mathrm{d}\delta/\mathrm{d}t$ was directly related to the error in δ, in essence amplifying the error in τ_{eff}. However, the errors in neighboring data points are correlated reducing the error in the rate. McKenna et al. also evaluated not only the original published Kovacs' data set but also evaluated the unpublished volume recovery data obtained in Kovacs' laboratory on the same material. Due to the large number of repeat experiments at various temperatures, McKenna concludes that the volume recovery data of PVAc at 40 °C for the largest up-jumps (≥5.0 K) supports the original contention of Kovacs that an expansion gap and the apparent τ_{eff} paradox exist at least down to values of δ of 1.6×10^{-4}. For the smallest up-jumps at 40 °C (≤2.5 K), there was no expansion gap. At lower aging temperatures, McKenna et al. claim that the existence of an expansion gap is not unambiguously supported due to the greater uncertainty in the values of τ_{eff} which arises from a decreased correlation in the error between successive data points, and hence an increased error in the rate $\mathrm{d}\delta/\mathrm{d}t$. This decreased correlation in the error in the data is due to the fact that Kovacs' data was obtained logarithmically rather than linearly in time coupled with longer time scales to achieve equilibrium at lower aging temperatures. In another work [7], McKenna and co-workers performed small temperature jumps ranging from 0.7 K up-jumps to 5.3 K down-jumps to smaller values of δ than accessible in Kovacs' work (1×10^{-6}) and concluded that an expansion gap did exist for the up-jumps although all the curves appeared to come together as $\delta=0$ resolving the τ_{eff} paradox. However, to obtain τ_{eff} in that work, volume recovery data was fit to a KWW or similar function with the result that τ_{eff} approaches infinity at $\delta=0$ for all curves.

The expansion gap and τ_{eff} paradox are important because the phenomenon is not predicted by the most widely used empirical models of structural recovery, the Kovacs–Aklonis–Hutchinson–Ramos (KAHR) model [8] and the Tool–Narayanaswamy–Moynihan model [9–11]. A coupling model of structural recovery developed by Ngai and co-workers was able to predict the expansion gap [12], but it has been pointed out [13] that the model is inconsistent with Boltzmann superposition, and further work applying the model to structural recovery has not been performed. On the other hand, the thermoviscoelastic model of structural recovery developed by Caruther and co-workers [14] based on Coleman's thermodynamic theory, also known as rational mechanics [15,16], can reasonably describe Kovac's τ_{eff} data and the expansion gap at 40 °C without adjustable parameters [17]; however, it appears that the model predicts that the effective relaxation time tends toward infinity at equilibrium ($\delta=0$), in contrast to experimental observations, presumably because Caruthers and co-workers represented the time-dependent relaxation functions in their model by KWW stretched exponential functions.

The present work is aimed at examining the expansion gap and τ-effective paradox for small temperature jumps, of 4 K and less, and closer to equilibrium than achieved by Kovacs. The objective is to examine to what value of δ the expansion gap and τ-effective paradox exist since this knowledge is important for testing models of structural recovery. In part we are able to accomplish our aim of examining the behavior at smaller δ because we obtain our data linearly in time, as discussed in McKenna's reanalysis [6] of Kovacs' data. In addition, the short-time resolution and long-term stability of our volume measurements is better than Kovacs', as discussed below.

2. Experimental

2.1. Materials

The sample studied is an epoxy material: diglycidyl ether of bisphenol A (DER 332, DOW Chemical Company, with a reported average molecular weight of 356 g/mol) cured with a stoichiometric amount of amine-terminated poly(propylene oxide) (Jeffamine D230, Huntsman, with a functionality of four and a reported average molecular weight of 230 g/mol). The material was cured at 100 °C for 24 h under nitrogen atmosphere following the protocol of Lee and McKenna [18] in a cylindrical mold 1.3 cm outer diameter and 4.0 cm in length after first mixing the two components until clear at 55 °C and then degassing for 60 min in a vacuum oven at room temperature. After curing, the sample was allowed to cool slowly to room temperature overnight to minimize residual stresses. A 0.3 cm hole was then drilled along the axis of the cylindrical sample to improve heat transfer. The final mass of the sample is 6.51 g. The density of the cured sample at 22 °C is 1.157 g/cm^3, as found by weighing the sample in air and in water. The dilatometric glass transition temperature was found to be 75.5 °C when cooled at a rate of 0.1 °C/min (see later). The sample is chemically stable throughout the course of the experiments; cooling runs completed before and after all isothermal experiments gave the same value of T_g to within 0.1 K.

