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MEMORY EXPERIMENTS IN PHYSICALLY AGING SYSTEMS: A TEST OF MULTIORDERING PARAMETER MODELS *

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ABSTRACT

An extension of a multiordering parameter model of volume and enthalpy recovery is tested by comparing calculated viscoelastic behavior with published creep data for memory like experiments. The calculated viscoelastic curves are qualitatively in agreement with published data. However, it has been determined from the creep data that the structure shift factor a_δ has an unexpected temperature dependence, which may indicate an additional temperature dependence for one of the underlying variables such as x, the structure partition parameter.

INTRODUCTION

When liquids or polymers are cooled rapidly such that the rate of cooling is much faster than the rate of structural recovery, it is found that the glass formed is not in structural equilibrium. Measurements of the properties of the glass, such as volume [1], enthalpy [2], dielectric loss [3] or viscoelastic behavior [4] after such a temperature jump result in the observation of changes in these properties as time progresses. These changes in material properties with time, known as physical aging, are commonly observed in polymeric glasses although simple liquids and inorganic glasses also are known to exhibit this type of behavior.

These time dependent phenomena which are characteristic of glasses have several distinct features such as: (1) the relaxation behavior is non-linear; (2) there is considerable asymmetry of the relaxation behavior for expansion and contraction isotherms; and (3) memory effects associated with complex thermal treatments are also observed.

In previous work, the KAHR model [1] was used to rationalize successfully volume and enthalpy relaxation behavior in glasses. This but one of

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several theoretical models which have now been developed. For this model, the volume (or enthalpy) relaxation is partitioned into i relaxation modes each with its corresponding relaxation time τ_i.

The partitioning of the response function into individual relaxation modes is both intuitively satisfying and necessary to explain memory behavior results from multiple T-jump experiments which cannot be reproduced using a single order parameter model [5].

While the KAHR model has been elucidated more rigorously in ref. 1, the main points of the model are reiterated here.

For the volume recovery of a glass, the volume departure from equilibrium, δ, is defined as

$$\delta = \frac{V - V_\infty}{V_\infty} \tag{1}$$

The total volumetric recovery is partitioned among the various recovery modes; for single temperature jump experiments starting from equilibrium, the following rate equation results for each mode of response, i

$$\frac{\mathrm{d}\delta_i}{\mathrm{d}t} = -\frac{\delta_i}{\tau_i(\delta)} \qquad 1 \leqslant i \leqslant N \tag{2}$$

Here δ_i is the normalized volume departure from equilibrium for the ith mode and τ_i is the relaxation time characteristic of that mode. It should also be noted that τ_i depends on the total departure δ, and not on δ_i alone according to eqn. (4) below. Having a dependence on δ couples the N rate equations, resulting in the complicated behavior observed in non-equilibrium glasses.

It is convenient to express the partitioning of the response function in terms of a volume distribution, $g(\tau_i)$, defined as

$$g(\tau_i) = \frac{\delta_{i,\mathrm{o}}}{\sum_{i=1}^{N} \delta_{i,\mathrm{o}}} \tag{3}$$

where the second subscript indicates values of δ_i immediately after the temperature jump. $g(\tau_i)$ is plotted in Fig. 1 for polyvinylacetate, PVAc. This distribution represents represents the normalized departure from equilibrium associated with each relaxation time $\tau_{i,\mathrm{r}}$ at the arbitrary reference temperature, $T_\mathrm{r} = 35\,°\mathrm{C}$.

