

# Principal Features of Structural Relaxation in Glassy Polymers. A Review

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The principal features of models of structural relaxation in the glassy state were reviewed. The concepts of fictive temperature as the structural parameter and nonexponentiality and nonlinearity of structural relaxations were described. Various expressions for the structural relaxation time were presented and compared. One particular model was selected and utilized in a parametric optimization study of structural relaxation. Model predictions were checked against experimental results obtained by volumetric and calorimetric measurements.

## INTRODUCTION

Glasses, which are by a broad definition amorphous solids, are among the oldest materials known to mankind. A recently renewed interest in glasses has been spurred by their newly found applications in advanced technologies, such as electronics, telecommunications, and aerospace. It is safe to say, however, that the technology of glasses is ahead of our understanding of their fundamental characteristics. Systematic studies of the glassy state have a much more recent origin.

The two most prominent features of the glassy state are the glass transition and the structural relaxation.

The glass transition is revealed by a change in the temperature dependence of some property of the material, such as enthalpy or volume, during heating or cooling through the transition region. Broadly defined, the material is liquid above the glass transition and solid below it. The temperature derivative of enthalpy (i.e. the heat capacity) or volume, in the liquid state, is usually larger than its counterpart in the glassy state.

Structural relaxation refers to the phenomenon which occurs when a liquid, originally equilibrated at a temperature  $T_1$  is suddenly cooled to a temperature  $T_2$ , where the structure first experiences an abrupt contraction and then undergoes a series of gradual rearrangements towards equilibrium. The instantaneous (elastic) contraction is the contribution of vibrational relaxations, whose origin is in the response

of atomic bonds, while the subsequent time-dependent decay represents structural relaxation. Experimentally, structural relaxation is detected by the corresponding changes in some structure sensitive property, such as enthalpy, volume or refractive index.

The ultimate goal of studying the relaxation phenomena is the development of a theory of the glassy state. The most important issue concerning the nature of the glassy state is whether the glass transition is a kinetic phenomenon or a manifestation of an underlying thermodynamic transition? Attempts to model the glassy state have been launched from both kinetic and thermodynamic points of view, but their respective implications remain to be fully corroborated by experimental evidence.

The objective of this paper is to present a concise review of the chronological development of models for structural relaxation in glassy materials. It was not our intention to include in this review a number of studies that report the change in some structure sensitive property of a glass without attempting to model it.

## BACKGROUND

### Kinetics

It is known that the inception of the glass transition region, marked by the appearance of a deviation of the monitored property from the equilibrium, shifts with the cooling rate. The slower the cooling rate, the lower the transition temperature; hence the experi-

mental time-scale determines whether the material appears to be in equilibrium or not. From the kinetic point of view, both the glass transition and the structural relaxation are kinetic phenomena and hence could be explained by the same mechanism. The observed similarity in the transitional behavior implies that different glasses should also exhibit common characteristics in their relaxational behavior. Because the structural relaxation proceeds slower than the glass transition, finer details of the mechanism can be deduced from the former.

### Thermodynamics

An explanation of the glassy state from the thermodynamic point of view has always been of great interest. Kauzmann pointed out that the extrapolated configurational entropy of supercooled liquid would become zero before the temperature reaches absolute zero (1). This would create a paradox (the "Kauzmann paradox") since the entropy of the supercooled liquid would equal that of the crystal at some finite temperature, thus contradicting the third law of thermodynamics (2). Kauzmann proposed that a pseudocritical point existed at a temperature below the glass transition, where the supercooled liquid and the crystal are energetically indistinguishable. A glass would relax either toward a supercooled liquid state, or, at temperatures below the pseudocritical point, a crystalline state, and the entropy of the glass would never fall below that of the crystal. Gibbs and DiMarzio held a different view (3). They theorized that a true second-order thermodynamic phase transition occurs below the glass transition temperature, and the glass transition is the kinetic manifestation of that thermodynamic transition. This concept was further expanded by Adam and Gibbs (4), who described structural rearrangements in the glassy state through cooperative movements of atoms. Within a cooperative unit, atoms must behave as one and a whole, with the size of a cooperative unit becoming larger as temperature decreases. When the size of the cooperative unit becomes comparable to the size of the sample, which occurs when the system approaches the second order transition temperature, the structural relaxation virtually ceases. Consequently, the second order transition can never be observed experimentally. Both theories have thus resolved the "Kauzmann paradox", although neither Kauzmann's claim of the eventual crystallization nor Gibbs and DiMarzio's postulation of a second order transition could be verified directly by experiment. More recently, Gutzow and Dobrev utilized irreversible thermodynamics to model the glassy state (5). Upon matching the model prediction with their experimental results, they were able to determine the "most probable values" for the following thermodynamic functions of typical glass forming materials:

$$T_g/T_m \cong 2/3 \quad T_0/T_m = x_0 \cong 1/2 \quad (1)$$

$$\Delta Cp/\Delta S_m \cong 3/2 \quad \Delta \alpha T_g \cong 1/8 \quad (2)$$

$$\Delta S_g/\Delta S_m \cong 1/3 \quad (3)$$

$$\Delta H_g/\Delta H_m \cong 1/2 \quad (4)$$

In Eqs 1 to 4,  $x$  is the relative temperature,  $\Delta \alpha$  the linear coefficient of thermal expansion, subscripts  $g$  and  $m$  denote glass and melt, respectively, and the other symbols have their usual meaning. At present, however, it is fair to say that the quest for a thermodynamic theory of the glassy state continues.

