

Effects of Annealing and Prior History on Enthalpy Relaxation in Glassy Polymers. 2. Mathematical Modeling

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ABSTRACT: A simple four-parameter model reproduces DSC data on the effects of annealing conditions, and thermal history before annealing, on the heat capacity of glassy polymers. The model is an application of the successful treatment of glass transition kinetics, due to Moynihan and co-workers, to thermal histories which include annealing. It is found that a nonexponential relaxation function is essential for the development of sub- T_g heat capacity peaks with annealing and that nonlinearity is important in accelerating their development to experimentally accessible aging times. Numerical integration allows accurate predictions of the effects of quench rate, annealing temperature, annealing time, and reheating rate on the magnitude and temperature of heat capacity peaks observed in DSC scans of annealed PVC (part 1) and other polymeric glasses.

I. Introduction

Glasses usually exist in a nonequilibrium state, and relaxation toward equilibrium is commonly referred to as physical aging or annealing. Aging affects a large number of properties such as density, modulus, and the rate of stress, strain, enthalpy, and volume relaxation.¹⁻³

The increased rate of aging as temperature approaches the glass transition temperature, T_g , and the elimination of aging effects after heating above T_g suggest a close connection between the aging and glass transition phenomena. Furthermore, Kovacs et al.^{2,3} and the present authors⁴ have demonstrated that the development of sub- T_g heat capacity peaks with aging is a consequence of the glass transition kinetics. The present paper explores in detail the relation between the glass transition phenomenon and aging effects. The approach used by Moynihan and co-workers⁵ to treat the glass transition is used to calculate the heat capacity as a function of glass transition kinetic parameters, annealing conditions, and thermal history before annealing. A comparison with experimental data given in part 1 is also made. We begin by reviewing some of the phenomenological aspects of the glass transition kinetics, as treated by Moynihan and co-workers.⁵

The kinetics of the glass transition and aging phenomena are both nonexponential and nonlinear. They are nonexponential in the sense that the relaxation toward equilibrium following a sudden perturbation (e.g., a temperature step) is described by a nonexponential decay function $\phi(t)$. This is formally equivalent to a distribution of relaxation times $g(\tau)$, related to $\phi(t)$ by

$$\phi(t) = \int_0^{\infty} g(\tau) e^{-t/\tau} d\tau \quad (1)$$

and constrained by the condition

$$\int_0^{\infty} g(\tau) d\tau = 1 \quad (2)$$

The description of a relaxation by a specific function for $g(\tau)$ does not necessarily imply separate relaxation mechanisms for the various relaxation time components of $g(\tau)$, since a single cooperative relaxation mechanism may produce a nonexponential form for $\phi(t)$. A well-known consequence of a nonexponential relaxation is the maximum in the response (e.g., volume) to two separate perturbations of opposite sign (e.g., temperature jumps).^{3,5} An empirical function which has been found to give an excellent fit to a wide range of relaxation processes in a large variety of amorphous materials is

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \quad (3)$$

where τ_0 is a characteristic time and β ($0 < \beta \leq 1$) is a direct measure of nonexponentiality. The corresponding $g(\tau)$ is asymmetric on a $\log \tau$ scale, with a skew toward short times.⁶ Plots of eq 3 are shown in Figure 1 for $\beta = 1.0$ (single relaxation time) and $\beta = 0.5$ (a representative value). Compared with the exponential function, $\phi(t)$ for $\beta = 0.5$ has both shorter and longer time components. This has important consequences for aging behavior which are discussed below. In this paper we shall accept eq 3 as an adequate description of the nonexponentiality of the glass transition and use it to model aging.

The kinetics of aging and the glass transition are also nonlinear in the sense that $\phi(t)$ depends on the degree of departure from equilibrium. This nonlinearity is most conveniently treated by making the average relaxation time a function of structure as well as temperature. It is an additional convenience to treat the structural state of a system, as measured by macroscopic properties such as volume or enthalpy, in terms of the fictive temperature T_f .⁷ In the general case, T_f is defined as the temperature at which the measured value of a property would be the equilibrium one. However, since T_f measures only the relaxational component of a specified property, values of T_f assessed from different properties for the same glass may differ. The equilibrium state well above T_g is characterized by the condition $T_f = T$, and relaxation from a nonequilibrium state is described by the decay of T_f toward T . Nonlinearity is treated phenomenologically by allowing τ_0 in eq 3 to be an explicit function of T and T_f , as in the expression of Gardon and Narayanaswamy^{8,9}

$$\tau_0 = A \exp \left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f} \right] \quad (4)$$

where A , x ($0 < x \leq 1$), and Δh^* are constants and R is the ideal gas constant. The parameter x is a direct measure of nonlinearity, with $x = 1$ for a linear relaxation. Equations 3 and 4 accurately describe both the decay of refractive index n in response to a single temperature jump and the maximum in n following two large temperature jumps of opposite sign for glassy B_2O_3 .⁵ The relaxation of enthalpy H following a large temperature jump (20 K) is also accurately described by eq 3 and 4 for the chalcogenide glass As_2Se_3 .⁵

