

Physical Aging Studies in Poly(vinyl methyl ether). 1. Enthalpy Relaxation as a Function of Aging Temperature

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ABSTRACT: A series of enthalpy relaxation experiments at different aging temperatures was conducted on a sample of poly(vinyl methyl ether) using a differential scanning calorimeter. The excess enthalpy was found to decay with aging time according to a previously determined empirical three-parameter model. The temperature dependence of the three aging parameters pertaining to this model was established. The data were also analyzed by using the single effective relaxation time model of Petrie and Marshall. A comparison was made between these two models.

Introduction

Physical aging involves changes in the physical properties of polymer glasses as a function of time. These changes occur when a polymer glass is prepared in such a manner as to produce a "nonequilibrium" thermodynamic state. The usual method of preparation is to quench the polymer rapidly at a given cooling rate, starting from an equilibrium state, which is 50–60 K above the glass transition temperature, T_g , down to the aging temperature, T_a , which is always less than the glass transition temperature, T_g .

Once the polymer glass has been quenched into a nonequilibrium state, physical properties such as the specific volume, V , enthalpy, H , and shear modulus, G , all move toward values which are characteristic of the thermodynamic equilibrium state at the particular aging temperature under consideration. Furthermore, the initial departure from the equilibrium state at the aging temperature, T_a , also depends on the thermal history which was used to reach this point. Physical aging experiments can be carried out on the same sample only if the effects of any previous thermal treatment have been erased by annealing at ca. $T_g + 60$ K for a sufficient length of time, and it has been found that an annealing time of 10–15 min is adequate.¹

Physical aging is important because polymers tend to become more brittle as they age and this could be vital in any long-term application of such materials. It must be stressed that physical aging effects should not be confused with chemical aging effects, where bond scission and/or chemical modification in the polymer matrix also give rise to changes in physical properties as a function of time. Photochemical processes and oxidation are two possible sources of chemical aging effects.

Currently, only a few physical aging studies on polymer blends have been reported in the literature,³ and these have been mainly concerned with changes in mechanical properties with aging time and temperature. To our present knowledge, enthalpic aging in miscible polymer blends has not yet received much attention. Conditionally miscible blends of polystyrene and poly(vinyl methyl ether), PVME, have been the subject of extensive examination,⁴ but no aging studies have yet appeared. Before one can investigate enthalpic aging in this blend system, one must have data for the aging characteristics of the parent homopolymers. While some enthalpic aging data are available for polystyrene, the only results for PVME come from our own preliminary study.¹ We now report a more comprehensive examination of enthalpic aging in PVME and in

a subsequent paper will report on our studies of the enthalpy relaxation in blends of PVME and polystyrene.

Experimental Section

Heat capacity (C_p) measurements were made by using a Perkin-Elmer DSC2, which was interfaced to an Apple II data collection and analysis system. A 12-bit analog to digital converter was used¹ because of the need to be able to detect enthalpy differences of the order of 2 J g⁻¹ with an accuracy of 1% or less. The differential scanning calorimeter (DSC) output voltage was taken at a point in the circuit before the range control and then fed into a DC amplifier before finally entering the ADC card in the Apple II computer. This arrangement resulted in a greater sensitivity and reproducibility for C_p measurements than was obtained previously.¹

All C_p measurements were taken by using the subambient mode of the DSC with liquid nitrogen as coolant, helium as purge gas, and sapphire as the C_p standard. As before,¹ the scan starting and finishing temperatures were 160 and 320 K, respectively, but only C_p data in the range $200 \leq T \leq 320$ K were used in the final enthalpy determinations. A heating rate of 20 K min⁻¹ and a cooling rate of 40 K min⁻¹ were used throughout this work.

The sample of PVME was a polydisperse material (Polysciences) which was "topped and tailed" with toluene and petroleum ether as solvent and nonsolvent, respectively. About 7 g of polymer with $M_n = 44000$ (as determined by membrane osmometry at 306 K in methyl ethyl ketone) was obtained from 12 g of starting material.

The thermal history which was used in this work is given below, and Figure 1 shows in diagrammatic form the corresponding changes in enthalpy as this aging history is applied to the polymer sample inside the DSC: (a) Anneal sample at $T = T_2$, where $T_2 \geq T_g + 60$ (=320 K for PVME) for 10–15 min. (b) Quench sample down to the aging temperature, T_a , at 40 K min⁻¹ and age it for " t_a " minutes. (c) Quench sample down to the scan starting temperature, T_1 , again at 40 K min⁻¹ ($T_1 = 160$ K for PVME). (d) Perform a heating scan from T_1 to T_2 , collecting all data.