### Viscoelasticity

The above described structural relaxation is triggered by a temperature jump. Another kind of relaxation of structure is caused by the application of a small external stress or strain (usually mechanical or electrical), and that is the subject of viscoelasticity. Viscoelastic analysis of materials initially in structural equilibrium is well documented in the classic texts (6-8). The problem is more complex when a small stress (or strain) is applied to a nonequilibrium structure, because in that case the viscoelastic response and the structural relaxation occur simultaneously. In the rubbery state, structural relaxation in a polymer proceeds extremely fast. The relaxation time is about one min around the glass transition temperature, and about  $10^{-10}$  min at  $30^\circ\text{C}$  above the glass transition temperature. As a result, polymers are always in equilibrium in the rubbery state, and structural relaxation does not affect stress relaxation. In the glassy state, however, structural relaxation is a very slow process; relaxation time is estimated at about  $10^{+10}$  min at  $30^\circ\text{C}$  below the glass transition temperature, and glasses are rarely in equilibrium. The rate of stress relaxation is either comparable (around  $T_g$ ) or faster (below  $T_g$ ) than the rate of structural relaxation. Thus stress relaxation in the glassy state proceeds in a medium that is still undergoing structural relaxation. Disentangling of structural units during stress relaxation is affected by the spatial arrangement of those units, which changes with the progress of structural relaxation. A comprehensive treatment of this subject appears in an excellent monograph by Struik (9) on physical aging (his term for structural relaxation) in various glasses.

## EXPERIMENTAL MEASUREMENTS OF STRUCTURAL RELAXATION

### Enthalpy Relaxation

The property most widely used to study structural relaxation is the enthalpy. This preference was established during the past decade, primarily as a result of the advancements in differential scanning calorimetry (DSC).

The enthalpy of a system in the glassy state is closely related to other thermodynamic properties, the entropy and the volume, as they all change during the course of structural relaxation. Experimentally, changes in enthalpy and entropy are obtained from the specific heat function, while changes in volume are measured directly. It was difficult and

time consuming to carry out the measurement of specific heat (with adiabatic calorimetry) before the development of DSC, and it still is a laborious endeavor to measure the specific volume. This observation is corroborated by the fact that systematic investigations of enthalpy relaxation were reported only in the past two decades. Theoretically, a case can be made that since enthalpy and volume relaxation are caused by the same structural relaxation, they should share the same phenomenological pattern. In fact, it has been shown (10) that phenomenological models derived from volume relaxation and enthalpy relaxation are equivalent.

Enthalpy relaxation can be studied with DSC using either the rate heating approach, which focuses on the effect of cooling (and/or heating) on the specific heat function in the transition range, or the isothermal approach, which follows the enthalpy change during isothermal aging in the glassy state. Both approaches have been applied to study various glasses in the past.

Systematic study of enthalpy relaxation with DSC, that led directly to the development of a model of structural relaxation, was pioneered by Moynihan and coworkers, who used the rate heating approach to study relaxation in several alkali glasses (11), a chalcogenide glass (12), a boron oxide glass (13), an organic molecule (5-phenyl-4-ether) (12), and a fluoride glass (14). Sasabe and coworkers applied the rate heating approach in their studies of soda-lime silica glass (15), and poly(vinyl acetate) (16). Gonchukova employed the rate heating approach to study a glass composed of 60% PbO and 40% SiO<sub>2</sub> (17). Gonchukova and Mazurin also investigated a metallic glass, SiCuPd (18). The isothermal approach was used by Chen to study PdNiP glass (19), and by Chen and Kurkjian to study a boron oxide glass (20).