Combination of eq 3 and 4 with the Boltzmann superposition principle (as described below) has been used by Moynihan and co-workers^{5,10-12} to give an accurate description of the heat capacity C_p as a function of temperature during rate cooling and reheating through the

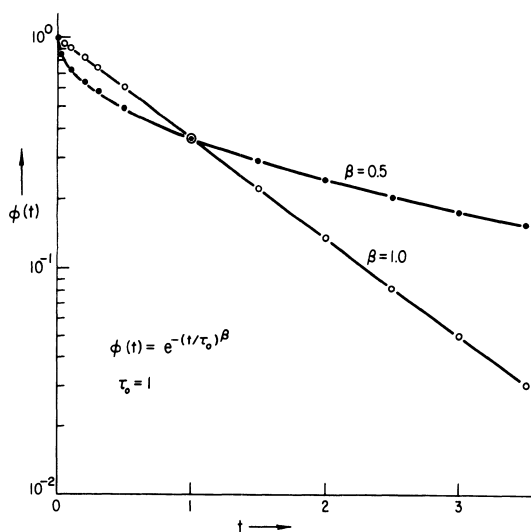


Figure 1. Plots of the decay function given by eq 3 for $\beta = 1.0$ and $\beta = 0.5$.

glass transition for a variety of glasses, including B_2O_3 ,¹⁰ As_2Se_3 ,¹⁰ $NaKSi_3O_7$,¹¹ "5-phenyl-4-ether" [$C_6H_5(OC_6H_4)_3OC_6H_5$],⁵ and poly(vinyl acetate) (PVAc).¹² In particular, the C_p overshoot near T_g during reheating after rate cooling as a function of cooling and heating rates is accurately described.

The development of sub- T_g heat capacity peaks with aging has been well established experimentally since the pioneering work of Illers¹⁵ (see part 1 for further references). We describe here a procedure for accurately calculating these peaks.

II. Model

We first give a summary of the relevant features of Moynihan's treatment of the glass transition kinetics^{5,10} and then describe how annealing is introduced.

The glass transition is treated as a straightforward application of the Boltzmann superposition principle of aftereffects, with the nonexponentiality and nonlinearity described by eq 3 and 4, respectively. For heating or cooling rate Q , the time t and temperature T variables are simply related as

$$dT = Q dt \quad (5)$$

so that the Boltzmann superposition integral over time can be replaced by a corresponding integral over temperature. Thus the response $T_f(T)$ to temperature perturbations is given by

$$T_f(T) = T_0 + \int_{T_0}^T dT' \left\{ 1 - \exp \left[- \left(\int_{T'}^T dT'' / Q\tau_0 \right)^\beta \right] \right\} \quad (6)$$

where T_0 is a starting temperature well above T_g , and T' and T'' are dummy temperature variables. The value of τ_0 varies continuously with T and T_f according to eq 4. A dimensionless heat capacity $C_p(T)$ is defined as

$$C_p(T) = dT_f/dT \quad (7)$$

and is calculated by differentiating eq 6 during cooling from T_0 to a temperature far below T_g and reheating to T_0 again. The relation between $C_p(T)$ and experimental data is described below. The calculated heat capacity during heating, corresponding to the usual DSC scans, therefore depends on both the heating rate and the previous cooling rate through T_g . Equations 4 and 6 comprise the model for the glass transition phenomenon. The present model for annealing is obtained by inserting the

annealing time into the cooling cycle at the annealing temperature in the manner described below.

III. Method of Computation

In practice, eq 6 must be integrated numerically. For this purpose continuous cooling or reheating at a rate Q is replaced by a series of temperature steps, ΔT , followed by isothermal holds of duration $\Delta t = \Delta T/Q$. The magnitude of ΔT must be sufficiently small to ensure linearity; $\Delta T = 1$ K is satisfactory¹⁰ and was used for all the calculations reported here. The evolution of T_f following n temperature steps is then expressed by rewriting eq 6 in the form

$$T_{f,n} = T_0 + \sum_{j=1}^n \Delta T_j \left\{ 1 - \exp \left[- \left(\sum_{k=j}^n \Delta T_k / Q_k \tau_{0,k} \right)^\beta \right] \right\} \quad (8)$$

where $\tau_{0,k}$ is given by

$$\tau_{0,k} = A \exp \left[\frac{x \Delta h^*}{RT_k} + \frac{(1-x) \Delta h^*}{RT_{f,k-1}} \right] \quad (9)$$

The heat capacity corresponding to eq 7 is given by

$$C_{p,n} = \frac{dT_f}{dT} = \frac{T_{f,n} - T_{f,n-1}}{T_n - T_{n-1}} \quad (10)$$

In fitting the model to experimental data, one must normalize the latter by extrapolating the experimental glass and rubber heat capacities into the glass transition region and expressing the measured heat capacities in excess of $C_p(\text{glass})$ as a fraction of the difference $C_p(\text{rubber}) - C_p(\text{glass})$. This normalized C_p has a value zero for the glass and unity for the liquid and is directly comparable with the calculated $C_p(T)$ given by eq 10.