The results of this treatment are indicated by the arrows on the cooling and heating enthalpy curves of Figure 1, and the physical aging takes place between points marked B and C on the same figure. If the sample was left to age for an infinitely long time, then point C would have moved down to point E on the equilibrium enthalpy versus temperature curve. In order to get a measure of how much the sample has aged, one must then compare an unaged sample with an aged sample.

It can be shown that the enthalpy difference, $H_B - H_C$ is given by the following integral:

$$H_B - H_C = \Delta H(t_a, T_a) = \int_{T_a}^{T_g} (C_p(\text{aged}) - C_p(\text{unaged})) dT \quad (1)$$

From now on, $H_B - H_C$ will be denoted by $\Delta H(t_a, T_a)$, the excess enthalpy lost on aging at a temperature T_a for an aging time of t_a minutes. In order to make the comparison, step e must be added to the thermal history shown above: (e) Repeat steps a–d above but use $t_a = 0$ min, i.e., quench from T_2 to T_1 without stopping at the aging temperature, T_a .

One reason for choosing this particular thermal history is that it has also been used by Hodge and Berens^{5a} in their phenome-

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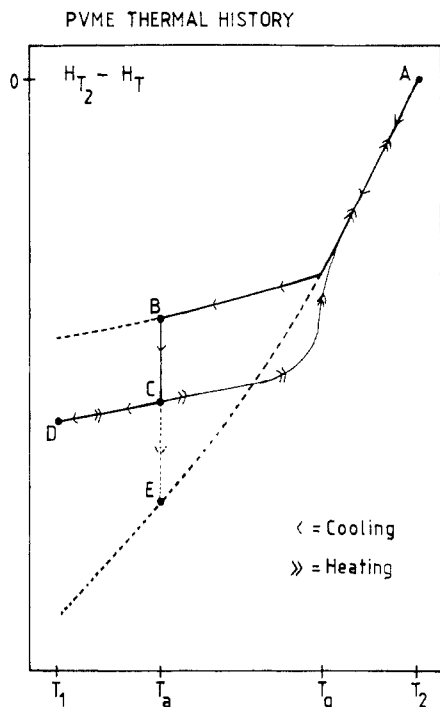


Figure 1. Illustration of thermal history used in enthalpic relaxation experiments via an enthalpy versus temperature plot.

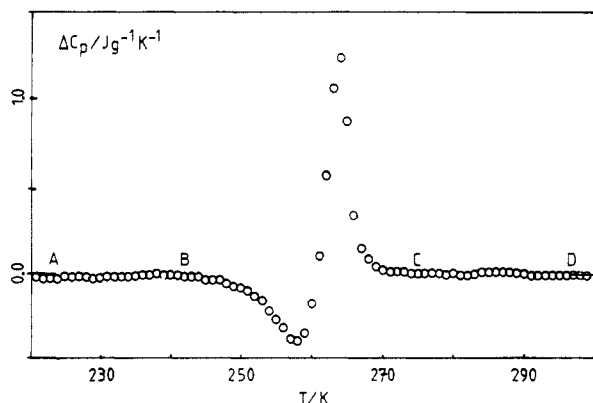


Figure 2. Typical PVME ΔC_p difference curve, with $\Delta C_p = C_p(\text{aged}) - C_p(\text{unaged})$ and C_p in $\text{J g}^{-1} \text{K}^{-1}$.

nological model of enthalpic relaxation in polymer glasses. We can easily obtain normalized heat capacity data which this particular model requires and so test its ability to predict our results for PVME. This comparison between the present method of interpreting enthalpic relaxation data and the Hodge/Berens approach will be the subject of a separate paper.⁶

An example of a typical experimental ΔC_p difference curve is shown in Figure 2. As mentioned previously,⁴ the excess enthalpy lost during aging, $\Delta H(t_a, T_a)$, was obtained by integrating a ΔC_p difference curve between two temperature limits, T_α and T_β . However, during the course of this study, it was found that the choice of T_α and T_β can occasionally influence the value of $\Delta H(t_a, T_a)$ which is obtained. A more reliable method for determining this quantity is (a) smooth the ΔC_p data between the points AB and CD shown in Figure 2 prior to evaluating the area $\Delta H(t_a, T_a)$ and then (b) pick several values for T_α and T_β and get the corresponding values of $\Delta H(t_a, T_a)$ by numerical integration. Finally, take an average. (c) T_α and T_β should not be selected to be too close to the transition region BC.

All of the $\Delta H(t_a, T_a)$ data obtained during this work were taken from two or more separate aging experiments in the DSC.