2.2. Dilatometric studies

The capillary dilatometer used in these experiments is based on the design of Plazek [19]. The dilatometer consists of approximately 5 cm of 4.68 mm diameter precision bore Pyrex capillary tubing connected to a thin-walled, removable stainless steel bulb via a Kovar glass to metal joint. The bulb is threaded in place and sealed by compression of a vyton o-ring. The sample is placed in the stainless steel bulb and mercury is used as the confining liquid. In order to collect the data automatically, an aluminum float is placed on top of the mercury and attached to the core of a linear variable differential transformer (LVDT) as in work by other researchers [20]. The LVDT of the capillary dilatometer is connected to an analog digital converter to amplify the voltage signal. A computer records both the LVDT output voltage and also the bath temperature measured by a platinum resistance thermometer. Data points are obtained every 1.5 s with data acquisition being controlled with a program written using Labview™ software from National Instruments. To eliminate recurring vibrations, a filtering technique was used which is analogous to a low pass filter as described in previous work [21]. The resulting noise due to the electronics is better than $\pm 2\times 10^{-6}$ cm^3/g.

Temperature jumps ranged from 1.0 to 4.0 K in magnitude and were made by first equilibrating the sample in an oil bath maintained at a temperature T_0 and then transferring the dilatometer to an oil bath maintained at an aging temperature T_a of either 75 or 77 °C. The values of T_0 and T_a were within 0.05 K of the nominal (integer) values desired based on measurements using a high-accuracy reference thermometer with a reported accuracy of 0.0013 K (Black Stack model 1560, Hart Scientific) for all runs except for two (one of the $77 \rightarrow 75$ °C runs and one of the $76 \rightarrow 77$ °C runs) in which both T_0 and T_a were 0.35 K low (shifting the equilibrium relaxation time by approximately 0.18 decades which is within the reproducibility of the measurements). In the Sections 3 and 4 to follow, integer values are used for T_0 and T_a although as discussed above the accuracy of the absolute temperature is in most cases better than ± 0.05 K. We note that stabilization of the sample at 73 °C took 20 days, and hence, 2.0 K up-jumps were the largest up-jumps made for the aging temperature of 75 °C.

The temperature baths used are Hart Scientific model 6025 and are filled with Rhodorsil silicone fluid from Chemsil Inc. The stability of the bath temperature is $\pm$ 0.005 K based on the product specification. The standard deviation of the mean temperature over a period of three days is 0.008 K; better temperature stability is observed over shorter periods of time. The long-term accuracy in our experiments due to temperature fluctuations in the bath is estimated to be better than 1.0×10^{-5} cm^3/g, whereas that in Kovacs' experiments was estimated [6] to be 1.7×10^{-5} cm^3/cm^3 $\approx 1.5\times 10^{-5}$ cm^3/g and that in McKenna's experiments was 1.5×10^{-5} cm^3/cm^3 $\approx 1.3\times 10^{-5}$ cm^3/g. However, as alluded to previously, the largest gain in accuracy in our work comes from taking data linearly in time (as opposed to logarithmically as in Kovacs' work) due to correlation in errors. In addition, short time experiments (on the order of several hours) have noise levels of $\pm 2\times 10^{-6}$ cm^3/g as mentioned above.

The transfer time between baths for temperature jumps is approximately 150 s and the thermal equilibration time is about 200 s to reach the aging temperature within 0.1 K and about 500 s to reach temperature within 0.01 K. Time zero for our temperature jump experiments is the time at which the bath transfer is initiated as in our previous work [20].

