Proposed correlation between enthalpic and viscoelastic measurements of structural relaxation in glassy polymers

Jovan Mijović* and Tai Ho†
Polytechnic University, Department of Chemical Engineering, 6 MetroTech Center, Brooklyn, NY 11201, USA
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An investigation was carried out seeking to correlate the results of enthalpic and viscoelastic measurements of the progress of structural relaxation in glassy polymers. Experimentally, changes in enthalpy were followed by calorimetry, and changes in the viscoelastic response by stress relaxation. The Narayanaswamy/Moynihan model was used in the simulation of enthalpy relaxation. An optimized set of model parameters was determined, for which the calculated enthalpy relaxation times were comparable to the experimental stress relaxation times, thus providing an empirical link between two different manifestations of the same process.

(Keywords: modelling; enthalpy; structural relaxation; stress relaxation; glassy state)

INTRODUCTION

The two principal phenomena that characterize the glassy state are the glass transition temperature and the structural relaxation. The glass transition is revealed by a change of some material property, such as enthalpy or volume, during heating or cooling through the transition range. Structural relaxation occurs when an equilibrated liquid is quenched to some lower temperature, where the structure first contracts abruptly and then undergoes a series of rearrangements towards the new equilibrium. The instantaneous contraction is due to the vibrational relaxation of atomic bonds, and the subsequent time-dependent change is referred to as structural relaxation. An excellent account of structural relaxation can be found in the book by Scherer[1].

The relaxation of structure in the presence of an externally applied stress or strain is the subject of viscoelasticity. Viscoelastic analysis of materials which are initially in equilibrium is well documented in the literature[2–4]. A more complex situation is encountered when a stress (or strain) is applied to a non-equilibrium structure, in which case the structural relaxation and the viscoelastic response occur simultaneously. A comprehensive treatment of viscoelastic analysis of glasses appears in the book by Struik[5] on physical ageing (his term) of polymers.

Structural relaxation in polymers has been studied predominantly by dilatometric[6,7] and calorimetric[8–11] measurements, and various models have been proposed to describe it[12–14]. Most models are based either on fundamental kinetic expressions[14] or empirical equations of the Kohlrausch–Williams–Watts type[5]. Various expressions for the relaxation time were used in the models, including those based on the generalized Arrhenius equation[15–17], the free volume concept[18,19], and the configurational entropy concept[20–23], which was introduced into expressions for relaxation times by Adam and Gibbs[24] in accordance with the thermodynamic theory of Gibbs and DiMarzio[25]. A comparison of various expressions for relaxation time can be found in the literature[1,26].

The immediate background for this study has been reported in a series of papers by our group published in the last two years[27–30], and will not be restated here. The Narayanaswamy/Moynihan model, which was successfully used to simulate enthalpy relaxation in a series of polymer blends, is also used in this work.

The main objective of this study was to seek a correlation between the results of enthalpy relaxation and stress relaxation which were generated during the course of structural relaxation in polymeric glasses.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA), poly(styrene-*co*-acrylonitrile) (SAN) and their blends were used in this study. PMMA was a low-T_g injection moulding grade Plexiglas VS-100 from Rohm and Haas. SAN was Tyril-1000 natural from Dow Chemical, containing 25.3 wt% acrylonitrile. Materials characterization and sample preparation were described in our earlier communications[27–30].

Processing

Samples were processed by twin-screw extrusion followed by compression moulding into 2 mm thick sheets.

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* To whom correspondence should be addressed
† Present address: Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC, WA 20375-5000, USA

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Techniques

Thermal analysis was performed in a Perkin–Elmer DSC Model 7. Both isothermal and rate-heating approaches were used, and they are described in detail elsewhere[29]. Ageing was conducted at three different temperatures ($T_g = 20$, 35 and 50°C) and at three different times (2, 4 and 8 h). Stress relaxation experiments were performed on samples cut from the moulded sheets. Testing was done in accordance with the procedure described elsewhere[27,30].