Results and Discussion

Glass Transition. Several definitions for the location of the glass transition temperature on a C_p versus T plot are currently in use, and the three most commonly used

are (a) the extrapolated onset T_g , (b) the midpoint T_g , and (c) the enthalpic T_g . For this latter case, T_g is defined by the intersection of the liquid and the glassy enthalpy curves.⁷ ΔC_p at T_g is defined as $\Delta C_p = C_p(\text{liquid}) - C_p(\text{glass})$ at $T = T_g(\text{mid})$, and $C_p(\text{liquid})$ and $C_p(\text{glass})$ are linear extrapolations of the liquid and glassy heat capacities, respectively, which are obtained by a linear least-squares analysis of the C_p data over the appropriate temperature ranges. When comparing reports from different workers on enthalpy relaxation/aging characteristics of polymers, it is very important that the same definition for T_g is used throughout, otherwise potentially misleading comparisons will be made. In the rest of this work, definition c above will be used for the glass transition temperature, since enthalpy data in the form of $H(T_2) - H(T_1)$ curves are readily available from the $C_p - T$ data.

This yields, for the sample of PVME under study, $T_g = 255.6 \text{ K}$ (T_g onset = 250.7 K and T_g midpoint = 254.1 K). The glassy and liquid heat capacities are both linear functions of temperature over the following ranges:

$$C_p(\text{glass}) = 1.113 + 4.183 \times 10^{-3}(T - 205), \quad 205 \leq T \leq 235 \text{ K}$$

$$C_p(\text{liquid}) = 1.762 + 1.798 \times 10^{-3}(T - 205), \quad 270 \leq T \leq 310 \text{ K}$$

A value of $\Delta C_p = 0.533 \text{ J g}^{-1} \text{K}^{-1}$ was obtained.

Enthalpy Relaxation/Physical Aging. It has already been found that $\Delta H(t_a, T_a)$ data for PVME aged at $T_a = 245 \text{ K}$ can be described by an empirical equation,¹ which has the following form:

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)[1 - \Phi(t_a)] \quad (2)$$

where

$$\Phi(t) = \exp[-(t/t_c)^\beta]$$

This equation has already been successfully applied to enthalpic aging data in the cases of plasticized PVC, polystyrene, and poly(vinyl acetate).⁸⁻¹⁰ The function $\Phi(t)$ is also known as the Williams-Watt relaxation function. An analogous equation has in fact been used by Moynihan to describe the volume relaxation in amorphous glasses.¹¹

The three parameters $\Delta H_\infty(T_a)$, t_c , and β are determined by using a nonlinear curve-fitting analysis. $\Delta H_\infty(T_a)$ corresponds to the enthalpy difference $H_B - H_E$ shown on Figure 1, and the t_c parameter is a characteristic time. The relaxation function $\Phi(t)$ describes the kinetics of the approach of the system to the equilibrium state. In addition, $\Phi(t)$ may also be analyzed in terms of a distribution of relaxation times, $\rho(\tau)$.

Most relaxation phenomena which occur in polymers can be understood in terms of a summation of many different elementary processes, where each elementary process is governed by a single relaxation time, τ . The connection between the distribution function $\rho(\tau)$ and the relaxation function $\Phi(t)$ is given by the following integral transform:

$$\Phi(t) = \int_{\tau=0}^{\infty} \rho(\tau) \exp(-t/\tau) d\tau \quad (3)$$

if $x = 1/\tau$ and $S = 1/t$ are substituted in this equation, then

$$\Phi(S) = \int_{x=0}^{\infty} (1/x^2) \rho(1/x) \exp(-Sx) dx \quad (4)$$

thus, the relaxation function $\Phi(S)$ is the Laplace transform of the function $(1/x^2)\rho(1/x)$, and in principal, $\rho(\tau)$ can be obtained by finding the inverse Laplace transform of the function $\Phi(S)$. This has been done for the Williams-Watt function¹² and the distribution of relaxation times $\rho(\tau)$ obtained. It must be mentioned that ob-