3. Results

The specific volume versus temperature curve for the sample was obtained on cooling at 0.1 K/min and is shown in Fig. 2. The thermal expansion coefficients, $\alpha = 1/V(\mathrm{d}V/\mathrm{d}T)$, are found to be 6.4×10^{-4} and 2.6×10^{-4} K^{-1} in the liquid and glassy regions, respectively. The difference in the thermal expansivities $\Delta\alpha$ at the glass transition temperature is 3.8×10^{-4} K^{-1}. The glass transition temperature is determined by the intersection of the extrapolated glassy and liquid lines and is 75.5 °C at 0.1 K/min cooling.

Volume recovery data for the up- and down-jumps from

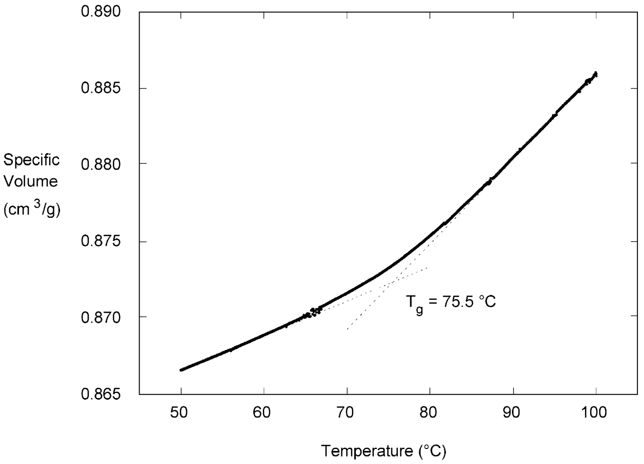

Fig. 2. Volume as a function of temperature obtained dilatometrically during cooling at 0.1 K/min.

T_0 to 75 °C are shown in Fig. 3, and analogous asymmetry of approach experiments at 77 °C are shown in Fig. 4. For both figures, the relative departure from equilibrium δ is plotted against the logarithm of time. Reproducibility of the data is shown by the two curves plotted for the 77–75 °C down-jump and by the two curves obtained for the 76–77 °C up-jump. The initial departure from equilibrium for a perfect quench δ_0 is given by $\Delta\alpha\Delta T$, where ΔT is the magnitude of the temperature jump. The magnitude of δ_0 for 1.0, 2.0, and 4.0 K jumps is 3.8×10^{-4}, 7.6×10^{-4} and, 1.52×10^{-3}, respectively. Comparing these values to the data in Figs. 3 and 4, it is clear that although the departure from equilibrium at the shortest times increases with increasing T_0, the values are lower than those calculated above assuming a perfect quench due to the volume relaxation that occurs during cooling and during the first 200 s before thermal equilibrium is obtained. This is especially true for the down-jumps because more volume relaxation occurs at the shortest times due to the higher mobility giving asymmetry at the shortest times. The isotherms approach equilibrium asymptotically and level off at long times as equilibrium is reached as expected. The contraction curves at positive δ show higher rates of recovery at the shortest times and show an autoretarded response on the logarithmic time scale, whereas the expansion curves show a slow response at earlier times, but the mobility increases with time as the volume increases leading to autocatalytic behavior on the logarithmic time scale.

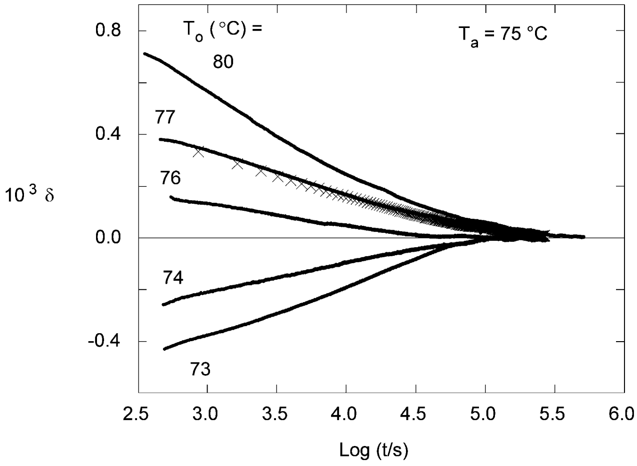

Fig. 3. Volume recovery at 75 °C for various down-jumps and up-jumps showing the asymmetry of approach. The values of the initial temperatures (T_0) from which each jump was made are indicated. Reproducibility of the response is shown by the two data sets for $T_0 = 77$ °C.