Several researchers have applied these techniques to study polymeric glasses. Petrie (21) and Marshall and Petri (22) employed the isothermal approach in their research on various polymers, including polycarbonate and poly(ethylene terephthalate). Ott used the isothermal approach in his study of poly(methyl methacrylate), poly(vinyl chloride), and polycarbonate (23). Chen and Wang also used the isothermal approach to study polystyrene (24). Hodge and coworkers applied both the isothermal and the rate heating approach in their investigations of poly(vinyl acetate), poly(vinyl chloride), poly(methyl methacrylate), polystyrene, and polycarbonate (25-29). Prest and coworkers also utilized both approaches in studies of copolymers of styrene and crown ether(4-vinylbenzo-18-crown-6), dispersions of polycarbonate with various small molecules, and blends of polystyrene with poly(2,6-dimethyl 1,4-phenylene oxide) (e.g. 30, 31). Mijovic and coworkers investigated a series of compatible polymer blends, including poly(methyl methacrylate)/poly(styrene-co-acrylonitrile), polystyrene/poly(2,6-dimethyl 1,4-phenylene oxide), and poly(methyl methacrylate)/poly(vinylidene fluoride) blends (32,

33). Cowie and Ferguson reported their results on the enthalpy relaxation in poly(vinyl ethyl ether) and poly(vinyl ethyl ether)/polystyrene blends (34, 35).

Those studies have provided experimental evidence for the occurrence of structural relaxation in various types of glasses; polymeric, inorganic, and metallic, thus suggesting that structural relaxation is a property of the glassy state regardless of the chemical nature of the constituent molecules.

### **Volume Relaxation**

A. J. Kovacs studied volume relaxation in glassy polystyrene, poly(vinyl acetate), polypiperidide, poly(morpholide acrylate), and glucose (36, 37), and found that it proceeded in the same manner for all these materials. This observation also suggests that volume relaxation or, by implication, structural relaxation, is one aspect of the glassy state which is independent of the type of molecules involved. Accurate measurements of the changes in specific volume remain a laborious endeavor, as evidenced by the fact that systematic research on volume relaxation has been carried out only by Kovacs and coworkers in the past four decades. Recently, positron annihilation lifetime spectroscopy has been employed to study volume relaxation in a glassy polycarbonate (38). This technique is based on the correlations between the measured lifetime of the ortho-positronium and the open(free) volume sites in amorphous glassy polymers.

### **Viscoelastic Properties**

Struik studied creep in various glasses (9) and found that with the progress of physical aging (his term for structural relaxation), the rate of creep becomes slower, which is partly due to the densification of the material. To minimize the effect of stress imposed on the sample during the test, he employed a momentary measurement technique. This technique has a shortened measurement time, so that the progress of structural relaxation during the measurement is negligible. Essentially, Struik's technique is an iso-structural measurement with which it becomes possible to study the effect of instantaneous structure on the viscoelastic behavior of glasses. An ample collection of examples of the use of viscoelastic measurements to follow the progress of structural relaxation in a vast array of organic and inorganic glasses can be found in Struik's book (9). The same technique was also used by Mijovic and coworkers in their studies of various polymer blends (39, 40), and by Lee and McKenna in their investigation of epoxy networks (41).

### **MODELING OF STRUCTURAL RELAXATION**

#### **Fictive Temperature as Structural Parameter**

Over the years, two principal characteristics of the structural relaxation have been established and must be accounted for in the modeling studies of the glassy state. They are 1) nonlinearity, and 2) nonexponen-

tiality or memory effect. We shall limit ourselves here to a brief description of those phenomena, as they have been discussed in detail by others, as excellently recapped in the book by Scherer (42). The dependence of structural relaxation on the direction and magnitude of the temperature jump implies nonlinearity. Asymmetry is *de facto* a manifestation of nonlinearity, in that the structural relaxations starting from the same amount of deviation but with the opposite signs in temperature follow asymmetric routes. Nonexponentiality or memory effect essentially signifies that structural relaxation is composed of numerous processes, each characterized by its own relaxation time. Thus a distribution of relaxation times must be included in the analysis to account for nonexponentiality. The unambiguous proof for the existence of the memory effect has come from the classic study of Kovacs, who established the influence of the past thermal history on the present behavior of glassy polymers (36, 37).

A major pioneering contribution to the development of the theory of structural relaxation was the introduction of the concept of fictive temperature by Tool (43). He recognized that a nonequilibrium glassy state could not be described by temperature and pressure only and suggested that the structural relaxation time must also be a function of The Changing Structure, the latter being described by a parameter termed the fictive temperature ( $T_f$ ). Let us assume that a material is cooled from the equilibrium state at  $T_0$  to the glassy state at  $T_1$ , along the path described in Fig. 1. At  $T_1$ , the glass is initially characterized by a structure sensitive property  $P(T_1)$ . The fictive temperature is obtained from Fig. 1 by extrapolating a line from  $P(T_1)$  with slope  $\alpha_{pg}$  to intersect with a line extrapolated from  $P(T_0)$  with a slope of  $\alpha_{pl}$ . Mathematically, fictive temperature is defined as:

$$\int_T^{T_1} [\partial(P - P_g) / \partial T] dT = \int_{T_f}^{T_1} [\partial(P_e - P_g) / \partial T] dT \quad (5)$$