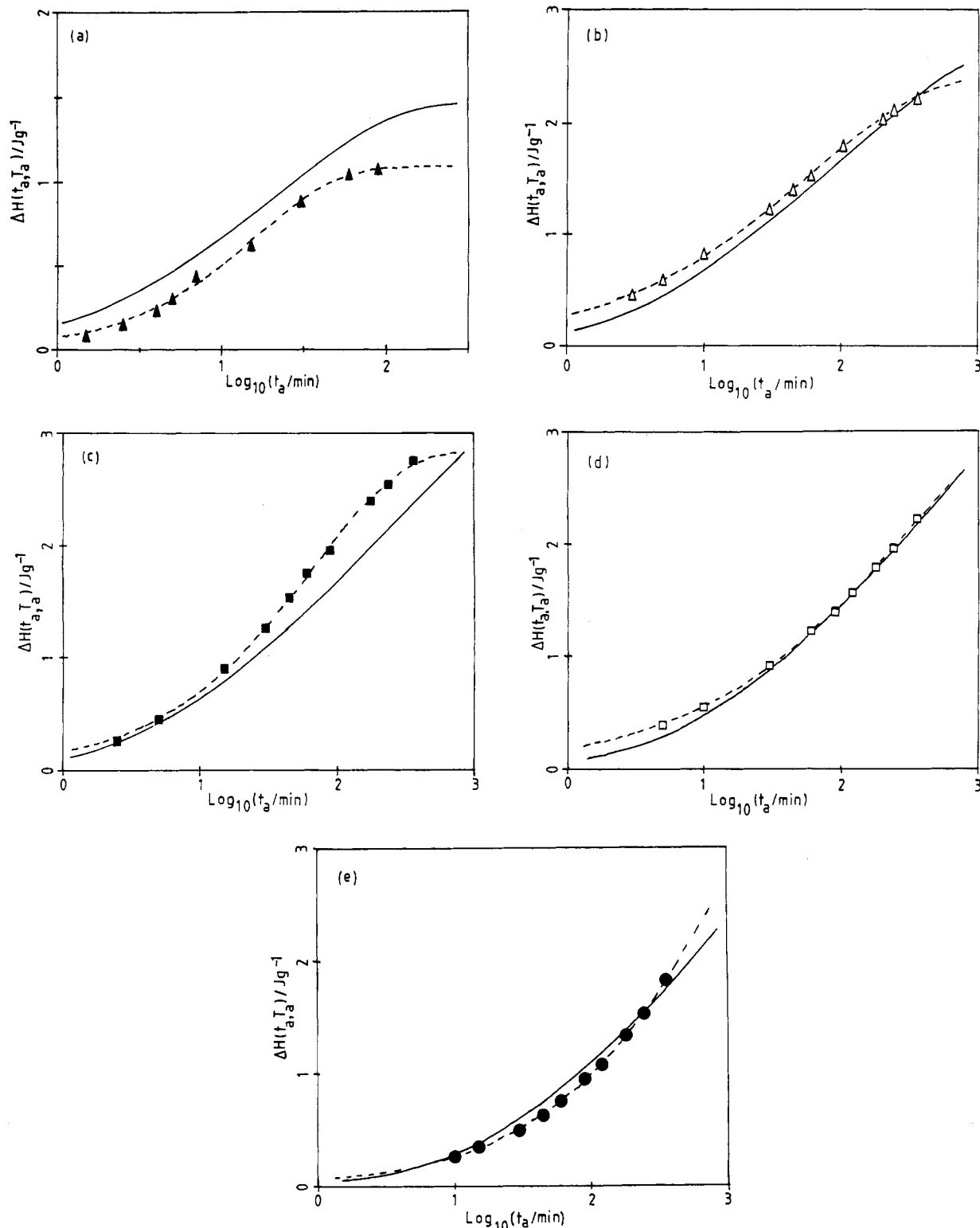


Figure 3. Poly(vinyl methyl ether), $\Delta H(t_a, T_a)$ versus $\log(t_a)$ plots for five aging temperatures. Dashed lines are the fits to the Cowie/Ferguson model, and the full lines are the predicted time dependences of $\Delta H(t_a, T_a)$ according to the Petrie/Marshall model. The plots are labeled (a) $T_a = 250$ (▲), (b) $T_a = 247.5$ (Δ), (c) $T_a = 245$ (■), (d) $T_a = 240$ (□), and (e) $T_a = 235$ K (●).

taining inverse Laplace transforms is by no means an easy process, and some caution must still be exercised when seeking to impart any physical significance to the $\rho(\tau)$ function which can be calculated in this way.¹²

However, despite these limitations, information about the relaxation time distribution for the Williams-Watt function can be derived. It can be shown that the β parameter of eq 2 can be related to the width of the distribution of relaxation times; a small value of β , e.g. $\beta = 0.2$, implies a very broad distribution, and β close to unity

implies a very narrow distribution of relaxation times. ($\beta = \text{unity}$ would mean that $\rho(\tau)$ was a Dirac δ function.) In addition, an average relaxation time, $\langle\tau\rangle$ can be calculated from $\langle\tau\rangle = t_c \Gamma(1 + 1/\beta)$, where $\Gamma(x)$ is the Γ function.¹² Thus the parameter t_c from eq 2 can be related to $\langle\tau\rangle$.