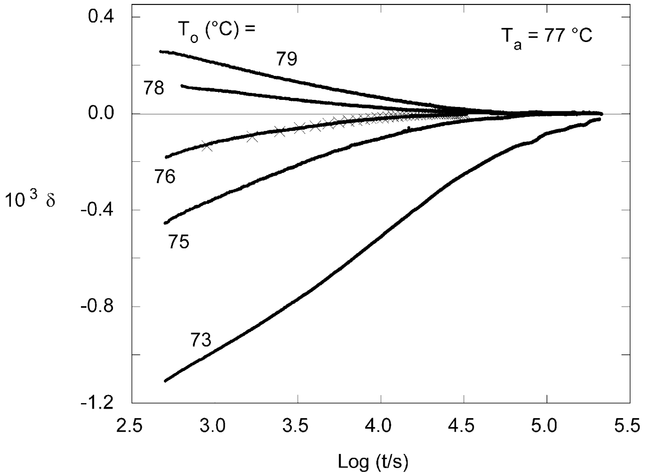

Fig. 4. Volume recovery at 77 °C for various down-jumps and up-jumps showing the asymmetry of approach. The values of the initial temperatures (T_0) from which each jump was made are indicated. Reproducibility of the response is shown by the two data sets for $T_0 = 76$ °C.

Values of τ-effective (τ_{eff}) as a function of aging time are calculated from the volume recovery data shown in Figs. 3 and 4 in several ways. In one case, τ_{eff} is calculated from Eq. (1) using an average slope in $\mathrm{d}\delta/\mathrm{d}t$ and an average value of δ, with both averages taken from a time t to a time $1.05t$, i.e. the data is averaged over 0.02 logarithmic units in time. Figs. 5 and 6 show the logarithm of τ_{eff} obtained in this way as a function of δ for jumps to 75 and 77 °C, respectively. For the aging temperature of 75 °C, τ_{eff} values from the expansion and the contraction curves merge as δ approaches zero at approximately the same value of $-\log \tau_{\mathrm{eff}} = -4.5 \pm 0.3$ (obtained by linear extrapolation of the data between $0 \leq |\delta| \leq 0.05$) and no expansion gap is observed. On the other hand, for aging at 77 °C, τ_{eff} merges at $\delta = 0$ to a value of $-\log \tau_{\mathrm{eff}} = -4.1 \pm 0.2$ only for the down-jumps and the smallest up-jump (obtained by linear extrapolation of the data between $0 \leq |\delta| \leq 0.05$). The 2.0 and 4.0 K up-jumps to 77 °C seem to show the expansion gap, with the 4.0 K jump being most obvious. The slightly larger standard deviation in the value of τ_{eff} at equilibrium for $T_a = 75$ °C is due to the longer aging times at this temperature, which are on the order of 1–3 days to achieve equilibrium (compared to 8 h to one day for most of the jumps to 77 °C), leading to increased noise at long times and small δ due to long-term temperature fluctuations in the bath. Kovacs' data also showed increased scatter in the values of τ_{eff} at equilibrium for the lower aging