where  $P_e$  is the actual (or extrapolated) equilibrium value of  $P$ ,  $P_g$  is the actual (or extrapolated) glassy state value of  $P$ ,  $T$  is the temperature of the given state,  $T_0$  is the temperature in the equilibrium liquid state and  $T_f$  is the fictive temperature. Taking the derivative with respect to temperature on both sides of Eq 5, an equivalent form is obtained, where  $R$  is the temperature derivative of  $P$ :

$$dT_f / dT = [(R(T) - R_g(T)) / (R_e(T_f) - R_g(T_f))] \quad (6)$$

The following equation was originally derived by Tool to describe the change in fictive temperature (thence structural relaxation) as a function of time:

$$dT_f / dt = (T - T_f) / \tau_p \quad (7)$$

where  $\tau_p$  is the structural relaxation time for property  $p$ . The function of fictive temperature in modeling relaxation phenomena is twofold: 1) at constant pressure, the fictive temperature and the temperature of the glass together describe the thermody-

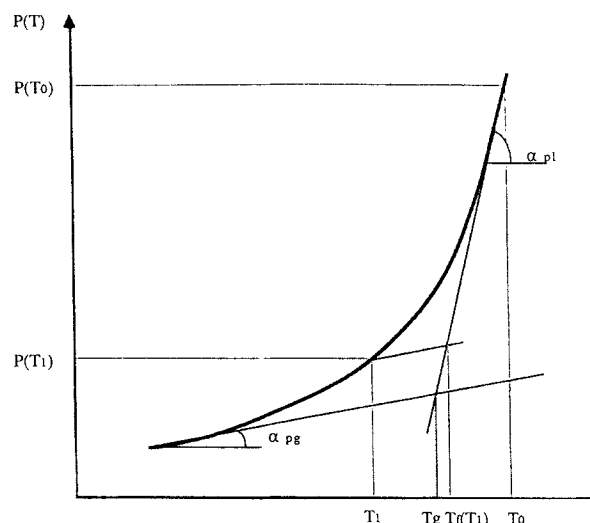


Fig. 1. Schematic of the determination of fictive temperature from a plot of structure sensitive property ( $P$ ) as a function of temperature.

amic state of the system, and 2) the temperature derivative of the fictive temperature corresponds to that of the relaxing property, as expressed in Eq 6, thus providing a link between changes in the thermodynamic state and the property of the system. The second role is significant, because, for a given set of treatments, fictive temperature can be established as a function of temperature through model calculations, the temperature derivatives of both the fictive temperature and the relaxing property can be conveniently obtained.

### Structural Relaxation Time

Following Tool's work, various expressions for the relaxation time have been put forward, all of them containing temperature and fictive temperature as variables in the exponential form. We classified them into the following three groups.

#### Expressions based on the generalized Arrhenius equation

These are usually referred to as the Narayanaswamy expression and have the following form:

$$\tau = A \exp[X \Delta h^* / RT + (1 - X) \Delta h^* / RT_f] \quad (8)$$

where  $T$  and  $T_f$  are as previously defined and  $\tau$  is the structural relaxation time. Parameter  $X$  ( $0 < X < 1$ ) partitions the activation energy  $\Delta h^*$  into two parts, characterizing the relative effects of temperature and structure, respectively, on the structural relaxation time. Expressions of this type have been used by Tool (44), Ritland (45), Narayanaswamy (46), Mazurin, *et al.* (47), Moynihan, *et al.* (11), and Kovacs, *et al.* (48).

#### Expressions based on the free volume concept (49-53)

These are of the form:

$$\tau = A \exp\{B / [R(T_f - T_2)] + E / RT\} \quad (9)$$

where  $A$ ,  $B$ , and  $E$  are constants, and  $T_2$  is the temperature of zero free volume. Expressions of this kind have been utilized by Macedo and Litovitz (54), and Mazurin, *et al.* (55).

#### Expressions based on the configurational entropy concept

Configurational entropy was introduced into expressions for relaxation time by Adam and Gibbs (4). In accordance with the Gibbs-DiMarzio thermodynamic theory of the glass transition (3), the expression for relaxation time becomes:

$$\tau = A \exp \left\{ B/RT \left[ \int_{T_2}^{T_f} (\Delta C_p/T) dT \right] \right\} \quad (10)$$

where  $A$  and  $B$  are constants,  $T_2$  is the second order transition temperature predicted by the Gibbs-DiMarzio theory,  $T_f$  is the fictive temperature, and  $\Delta C_p$  is the configurational heat capacity. Expressions of this type have been used by Howell, *et al.* (56), Plazek and Magill (57), Scherer (58), Matsuoka (59), and Hodge (29). A similar expression was also utilized by Gutzow (60).