Figure 3 shows plots of $\Delta H(t_a, T_a)$ versus $\log(t_a)$ for five different aging temperatures, viz., $T_a = 235, 240, 245, 247.5$, and 250 K, for PVME. Also shown in this figure are theoretical curves which were obtained by using both the CF model and the Petrie/Marshall model. Figure 4 depicts

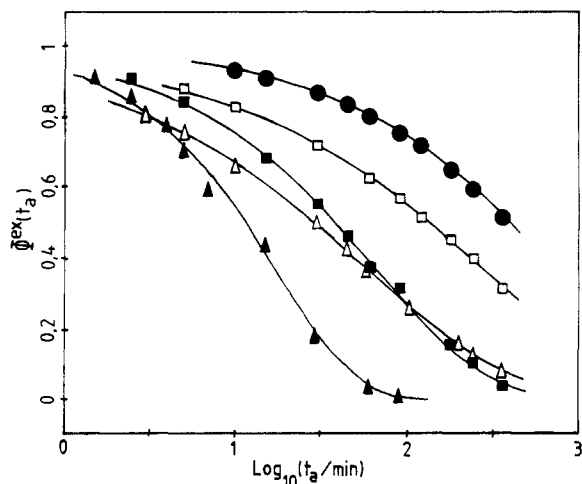


Figure 4. $\Phi^{\text{ex}}(t_a)$ versus $\log(t_a)$ plot for five aging temperatures as given in Figure 3.

Table I
Parameters and Error Limits Obtained from the
Levenberg-Marquardt Nonlinear Least-Squares Curve Fit
of PVME Enthalpic Relaxation Data to Equation 2^a

T_a , K	$\Delta H_{\infty}(T_a)$, J g^{-1}	$\log(t_c)^b$	β	$\Delta H_{\infty}(T_a)^c$, J g^{-1}
250.0	1.08 ± 0.01	1.23 ± 0.01	0.914 ± 0.020	1.45
247.5	2.43 ± 0.02	1.77 ± 0.02	0.511 ± 0.007	2.63
245.0	2.83 ± 0.02	1.82 ± 0.01	0.661 ± 0.007	3.90
240.0	3.24 ± 0.13	2.44 ± 0.06	0.501 ± 0.010	6.61
235.0	3.77 ± 0.40	2.84 ± 0.11	0.617 ± 0.015	9.45
245.0 ^d	3.48^d	1.29^d	0.462^d	

^a With $\log t_a$ as the dependent variables (see text for details). ^b t_c is the characteristic time in minutes. ^c Obtained from Petrie/Marshall model, eq 8. ^d Obtained from eq 2 using t_a and not $\log t_a$ as the dependent variable.¹

the corresponding plots of $\Phi^{\text{ex}}(t)$ versus $\log(t_a)$, where $\Phi^{\text{ex}}(t) = 1 - \Delta H(t_a, T_a)/\Delta H_{\infty}(T_a)$, and $\Delta H_{\infty}(T_a)$ is obtained from the nonlinear least-squares curve fit by eq 2, where $\log(t_a)$ is the dependent variable. The resulting values (and error limits) of $\Delta H_{\infty}(T_a)$, $\log(t_c)$, and β are listed in Table I. This table also gives the values of these parameters which were obtained from a previous set of data¹ for PVME aged at 245 K. This previous data set was fitted to eq 2 with t_a as the dependent variable. It was found that plotting the data on a logarithmic time scale gave more equal weighting to both the very short and long aging time portions of the enthalpy data. Equation 2 in terms of $\log t_a = x_a$ and $\log t_c = x_c$ becomes $\Delta H(t_a, T_a) = \Delta H_{\infty}(T_a)[1 - \exp(-u)]$, with $\log u = \beta(x_a - x_c)$.

Temperature Dependence of the Aging Parameters. For PVME, the behavior of $\Delta H_{\infty}(T_a)$ as a function of the temperature difference between the glass transition and the aging temperature is a linear function of $T_g - T_a$ for $8 < (T_g - T_a) < 21$ K as given by

$$\Delta H_{\infty}(T_a) = 1.650 + 0.103(T_g - T_a) \quad (5)$$

where $\Delta H_{\infty}(T_a)$ is in J g^{-1} .

A plot of $\ln(t_c)$ versus $T_g - T_a$ is shown in Figure 5. These data can be described by using a pseudo-WLF type of equation, viz.

$$\ln(t_c) = C_0 + \frac{C_1(T_g - T_a)}{C_2 + (T_g - T_a)} \quad (6)$$

where $C_0 = 0.78$, $C_1 = 19$, and $C_2 = 47$ K (cf. $C_1 = 17.44$ and $C_2 = 51.6$ K from other sources).

The best fit values of C_0 , C_1 , and C_2 were obtained by using a nonlinear least-squares curve fit to eq 6. For the

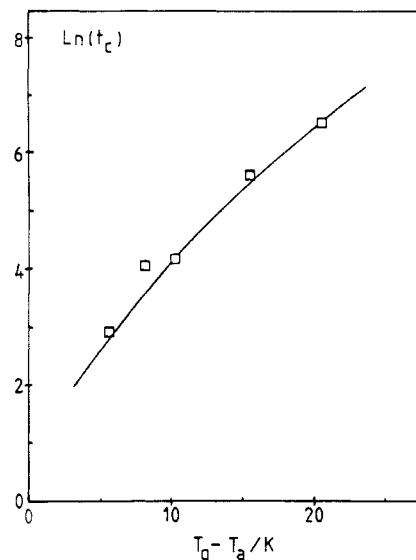


Figure 5. $\ln(t_c)$ versus $T_g - T_a$ plot; t_c in minutes.