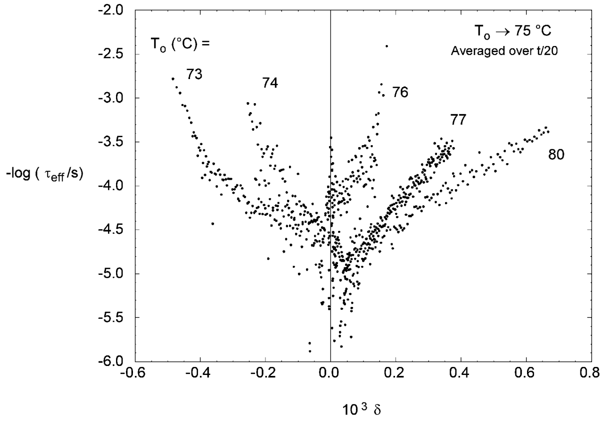

Fig. 5. τ-effective plot for aging at 75 °C. The values of τ_{eff} were determined from the slope ($d\delta/dt$) and average δ value obtained from time t to $1.05t$ (i.e. over a logarithmic time interval of 0.02) for the volume recovery curves shown in Fig. 3. The values of the initial temperatures (T_0) from which each jump was made are indicated. No expansion gap is observed.

temperatures although in Kovacs' case the problem was amplified because data was collected logarithmically rather than linearly in time.

Another approach for examining the τ_{eff} paradox which was used by McKenna et al. [6] is to determine the value of τ_{eff} from a plot of ln δ versus t over various ranges of $|\delta|$ in order to observe how fast the expansion gap and τ_{eff} paradox disappear as δ approaches zero. A series of four plots of τ_{eff} versus T_0 for various ranges of δ from 3.3×10^{-4} to 7.5×10^{-6} are shown in Figs. 7 and 8 for the data taken at 75 and 77 °C, respectively. For the 75 °C data, there is no obvious expansion gap over any of the ranges of δ examined; in addition, it is clear that the value of $-\log\tau_{\mathrm{eff}}$ decreases as the range of $|\delta|$ gets closer to equilibrium and that the values appear to show less scatter for the smallest δ range, $6.1\times10^{-6}\leq|\delta|\leq1.7\times10^{-5}$. On the other hand, the data at 77 °C show what appears to be a sigmoidal dependence on T_0 for the largest δ ranges examined, with the largest (2.0 and 4.0 K) up-jumps showing an expansion gap down to a δ of 1.7×10^{-5}. For the smallest δ range, the gap disappears for the 2.0 K up-jump; data is unavailable in this range to determine whether the gap is still present for the 4.0 K jump. The sigmoidal shape of $\log(\tau_{\mathrm{eff}})$ versus T_0 was also observed by McKenna and co-workers in their reanalysis of Kovacs' data set. However, in that work, it was found that only Kovacs' data at 40 °C unambiguously supported the existence of the expansion gap, and then only down to δ values of 1.6×10^{-4} for up-jumps greater than 5 K. On the other hand, we observe the expansion gap for smaller up-jumps and much closer to equilibrium, i.e. for up-jumps of 2.0 and 4.0 K for the range $1.7\times10^{-5}\leq|\delta|\leq4.5\times10^{-5}$ for our highest aging temperature. However, as in the work by McKenna and co-workers [7], in McKenna's reanalysis of Kovacs' data [6], and as inferred by Struik [5] in his reanalysis of Kovacs' data, the τ-effective paradox and the

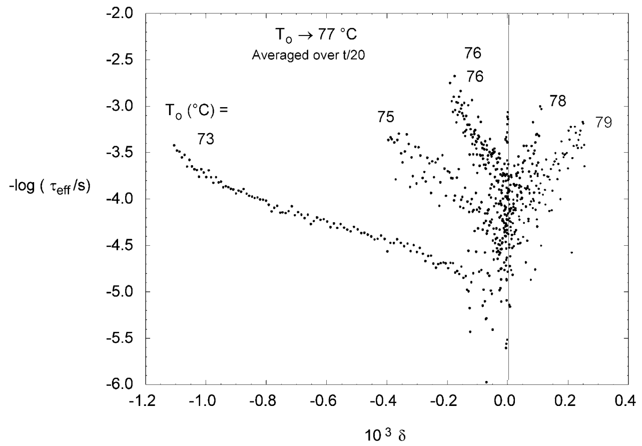

Fig. 6. τ-effective plot for aging at 77 °C. The values of τ_{eff} were determined from the slope ($d\delta/dt$) and average δ value obtained from time t to $1.05t$ (i.e. over a logarithmic time interval of 0.02) for the volume recovery curves shown in Fig. 4. The values of the initial temperatures (T_0) from which each jump was made are indicated. An expansion gap is observed for the largest up-jumps.