The relaxation times depend on structure (δ) and temperature. Several expressions relating the dependence of structure and temperature have been developed, but near T_g all these functions reduce to the expression first suggested by Toole [6]

$$\begin{aligned}\tau_i(\delta, T) &= \tau_{i,\mathrm{r}} \exp[-\theta(T - T_\mathrm{r})] \exp\left[\frac{-(1-x)\theta\delta}{\Delta\alpha}\right]\\ &= \tau_{i,\mathrm{r}} a_T a_\delta \end{aligned} \tag{4}$$

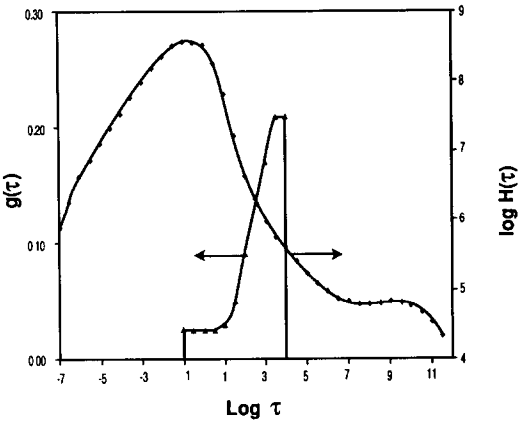

Fig. 1. Volume distribution $g(\tau)$ and relaxation spectrum $H(\tau)$ at 35 °C.

where $\tau_{i,r}$ is the value of the ith relaxation time at the reference temperature and at volume equilibrium, $\theta = E_a/RT$, where E_a is the activation energy of the process, $\Delta\alpha = \alpha_l - \alpha_g$, α_l and α_g being the coefficients of thermal expansion for the liquid and glass respectively, and x is the structure partition factor which determines the relative effect of structure and temperature on the relaxation times. $x = 1$ indicates purely thermal dependence, while $x = 0$ indicates purely structural dependence. While $\Delta\alpha$ is a material constant, for most polymers $\Delta\alpha \approx 4 \times 10^{-4}$ K^{-1}. For our calculations, we have used the following: $\theta = 1.0$ K^{-1}; $x = 0.4$.

VISCOELASTIC BEHAVIOR DURING VOLUME RECOVERY

The mechanical properties of polymeric glasses quenched from above T_g change as a function of time. In Struik's short time creep experiments [7], for example, the creep curves shifted to longer times as aging progressed. Stress relaxation experiments, carried out by Matsuoka et al. [8], show similar behavior (Fig. 2).

The observed shifting of the viscoelastic curves can be attributed to the structural relaxation in the glass during physical aging in a manner identical to that invoked to explain the asymmetry observed in volume and enthalpy recovery [1]. When a glass is quenched from equilibrium, the volume of the quenched sample is greater that its equilibrium volume. As the sample ages, the volume decreases which causes the configurational mobility of the polymer chains to decrease also. Consequently, the relaxation times increase, or move to longer time scales. This is what is observed when physically aging glasses are subjected to viscoelastic experiments: the underlying relaxation times move toward longer time scales as time progresses. The viscoelastic curves do not shift indefinitely; after a certain period of time, the curves

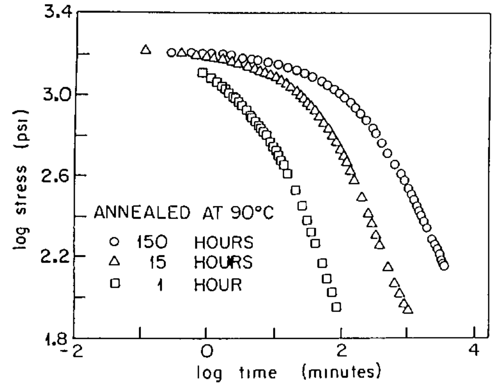

Fig. 2. Stress relaxation behavior of polystyrene at different aging times as indicated (ref. 8).

stop shifting, and the succeeding viscoelastic curves measured at even still longer "aging" times are all identical. The curves stop shifting ostensibly because the sample has reached structural equilibrium.

A convenient way of quantifying the relationship between the individual viscoelastic curves in simple aging experiments is through the shift rate, μ [7].

$$\mu = -\frac{\mathrm{d}\log a}{\mathrm{d}\log t_a} \tag{5}$$

where d log a is the horizontal shift necessary to superpose two curves of different aging times and d log t_a is just the difference in the logarithms of aging times.