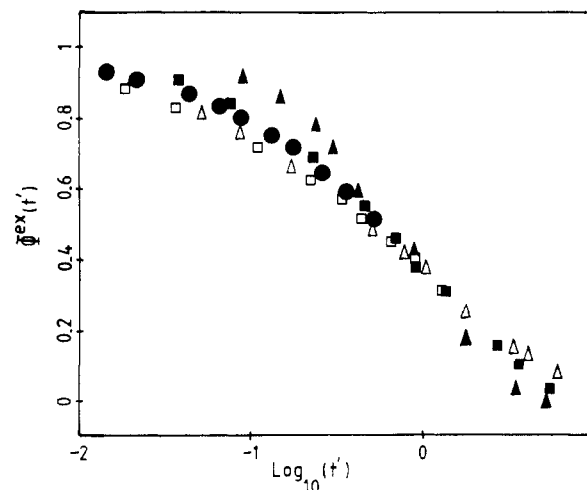


Figure 6. $\Phi^{\text{ex}}(t')$ versus $\log(t')$ plot for five aging temperatures as given in Figure 3.

four aging temperatures which were more than 5 K lower than the T_g of PVME, β was essentially constant. Averaging the four β values for $235 \leq T_a \leq 247.5$ K gives $\beta = 0.572 \pm 0.079$. At aging temperatures close to T_g , β approaches unity ($T_a = 250$ K gave $\beta = 0.914$).

Figure 6 is a reduced plot of $\Phi^{\text{ex}}(t')$ versus $\log(t')$ for the five aging temperatures, where $t' = t_a/t_c$ is a reduced aging time. Except for the $T_a = 250$ K case, the reduced data lie on approximately the same curve, and hence the parameter $\log(t_c)$ can also be interpreted as a shift factor in the time domain.

The Petrie/Marshall Analysis. A different way of interpreting enthalpic aging data employs the concept of a single effective relaxation time, τ , which is also a function of aging time. The relevant equations are given below

$$\Delta H(t_a, T_a) = \Delta H_{\infty}(T_a)[1 - \Phi(t_a)] \quad (7)$$

where

$$\Phi(t) = \exp[-t/\tau]$$

and $\Delta H_{\infty}(T_a)$ is now obtained by an extrapolation of the liquid enthalpy curve of the reference unaged sample via

$$\Delta H_{\infty}(T_a) = \int_{T_a}^{T^*} C_{p(\text{liq})}(T) - C_p(T) dT \quad (8)$$

Here T^* , the upper limit in this integral, is taken at least 30 K above T_g , $C_{p(\text{liq})}(T)$ is a linear least-squares fit to the

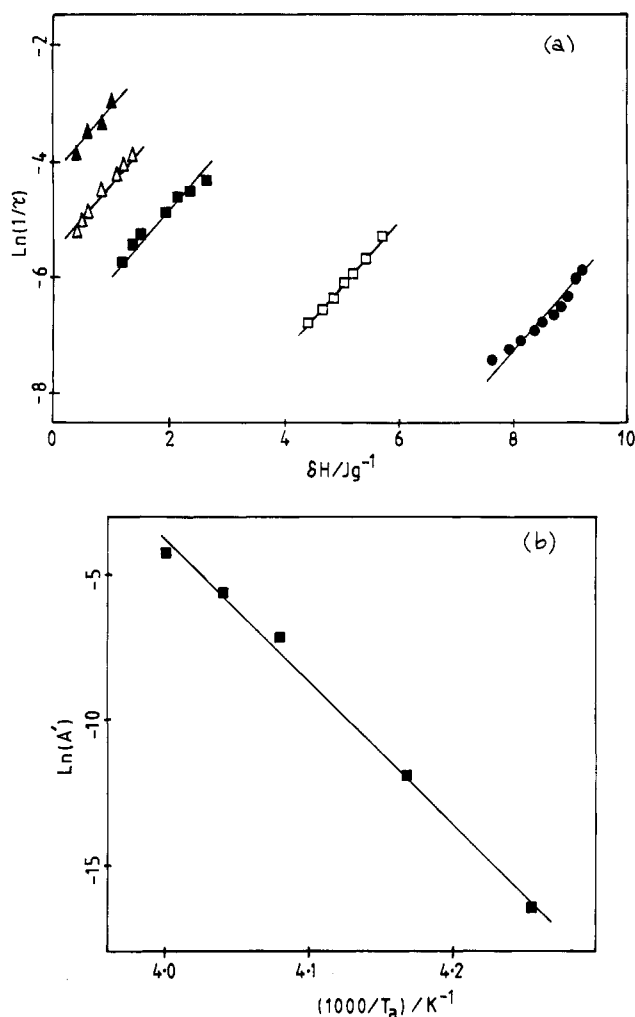


Figure 7. (a) Petrie/Marshall $\ln(1/\tau)$ versus δH plot for five aging temperatures as given in Figure 3. (b) Petrie/Marshall Arrhenius plot of $\ln(A')$ versus $1000/T_a$ (see text for details).

heat capacity of the unaged sample in the liquid state, and $C_p(T)$ is the experimentally determined heat capacity of the unaged sample.