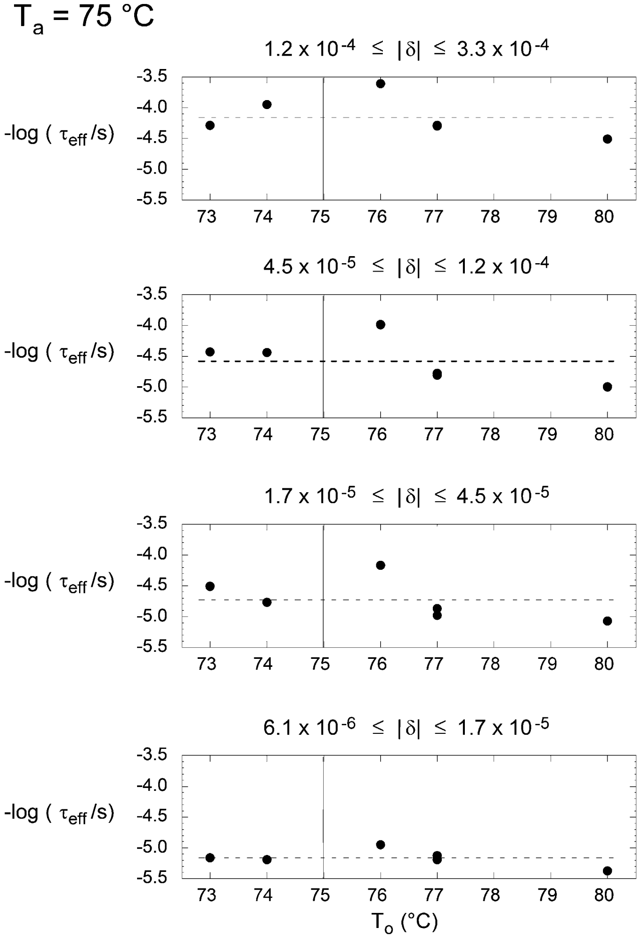

Fig. 7. Plots of $-\log(\tau_{\mathrm{eff}})$ versus the initial temperature T_0 for volume recovery at 75 °C. The values of τ_{eff} were determined over the range of $|\delta|$ indicated above each graph. The dashed lines indicate the trend in the data and show that no expansion gap is observed.