Although the value of the shift rate changes with aging time, it was determined by Struik and others [7–9] that maximum value of the shift rate is often close to 1.0 at temperatures in the glass transition range.

While multiordering parameter models have been very successful in the treatment of volume and enthalpy recovery in non-equilibrium glasses, there have been few attempts to rationalize viscoelastic behavior of physically aging glasses using the KAHR or other models [10,11].

As a starting point for our extension of the KAHR model to treat viscoelastic behavior we will assume that both structural recovery and changes in mechanical behavior of an aging glass can be explained by a kinetic process wherein the distributions of relaxation times move in accordance with the change in configurational mobility. Thus distributions of relaxation times for both viscoelastic and structural recovery are assumed to shift in the same way, because on any particular time scale the same underlying modes of molecular motion which contribute both to viscoelastic and structural relaxation. Therefore, the equations which characterize the dependence of the relaxation times in structural recovery could also be used in viscoelastic recovery.

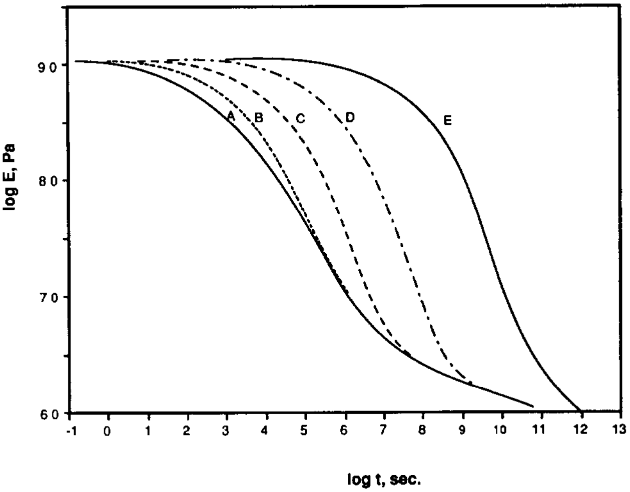

Fig. 3. Calculated stress relaxation curves for PVAc quenched from 35 ° C to 15 ° C with aging times (s): A, 0; B, 10^5; C, 10^7; D, 10^9. E is at volume equilibrium.

The stress relaxation modulus $E(t)$ is related to the relaxation spectrum $H(\tau)$ as

$$E(t) = \int_{-\infty}^{\infty} H(\tau)\, \mathrm{e}^{-t/\tau} \mathrm{d} \ln \tau \tag{6}$$

$H(\tau)$ for PVAc at 35 ° C is shown in Fig. 1, and was determined by using the 2nd approximation method of Ferry [12,13]. An assumption made in deriving the spectrum from the experimental data is that the viscoelastic behavior of PVAc is "thermo-rheologically simple", i.e. under isothermal conditions, the shape of the relaxation spectrum does not change with changes in temperature [14] but rather moves along the logarithmic time-scale one way or the other subject to temperature increases or decreases.

Physical aging is more complicated. While the shape of the distribution of relaxation times remains unchanged, the same is not true of the viscoelastic response function. Equation (6) can be generalized to treat physically aging systems as

$$E(t) = \int_{-\infty}^{\infty} H(\tau)\, \mathrm{e}^{-t/\tau a_T a_\delta}\, \mathrm{d} \ln \tau \tag{7}$$

Calculated stress relaxation behavior of PVAc during a simple aging experiment is shown in Fig. 3. Here the PVAc was quenched from 35 ° C to the measurement temperature of 15 ° C and annealed at this temperature for the various aging times indicated before starting the stress relaxation experiment. Curve A, for example, is a calculation of a sample quenched from 35 ° C to 15 ° C with the stress relaxation experiment started immediately after the quench, i.e. no aging period. For sample B, 10^5 s elapsed between the quench and the start of the stress relaxation experiment.

