Enthalpy Recovery and Its Relation to Shear Response in an Amine Cured DGEBA Epoxy

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KEYWORDS: Enthalpy relaxation; shear relaxation; epoxy

Abstract

A description of enthalpy recovery for an amine-cured, diglycidyl ether of bisphenol A (DGEBA) epoxy (Epon 828/ Jeffamine T403) was acquired through a series of experiments targeting the effects of the individual parameters: cooling rate, heating rate, aging temperature, and aging time. From these experiments, the peak temperature, T_p , and fictive temperature, T_f , were tracked as measures of the extent of structural relaxation. The KAHR formalism provides a standard for comparison to similar epoxies and was parametrized using the peak shift method. The resulting parameterization was then used to assess the relation between volumetric and shear relaxation. In particular, the KAHR model was used to predict volumetric relaxation time-temperature shift factors that are directly compared to measured time-temperature shift factors in shear. This unique methodology to assess equivalence between volumetric and shear relaxation shift factors, a key assumption in constitutive models based on rheological simplicity, further establishes the basis for the assumption of continuum assumptions of equivalency.

1. Introduction

Experiments designed to probe the “structural” or “physical” aging [1, 2] process typically involve three steps: 1) cooling at a rate q_1 from above T_g to an “aging temperature”, T_a , below T_g ; 2) holding at T_a for an “aging time”, t_a ; and 3) heating at a rate q_2 back to the start temperature above T_g . The material properties most commonly tracked are the volume and the enthalpy. The value of these quantities will return to their initial values after concluding the heating step, as the material returns to an equilibrium state (i.e., its history is “erased”). The detailed dynamics of the “relaxation” or “recovery” of the volume or enthalpy depends sensitively on the parameters mentioned above: T_a , t_a , q_1 , and q_2 . A number of models have been developed that package this complex aging process into differential equations. Naturally, each polymer glass needs to be characterized so that the mathematical models can be “populated” with materials specific parameters.

The primary goal of the present work is to provide a reliable data set of enthalpy recovery experiments from conventional cool/age/heat cycles for the epoxy of interest. The reliability of the data set is verified by demonstrating its consistency with the Kovacs, Aklonis, Hutchinson, Ramos (KAHR) model (discussed below) and by comparisons with previous studies of similar materials. More advanced model development relying on this data set is planned and will permit better prediction of material evolution during its life cycle and of the effect of physical aging on application performance.

These relaxation phenomena are for “bulk”, or volumetric, relaxation. A second goal of the present study is to compare the bulk and shear relaxation responses. To this end, the time-temperature shift factors from shear mastercurve construction are compared to predicted

values from the KAHR analysis. In this manner, it is shown that the bulk and shear relaxation timescales are equivalent over the range of temperatures studied in the enthalpic aging experiments. The equivalence of bulk and shear relaxation time scales has been observed in other experiments (see Grassia and D'Amore [3] and references therein); however, the use of the KAHR model in this analysis is a unique methodology to make this comparison.

The present work will examine an epoxy commonly used in aerospace applications [4]. The resin is a diglycidyl ether of bisphenol A (DGEBA) (Epon 828) and the curative is a polyether amine (Jeffamine T-403). This is an attractive epoxy for a number of reasons. It has simple, easily modeled reaction kinetics. It proceeds to full cure during typical manufacturing processing, and, consequently, there is little drift of properties due to additional post-processing cure. Finally, the reactants contain no proprietary accelerants that would be susceptible to supplier variation and potentially require redesigning the manufacturing process for changes in the formulation. Although this is a relatively well-characterized epoxy [5-7], studies of its physical aging are lacking.

Before introducing the technical details, a brief overview of this class of aging studies will be given. Although termed “enthalpy relaxation (or recovery)”, enthalpy is not directly measured. Instead, the rate of heat flow is tracked as the temperature is changed in a differential scanning calorimeter (DSC). The effect of physical aging is superimposed on the glassy to rubbery transition typical of un-aged materials. The characteristic signature seen on heating of an aged glass is an enthalpic peak in the DSC signal just above T_g . In particular, the peak becomes more pronounced with increased aging time; however, it is necessary to

disentangle the individual effects of cooling rate, heating rate, aging temperature, and aging time.

Fig. 1 schematically describes the thermal histories utilized in the present physical aging studies. Starting in the equilibrium state at position A with temperature T_0 , the material is cooled at rate q_1 through the glass transition to the aging temperature T_{a2} . At T_{a2} , the material is allowed to relax for the time, t_a , which determines how far the material departs, $\bar{\delta}_H$ $= (H_i - H(t))$, from its original structure. Here $H(t)$ is the enthalpy at time t and H_i is the enthalpy at the beginning of the aging cycle. After

isothermally aging, the material is rapidly cooled to T_1 and reheated through T_g at rate q_2 to measure the response. Rapidly cooling to T_1 prohibits any additional aging from taking place, and is performed so that there is a large linear region in the heat capacity response during the heating ramp which facilitates numerical analysis of the data.

At a fixed T_a , the rate that $\bar{\delta}_H$ increases depends on temperature in two ways. Consider temperature T_{a1} in the figure. Here, the temperature is only slightly below T_g so the material has relatively high mobility and will “quickly” approach the equilibrium state (the red dashed line in the figure); however, because the equilibrium line is only slightly below the un-aged state (point B), the driving force (the deviation from equilibrium) is small and the material does

Fig. 1 Schematic of cooling and heating cycles for short time, high temperature aging (AB), long time, low temperature (AC), and subsequent cooling/heating (AD).

not relax as quickly as one would expect from the high mobility alone. On the other hand, at T_{a2} , the molecular mobility is small and relaxation is slowed; however, the driving force is large (point C is far from equilibrium) and relaxation is faster than would otherwise be expected. Consequently, the temperature where most rapid aging is seen is expected to be near but slightly below T_g . Figures 5 and 6 in Montserrat [8] show an example of this behavior. Details of the analysis of these measurements will be discussed after specifics of the materials and experiments are presented.

A

2. Materials and Experimental Method

The subject of the present research is a polyetheramine cured epoxy, henceforth referred to as

B

Fig. 2. A) EPON 828 DGEBA resin molecule, $n=0.14$ B) Jeffamine T-403 curative molecule.