RESULTS AND DISCUSSION

We begin our discussion with a brief description of the main features of the analysis of calorimetric data generated in isothermal and rate-heating tests. The starting point in our analysis is the Kohlrausch–Williams–Watts equation[31], which has been used by Moynihan and co-workers[5] to describe isothermal structural relaxation in the following form:

$$\phi(t-t_1,t)=(P-P_e)/(P_0-P_e)=\exp\left[-\left(\int_{t_1}^{t}\mathrm{d}t'/\tau\right)^{\beta}\right] \tag{1}$$

where t_1 is the time when the temperature change occurs, P_0 is the value of P at t_1, P_e is the equilibrium value of P, and β is a constant ($0 \leqslant \beta \leqslant 1$). The relaxation time τ is expressed in the Narayanaswamy form[17] as follows:

$$\tau = A\exp[X\Delta h^*/(RT)+(1-X)\Delta h^*/(RT_f)] \tag{2}$$

where A is a constant, Δh^* is a characteristic activation energy, X is a partitioning parameter ($0 \leqslant X \leqslant 1$) that separates Δh^* into two parts, which characterize temperature and structure dependence, respectively, R is the ideal gas constant, and T_f is the fictive temperature[15]. The following correlation relates the fictive temperature to the property P, during the isothermal relaxation after a temperature jump from T_0 to T_1:

$$\phi(t-t_1,t)=(P-P_e)/(P_0-P_e)=[T_1-T_f(t)]/(T_1-T_0) \tag{3}$$

In non-isothermal situations, taking the relaxation function to be linear with respect to temperature jumps, the net response of the system can be formulated as the superposition of responses to the series of temperature jumps that constitute the thermal history. The resulting equation is:

$$T_f(T)=T_0+\int_{T_0}^{T}\mathrm{d}T'\left[1-\exp\left(-\left(\int_{t(T')}^{t(T)}\mathrm{d}t/\tau\right)^{\beta}\right)\right] \tag{4}$$

where T_0 is the initial temperature.

The structural relaxation of P can be obtained by solving equations (2) and (4) simultaneously. We shall refer to the phenomenological model of structural relaxation composed of equations (2) and (4) as the Narayanaswamy/Moynihan model, although many other researchers have contributed to its development.

Equations (2) and (4) must be rewritten first in discrete form and then solved numerically. For simple thermal histories the conversion from continuous to discrete form is straightforward, but the procedure is more involved when the thermal history contains both isothermal and rate-heating steps. A complete set of equations and further details of the calculation procedure for simulation of structural relaxation during an arbitrary thermal history have been described in our previous communication[29] and will not be restated here.

Let us now digress and briefly recap the main features of our viscoelastic analysis. Stress relaxation tests were conducted in a series of 'isostructural' measurements and the data were analysed with the Kohlrausch–Williams–Watts equation in the manner described before[27,30]. One major finding in our analysis was that the stress relaxation time for a series of polymer blends depended on the blend composition, ageing temperature and ageing time, according to the following expression:

$$\ln\tau = C_w + C_T\ln(T_g - T) + C_t\ln t_a \tag{5}$$

where C_w, C_T and C_t are the compositional coefficient, the ageing temperature coefficient and the ageing time coefficient, respectively. The ageing time coefficient has been investigated in depth by Struik[5], while the ageing temperature coefficient has not been reported before. For comparison purposes we made use of some of Struik's data for PMMA and SAN by replotting them in the form of $\ln\tau$ *versus* $(T_g - T)$, which enabled us to calculate the value of C_T for each polymer. The observed agreement between Struik's results for the ageing time and the ageing temperature coefficients and our values was excellent[30].

We then re-examined the results of our calorimetric studies and found out that a relationship of the type given by equation (5) could also describe the isothermal relaxation times obtained using the Narayanaswamy/Moynihan model simulation. For example, we determined the optimum model parameters for SAN and used them to calculate the corresponding relaxation times at three different ageing temperatures. The results are displayed in *Figure 1*, where calculated relaxation times are plotted as a function of ageing time. On a double logarithmic plot, the relaxation time curve consists typically of three distinct parts; an initial stage where relaxation time increases almost negligibly with ageing time; a second stage where relaxation time increases rapidly and linearly with ageing time; and a final stage where relaxation time levels off. The onset of the second and third stages shifts to longer ageing times with decreasing temperature. At ageing temperatures utilized in this study (i.e. $T_g = 20$, 35 and 50°C), there exists a common linear interval on the ageing time scale for all three curves, which extends from 10^4 to 10^7 min, as seen in *Figure 1*. A regressional analysis