While the uppermost portion of the curves are all very similar except for a horizontal shift, the complete curves are actually very different—the unannealed sample, A, showing the largest discrepancy from the rest. The behavior exhibited in the calculated manifold of curves can be understood easily. When the stress relaxation measurement time is less than the annealing time, the relaxation spectrum $H(\tau)$ is stationary. If however, the stress relaxation measurement time is greater than or equal to the annealing time, the relaxation spectrum then shifts to longer time scales during the mechanical measurement. Suppose a sample which has been aged for some amount of time t_a is subjected to a stress relaxation experiment at the measurement time t_m. The total time that the sample has aged will be $t_m + t_a$. If $t_m \ll t_a$, the total aged time will be approximately t_a and the total aged time is essentially unchanged for this part of stress relaxation experiment. The volume of the sample remains fixed, and the distribution of relaxation times does not shift during the stress relaxation measurement. When all of these conditions apply, the stress relaxation curves at different aging times can be superposed by a simple horizontal shift attributed to the volume difference between the samples.

However, when $t_m \approx t_a$, the stress and volume relax simultaneously, causing the relaxation times to shift to longer time scales during the stress relaxation experiment. For example, curve B, which was annealed for 10^5 s, has approximately the same shape as the equilibrium volume curve E at times less than t_a; it is roughly at $t_m = t_a = 10^5$ s that the relaxation times start to shift to longer times, since the total aged time $(t_m + t_a)$ becomes 2×10^5 s and the volume becomes significantly less than at the start of the stress relaxation experiment when the total aged time was 10^5 s.

While the calculated curves in Fig. 3 do not look very much like the experimental stress relaxation data of Matsuoka et al [8] they are actually in good agreement. This accord becomes clear when we note that the experimental data spans a narrow window of modulus equivalent to only the topmost portion of our calculated curves. In fact, our calculated curves show stress relaxation behavior of glasses at various aging times which are superposable by simple horizontal shifts, as experimentally demonstrated by Matsuoka's data.

At least one major problem exists with extending the KAHR model to treat physical aging in this way. The shift rate for the calculated stress relaxation curves are not in accord with the experimental behavior. Within the framework of the model and using parameter values chosen to reproduce the kinetics of volume relaxation, the maximum value of μ is about 0.6, in contrast with the maximum experimental shift rate of around 1.0 ($\mu_{max} \approx 0.65$ in Fig. 3). In fact Chen and Aklonis [10] have analyzed the dependence of the shift rate on various factors, such as the type of distribution function used and the values of the parameters x and θ. They found that with distributions of relaxation times which spanned more than two decades of log time, the maximum shift rate attained was considerably less than 1.0. In order to get a maximum shift rate close to 1.0, a very narrow distribution such as a single relaxation time had to be used.

It is universally accepted that such a distribution cannot satisfactorily reproduce many aspects of the complicated kinetics of glass transition phenomena. For the time being we have made an 'ad hoc' assumption for the purpose of calculating physical aging behavior which is in agreement with experiment.

For volume (and enthalpy) relaxation the value of a_δ is that given in eqn. (4) with the value of the parameters mentioned above. The a_δ used to determine the position of $H(\tau)$ during an aging experiment must be modified as follows

$$a_\delta = \exp\left\{\frac{-1.8(1-x)\theta\delta}{\Delta\alpha}\right\} \tag{8}$$

The underlying molecular reasons for the necessity of the two different a_δ functions are not entirely clear to us but we believe that the coupling model [15] of Ngai and Rendell may be able to rationalize the difference in shift rates.

MEMORY EXPERIMENTS

The volumetric response in a memory experiment is considerably more complicated than in a simple aging experiment, as is demonstrated in Fig. 4.

This type of behavior is evoked by subjecting a glass former to a quench from equilibrium followed by annealing at a temperature below what will be the experimental temperature. After a suitable annealing period, which is determined by trial and error, the sample is quickly warmed to the experimental temperature where the volume of the sample is equal to its equilibrium volume. Rather than maintain this condition where $\delta = 0$, the

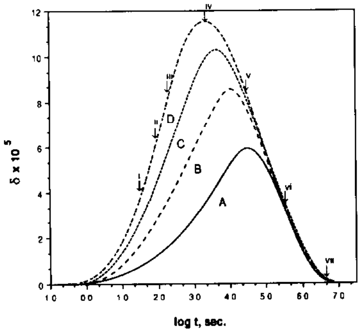

Fig. 4. Volume relaxation during memory experiments A–D.