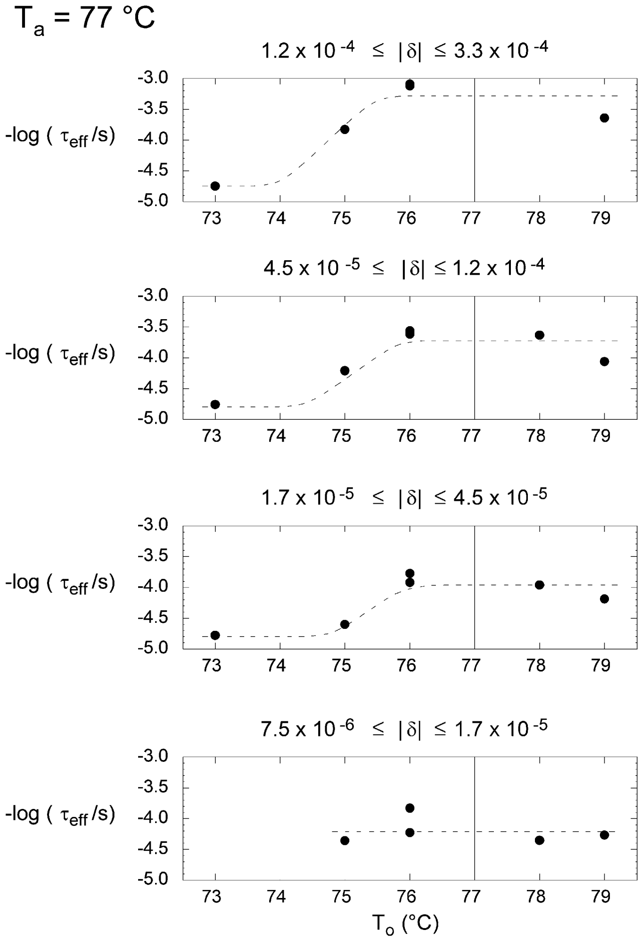

Fig. 8. Plots of $-\log(\tau_{\text{eff}})$ versus the initial temperature T_0 for volume recovery at 77 °C. The values of τ_{eff} were determined over the range of $|\delta|$ indicated above each graph. The dashed lines indicate the trend in the data and show that the expansion gap is observed for the 2.0 and 4.0 K up-jumps but disappears for the smallest range of $|\delta|$.

expansion gap appear to resolve themselves and disappear as $|\delta|$ approaches zero.

4. Discussion

Although the τ-effective paradox is resolved at the smallest δ values examined, we emphasize that the paradox itself is real, i.e. that the effective characteristic relaxation times for up-jumps and down-jumps are not the same as one approaches equilibrium. The expansion gap was observed in the present work for 2.0 and 4.0 K up-jumps but not for the 1.0 K up-jump at 77 °C; similarly in McKenna's reanalysis of Kovacs' work, the expansion gap was confirmed for up-jumps of 5 K and greater at the highest aging temperature and not for the smallest 2.5 K up-jump. The implication is that the non-linearity of the response plays a role in the expansion gap. The fact that a gap has not been observed for down-jump experiments, however, indicates that the situation is more complex than simply being a matter of linearity or lack thereof.

The expansion gap exists even at very small $|\delta|$ near equilibrium; this indicates that the relaxation time, or its distribution, depends on thermal history [17], in addition to depending nominally on the temperature and volume (or fictive temperature) of the glass as assumed by the KAHR and TNM models [8–11] of structural recovery. Other recent work [22] in our laboratory using a unique temperature perturbation experiment [21] indicates that the relaxation time also depends on thermal history. This is consistent with recent work investigating volume recovery after plasticizer jumps from the laboratory of McKenna and co-workers [23, 24] that indicates that the plasticizer/temperature history affects relaxation times.

Microscopic pictures of the glassy state, including the landscape picture of glass-formers [25–29], are also consistent with the conclusion that the relaxation time depends on thermal history. In the landscape paradigm, the material can explore many potential energy wells when it is in the equilibrium state above T_g where there is sufficient mobility and energy. In the glass where mobility is lowered due to high packing, however, the material gets 'stuck' in potential wells which do not have the lowest free energy. Within this framework, it is easy to visualize how the same macroscopic volume, arrived at via different paths, could give rise to different degrees of frustration at the local level. The result could very well be that the characteristic relaxation time for macroscopic volume recovery would depend on thermal history rather than simply on the instantaneous state of the material, a fundamental assumption of the KAHR and TNM models of structural recovery [8–11]. A similar argument can be made concerning the dynamic heterogeneities [30–34] that have been recently observed in glass-forming systems. At the nanoscale, different nanoregions appear to have differing mobilities and these will affect the observed macroscopic relaxation; it is quite possible that the nanoscale dynamic heterogeneity in the glass depends on path and, hence, macroscopic relaxation times would also be expected to be path-dependent.