The obvious question regarding which of the expressions for relaxation time is the most accurate one has been debated in the literature (30, 42, 59). Best fits of the experimental data have been obtained with the Narayanaswamy and the Adam-Gibbs type expressions, with the former being easier to manipulate. The critics of the Narayanaswamy expression point to its empirical character, the uncharacteristically large values of the activation energy, and the fact that the equation reduces to the Arrhenius form at equilibrium instead of the well-known Williams-Landel-Ferry (WLF) or Vogel-Fulcher forms. The Adam-Gibbs equation has gained popularity in recent years due to its fundamental character and good fits of data. The inherent assumption in the Adam-Gibbs equation that  $\Delta C_p$  is a measure of structural relaxation has been challenged by Goldstein (61), who argued that a considerable part of the  $\Delta C_p$  value arises from anharmonic vibrations and secondary relaxations which should be considered separately from structural relaxation. Matsuoka (59) has pointed out that the Adam-Gibbs equation modified to account for the nonequilibrium state gives the correct form of the relaxation time, since it is capable of predicting the behavior in the equilibrium state as well, where it assumes the well-known Vogel-Fulcher form. Nevertheless, the Narayanaswamy expression has been used widely and with success for prediction of structural relaxation in numerous glasses.

#### Phenomenological Models of Structural Relaxation

Tool's equation was successful in describing the dependence of the glass transition temperature on the cooling rate, but it contained a single relaxation time and hence couldn't account for the nonexponentiality (or memory effect). In terms of the viscoelastic analogy, it would correspond to the situation where a

single Maxwell element is used to describe stress relaxation of a polymer. The deficiencies of Tool's equation were demonstrated by several researchers (e.g. 45, 46), and it was recognized that in order to account for the distribution of relaxation times, models with a single relaxation time had to be modified. The next major contribution in that direction was made in the classic studies by Gardon and Narayanaswamy (62), and Narayanaswamy (46), who accounted for both nonlinearity and nonexponentiality of the structural relaxation. Narayanaswamy pointed out that nonlinearity results from the time dependence of the structural relaxation and that linearity can be restored by using the reduced time,  $\xi$ :

$$\xi = \int_0^t \phi(T, T_{fp}) dt' \quad (11)$$

where  $\phi$  is the shift function defined as the ratio of the instantaneous viscosity and a reference viscosity measured at some reference temperature. Nonexponentiality was accounted for by introducing the memory integral and calculating the fictive temperature by adding to the actual temperature the part of the temperature change that is "remembered" in the structure. By assuming thermorheological simplicity he was able to describe the relaxation function for an arbitrary temperature jump. Narayanaswamy expressed the structural relaxation time with a generalized Arrhenius equation, with parameter  $X$  inserted to partition the relative effects of temperature and structure on the structural relaxation time. Although essentially phenomenological, Narayanaswamy's approach has met with considerable success in describing experimental results on a host of glasses.

Two principal routes to the subsequent development of structural relaxation models containing a relaxation spectrum are based on the use of:

- 1) Multi-parameter mechanism, as in the Kovacs-Aklonis-Hutchinson-Ramos (KAHR) model (48), and
- 2) The Kohlrausch-Williams-Watts (KWW) equation, as in the model developed by Moynihan and coworkers (11, 13).

Naturally, an equation for structural relaxation time is needed in either approach. And while Moynihan and coworkers (11, 13), Kovacs and coworkers (48), and Mijovic and coworkers (33) obtained excellent results using the Narayanaswamy type expression for the relaxation time, Matsuoka and coworkers (63), and Hodge (29) were equally successful in describing their data with the Adam-Gibbs equation. A common thread between the above cited approaches is that they all postulate:

- 1) the existence of a spectrum of relaxation times, and
- 2) thermorheological simplicity.

In the KAHR model, mathematical manipulations are simplified by expressing the relaxation through a new

variable,  $W$ , which is proportional to the difference between  $P$  and  $P_{eq}$ , the latter being the equilibrium value of  $P$  at the same temperature. The relaxation of  $P$  is described by the following set of kinetic equations:

$$d\delta_i/dt = -\delta_i/\tau_i - \Delta\alpha_i q \quad 1 < i < N \quad (12)$$

$$\begin{aligned} \tau_i &= \tau_{i,r} \exp[-\theta(T - T_r)] \exp[-(1 - X)\theta\delta/\Delta\alpha] \\ &= \tau_{i,r} a_T a_\delta = \tau_{i,r} a \end{aligned} \quad (13)$$

and

$$\delta = \sum_{i=1}^N \delta_i \quad (14)$$

In the above equations,  $\delta_i$  is the contribution to  $\delta$  from the  $i$ -th mechanism,  $\tau_i$  is the  $i$ -th relaxation time,  $a_T$  and  $a_\delta$  are the shift factors,  $\theta$  is the scaling factor,  $X$  the partitioning parameter,  $\Delta\alpha$  is the excess temperature coefficient of the liquid with respect to the glass,  $\Delta\alpha_i$  is the contribution to  $\Delta\alpha$  from the  $i$ -th mechanism, and  $q$  is the heating ( $q > 0$ ) or cooling ( $q < 0$ ) rate. The simulated relaxation of  $P$  can be obtained by solving Eqs 12 to 14 simultaneously.