828/T403. The resin, EPON 828 (epoxide equivalent weight: 185-192g/eq., Momentive Corp.), is the diglycidyl ether of bisphenol A shown in Fig. 2.A. The curative molecule, Jeffamine T-403 (epoxide equivalent weight: 81g/eq., Huntsman Corp.) shown in Fig. 2.B, possesses three primary amine groups which react with the epoxide. A stoichiometric mix ratio of 100:43 parts by weight of resin to curative was selected to produce the thermoset material. Preheated resin and curative were mixed, poured into a preheated aluminum plaque and cured at 80°C for 24 hrs. Samples for DSC analysis were prepared from cured epoxy plaques with a 3/16" hole punch for use with Tzero hermetic aluminum pans (TA Instruments). Sample masses were 12±1mg. A TA Instruments Q2000 differential scanning calorimeter was employed, and ramp rates, aging times, and aging temperatures were varied.

Variation in cross-link density can cause differences in the glass transition temperature, T_g [9].

As a quality assurance, the glass transition temperature (taken, in this case, as the onset transition temperature upon heating when no structural relaxation is present) was measured for every batch by cooling and heating, both at a rate of

10°C/min. All batches measured within 2°C of each other

in this analysis. Additionally, the peak temperature for a known thermal history (cooled from equilibrium at 1C/min and referred to as the “annealed” history), was measured for each batch at a heating rate of 10°C/min. All batches measured within 1°C of each other in this analysis. Batches which did not satisfy both criteria were discarded. These elimination criteria experiments were performed after

Table 1. List of experimental variables altered in subsequent experiments.

Variable	Value
Ta (°C)	60, 65, 70, 72, 74, 75, 76, 78, 80, 82, 84, 86
Ta (hrs)	3, 6, 24, 72, 144, 240
q1 (°C/min)	0.25, 0.5, 0.75, 1, 2.5, 5, 7.5, 10, 12.5, 15
q2 (°C/min)	2.5, 5, 10, 15, 20

annealing samples at 110°C, for 30 min. to remove residual stresses induced in the sample during the manufacturing process or during post-manufacture processing. Fewer than 10% of samples were eliminated. As samples were subjected to numerous thermal cycling experiments, (the upper temperature of which was 150°C), chemical aging associated with the elevated temperature exposure was a concern. To mitigate this concern, “annealing” cycles as described above were performed to verify that the sample had not undergone irreversible changes within the limits of detection. No noticeable changes in T_g ’s were observed between the pre-test and post-test anneal cycles indicating that no significant degradation or additional cure took place during the testing.

Again, an aim of the present research was to isolate the individual effects of the experimental variables: cooling rate, heating rate, isothermal aging temperature, and isothermal aging time. The spectrum of variables utilized can be found in Table 1 and the exact temperature programs are identified on the experimental heat capacity data shown in the present work. Where possible, experiments were performed entirely in the DSC chamber as “down jumps”. Down jumps were cooled at a rate q_1 from above T_g to T_a and isothermally held for some amount of time, t_a , before quenching to room temperature at $35^\circ\text{C}/\text{min}$. Samples were then immediately reheated at q_2 through T_g .

In some cases, namely the isothermal experiments at 60°C and 70°C where aging time exceed 24 hrs, the use of an external oven was employed. These experiments were cooled through T_g to room temperature at a rate of $1^\circ\text{C}/\text{min}$ and then transferred to a preheated isothermal aging oven. After isothermally aging in the oven, the samples were cooled to room temperature at approximately $1^\circ\text{C}/\text{min}$ and immediately transferred to the DSC to be reheated at $10^\circ\text{C}/\text{min}$. Error bars associated with data points such as peak temperatures were based on 3-4 samples of different batches for a given history.

Shear relaxation mastercurves were constructed from torsion-bar test data collected on an ARES M rheometer (Rheometrics). Isothermal frequency sweeps (0.1 to 100 rad/sec) were performed at 5°C intervals from 130°C to 35°C . Samples were equilibrated in the instrument for 5 min. at each temperature step and, when the time needed for the sweeps is included, resulted in a cooling rate of about $0.1^\circ\text{C}/\text{min}$. Strain amplitude was 0.1%. Nominal sample dimensions were: 50X13X5mm. The master curve was constructed so that a Havriliak–Negami [10] functional form was followed.

The glass transition temperature was evaluated in a number of manners. First, $\tan(\delta_R)$ and G'' were found from a $1^\circ\text{C}/\text{min}$ cooling ramp at frequency of 1Hz where δ_R is the rheological phase lag and G'' is the loss modulus. The peak in $\tan(\delta_R)$ occurs at 99°C and the peak in G'' occurs at 92°C . Onset, midpoint and peak temperatures for a $10^\circ\text{C}/\text{min}$ DSC heating ramp (following a $10^\circ\text{C}/\text{min}$ cool from an equilibrated sample well above T_g) are commonly used [11] as measures of T_g . For this system, these are, respectively, 80°C , 85°C , and 92°C . During cooling ramps, the temperatures associated with the transition are lower with onset, midpoint and endpoint of 77°C , 73°C , and 70°C for $10^\circ\text{C}/\text{min}$. Unless otherwise stipulated, we adopt the peak temperature in G'' (i.e., 92°C) as the glass transition temperature. The only place we report a non- G'' value of T_g is for Fig. 8 where T_f' fictive temperatures for cooling are reported (see next section for description of calculation of T_f'). The T_f' value of T_g at a cooling rate of $10^\circ\text{C}/\text{min}$ is $76.5^\circ\text{C}/\text{min}$.

3. Data Analysis of Enthalpy Recovery

The collected heat flow signatures fall under one of two descriptions that dictate how the data was analyzed. Entering the transition during the heating ramp, the response can appear as an “undershoot,” where the response appears to span a wide temperature range and no peak is apparent, or, alternatively, it can appear as an “overshoot.” An overshoot observed in a fully cured epoxy is the result of structural relaxation [12] and is understood as follows. During physical aging the enthalpy decreases as the molecules undergo slow structural rearrangement. The heating rate q_2 is faster than the structural relaxation time until the temperature is above T_g . At this point, all the enthalpy “lost” during the physical aging process

is "recovered" in a short time and the epoxy returns to its equilibrium state. This sudden recovery of the enthalpy results in an endothermic peak in the DSC thermogram. The blue line in Fig. 3 A is an example of this behavior. The red curve in Fig. 3 A, is indicative of "undershoot" behavior. A typical history that might show undershoot behavior is cooling at a fast rate and heating at a slow rate.

The fictive temperature, T_f , has long been used as a measure of the degree of structural relaxation. It is a function of the experimental parameters that directly impact the departure of the material from equilibrium (namely q_1 , T_a , t_a , and q_2). Quantitatively, T_f has been defined as the intercept of the extrapolated glassy and equilibrium lines [13]. Conceptually, it is the temperature at which the glass forming material would fall out of equilibrium if it were cooled from high temperature at some (slow) rate to yield a non-equilibrium state identical to that of the aged material.