Aging at temperature T_k is introduced into the calculation, in essence, by replacing the term $\Delta T_k/Q_k$ in eq 8 with the annealing time t_e . In the preliminary communication of this model,⁴ t_e was inserted directly into eq 8 in this way during the cooling cycle. The calculation proceeded by cooling at a rate Q_C to the aging temperature T_e , holding at that temperature for time t_e , cooling at the same rate to room temperature (300 K), and reheating immediately at heating rate Q_H . The relaxation time τ_0 of eq 3 was assumed constant over the time t_e ; i.e., no account was made of the self-retarding (nonlinear) aging kinetics. Although this approximation is sufficiently good to permit the prediction of general changes in the heat capacity maximum ($C_{p,\text{max}}$) and the temperature at which it occurs (T_{max}) with t_e and T_e for PVC,⁴ it was necessary to make the parameter x increase explicitly with T_e to give a quantitative account of the experimental data. This shortcoming is largely removed in the computation procedure described here, which incorporates the self-retarding kinetics of aging. The present calculation fits experimental data reasonably well with a single set of four parameters (two of which are constrained by the value of T_g and its variation with quench rate). The self-retarding kinetics were introduced by dividing the aging time into 10 subintervals and calculating T_f and τ_0 at the end of each. Because of the well-established dependence of aging effects on $\log t_e$, the subintervals were determined by dividing t_e into even logarithmically spaced intervals.

During annealing, T is, of course, held constant so that $Q_C = 0$, and eq 8 must be modified to prevent a singularity in the summation over k . This was done by truncating the sum over j in eq 8, with the maximum value of j held fixed at the value at the beginning of the annealing time ($j = n_A$). The summation over k was not truncated, the max-

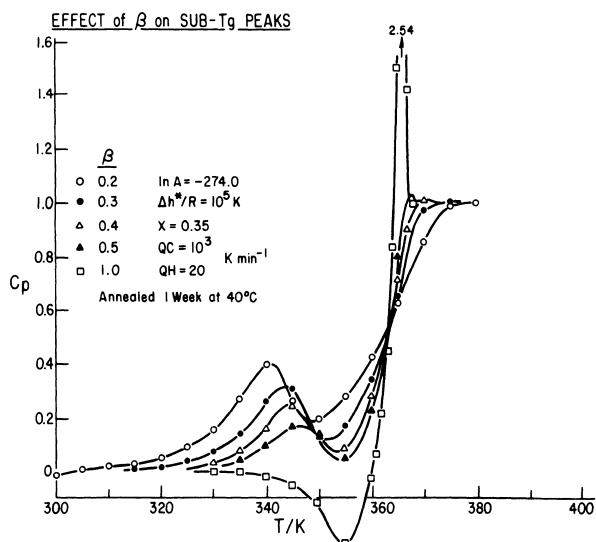


Figure 2. Calculated effect of the nonexponentiality parameter β (eq 3) on the development of sub- T_g heat capacity peaks after annealing at 40 °C for 1 week.

imum value of k being incremented for each subinterval of the aging time. Thus, during annealing eq 8 was modified to

$$T_{f,n} = T_0 + \sum_{j=1}^{n_A} \Delta T_j \{1 - \exp[-(\sum_{k=n_A}^n \Delta t_{e,k} / \tau_{0,k})^\beta]\} \quad (11)$$

where $n_A + 10 \geq n > n_A$ and

$$\Delta t_{e,k} = t_e^{1/10} \quad k = n_A + 1$$

$$\Delta t_{e,k} = t_e^{(k-n_A)/10} - t_e^{(k-n_A-1)/10} \quad k > n_A + 1$$

Equation 11 is a summation version of the integral expressions of Moynihan et al.^{5,10} At the first temperature step after annealing, the upper limit of j was increased from n_A to $n_A + 1$ and the summation over j recommenced using eq 8. As before,⁴ annealing was introduced during the cooling cycle. This is clearly an approximation to most experimental thermal histories, but since these are rarely specified exactly the precise difference is not known.