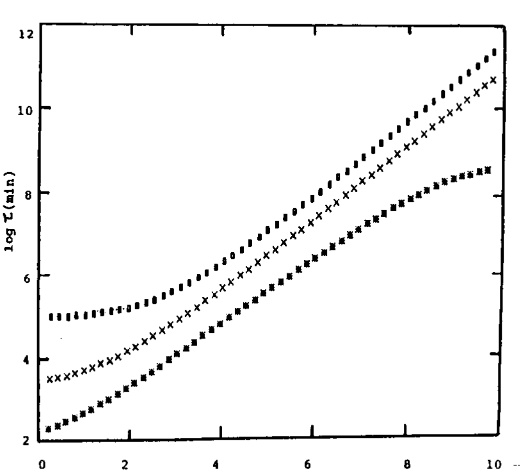

Figure 1 Isothermal relaxation time as a function of ageing time for SAN at different ageing temperatures: □, $T_g = 50°C$; ×, $T_g = 35°C$; *, $T_g = 20°C$

of the values of isothermal relaxation time in this linear interval yielded a power law relationship between the relaxation time and both ageing time and temperature, which can be described by equation (5). The ageing time coefficient was calculated to be 0.79 at $T_g = 20°C$ and 0.88 at $T_g = 35$ and $T_g = 50°C$, while the ageing temperature coefficient was 3.68 for all ageing times and temperatures within that interval. These numbers are extremely close to those obtained from stress relaxation experiments, where C_t was found to vary from 0.88 and 1.01, while C_T was constant and equal to 3.33[30].

The observed similarity between the isothermal relaxation times calculated from enthalpy relaxation and from stress relaxation suggests that there might be a connection between the two. We then proceeded with an attempt to find and describe that connection in terms of the Narayanaswamy/Moynihan model parameters.

First, we performed a set of parametric calculations intended to identify a range for each parameter where the Narayanaswamy/Moynihan model simulation yields isothermal relaxation times which possess the following characteristics of the stress relaxation times:

(i) The ageing temperature coefficient $C_T \geq 3.3$.

(ii) The ageing time coefficient $C_t \leq 1.0$.

(iii) The inception of the linear region (the second stage defined above and shown in *Figure 1*) is of the order of 10 min.

Four adjustable parameters used in the simulation of enthalpy relaxation with the Narayanaswamy/Moynihan model (X, Δh^*, β and A) are considered material characteristics despite their unclear physical meaning. The fifth quantity, $\Delta T(i)$, is used to vary the size of the temperature increment in the simulation of cooling and/or heating. The effect of varying ΔT was determined by comparing the results obtained with two different values of ΔT; 0.5 and 1.0 K. For convenience, we chose the same temperature increment for simulations of both cooling and heating, i.e. $\Delta T = \Delta T(i)_{\text{heating}} = \Delta T(i)_{\text{cooling}}$. The observed difference between the results obtained with $\Delta T = 0.5$ and $\Delta T = 1.0$ was negligible and the latter value was selected for use since it required less computational time. Parametric studies of this kind have been carried out to establish the effect of variation of each adjustable parameter on the calculated results[11,29,32]. An optimization procedure must be executed in order to establish a set of parameters that best describe the relaxing property. A similar modelling approach was also used by ten Brinke[33] in his investigation of the interfacial region in block copolymers.

We shall now consider the effect of the variation of the other four model parameters on the isothermal relaxation time.

The effect of X on the isothermal relaxation time is shown in *Figure 2*. It was generally observed that an increase in X delays the inception of the linear relaxation time region. At low values of X, below 0.1, there are only negligible differences between results with different X values. The observed linear relationship between relaxation time and ageing time from about 50 min up suggests that $X \leq 0.1$ constitutes the proper range for X in the simulation of stress relaxation in this study.