A popular method for analyzing T_f uses the approximation in eq. 1 where T is a temperature well above T_g [12, 14]. This technique is convenient for analysis because only the

Fig. 3. Graphical interpretations of T_f for physically aged samples which exhibit "undershoot" (red), and "overshoot" (blue) from the A) raw heat capacity data, C_p , B) $C_p - C_{pEQ}$, and C) enthalpy, $H - H_{\infty}$.

extrapolated equilibrium line with slope $C_{p,Eq}$ is necessary and is found from the heat capacity above T_g . By eliminating the need for the second extrapolation of the glassy C_p , the technique essentially reduces the error associated with fitting two extrapolated lines where data distortion effects, like slight variation in the experimental heat capacity, can produce large error amongst data sets and obscure small changes in T_f .

$$\int_{T_f}^T (C_p - C_{p,Eq}) dT = 0 \quad (1)$$

This method of analysis, however, is restricted to data sets where there is a clearly defined enthalpy relaxation peak. For data sets where the enthalpy relaxation peak is not clearly defined or is not present, such as when T_a is far below T_g or t_a is short, T_f cannot be accurately approximated by Eq. 1. In the analysis of the current work, T_f' , has been defined as a substitute when T_f cannot be found using Eq.1; T_f' is the *limiting fictive temperature* [15, 16]. The graphical analysis of both temperatures will now be discussed.

Fig. 3 A is a schematic of the experimental heat capacity for “overshoot” (blue) and “undershoot” (red) scenarios. In the graphical analysis of the fictive temperature, T_f , the heat capacity curves for a constant set of experimental conditions are plotted together as seen in Fig. 3. The slope of the heat capacity above T_g , $C_{p,Eq}$, is extrapolated as a linear best fit curve in the equilibrium region and subtracted from the experimental data to obtain Fig. 3 B. Integration of $(C_p - C_{p,Eq})$ over temperature produces the curves in Fig. 3 C. Using the approximation in Eq.1 for the calculation in the case of an overshoot, T_f is where the enthalpy curve intersects the x-axis, as shown. In the case of an undershoot, the glassy line is linearly extrapolated from far below T_g on the enthalpy curve in Fig. 3 C and the intersection of that

line with the x-axis is defined as T_f' . T_f' has been defined previously for heating curves by Gao *et al.* [14] and, T_f' will be applied here as a measure of the glass transition, T_g , for cooling curve analysis as well as an approximation for T_f in heating curve analysis where the peak is not present. (Also see discussion of T_g in Sec. 2.)

The limiting fictive temperature, T_f' , is often calculated from a rapid heating that followed a slow cooling [16]. In this case, T_f' is less than T_g (when defined as the midpoint of the transition on cooling). In the present paper, the cooling curve is used to determine T_f' . In this case, T_f' is roughly 1°C higher than the same measure of T_g and is used as an approximation for T_g .

The peak temperature, T_p , is taken as the temperature at which the heat capacity exhibits a local maximum during a heating profile that is portrayed as endotherm up, as shown in Fig. 3 A. This value was chosen as a primary descriptor of the aging process because, as others have suggested, it is a very robust measurement in so far as data distortion effects are concerned [17, 18].

The difference in the heat capacity, $\Delta C_p = C_{pEq} - C_{pG}$, was calculated from the extrapolated equilibrium and glassy lines at the peak temperature [19]. ΔC_p upon heating at the onset T_g yields comparable values [8]. All specimens showing a distinct enthalpy relaxation peak were utilized for the calculation. ΔC_p was found to be 0.435 +/- 0.028 J/g°C, which is in good agreement with similar DGEBA epoxies [20].

We have used the Kovacs-Alkonis-Hutchinson-Ramos (KAHR) model as a guide in selecting the series of experiments performed as well as in plotting data. [19, 21] This model is briefly reviewed in the Appendix. Here we state the derivatives that are typically expected to

be constants in the KAHR model. In the Results and Discussion section, we will plot data so that the degree to which these slopes are constant can be assessed. In addition, the materials constants used for parameterization in the KAHR model will be evaluated and compared to similar materials, as well as compared to shift factors deduced from rheological master curves.

The deviation from equilibrium is defined by $\delta_H = (H(t) - H_\infty)$ without an over-bar where $H(t)$ is the enthalpy at time t and H_∞ is the equilibrium value of the enthalpy (note that H_∞ is a function of T). For a series of runs where the cooling rate, q_1 , is varied, the glass transition temperature is expected to vary linearly with the logarithm of q_1 . The slope is the inverse of the KAHR θ parameter:

$$\left(\frac{\partial T_g}{\partial \ln(q_1)} \right) = \theta^{-1} \quad (2)$$

For the series of cycles with cooling rate, q_1 , aging temperature, T_a , and aging time, t_a , all held fixed, the peak temperature, T_p , is expected to vary linearly with the logarithm of q_2 . The slope is the inverse of the product of the KAHR χ and θ parameters:

$$\theta \left(\frac{\partial T_p}{\partial \ln(q_2)} \right)_{q_1, T_a, \delta_H} = \chi^{-1} \quad (3)$$

For the cycle where the cooling and heating rates, q_1 and q_2 , and the aging temperature are held fixed, but the aging time is varied, the peak temperature is expected to vary linearly with the fictive temperature, T_f . The slope is 1 minus the inverse of the KAHR parameter χ :

$$\left(\frac{\partial T_p}{\partial T_f} \right)_{q_1, T_a, q_2} = 1 - \chi^{-1} \quad (4)$$

This equation can also be written in terms of $\Delta T_f = T_{f0} - T_f$ where T_{f0} is the fictive temperature calculated for the case of $t_a = 0$. Since T_{f0} is constant over the set of experiments, one finds

$$\left(\frac{\partial T_p}{\partial \Delta T_f} \right)_{q1, Ta, q2} = C^{-1} - 1 \quad (5)$$

4. Results & Discussion

As indicated above, a large number of aging cycles were performed by varying cooling and heating rates as well as by varying aging temperatures and times.

First, we present the results so as to show consistency with the KAHHR model, and, consequently, to show the internal consistency of our experiments. Second, the relation of the KAHHR predictions with the rheological shift factors is shown.