Besides expressions derived from the first principles, as in the case of the KAHR model, there are empirical expressions that describe relaxation in the glassy state. Moynihan and coworkers obtained an excellent fit of data using the Kohlrausch-Williams-Watts equation in the following form:

$$\phi(t - t_1, t) = (P - P_e)/(P_0 - P_e) = \exp\left[-\left(\int_{t_1}^t dt'/\tau\right)^\beta\right] \quad (15)$$

where  $t_1$  is the time when the change in temperature occurs,  $P_0$  is the value of property  $P$  at time  $t_1$ ,  $P_e$  is the equilibrium value of  $P$  at the final temperature,  $\beta$  is a constant, and  $\tau$  the characteristic relaxation time expressed in the narayanaswamy form given by Eq 8. The above model can be extended to nonisothermal situations by assuming that the relaxation function can be represented by the supersposition of responses of the system to the series of temperature jumps that constitute the thermal history. The model then assumes the form:

$$T_f(T) = T_0 + \int_{T_0}^T dT' \left\{ 1 - \exp\left[-\left(\int_{t(T')}^{t(T)} dt/\tau\right)^\beta\right] \right\} \quad (16)$$

where  $T_0$  is the initial temperature.

The fictive temperature  $T_f$  is related to property  $P$  and the normalized relaxation function  $\phi$ , as follows:

$$\begin{aligned} \phi(t - t_1, t) &= (P - P_e)/(P_0 - P_e) \\ &= [T_1 - T_f(T)]/(T_1 - T_0) \end{aligned} \quad (17)$$

The simulated relaxation of  $P$  can be obtained by solving Eqs 16 and, 8, 9, or 10, simultaneously.

It is instructive to note that Chow and Prest (10) have shown that the above described models are essentially equivalent, in that the Moynihan model

can be derived from the KAHR model when the number of mechanisms in the latter ( $N$  in Eq 14) is infinite.

### Optimization of Model Parameters

As an example of modeling sequence we shall consider the optimization procedure based upon the use of an equation for fictive temperature in the form written by Moynihan (13), coupled with the Narayanaswamy expression for structural relaxation time. The choice of the model merely reflects the good agreement with experimental results obtained in our laboratory, and is not meant to promote one type of model or expression for the structural relaxation time over the other. To accommodate the discrete nature of numerical calculations, we begin by rewriting Eqs 16 and 8 as follows:

$$\begin{aligned} T_f(m) &= T_0 + \sum_{j=1}^m \Delta T(j) \\ &\times \left\{ 1 - \exp\left[-\left(\sum_{k=j}^m \Delta t(k)/\tau(k)\right)^\beta\right] \right\} \end{aligned} \quad (18)$$

and

$$\begin{aligned} \tau(k) &= A \exp\{X\Delta h^*/[RT(k)] \\ &+ (1 - X)\Delta h^*/[RT_f(k)]\} \end{aligned} \quad (19)$$

In Eqs 18 and 19,  $m$  is an iteration index, and  $j$  and  $k$  are dumb indices. A caution must be exercised in that  $T_0$ , the starting temperature for the simulation, must be sufficiently high, so that the system is initially in equilibrium at that temperature. This is a necessary condition since the properties of glasses are route dependent, and every step in the thermal history continues to affect their current response. For simple thermal histories the conversion from continuous to discrete form can be performed in a straightforward manner, while a more complex picture emerges when thermal history includes both isothermal and rate heating steps. Let us consider a thermal history sequence consisting of a cooling step (from  $T_0$  in the rubbery state to  $T_1$  in the glassy state), an isothermal step (relaxation in the glassy state for time  $t_a$ ), and a heating step (from  $T_1$  in the glassy state back to  $T_0$  in the rubbery state). To model this sequence it is necessary to rewrite Eq 18 separately for each step in the sequence as follows:

For the cooling step:

$$\begin{aligned} T_f(m) &= T_0 + \sum_{j=1}^m \Delta T(j) \\ &\times \left\{ 1 - \exp\left[-\left(\sum_{k=j}^m \uparrow \Delta T(k)/q(k)/\tau(k)\right)^\beta\right] \right\} \end{aligned} \quad (20)$$

and  $1 \leq m \leq IM$

For the isothermal step:

$$T_f(n) = T_0 + \sum_{j=1}^m \Delta T(j) \times \left\{ 1 - \exp \left[ - \left( \sum_{k=j}^m \uparrow \Delta T(k)/q(k) \right) / \tau(k) + \sum_{k=m+1}^m \Delta t(k)/\tau(k)^\beta \right] \right\} \quad (21)$$

and  $IM \leq n \leq IN$ .