The effect of variation of β is shown in *Figure 3*. Two values were used in the calculations; 0.27 and 0.46. The change in β results in a variation in the horizontal distance between the isothermal curves, which is the property described by the ageing temperature coefficient C_T in equation (5). By an extension of equation (5), C_T can be calculated from the isochronous data from the following equation:

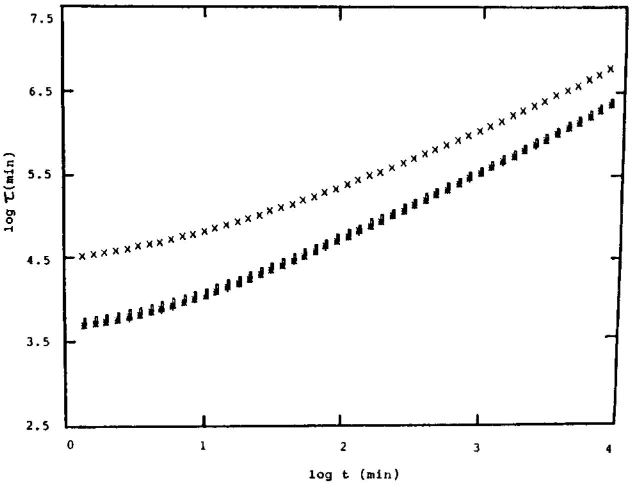

Figure 2 Effect of change in X on isothermal relaxation time as a function of ageing time at $T_g = 20°C$; ×, $X = 0.1$; □, $X = 0.01$; *, $X = 0$

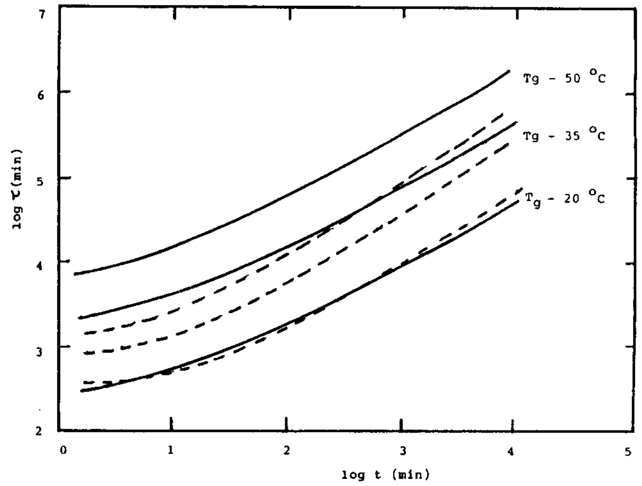

Figure 3 Effect of change in β on isothermal relaxation time as a function of ageing time with ageing temperature as a parameter: ——, $\beta = 0.27$; – – –, $\beta = 0.46$

$$C_T = \ln(\tau_1/\tau_2)/\ln[(T_g - T_1)/(T_g - T_2)] \qquad (6)$$

The results obtained between the ageing times of 100 and 10 000 min indicate a constant C_T for each β; $C_T = 3.74$ for $\beta = 0.27$, and $C_T = 2.18$ for $\beta = 0.46$. Hence, to achieve $C_T = 3.3$, a value of β between 0.27 and 0.46 should be used.

Figure 4 shows the effect of $\Delta h^*/R$ on the isothermal relaxation time. At lower levels of $\Delta h^*/R$, below 120×10^3 K, the slope of the curve $d(\ln \tau)/d(\ln t_a)$ ($= C_t$) increases with $\Delta h^*/R$, but above that value the change in slope becomes negligible. The results, therefore, suggest that a $\Delta h^*/R$ value higher than 120×10^3 K is required to obtain a C_t value close to unity.

Based upon the results of the parametric study we assembled the following set of parameters: $X = 0.1$; $\beta = 0.3$; $\Delta h^*/R = 120 \times 10^3$; $\ln A = -358.7$. With these parameters, the model calculations yield isothermal relaxation times with the characteristics of the stress relaxation times. Compared with the optimum parameters calculated for

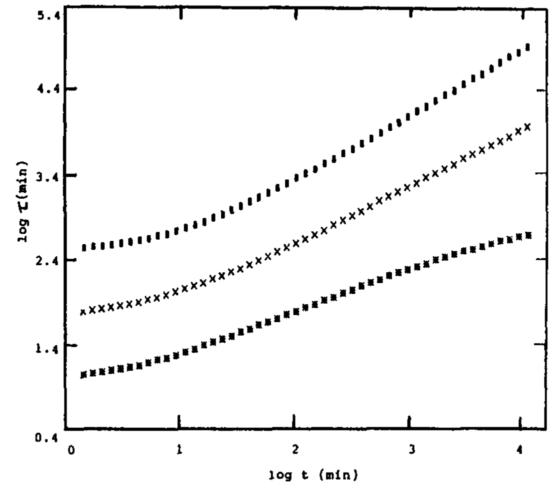

Figure 4 Effect of change in $\Delta h^*/R$ on isothermal relaxation time as a function of ageing time at $T_g=20°C$: □, $\Delta h^*/R=120000$ K; ×, $\Delta h^*/R=80000$ K; *, $\Delta h^*/R=40000$ K