An overview of the effects of variation of the experimental parameters on the heating thermograms is shown in

Fig. 4. Relative heat capacity profiles demonstrating variation with A) cooling rate, q_1 , B) aging temperature, T_a , C) aging time, t_a , and D) heating rate, q_2 . The independent variable is indicated against the legend with the exception of Fig. 4 A in which cooling rates are color coded as 0.25 (dark blue), 0.5 (dark purple), 0.75 (dark green), 1 (green), 2.5 (pink), 5 (cyan), 7.5 (orange), 10 (light purple), 12.5 (light pink), 15 (black); heating rate is indicated against the curve and arbitrarily shifted along the vertical axis. Units are in °C/min for all heating and cooling rates.

Fig. 4. The simplest cycles cool the sample and then reheat it with no isothermal aging phase (i.e., $t_a = 0$). Thermograms of these cool/heat runs are shown in Fig. 4 A, where curves for fixed heating rates have been shifted along the vertical axis to distinguish amongst data sets.

Contrary to what one might expect, a pronounced enthalpic peak is often observed even though there is no extended isothermal aging phase. Clearly, slow cooling (small q_1) results in the most pronounced peak while rapid cooling (large q_1) results in no peak. This is understood because the material begins to age as soon as its temperature drops below T_g . If the cooling rate is small, the material will spend a considerable time in the temperature range just below T_g where aging is rapid, resulting in a pronounced enthalpic peak. Heating rates also have an effect on the peak.

For slow heating (small q_2), the peaks in Fig. 4 A are reduced in height and broadened. This is understood from a perspective analogous to that used to understand the effect of q_1 . If the material is heated quickly, recovery of the enthalpy lost during aging is not observed until the molecular mobility is high enough that significant motion is possible on the timescale of the temperature change. This does not occur until above T_g and results in a pronounced peak at a high T_p . On the other hand, if the material is heated slowly, enthalpy recovery is observed at lower temperatures since the longer timescale of the temperature change allows for significant motion even when the molecular mobility is not as high. This results in a broad peak at a lower T_p . Despite these differences in peak shape, the total enthalpy recovered from the aging resulting for a given q_1 (and T_a and t_a) when the glass is heated from T_a to T_0 is the same for all heating rates because enthalpy is a conserved state function.

The effect of aging temperature is investigated next with a series of rapid cools ($q_1 = 15^\circ\text{C}/\text{min}$) or “down-jumps” to different temperatures where the sample is aged for 3 hours. After aging, the sample is heated at a relatively rapid heating rate of $q_2 = 10^\circ\text{C}/\text{min}$. Results are shown in Fig. 4 B for T_a varying from 70°C to 86°C . For aging temperatures far below T_g , the

peak is small, if evident at all. At these temperatures the molecular mobility is small and the aging time is insufficient for any appreciable enthalpy loss. As the aging temperature is increased, the increase in molecular mobility leads to more enthalpy loss over the 3 hour aging period and the peak during heating becomes more pronounced and moves to higher temperature. This increase of peak height continues until the aging temperature is increased above 80°C (which is approximately the onset of the glass transition as measured in DSC). For aging temperatures in the 80°C to 86°C range, the peak height decreases even though the mobility continues to increase. This is because the deviation from equilibrium, δ , is small in this range and the material either relaxes completely to equilibrium and then stops, or sluggishly moves towards equilibrium because the driving force for aging, δ , is small. In either case, less enthalpy is lost, and, consequently, the recovery peak is attenuated. That physical aging can occur well above the onset of the glass transition range is recognized and highlights that the glass transition is a complex dynamic process that occurs over a range of temperatures [8, 22].

It is expected that the effects of physical aging would be measurable for lower temperatures if the aging time, t_a , was increased. To examine this, a series of aging runs were performed with T_a at 60°C and 70°C. Results are shown in Fig. 4 C, where the cooling rate was chosen to imitate realistic cooling rates for large components. For these experiments, a significant amount of physical aging occurs during the slow cooling ramp. Consequently, in order to see additional aging effects at these relatively low aging temperatures, extended aging times, up to 10 days, were necessary.

The degree to which a sample ages during the cooling ramp can be seen by inspecting the $t_a=0$ run in Fig. 4 C. This should be compared to the thermograms with progressively longer

aging up to to 240 Hrs (with t_a 's selected to be roughly on a logarithmic scale). As t_a increases, the onset of the enthalpic peak shifts to higher temperatures, as explicitly shown in Fig. 5 C. In addition, the peak height increases with increasing aging time. A lower T_a , 60°C, (not shown) exhibits the same qualitative behavior as at 70°C, but, for a given t_a , and T_p the peak height is smaller at 60°C indicating slower aging for the lower molecular mobility condition.

The final set of thermograms considered explores the effect of the heating rate, q_2 , and is shown in Fig. 4 D. These runs have fixed q_1 , T_a and t_a so that at the beginning of the heating ramp, all samples are identical. One would expect that the peak location would shift to higher temperature as the scan rate increases

because the rate that the enthalpy is recovered is in competition with the ramp rate and a faster ramp rate will carry the material further into the high(er) temperature/mobility region before the enthalpy recovery is observable. The KAHR model predicts that the peak temperature should vary linearly with the logarithm of the heating rate, which is, to good approximation, what is seen here and in Fig. 5 D [19].

Fig. 5. Peak temperature, T_p , dependence on the cycle parameters A) q_1 , B) T_a , C) t_a , and D) q_2 , when all other parameters are held constant. B) X-axis has been normalized to $\Delta T_a = T_f' - T_a$.

A common way to deduce the KAHR model parameters is by evaluating the peak temperature, T_p , as a function of the experimental parameters, q_1 , q_2 , T_a , and t_a . First

consider the response of T_p of un-aged ($t_a=0$) samples to variations in $\ln(q_1)$ shown in Fig. 5 A. Three different sets of heating rates are considered and there seems little consistency within the data. Non-monotonic behavior such as this has previously been observed experimentally [23, 24]. In that work, it was found [23, 24] that at low q_1 the peaks are sharp and well defined with considerable enthalpy recovered, and T_p is found to *decrease* linearly with increasing $\ln(q_1)$. On the other hand, at high q_1 , the peaks are broad with little enthalpy released and T_p *increases* linearly with $\ln(q_1)$. In the cited literature, T_p was tracked over nearly 3 orders of magnitude in q_1 for polycarbonate and clearly illustrates the non-monotonic behavior described above [24]. Because we have explored only about 1.5 orders of magnitude in q_1 , it is perhaps not surprising that we do not see as well defined a “turn-around” in T_p as in the literature [24].