5. Conclusions

Volume recovery after small temperature jumps, ranging from 1.0 to 4.0 K, has been studied for an epoxy material at two aging temperatures. The results after temperature up-jump and down-jump experiments are consistent with those of Kovacs [1] showing auto-acceleration and auto-retardation, respectively. The τ_{eff} plots show that at the lowest aging temperature, no expansion gap or τ_{eff} paradox exists. However, at the higher aging temperature, we observe a sigmoidal shape of $\log(\tau_{\text{eff}})$ versus T_0 with the expansion gap existing for up-jumps of 2.0 and 4.0 K down to a $|\delta|$ range of $1.7\times10^{-5}\leq|\delta|\leq4.5\times10^{-5}$. For smaller ranges of $|\delta|$, the expansion gap disappeared and the τ_{eff} paradox was resolved. The results are consistent with McKenna's reanalysis [6] of Kovacs' data [1], but show the existence of the expansion gap for smaller temperature jumps and to smaller δ values due to the higher resolution of our volume measurements, coupled with our taking the data linearly in time. The results are important for testing models of structural recovery.

Acknowledgements

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References

[1] Kovacs AJ. Adv Polym Sci 1963;3(3):394–597.
[2] Angel CA, Ngai KL, McKenna GB, McMillan PF, Martin SW. J Appl Phys 2000;88(6):3113–57.
[3] McKenna GB. Glass formation and glassy behavior. In: Comprehensive polymer science, vol. 2 p. 311–62.
[4] Tant MR, Wilkes GL. Polym Eng Sci 1981;21(14):874–95.
[5] Struik LCE. Polymer 1997;38(18):4677–85.
[6] McKenna GB, Vangel MG, Rukhin AL, Leigh SD, Lotz B, Straupe C. Polymer 1999;40:5183–205.
[7] McKenna GB, Leterrier Y, Schultheisz CR. Polym Eng Sci 1995; 35(5):403–10.
[8] Kovacs AJ, Aklonis JJ, Hutchinson JM, Ramos AR. J Polym Sci, Polym Phys Ed 1979;17:1097–162.
[9] Tool AQ. J Am Ceram Soc 1946;37:73–90.
[10] Moynihan CT, Macedo PB, Montrose CJ, Gupta PK, DeBolt MA, Dill JF, et al. Ann NY Acad Sci 1976;279:15–35.
[11] Narayanaswamy OS. J Am Ceram Soc 1971;54:491–8.
[12] Rendell RW, Ngai KL, Plazek DJ. J Non-Cryst Solids 1991;131–133: 442–50.
[13] Hodge IM. J Non-Cryst Solids 1994;169:211–66.
[14] Lustig SR, Shay Jr RM, Caruthers JM. J Rheol 1996;40(1):69.
[15] Coleman BD. Arch Ration Mech Anal 1964;17:1.
[16] Coleman BD. Arch Ration Mech Anal 1964;17:230.
[17] McWilliams DS. PhD Thesis, Purdue University; 1995
[18] Lee A, McKenna GB. Polymer 1988;29:1812–7.
[19] Bero CA, Plazek DJ. J Polym Sci: Part B: Polym Phys 1991;29:39–47.
[20] Duran RS, McKenna GB. J Rheol 1990;34:813–39.
[21] Bernazzani P, Simon SL. J Non-Cryst Solids 2002;307–310:470–80.
[22] Bernazzani P, Simon SL. In preparation
[23] Alcoutlabi M, Briatico-Vangosa F, McKenna GB. J Polym Sci Part B-Polym Phys 2002;40(18):2050–64.
[24] Zheng Y, McKenna GB. Macromolecules 2003;36(7):2387–96.
[25] Stillinger FH, Weber TA. Phys Rev A 1982;25(2):978–89.
[26] Stillinger FH. Science 1995;267:1935–9.
[27] Stillinger FH, Debenedetti PG. J Chem Phys 2002;116(8):3353–61.
[28] Richert R, Angell CA. J Chem Phys 1998;108(21):9016–26.
[29] Lei YN, Cummins K, Lacks DJ. J Polym Sci Part B-Polym Phys 2003; 41(19):2302–6.
[30] Richert R. J Phys: Condens Matter 2002;14:R703–R38.
[31] Ediger M. Annu Rev Phys Chem 2000;51:990128.
[32] Glotzer SC. J Non-Cryst Solids 2000;274:342–55.
[33] Bohmer R. Phase Trans Part B 1999;65:211–31.
[34] Bohmer R. Curr Opin Solid State Mater Sci 1998;3:378–85.