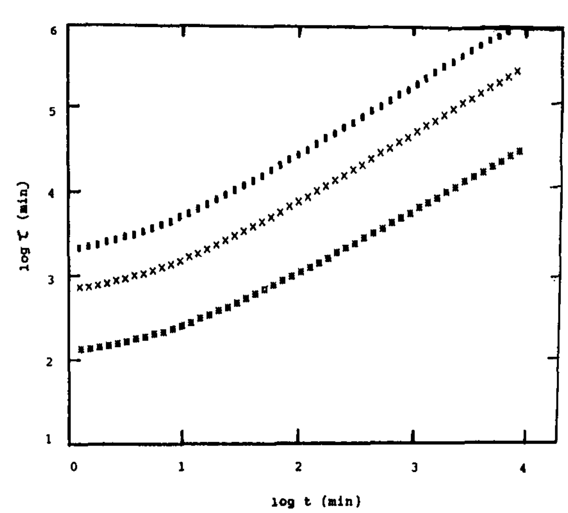

Figure 5 Calculated isothermal relaxation time as a function of ageing time with ageing temperature as a parameter: □, $T_g=50°C$; ×, $T_g=35°C$; *, $T_g=20°C$

the simulation of enthalpy relaxation of polymer blends[29], the above set of parameters has similar β, $\Delta h^*/R$ and $\ln A$, but a lower X (0.1 *vs.* 0.14–0.34). The low X value, according to equation (2), indicates a structure dominated relaxation.

The calculated relaxation times are plotted in *Figure 5*. The isothermal relaxation time changes linearly with ageing time when the latter is longer than 50 min. The slope (the ageing time coefficient, C_t) varies from 0.68 for $T_g=20°C$ to 0.75 for $T_g=50°C$, while the ageing temperature coefficient, C_T, calculated from equation (6), equals $3.5 \pm 1\%$ for ageing times between 10^2 and 10^4 min.

We can thus state that the relaxation times calculated from the model simulation compare favourably with the experimental stress relaxation data in terms of: (i) the inception of the linear relaxation time region; (ii) the ageing time coefficient; and (iii) the ageing temperature coefficient. Our results suggest that the Narayanaswamy/Moynihan model is capable of predicting isothermal relaxation times with the characteristics of stress relaxation times. This further implies that if a material property were identified whose relaxation could be described by the Narayanaswamy/Moynihan parameters, that property could be used to link the enthalpic and viscoelastic parameters which describe the progress of structural relaxation in glassy polymers.

Finally, we would like to emphasize that the correlations reported here are empirical and their applicability to other systems must be established independently. In addition, although the Narayanaswamy/Moynihan modelling approach has been successfully applied to a number of systems, its critics are quick to point out its phenomenological nature, the inadequacy of the expanded Arrhenius type expression for calculations of relaxation times of polymers, the observed variations in the model parameters with ageing time and temperature, and the oversimplification inherent in the concept of fictive temperature (see, for example, refs. 23, 34 and 35).

CONCLUSIONS

We have completed an investigation of structural relaxation in glassy poly(methyl methacrylate), poly(styrene-*co*-acrylonitrile), and their blends. The progress of structural relaxation was followed by monitoring the changes in enthalpy and viscoelastic properties at different ageing times and temperatures. From the stress relaxation measurements an expression was established for the stress relaxation time as a function of ageing time and temperature. A model simulation based on the Narayanaswamy/Moynihan approach was carried out using the calorimetric data. The simulation study yielded an optimum set of parameters with which the enthalpy relaxation time was expressed as a function of ageing conditions. Despite the fundamental difference between enthalpic and viscoelastic measurements, the two relaxation times showed remarkably similar dependence on the ageing conditions, as judged by the similar values of the ageing time and ageing temperature coefficients. The observed correspondence suggests that empirical correlations between calorimetric and viscoelastic changes during structural relaxation are feasible.

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