For the heating step:

$$T_f(n) = T_0 + \sum_{j=1}^m \Delta T(j) \times \left\{ 1 - \exp \left[ - \left( \sum_{k=j}^m \uparrow \Delta T(k)/q(k) \right) / \tau(k) + \sum_{k=m+1}^m \Delta t(k)/\tau(k) + \sum_{k=n+1}^c [\Delta T(k)/q(k)]/\tau(k)^\beta \right] \right\} + \sum_{j=n+1}^c \Delta T(j) \times \left\{ 1 - \exp \left[ - \left( \sum_{k=j}^m \uparrow \Delta T(k)/q(k) \right) / \tau(k)^\beta \right] \right\} \quad (22)$$

and  $IN \leq c \leq IC$ .

In Eqs 20 to 22,  $m$ ,  $n$ , and  $c$  are iteration indices,  $j$  and  $k$  are dumb indices, and  $IM$ ,  $IN$ , and  $IC$  mark the last iterations in the cooling, isothermal, and heating steps, respectively. The values of  $IM$ ,  $IN$ , and  $IC$  are determined by parameters  $T_0$ ,  $T_1$ ,  $t$ ,  $\Delta T(j)$ , and  $\Delta t(j)$ . If the temperature increments are uniform during cooling, i.e.  $\Delta T = \Delta T(j)$ , then  $IM = (T_1 - T_0)/\Delta T$ . In this case  $\Delta T$  is negative, as it should be for the cooling step. The reader will note that an expression for the relaxation time must be chosen and inserted into Eqs 20 to 22. If, for instance, the Narayanaswamy type equation is chosen, it should be used in the form given by Eq 19. The two principal characteristics of structural relaxation are implicitly accounted for in Eqs 19 to 22 by the following inequalities;  $\beta \neq 1$  (nonexponentially) and  $X \neq 1$  (non-linearity). Finally, the temperature derivative of the fictive temperature in the  $i$ -th interval during cooling or heating can be approximated by:

$$dT_{f(i)}/dT = [T_{f(i+1)} - T_{f(i)}]/[T_{(i+1)} - T_i] \quad (23)$$

From Eqs 19 to 22, the model yields the  $T_f$  of the system as a function of the thermal history, while from Eq 23 one obtains the temperature derivative of the fictive temperature. The latter is related to the

relaxing property, such as the volume in the case of volume relaxation or enthalpy (or its derivative, i.e. the specific heat) in the case of enthalpy relaxation, by Eq 6. In this manner it is possible to compare the model prediction with the experimental results and hence check the validity and accuracy of the model.

When Eqs 20 to 22 are used in conjunction with the Narayanaswamy expression, four adjustable parameters are needed to simulate structural relaxation;  $X$ ,  $\beta$ ,  $\Delta h^*$ , and  $A$  (see Eq 8 or 19). They are considered material characteristics despite the unclear physical meaning. The quantity  $\Delta T_i$  is used to vary the size of the temperature increment in the simulation of various steps in the thermal history. Parametric studies of this kind have been carried out to establish the effect of variation of each adjustable parameter on the calculated results (28, 29, 41). An optimization procedure must be executed in order to establish a set of parameters that best describe the relaxing property. Further details of the effect of various model parameters on the shape of the relaxation property curve have been published in the literature (e.g. 41). Similar modeling approach was recently used by ten Brinke (64) in his investigation of the interfacial region in block copolymers.

We shall next present in a somewhat different but convenient form some of the most recent results obtained in our laboratory, using the above described modeling procedure to simulate the enthalpy relaxation of several polymeric glasses. Using the above outlined procedure, we obtained the optimum model parameters for isothermal relaxation of a series of compatible polymer blends, and calculated the heat capacity ( $C_p$ ) as a function of temperature. A numerical integration of  $C_p$  along the heating step from the aging temperature ( $T_a$ ) to  $T_1$  in the rubbery state, yields the enthalpy difference between the equilibrium state at  $T_1$  and the state at  $T_a$ , the latter being characterized by the corresponding isothermal aging time,  $t_a$ . We term that quantity  $\Delta H(t_a, T_a)$ . An additional integration performed on the extrapolated equilibrium  $C_p$  function yields the extrapolated difference in enthalpy between the equilibrium states at  $T_a$  and  $T_1$ . We term that quantity  $\Delta H_e(T_a)$ . The extent of enthalpy relaxation can be expressed in terms of function  $\phi$ , as follows:

$$\phi(t, T_a) = [H_i(t, T_a) - H_e(T_a)]/[H_0(T_a) - H_e(T_a)] \quad (24)$$

In terms of the above described quantities, Eq. 24 can be rewritten as:

$$\phi(t_a, T_a) = [\Delta H_e(T_a) - \Delta H(t_a, T_a)]/[\Delta H_e(T_a) - \Delta H(0, T_a)] \quad (25)$$