It was shown in Fig. 4 that increases in the aging temperature (with q_1 , q_2 and t_a fixed) increased T_p . In Fig. 5 B, it is seen that the relation is a linear one. In order to make this comparison, it was useful to correct for small batch-to-batch variations. This was done by plotting against ΔT_a , where $\Delta T_a = T_f' - T_a$. Here T_f' was found from a common reference ($q_1=q_2=10^\circ\text{C}/\text{min}$ and $t_a=0$) which showed undershoot behavior. It should also be noted that the large values of q_1 and q_2 ensured that the aging effectively occurred only during the isothermal aging cycle and not during the temperature ramps. As seen in the figure, the slopes for the 3 and 6 hr aging times were equivalent with values of -0.24 ± 0.02 . In the next set of experiments, the timescale is increased to weeks in order to observe a quantifiable effect at T_a of 60°C and 70°C for a slowly cooled sample.

The set of extended aging runs displayed in Fig. 4 C shows a noticeable linear variation of T_p with the logarithm of aging time as seen in Fig. 5 C. This effect is shown both for the set of runs at 70°C and for the set deep in the glass at 60°C. Comparing with the 3 and 6 hr results in Fig. 5 B shows how little difference would be expected between these two short runs. The slopes of the lines in Fig. 5 C are the same within experimental error and equal to 1.83 ± 0.15 K, despite some evidence in the literature that suggests that the monotonic dependence of T_p on $\ln(ta)$ should change with increasing t_a because at higher temperatures the material is closer to equilibrium and physical aging would saturate [20, 22, 23]. It is particularly significant that linear behavior of T_p with respect to $\ln(ta)$ is seen in both cases. In addition, the lines can be superimposed with the shift factor, $a(T)$, in aging time of $\ln(a(70^\circ\text{C})/a(60^\circ\text{C})) = -3.05$. By assuming that $\ln(a)$ varies linearly over this temperature range, one predicts $\ln(a) = \ln(a(60^\circ\text{C})) - 0.30\text{K}^{-1}(T - 60^\circ\text{C})$.

Although the KAHR model does not transparently predict that T_p is a linear function of $\ln(ta)$, this has been seen experimentally [25] for a number of anhydride cured-DGEBA epoxies. The slope was found to be sensitive to the detailed nature of the hardener with a range of 2.7K to 3.45 K reported (in base 10). The T403 hardener used in the present study is considerably different than these and it is not surprising that, although displaying linear behavior, the slope falls outside of the anhydride range. Specifically, when expressed in log base 10, the slope in Fig. 5C is 4.21 ± 0.35 K.

The final cycle parameter that directly affects T_p is the heating rate, q_2 , and this is shown in Fig. 5 D. The peak shift method predicts T_p to be linear with $\ln(q_2)$ [19]. Fig. 5 D corroborates this. The slope of the line is 2.65 ± 0.35 K. From Eqn. 3, the product $\theta\chi$ is calculated to be 0.38 ± 0.04 K⁻¹. Notice that the T_p dependence in Fig. 5 D was not extracted from “intrinsic” cycles which Hutchinson and Ruddy [19] suggested as a direct evaluation of the material KAHR parameter, θ , from heating rate data [19]. Instead, the experiments in Fig. 5 D were run as “conventional” cooling and heating cycles where q_1 and the isothermal aging histories were constant. This was done to observe the effect of q_2 alone. All of the heating cycles shown have the same history to the beginning of the heating ramp, and, consequently, have the same “amount” of enthalpy to recover.

A complicating factor in the analysis of the effect of heating rate, q_2 , however, is that thermal lag can play a role at high scan rates. Distinguishing between thermal lag and the rate dependence of recovery is a challenge and an early method for identifying thermal lag and making corrections based on peak width was suggested by Hutchinson *et al* [26]. The

Fig. 6. Fictive temperature, T_f , dependence on A) q_1 , B) T_a , C) t_a , and D) q_2 . $\Delta T_f = T_f'(\text{unaged}) - T_f(\text{aged})$.

present work has forgone making such corrections based on the strong linearity seen in Fig. 5 D, which, for cases where thermal lag is appreciable, has been shown to be noticeably non-linear [26].

Commonly, the amount of enthalpy loss due to aging is expressed in terms of the fictive temperature, T_f . Here T_f was calculated using the well-established approximation given in Eq. 1 and the dependencies of the fictive temperature on the cycle parameters q_1 , q_2 , T_a , and t_a are shown in Fig. 6. Error bars for T_f were based on the variability in the slope of the raw heat capacity data and its effect on T_f .

The cooling rate has a clear effect on the fictive temperature. This is seen in Fig. 6 A where T_f has been plotted as a function of q_1 for three constant heating rates: 5, 10, and 15°C/min. The smaller q_1 is, the more physical aging can occur during cooling, and, consequently, the lower T_f is. This is clearly seen for all q_2 's. However, the relation is not a simple linear one, nor is it expected to be. Since the calculation of the fictive temperature is sensitive to the details of the enthalpic relaxation process, the variation of T_f with heating rate, q_2 , is non-trivial. Further, for a heating rate of 5°C/min, higher T_f 's are seen compared to T_f 's of the faster q_2 's. This indicates that some enthalpic recovery occurs before the peak region as q_2 decreases.

For a fixed aging time, t_a , the fictive temperature is expected to vary with aging temperature, T_a . This is seen in Fig. 6 B where T_a is plotted against ΔT_f . As before, the data has been renormalized for small batch-to-batch differences where ΔT_f is $T_{f,ref}' - T_f$, and $T_{f,ref}'$ is the common reference history mentioned previously. For low T_a , there is little or no peak and the alternative extrapolation for the fictive temperature must be used (denoted as T_f'). There was

good agreement between T_f' and T_f for heavily aged histories. Thus justifying the use of T_f' when no clear enthalpy relaxation peak exists. Generally, ΔT_f is small both for T_a close to T_g , where the displacement from equilibrium is small, and for T_a far below T_g , where physically aging occurs more slowly since the relaxation time is very large. Similar studies have shown that as T_a approaches T_g , T_f will equal T_a , which is the case here as ΔT_f appears to be getting smaller as T_a increases [27].

As one would expect, aging time also plays a role. This is shown in Fig. 6 C. While T_p was clearly linear with $\ln(t_a)$, corrections to T_f , to account for material batch-to-batch differences, were necessary to observe a trend with aging time. The result was also a linear dependence. Note the y-axis in Fig. 6 C has been normalized to $\Delta T_f = T_{f,ref}' - T_f$, where $T_{f,ref}'$ is found as in Fig. 6 B. Like its counterpart in Fig. 5 C, ΔT_f is larger for the higher aging temperature of 70°C as compared to 60°C. This is because as structural relaxation proceeds with increasing t_a , the material moves more quickly towards structural equilibrium at the higher temperature. One would expect this effect to saturate because, at higher T , δ is smaller so the structure does not need to travel as far to obtain structural equilibrium just below T_g (as depicted in Fig. 1). In addition, once at equilibrium no further aging takes place and T_f would remain constant for additional aging time. The timescale for the material to reach equilibrium at $T_a=60^\circ\text{C}$ and 70°C appears to exceed the experimentally examined timescale.