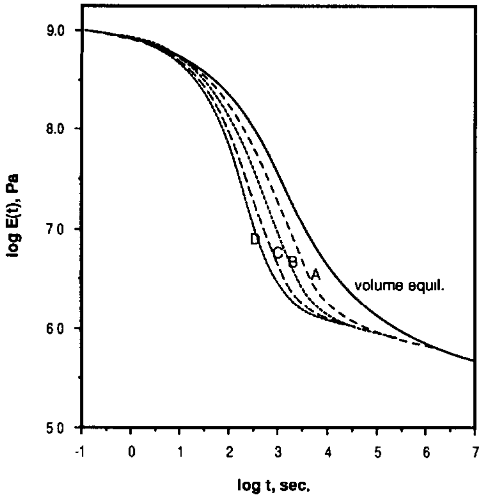

Fig. 5. Calculated stress relaxation curves of PVAc during memory experiments A–D.

sample spontaneously and isothermally increases in volume and then decreases in volume back to $\delta = 0$, the true equilibrium condition. This is the behavior shown in Fig. 4 for several different annealing times and temperatures. Since the volume both increases, and then decreases with aging time, we would also expect complicated viscoelastic behavior for a glass in a memory experiment. The thermal treatments used to treat the sample to stimulate the volume and stress relaxation behavior shown in Figs. 4 and 5 are shown in Table 1.

The mechanical experiments were started immediately after the sample reached its "equilibrium" volume at 30 °C; the calculated stress relaxation behavior during such memory experiments is shown in Fig. 5. In addition, the mechanical behavior at volume equilibrium is also shown.

The striking feature of these stress relaxation plots is that they are not superposable, even at the top portion of the curves. Because the volume changes for the samples are bigger when the *T*-jumps are larger, the relaxation times shift more for these experiments and steeper slopes in the stress relaxation plots for larger *T*-jumps are evident.

TABLE 1

Thermal treatments used

Thermal treatment	ΔT_1 (°C)	ΔT_2 (°C)	log(annealing time) (s)
A	−10	5	5.522
B	−15	10	5.799
C	−20	15	6.008
D	−25	20	5.856

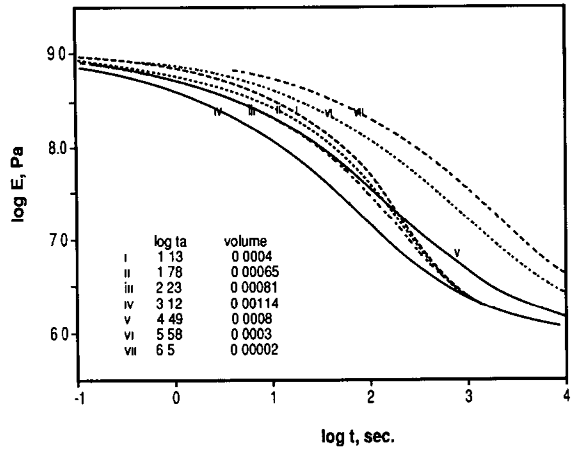

Fig. 6. Calculated stress relaxation curves at different points during memory experiment D.