The parameter $1/\tau$ appearing in eq 7 is a measure of the rate of relaxation of the system as it approaches thermodynamic equilibrium. This parameter can be obtained from rearrangement of eq 7, which yields

$$\frac{1}{\tau} = -\frac{1}{t} \ln(\Phi) = -\frac{1}{t} \ln \left[1 - \frac{\Delta H(t_a, T_a)}{\Delta H_\infty(T_a)} \right] \quad (9)$$

Figure 7a shows a plot of $\ln(1/\tau)$ versus $\delta H = \Delta H_\infty(T_a) - \Delta H(t_a, T_a)$, the departure from equilibrium, for all five aging temperatures investigated during this study. The aging data can be described by an equation first proposed by Petrie and Marshall,² namely:

$$\ln(1/\tau) = \ln(A') + C\delta H \quad (10a)$$

where

$$\ln(A') = \ln(A) - E_H/RT_a \quad (10b)$$

Here, τ is in minutes, A is in min^{-1} , E_H is an apparent activation energy for enthalpy relaxation in kJ mol^{-1} , and C is a constant. First, best-fit values of $\ln(A')$ and C were determined from linear regression analysis to eq 10a for each aging temperature. The average value of C taken over all five aging temperatures was found to be $C = 1.14 \pm 0.19 \text{ g J}^{-1}$. The set of parallel straight lines also shown in Figure 7a have a slope = 1.14. Values of $\ln(A')$ for each aging

temperature were then redetermined by a further linear regression to eq 10a with C held constant at the averaged value of 1.14. Finally, the activation energy and preexponential constant of eq 10b were determined from a linear regression of $\ln(A')$ against $1/T_a$, and Figure 7b is the corresponding Arrhenius plot.

Using the above-mentioned method of analysis, the following values for the Petrie/Marshall (PM) parameters were found: $\ln(A) = 192.3$, $E_H = 407.4 \text{ kJ mol}^{-1}$, and $C = 1.14 \text{ g J}^{-1}$. These results may be compared with enthalpic aging data for a polystyrene sample studied by Petrie and Marshall,² which gave $\ln(A) = 367$, $E_H = 1192 \text{ kJ mol}^{-1}$, and $C = 2.92 \text{ g J}^{-1}$.

The lower value of E_H for PVME could result from a lower energy barrier for limited main-chain segmental motion in this polymer compared with the situation encountered in polystyrene where there would be greater steric hindrance to main-chain segmental motions because of the presence of bulky phenyl side groups. If the C parameter are compared in terms of the monomer repeat unit, then $C = 0.020 \text{ mol J}^{-1}$ for PVME, and $C = 0.028 \text{ mol J}^{-1}$ for PS, and hence better agreement is found on this basis. The above implies that PVME relaxes faster than PS for the same value of $T_g - T_a$.

Comparison of the Two Models for Describing Enthalpic Relaxation in PVME. The two models considered in this study will be denoted by CF (Cowie/Ferguson) and PM (Petrie/Marshall) in the following discussion.

While inspection of Figure 3 shows that in most cases the CF model gives a visually superior fit to the aging data, this observation alone does not provide an adequate basis for concluding that this is the case. It might be argued that the PM model uses three adjustable parameters whereas the CF model uses four parameters, thus automatically leading to an improved fit. Calculations using a statistical "F test" on all of our curve fits showed that the CF model did in fact give a statistically significant improvement over the PM model.

The CF model uses the concept of a distribution of relaxation times as embodied in the Williams-Watt relaxation function, whereas the PM model uses a single effective relaxation time which is a function of both aging time and the departure from equilibrium.

Both models use extrapolations to obtain $\Delta H_\infty(T_a)$; in the case of the CF model an explicit form is assumed for the relaxation function $\Phi(t)$ and $\Delta H_\infty(T_a)$ found by a least-squares curve fit, whereas in the PM model $\Delta H_\infty(T_a)$ is obtained directly by extrapolating the liquid enthalpy curve down into the glassy region.