Finally, the heating rate, q_2 , also has an effect on T_f . One would expect that slow q_2 's would permit additional aging as the sample is heated. This is, indeed, what is seen in Fig. 6 D which shows a linear dependence of T_f on $\ln(q_2)$. It is worth mentioning that the increasing the aging time, t_a , at T_a helps to make T_f a more consistent measure of the degree of aging. This is because the enthalpic peak is more

pronounced and $H-H_\infty$ crosses zero in the linear region of the curve (see Fig. 3 C)

The KAHR model predicts that $(dT_p/dT_f)_{T_a, q_1, q_2}$ is linear. In addition, the difference of $T_f - T$ is proportional to d_H , and, consequently, $d_H - d_{H, Ref}$ is proportional to $\Delta T_f = T_f - T_{f, Ref}$ where "Ref" denotes a reference case. It follows that

$(dT_p/d \Delta T_f)_{T_a, q_1, q_2}$ will be constant, as Zheng *et al.* suggested in a previous discussion of the peak

shift method [28]. In Fig. 7, T_p vs ΔT_f is shown for the 60°C and 70°C aging histories from Fig. 4

C. There is good agreement between the plot results and the model prediction of linearity. The slopes of the lines in Fig. 7 are both 1.24 ± 0.1 . The slope of $(dT_p/d \Delta T_f)_{T_a, q_1, q_2}$ can be used to calculate χ using Eqn. 5, and χ is found to be 0.45 ± 0.02 . Combined with the previous value of $\Theta\chi = 0.38 \pm 0.04 \text{ K}^{-1}$, gives $\theta = 0.84 \pm 0.05 \text{ K}^{-1}$.

Fig. 7. T_p versus ΔT_f for aging time experiments at T_a equals 60°C and 70°C.

The variation of the glass transition during the cooling ramp is also significant to the parameterization of the KAHr model. However,

the glass transition temperature from DSC cooling data is notoriously difficult to resolve because as cooling rate, q_1 , becomes small, the noise to signal ratio becomes too large. In Fig. 8, T_g is reported versus $\ln(q_1)$ for the range of q_1 above the unintelligible noise to signal

threshold. T_g in Fig. 8 has been calculated using

the a method similar to that suggested by Gao

and Simon [15]. It is also similar to the

procedure used to calculate T_f' . The $C_{p,Eq}$ is subtracted from the signal before integrating and

extrapolating the non-equilibrium response to find the enthalpy=0 intercept. Since these are

cooling curves, there is no enthalpic peak to obscure the signal of the transition. These T_g 's

correspond to the low temperature onset of the transition. As q_1 decreases, T_g decreases,

which is in excellent agreement with free volume theory and with KAHr model predictions. The

slope of T_g vs $\ln(q_1)$ is found to be $1.38 \pm 0.15K$, and, using Eqn. 2, gives $\theta = 0.73 \pm 0.08 K^{-1}$. Within

the uncertainties, this value of θ is in agreement with that found in the previous analysis.

The KAHr parameters are similar for all glasses with χ in the range of 0.2 to 0.5, with θ in the range $0.5K^{-1}$ to $2.0K^{-1}$, and with $\chi\theta$ in the range $0.1K^{-1}$ to $0.4K^{-1}$. This is in keeping with a free volume interpretation of the physical aging. However, one also expects the detailed chemistry of the glass former to play a role. Even within epoxies, experimental evidence

Figure 8. Glass transition as a function of $\ln(q_1)$.

suggests a modest parameter variation [25]. Representative parameters for epoxies (Table 2) show χ to vary by about 20% while θ varies by about 40%.

Table 2. KAHr parameter values for various glass forming materials.

Material	χ	ΔC_p J/g°K	Θ K ⁻¹	$\theta\chi$ K ^[22]	Ref.
EPOXY 828/T403	0.45+/- 0.02	0.435 +/- 0.03	0.84 +/- 0.05 0.73 +/- 0.08	0.38 0.33 0.30	Present work
EPOXY CY100 ^A	0.42 +/- 0.03	0.336±0.002	0.95 0.99 ^E	0.40	[20] [25]
EPOXY CY070 ^B	0.41+/-0.03	0.407	0.70 ^E	0.29	[39] [25]
EPOXY FRD50 ^C	0.37 +/- 0.02	0.37	0.83 ^E	0.31	[25]
PVAc	0.35	-	0.74	0.26	[33]
	0.41		0.74	0.30	[33]
	0.27		0.92	0.25	[33]
PS	0.46	-	0.58	0.27	[33]
	0.48	-	0.56	0.27	
	0.44	-	0.60	0.26	
PVC	0.23	-	1.74	0.40	[33]
	0.27	-	-		[33]
	0.27-0.29	0.335+/- 0.015	1.1-1.21	0.30-0.35	[40]
A-PMMA	0.19, 0.25-0.32	-	0.98, 0.75	0.14-0.24	[20], [41]
S-PMMA	0.20, 0.12-0.38	-	0.87	0.10-0.33	[33],[41]
I-PMMA	0.22, 0.1-0.21	-	0.76	0.08-0.17	[33],[41]
EG ^D (22 mol%, H2O)	0.46	-	0.53	0.24	[33]

^A Epoxy CY100: CY255/HY225; 100% conversion

^B Epoxy CY070: CY255/HY 225; 70% conversion

^C Epoxy FRD50: Araldite F resin, 50 pbw Araldite DY026, HY 905; 100% conversion

^D Ethylene Glycol (EG)

^E Values of Θ approximated from the expression $\theta \cong \frac{\Delta H^*}{RT_g^2}$ using information from Cortes et al.[25]

The results of the analysis of the enthalpic aging study can also be used to comment on relaxation shift factors in the sub- T_g regime. As discussed in the appendix, the KAHR expression for the relaxation time is

$$t_i = t_{i,0} \exp\left(-q(T - T_R)\right) \exp\left(-(1-c)qd / DC_p\right). \quad (6)$$

For cooling of the material at a constant, relatively rapid, rate, δ can be approximated as $\delta = \Delta C_p(T - T_g)$. By taking the reference temperature to be T_g , and by assuming that time-temperature superposition holds, one finds the shift factor, a , to be

$$\ln(a) = -cq(T - T_g) \quad (7)$$

where $\ln(a(T))$ is defined as $\ln(\tau_g/\tau(T))$.