Even more dramatic changes in viscoelastic behavior are demonstrated in Fig. 6. These calculated stress relaxation plots correspond to mechanical experiments initiated after various annealing times, t_a, along the memory experiment curve D, which are indicated in Fig. 4. Curve ii, for example, involved annealing the sample for just over one minute after thermal treatment D, and then initiating the stress relaxation experiment. For curve ii, since the annealing and the stress relaxation experimental times are comparable over most of the relaxation time scale, the viscoelastic distribution $H(\tau)$ initially moves to shorter times causing the stress relaxation behavior to accelerate as indicated by a steepening of the slope. This acceleration is most dramatic for curve i which experiences the maximum volume change after the start of the mechanical experiment. Similar behavior occurs for curve ii, except that it is shifted to shorter times because the sample volume at the start of the mechanical experiment is greater here than for curve i. The subsequent curves (iii and iv) also shift to shorter times for the same reason. When the volume maximum is reached (curve iv), the trend changes. Now the experimental stress relaxation time over its entire span is less than the annealing time, which causes the volume to remain essentially unchanged during the mechanical experiment. Accordingly, the resulting stress relaxation curves have the same shape as the equilibrium volume curve and are merely shifted to longer times as subsequent long term annealing occurs (curves iv to vii).

Recently, Struik published experimental results [16] similar to those we have calculated. He subjected polystyrene, poly(vinyl chloride) and polycarbonate to thermal treatments which resulted in a type of memory behavior, and performed short term creep experiments on the samples. We believe that there is no fundamental difference between his having used creep and our consideration of stress relaxation behavior as far as the shifting of these time dependent mechanical property curves are concerned.

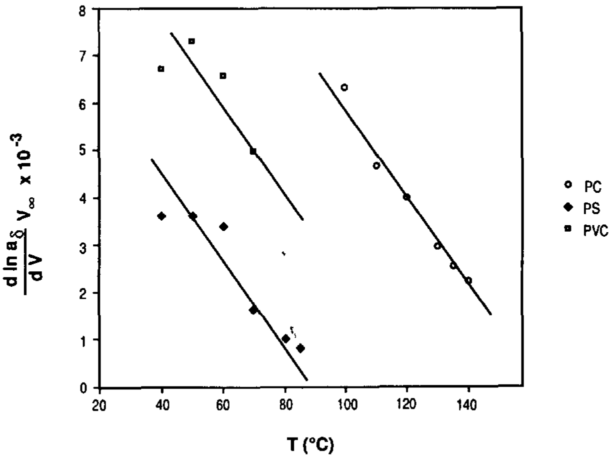

Fig. 7. Temperature dependence of the structure shift factor, a_δ.

His experimental results are qualitatively in agreement with what we have calculated using the KAHR model. The creep curves shift to short times until the maximum volume is reached and then shift to longer times, as is expected from the model. The lack of superposability of the curves at short annealing times as well as the superposability at longer annealing times predicted by the model is not observed due to the short duration of the creep experiments. Struik's data is particularly attractive in that it allows a very sensitive test of some of the tenets of all of the multiordering parameter models. If one takes the derivative of eqn. (8) and rearranges some terms one obtains

$$\left[\frac{\mathrm{d}\ln a_\delta}{\mathrm{d}V}\right]_T V_\infty = \frac{(1-x)\theta}{\Delta\alpha} \tag{9}$$

The terms on the left hand side of the equation can be extracted from Struik's experimental data, and are plotted for various temperatures and various materials in Fig. 7. It should be emphasized that each point on this plot represents a large number of aging experiments done at a single measurement temperature. The right hand side of eqn. (9) is assumed to be temperature independent. Thus it is expected that Fig. 7 should be composed of three horizontal lines, perhaps at somewhat different heights. In fact, the results show that the effective temperature structure shift factor, at least for memory like behavior, is not separable into two multiplicative terms, one temperature dependent and the other not, as assumed in eqn. (4). Rather, the analysis of Struik's data indicates that a temperature dependent factor must be directly included in the "a_δ" term, for example by making one of the parameters such as x temperature dependent. Such a temperature dependence has previously been suggested by O'Reilly et al. [17] in treating enthalpy relaxation of glasses via DSC experiments. However, the change in

x which would be needed to make the right hand side of eqn. (9) agree quantitatively with experimental data is much greater than that suggested by the analysis of O'Reilly et al.

It is evident that this new temperature dependence is similar for all the glassy polymers studied.

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