Further, Eqs 24 and 25 can be combined into the following form:

$$\phi(t_a, T_a) = 1 - [\Delta H(t_a, T_a) - \Delta H(0, T_a)]/[\Delta H_e(T_a) - \Delta H(0, T_a)] \quad (26)$$

or equivalently:

$$\Delta H(t_a, T_a) - \Delta H(0, T_a) = (1 - \phi)[\Delta H_e - \Delta H(0, T_a)] \quad (27)$$

By taking the logarithm of both sides of Eq 27:

$$\log[\Delta H(t_a, T_a) - \Delta H(0, T_a)] = \log(1 - \phi) + \log[\Delta H_e(T_a) - \Delta H(0, T_a)] \quad (28)$$

The bracketed expression on the left hand side of Eq 28, renamed  $\Delta Ht_a$ , is plotted as a function of the logarithm of aging time ( $\log t_a$ ) in Fig. 2. The results were obtained on glassy poly(methyl methacrylate) aged at 20, 35, and 50°C below its glass transition temperature. One  $H$  unit on the ordinate corresponds to six Joules. The displayed data were vertically shifted by:  $-0.06$  at  $T_g - 50^\circ$ ;  $-0.10$  at  $T_g - 35^\circ$ , and  $-0.18$  at  $T_g - 20^\circ\text{C}$ . The model predictions were obtained with the following parameters:  $X = 0.338$ ;  $\beta = 0.265$ ;  $\Delta h^*/R/1000\text{K} = 132.2$ , and  $\ln A = -359.8$ . The agreement between the model prediction (solid curves) and the experimental results (discrete symbols) is quite good.

### Correlations Between Structural Relaxation and Viscoelastic Relaxation

Structural relaxation is accompanied by a simultaneous change in all structure sensitive physical/mechanical properties. Naturally, a fundamental correlation between structural relaxation and the changing properties of the glass would be of great interest to scientists and engineers. Changes in mechanical and dielectric properties during the course of structural relaxation are of particular interest, but one must remember that their measurements involve the use of an external stress (or strain) which, regardless of its magnitude, will affect the ongoing structural relaxation. The application of even smallest stress or strain could shorten the relaxation time by order(s) of magnitude and hence caution must be exerted in seeking correlations between volume and enthalpy relaxation on the one hand, and viscoelastic (mechanical or dielectric) measurements on the other hand. The two approaches can be viewed as manifestations of the same structural relaxation although one must bear in mind that they differ fundamentally in terms of the cause and the effect. A good starting point for theoretical analysis is Robertson's model (65) of strain induced density fluctuations that lead to an increase in the configurational entropy and a simultaneous decrease in the relaxation time. And while the theoretical background of correlations between structural and viscoelastic relaxations has not been explored, empirical correlations between the two have been reported. In our recent investigation of volume relaxation and dynamic mechanical relaxation of amorphous poly(ether ether ketone) (PEEK) in the glassy state (66), a linear correlation between changes in volume and storage modulus at a series of temperatures below the glass transition was ob-

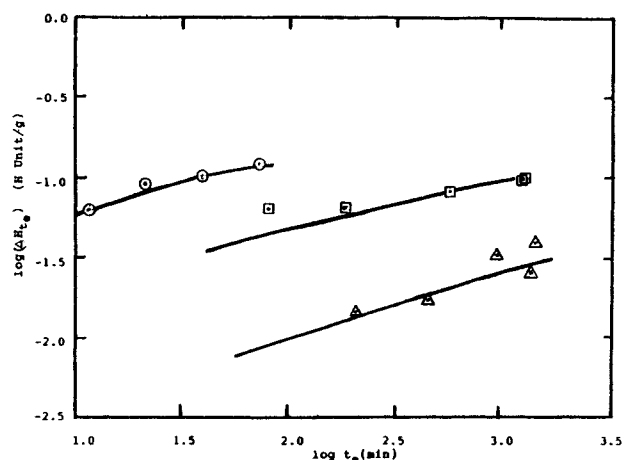


Fig. 2.  $\Delta Ht_a$  as a function of aging time for PMMA. Data are for aging at  $T_g - 50^\circ$  ( $\Delta$ ),  $T_g - 35^\circ\text{C}$  ( $\square$ ), and  $T_g - 20^\circ\text{C}$  ( $\circ$ ). Solid curves represent the model predictions.

served. Although intuitively expected, the produced trend is empirical in nature, and further research is required to establish the theoretical background for the observed results. Comprehensive efforts along those lines are currently underway at the Polytechnic University and the University of Naples.

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