We find the value of $\chi\theta$ to be $0.38K^{-1}$ from the above peak shift analysis. In addition, for aging in the $60^\circ C$ to $70^\circ C$ range, we directly fit a shift factor to be $\ln(a) = \ln(a(60^\circ C) - 0.30K^{-1}(T - 60^\circ C))$.

Shift factors can also be assessed via master curve construction from dynamic mechanical analysis (DMA) experiments. In Fig. 9, we show shift factors obtained from a shear master curve construction on $\tan(\delta_R)$, where

Fig. 9 Top: Shift factors from shear master curve analysis (symbols). KAHR model (Red line, slope of $-0.38K^{-1}$). Aging T_p shift factor analysis (Green line, slope of $-0.30K^{-1}$). Vogel-Fulcher fit (dashed line), $\ln(a) = -23.1 + 706K/(T - 59C)$. Bottom: $\tan(\delta)$ resulting from shifting. Red line is Havriliak–Negami fit.

δ_R is the phase lag and the reference temperature is 90°C. Above T_g , the results are well fit to a Vogel-Fulcher (VF) function with $\ln(a) = -23.1 + 706K/(T - 59C)$. Below T_g , the material falls out of equilibrium and shift factors rise in a sub-VF fashion. The shift factor predictions based on the enthalpic analysis discussed above are shown in the region below T_g , with lines extending roughly over the range of temperatures where the aging experiments were done. This suggests that the product $\chi\theta$ decreases from $0.38K^{-1}$ just below T_g to $0.30K^{-1}$ (and perhaps lower) deep in the glass. The master curve is also shown in Fig. 9. It is seen to be well fit by the Havriliak–Negami [10] functional form (shown by the red line). The terminal power-laws are 0.29 (high frequency) and 0.69 (low frequency).

The close agreement between structural relaxation and shear master curve shift factors is notable and is another step towards justifying the rheological simplicity assumption embedded in many continuum mechanics constitutive representations of viscoelastic materials. Our unique approach to the problem builds upon the work of others on this topic. For instance, an early justification for the equivalence of bulk and shear relaxation shift factors was through the free volume theory of relaxation (see discussion by Rychwalski et al. [29]). Kovacs et al. [30] originally explored this by tracking volume relaxation in a dilatometric up-jump experiment and comparing to master curve shift factors. They performed a free-volume based analysis, which, in effect, makes a connection between volumetric and shear relaxation. Kovacs et al. used carefully equilibrated samples below T_g to get the relaxation times and enable a free volume analysis using the Doolittle equation. They compared this to non-equilibrium volume relaxation. We, on the other hand, cool our samples during master curve studies at a relatively steady rate ($\sim 0.1^\circ C/min$) and compare to aging studies. Consequently, shift factors from shear response in

the non-equilibrium glass are compared to peak shift analysis of the bulk relaxation in the (non-equilibrium) glass.

An even more direct comparison between shear and bulk relaxation in the glassy state has been made by Sane and Knauss [31] on Poly(methyl methacrylate) (PMMA). They performed dynamic bulk compliance measurements and compared to earlier shear compliance results [32], and find that below T_g , the shift factors are nearly identical for shear and bulk response.

Of course, these conclusions are for aging under the relatively benign conditions of a few tens of degrees below T_g and without additional drivers of mobility such as an external load. It is an open question as to what degree shear and bulk relaxation remain equivalent across a wider experimental parameter space.

5. Conclusions

In the present study, the structural relaxation of the 828/T403 epoxy has been characterized using four unique classes of experiments designed to isolate the experimental parameters that make up the thermal history and response, i.e. the cooling rate, q_1 ; heating rate, q_2 ; aging temperature, T_a ; and aging time, t_a . The effect of these parameters on three calculated quantities was evaluated: the peak temperature, T_p , during enthalpy recovery; the fictive temperature, T_f , which is a measure of the degree of aging; and, finally, the glass transition temperature, T_g , during cooling. It was demonstrated that the data set generated was internally consistent and accurate by comparisons with KAHR model predictions and by comparisons with literature studies of similar systems

The peak shift analysis for the 828/T403 material was shown to be reasonable by comparisons with literature values (Table 2) for the KAHR parameters θ and χ . It is seen that χ is on the high end of the range of similar epoxies in the literature. The θ parameter is less frequently reported in the literature, but our results for 828/T403 appear to be in the middle of the range of similar epoxies. Table 2 includes other representative glass formers to illustrate the range of the values that the KAHR parameters are found to adopt. The accuracy and consistency of the results from a peak-shift analysis may be attributed to (as Svoboda has suggested in his analysis of the apparent activation energy of structural relaxation, Δh^* , from various methods) the fact that T_p appears to be relatively insensitive to data distortion effects from thermal lag, baseline subtractions, etc. as evidence in Fig. 5 D [18]. The T_f analysis is more difficult to implement, however, and the use of a reference case was helpful.

Comparisons between KAHR model predicted time-temperature shift factors and those measures through the construction of a shear mastercurve demonstrated that the (enthalpic) bulk and shear relaxation times have roughly the same temperature dependence in the region immediately below the glass transition temperature. Previous work has also made this claim [3, 30, 31] but arrived at the conclusion in a different manner. Interestingly, the Sane and Knauss [31] study of PMMA bulk and shear shift factors show agreement below T_g with $d\ln(a)/dT = -0.2K^{-1}$, which is roughly the same as the KAHR $\chi\theta$ reported in Hodge [33] as $0.15K^{-1}$ to $0.2K^{-1}$. In these comparisons it is important that the thermal history imposed during the rheological test be accounted for in the KAHR model comparison. For instance the work of Bero and Plazek [34] on the relaxation time in the sub- T_g region for an epoxy is based on temperature jumps so that δ at the beginning of each relaxation at each temperature would be constant. Consequently,

the value of $d\ln(a)/dT$ in this case would be $-\theta$ which is found to be -0.92 and is in good agreement with its value for other epoxies.

Future work will involve incorporating the data set generated in the present study in more detailed modeling, both using the simple KAHR differential equation and more advanced constitutive modeling. The ability to predict stress evolution in confined materials associated with the structural relaxation process is of considerable interest.