IV. Calculation Results

We present the model predictions in three sections. In the first, the effects of varying the model parameters are investigated, with the annealing conditions and other aspects of the thermal history held constant. In the second, the model parameters are held fixed and the predicted effects of changes in annealing conditions and thermal history (such as cooling rate before annealing) are presented. In the Discussion the model predictions are compared with experimental data, some of which were presented in part 1. Some additional results of special interest are also given in the Discussion.

The results presented here are the calculated C_p curves for the reheating cycle, corresponding to the experimental DSC scans. In most cases the value of T_g was fixed at 363 K, close to that of PVC. For this purpose, T_g is defined as the temperature at which the normalized C_p is 0.5 during heating at 20 K min⁻¹ after cooling at 10³ K min⁻¹.

A. Variation of Model Parameters. Variations in the nonexponentiality parameter β (eq 3), nonlinearity parameter x (eq 4), activation enthalpy Δh^* (eq 4), and preexponential factor A (eq 4) were studied. The parameters β and x were each varied individually, with the other three held fixed, and Δh^* and A were varied together to keep T_g constant at 363 K. To assess the importance of

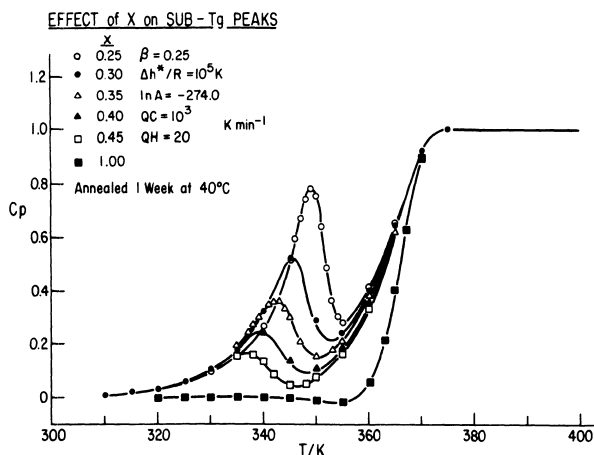


Figure 3. Calculated effect of the nonlinearity parameter x (eq 4) on the development of sub- T_g heat capacity peaks after annealing at 40 °C for 1 week.

the relative difference between T_e and T_g , the parameter A was also varied alone to change T_g .

1. Nonexponentiality Parameter β . The dimensionless parameter β is a direct measure of nonexponentiality or, equivalently, the breadth of the distribution of relaxation times. Smaller values of β correspond to increased nonexponentiality. Typically, β lies in the range 0.4–0.6 for the glass transition.⁵ The calculated effects of changing β on C_p during reheating of an aged glass are shown in Figure 2. The other parameters were fixed at $\Delta h^*/R = 1.0 \times 10^5$ K, $A = 1.01 \times 10^{-119}$ s, and $x = 0.35$, and the experimental variables were fixed at $T_e = 40$ °C, $t_e = 1$ week, $Q_C = 10^3$ K min⁻¹, and $Q_H = 20$ K min⁻¹. Note that A is an empirical parameter with no direct physical significance. The value of Q_C is an estimate of the rate usually referred to in the literature as a “rapid quench”. Figure 2 demonstrates that a distinct sub- T_g heat capacity peak is predicted to occur when $\beta < 1$ but not when $\beta = 1.0$. The peaks are asymmetric, with a low-temperature tail and relatively sharp high-temperature edge. This asymmetry is observed experimentally (e.g., see part 1). The results shown in Figure 2 also indicate that T_{\max} decreases and $C_{p \max}$ increases with decreasing β , and this trend continues for values of β between 0.5 and 1.0 (not shown). The limiting case of $\beta = 1.0$ is considered in the Discussion. The glass transition broadens with decreasing β , as expected, but T_g ($C_p = 0.5$) is unaffected.

2. Nonlinearity Parameter x . The effects of changing x on the calculated C_p scans are shown in Figure 3. The other model parameters and the experimental variables are given in the figure. The calculations indicate that both T_{\max} and $C_{p \max}$ increase with decreasing x (increasing nonlinearity). The effect on $C_{p \max}$ is the same as, and that on T_{\max} the opposite of, decreasing β . This difference in response to variations in x and β permits an unambiguous choice of these parameters when fitting the model to experimental data. Indeed, the calculations performed to date suggest that the development of C_p peaks with annealing is more sensitive to x and β than are the shape of the glass transition and the overshoot behavior at T_g as a function of relative cooling and reheating rates. The limiting case of $x = 1$, where $C_{p \max} = 0$, is considered in the Discussion.

3. Activation Enthalpy Δh^* . The parameter Δh^* (eq 4) can be obtained from the dependence of the frozen-in fictive temperature, T'_f , on cooling rate¹⁰ and is not considered as adjustable in the analysis of the kinetics of the glass transition.¹⁰ However, for the purposes of illustrating how annealing behavior is affected by Δh^* , we shall regard