Columns 2 and 5 of Table I list the values of $\Delta H_\infty(T_a)$ which were found from the two models, and inspection of these results shows that for all of the aging temperatures investigated in this study the PM model gives higher values for $\Delta H_\infty(T_a)$ than the CF model. Another way of highlighting the differences in $\Delta H_\infty(T_a)$ is to calculate t_e , the time taken for the excess enthalpy of a sample of PVME which has been quenched to $T_g - 15 \text{ K}$ ($=240 \text{ K}$) at 40 K min^{-1} from a temperature well above T_g to come to within 99.9% of thermodynamic equilibrium for each of the two models under consideration.

If eq 2 is employed, a time of $t_e = 8.08 \times 10^3 \text{ min} \approx 5.6$ days is obtained from the CF model, whereas from eq 7, the PM model, $t_e = 9.76 \times 10^5 \text{ min} \approx 678$ days. This difference in t_e might prompt one to consider what is physically the most realistic way of evaluating $\Delta H_\infty(T_a)$.

As has already been mentioned, the Petrie/Marshall model employs an extrapolation of the liquid enthalpy curve down into the glassy state to get access to the im-

portant quantity, $\Delta H_{\infty}(T_a)$. This extrapolation assumes that the heat capacity of most linear polymers in the liquid state at temperatures not too far above the glass transition region (e.g., PVME, $T_g + 15 \leq T \leq T_g + 55$ K) can be represented by a linear function of temperature. This assumption may not be strictly correct. Moreover, in the derivation of $\Delta H_{\infty}(=Q_E)$ which Petrie and Marshall give in ref 2, the glassy and liquid heat capacities are both assumed to be temperature independent. Thus, it can be concluded that the reliable estimation of $\Delta H_{\infty}(T_a)$ in terms of the PM model is not yet assured. Another shortcoming of this model is the lack of a distribution of relaxation times.

Several additional long time aging experiments in the DSC, with $t_a = 6-7$ days at an aging temperature of 240 K, were performed on a PVME sample with a view to resolving the question of which model (PM or CF) best describes enthalpic aging processes in PVME. However, no conclusive results could be obtained from these experiments because of practical difficulties which were encountered in maintaining thermal equilibrium inside our Perkin-Elmer DSC II under subambient conditions for extended periods of time. Once this problem has been dealt with, it is hoped that more definitive answers to some of the above questions will be found.

While only two models for describing enthalpic aging effects in polymer glasses were considered in this work, it should be noted that there are other ways of analyzing enthalpic aging data, e.g., the theoretical models of Hodge⁵ and Kovacs¹³ and the peak-shifting technique of Hutchinson.¹⁴ These models mainly deal with the shape and position of the peak(s) in the $C_p(T)$ curve and not directly with enthalpy differences which are our main concern.¹⁰

However, it can be shown that the isothermal single relaxation time KAHR model¹³ can be directly related to the Petrie/Marshall model. The results for PVME can be stated in terms of this model (with a reference temperature $T_r = T_{g(\text{midpt})} = 254.1$ K) as follows: $\theta = E_H/RT_r^2 = 0.76$, the structure parameter $x = 1 - C\Delta C_p/\theta = 0.20$, and $\ln(\tau_r) = E_H/RT_r - \ln(A) = 0.54$ (i.e., $\tau_r = 1.72$ min). These values are not unreasonable and fall within the limits of those anticipated for polymer glasses.¹³

The analysis of the shapes of our PVME C_p curves in terms of the phenomenological model of Hodge will be the subject of a separate publication.⁶

Conclusions

Enthalpic aging data for poly(vinyl methyl ether) covering several aging temperatures have been subjected to analysis by two different models of physical aging in polymer glasses, and the temperature dependence of the parameters of the Cowie/Ferguson model have been established. Additional work will seek to both (a) establish what is the most realistic model physically for enthalpy relaxation and (b) investigate enthalpy relaxation/physical aging effects in miscible polymer blends.

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Registry No. PVME, 9003-09-2.

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Physical Aging Studies in Polymer Blends. 2. Enthalpy Relaxation as a Function of Aging Temperature in a Poly(vinyl methyl ether)/Polystyrene Blend

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ABSTRACT: A series of enthalpy relaxation experiments at different aging temperatures was conducted on a poly(vinyl methyl ether)/polystyrene blend using a differential scanning calorimeter (DSC). The enthalpic aging data were analyzed in terms of two models for describing physical aging in polymer systems. Comparisons were also made between blend and homopolymer aging data. It has been found that the PVME component in the blend appears to age independently of the PS component and is responsible for essentially all of the aging effects measured. The PS component will, however, retard the physical aging processes of PVME in the blend.

Introduction

The long-term stability of polymers and their property retention are influenced by two possible processes. The

first process is chemical degradation which involves chemical bond modification and/or rupture, and the second process is physical aging. While physical aging is less obvious than the former process, it is nevertheless quite important as it may lead to noticeable changes in polymer properties over long periods of time such as embrittlement.

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