Acknowledgements

The assistance of Mary Ruff and Kathryn Mireles in the DMA testing reported here is gratefully acknowledged.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Appendix: The KAHR Model and the Peak Shift Method

A well established description of physical aging is the Kovacs-Alkonis-Hutchinson-Ramos (KAHR) model [21]. This model incorporates both the rapid material response due to the glassy heat capacity and the slow relaxation characteristic of physical aging. In the current paper, we do not undertake detailed KAHR modeling, however, because many of the plots were motivated by this model, we review it briefly. For additional details, the reader is referred to the extensive literature on the subject [21, 24, 35-37].

In the KAHR model, the mobility of the material is assumed to be separable into a number of relaxation “modes”. Here we will first assume a single mode and then generalize to multiple modes.

The deviation from equilibrium is defined by $\delta_H = (H(t) - H_\infty)$ where $H(t)$ is the enthalpy at time t and H_∞ is the equilibrium value of the enthalpy (and is a function of T) as seen in Fig. 1. If there is no physical aging (e.g., a rapid cool), the enthalpy below T_g is $H(t) = H_g + C_{pg}(T - T_g)$. The equilibrium enthalpy below T_g is extrapolated as $H_\infty = H_g + C_{peq}(T - T_g)$ where H_g is the enthalpy at the glass transition. Consequently, the unaged δ_H is $\delta_H = \Delta C_p (T_g - T)$. The fictive temperature, T_f , is a convenient way of expressing the departure due to physical aging, $\delta_H = \Delta C_p (T_f - T)$. In the following discussion we drop the “H” from δ_H for compactness.

For changes in temperature at a fixed degree of aging (i.e., fixed T_f), the variation of δ is

$$\frac{d\delta}{dt} = -\Delta C_p \frac{dT}{dt} \quad (\text{constant } T_f) \quad (\text{A.1})$$

If, on the other hand, the temperature is held fixed ($T < T_g$), then $d\delta/dt$ slowly decays to zero as the material progresses towards H_∞ . The deviation from equilibrium, δ , is assumed to be a driving force for the relaxation and, for constant temperature, gives a relaxation equation:

$$\frac{d\delta}{dt} = -\frac{\delta}{\tau} \quad (\text{constant } T) \quad (\text{A.2})$$

where τ , the relaxation time, is a function of both T and δ . If the relaxation time were not a function of δ , this equation could be integrated to give an exponential decay.

The general KAHR equation is a combination of the above two effects:

$$\frac{d\delta}{dt} = -DC_p \frac{dT}{dt} - \frac{\delta}{\tau} \quad (\text{Single mode KAHR Equation}) \quad (\text{A.3})$$

Typically the multi-mode generalization is used

$$\frac{d\delta_i}{dt} = -DC_{p,i} \frac{dT}{dt} - \frac{\delta_i}{\tau_i} \quad (\text{Multi-mode KAHR Equation}) \quad (\text{A.4})$$

where $\delta = \sum_i \delta_i$ and $DC_p = \sum_i DC_{p,i}$.

Although much of the general system behavior is reasonably well captured by the KAHR equation, much of the physics is also embedded in the dependence of τ on T and δ . The KAHR expression for τ is

$$\tau = \tau_0 \exp(-q(T - T_R)) \exp(-(1 - c)q\delta / DC_p) \quad (\text{Single Mode}) \quad (\text{A.5})$$

where T_R is a reference temperature, and θ , χ , and ΔC_p are the material constants that are needed to populate the KAHR model. The multi-mode generalization is

$$\tau_i = \tau_{i,0} \exp(-q(T - T_R)) \exp(-(1 - c)q\delta / DC_p) \quad (\text{Multi-mode}) \quad (\text{A.6})$$

where the shape of the distribution of the relaxation times seen at T_R is preserved as temperature and δ are varied, thus enforcing thermo-rheological simplicity over a range of equilibrium and non-equilibrium states. This equation suggests a number of ways to extract the constants θ and χ from experiment.

First, consider a material cooled from above the glass transition, T_g , deep in the rubbery state, at some cooling rate, q_1 . Upon cooling, δ (at a particular T) depends exclusively on q_1 . Where T_g occurs $\delta=0$ and $\tau \sim 1/q_1$. The right hand side of equation A.5 then simplifies to a pure temperature dependence and the material parameter, Θ , can be inferred to be:

$$\left(\frac{\partial T_g}{\partial \ln(q_1)} \right) = \theta^{-1} \quad (\text{A.7})$$

Next, consider the case of a series of cycles where the cooling rate q_1 , aging temperature, T_a , and aging time, t_a , are held fixed so that δ at the beginning of the heating ramp is constant. As the aged sample is heated at rate q_2 , the enthalpy follows a path with slope C_{pg} , holding on to much of its aged enthalpy and causing δ to become negative as the equilibrium line is crossed. When the temperature is sufficiently high, the relaxation time becomes comparable to $1/q_2$, and most of the enthalpy is recovered over a narrow temperature range resulting in an “enthalpic peak” with a maximum at T_p . Consequently, by tracking the change in T_p with q_2 , the nonlinearity parameter, χ , can be found from experimental conditions through the relationship [19]:

$$\theta \left(\frac{\partial T_p}{\partial \ln(q_2)} \right)_{q_1, T_a, \bar{\delta}_H} = \chi^{-1} \quad (\text{A.8})$$

Finally, consider a cycle where q_1 , q_2 , and T_a are held fixed and t_a is varied such that the departure from equilibrium at the beginning of the heating cycle is a function of t_a alone. If q_2 is relatively fast so that no additional aging takes place during heating, then the enthalpy H increases linearly on a line with the slope of the glassy specific heat and, consequently, $\delta = \Delta C_p(T_f - T)$. By substituting this expression in for δ in Eqn A.5 and identifying T_p with the temperature where the relaxation time is $1/q_2$, the rate of change of T_p with T_f is found to be

$$\left(\frac{\partial T_p}{\partial T_f} \right)_{q_1, T_a, q_2} = 1 - C^{-1} \quad (\text{A.9})$$

Or, if expressed in terms of $\Delta T_f = T_{f, \text{ref}} - T_f$,

$$\left(\frac{\partial T_p}{\partial \Delta T_f} \right)_{q_1, T_a, q_2} = \chi^{-1} - 1 \quad (\text{A.10})$$

where $T_{f, \text{ref}}$ is the fictive temperature of a sample with $t_a = 0$.

This method of examining the peak temperature dependence on experimental variables is the ‘peak shift’ method introduced by Hutchinson and Ruddy and provides a convenient and informative way to analyze structural relaxation [19]. Additionally, implementation and critique of the peak shift [18, 19, 24, 38] method over the last three decades has provided a foundation for comparison of the experiments conducted in the present work to previous work on similar materials.

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