Physical ageing of poly(methyl methacrylate) from enthalpy relaxation measurements

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(Received 7 April 1992; revised 14 August 1992)

The enthalpic ageing behaviour of poly(methyl methacrylate) was studied by differential scanning calorimetry for several ageing temperatures, and ageing times up to 10^4 min. The data are interpreted in terms of both the phenomenological multiparameter model and the Cowie–Ferguson model. The phenomenological multiparameter model was found not to provide an adequate description of the enthalpic ageing process(es) occurring in poly(methyl methacrylate). Problems encountered in defining the equilibrium glassy state by extrapolating from liquid enthalpy data are also discussed.

(Keywords: physical ageing; enthalpic ageing; poly(methyl methacrylate); differential scanning calorimetry)

INTRODUCTION

The long-term stability of polymers and their property retention is of continuing importance to all producers and users of these materials. Physical ageing in polymeric systems is the term used to describe the time dependence of changes in the behaviour of an amorphous polymer held at temperatures below the glass transition; such changes are normally the result of continuous slow relaxation of the glass from its initial non-equilibrium state towards its final thermodynamic equilibrium state. Volume relaxation and enthalpy relaxation are two manifestations of physical ageing, and they can be used to follow this process. Physical ageing must not be confused with chemical ageing or degradation, where changes in the physical properties of a polymer occur by means of chemical processes such as oxidation and/or photodegradation, which may eventually lead to the breaking of chemical bonds.

The enthalpic ageing behaviour of poly(methyl methacrylate) (PMMA) has been investigated by others[1–3], and the data interpreted mainly in terms of the multiparameter phenomenological (MP) model[4–7]. Tribone[3] also considered the effects of tacticity and deuteration on the enthalpic ageing of PMMA. In these studies, however, the MP model could not give an adequate description of the ageing characteristics of PMMA, and the MP model parameters were found to depend on the thermal history imposed on the polymer sample. A further deficiency of the MP model was that when the fitted and the experimental normalized heat capacity (C_p) curves were compared, the theoretical curves were always narrower than the experimental normalized C_p curves, and the discrepancy was found to be worst when thermal histories which involved long ageing times were used[2]. In early references to the MP model[4–7], the MP parameters were thought to represent fundamental properties of the polymer and so be invariant with respect to ageing time and temperature; however, this has not proved to be so.

In the study by Gomes Ribelles *et al.*[2], the predicted values of the enthalpy lost on ageing from the MP model were also found to be significantly larger than those measured experimentally. A recent study of volume ageing in polystyrene by Lee and McGarry[8] has also raised serious doubts as to the validity of extrapolating rubbery state data in order to obtain values for the equilibrium volume after an infinite ageing time. This observation is very important, because a large number of workers in this field have assumed that the equilibrium glassy enthalpy at an ageing temperature T_a can be obtained from an extrapolation of the liquid state enthalpy data. However, a study by Cowie and Ferguson on enthalpic ageing in poly(vinyl methyl ether) found that the equilibrium values for the enthalpy lost on ageing, $\Delta H_\infty(T_a)$, were significantly smaller than those obtained from such an extrapolation[9].

It should be noted that the multiparameter phenomenological models were first developed and tested on ageing data obtained from inorganic glasses[4,5], polymeric glasses were only considered at a later stage[6,7], and another implicit assumption was that polymeric glasses would age in a similar manner to inorganic glasses. This latter assumption is probably not strictly valid, because polymer glasses possess additional topological constraints such as chain entanglements. Another problem with the phenomenological MP models is that they do not consider the enthalpy lost on ageing directly, instead they deal with the first derivative of enthalpy with respect to temperature, i.e. they consider the shapes of heat capacity curves.

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0032-3861/93/102135-07

A different approach for studying the enthalpic ageing of polymer glasses is to consider the enthalpy lost on ageing after an ageing time of t_a minutes at an ageing temperature of T_a(K), which is designated as $\Delta H(t_a, T_a)$ in this work. This has been done for several polymer systems[9–11], and has the additional advantage that one can directly compare rates of enthalpic and volumetric ageing[12]. The experimental enthalpic ageing data can be described by an empirical equation first proposed by Cowie and Ferguson (the CF model)[9,10]:

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)(1-\phi(t_a)) \qquad (1)$$

where $\phi(t) = \exp[-(t/t_c)^\beta]$ is the Williams–Watts relaxation function, with parameters t_c and β. Here, t_c is a characteristic time (i.e. $\phi(t_c) = 1/e$) and β is related to the width of the relaxation time spectrum for the relaxation function $\phi(t)$. The quantity $\Delta H_\infty(T_a)$ is the enthalpy lost on ageing after the sample attains its thermodynamic equilibrium state. Again, it should be emphasized that unlike other treatments which obtain this quantity by assuming the validity of extrapolating the liquid enthalpy curve of the polymer down to temperatures below the glass transition region, $\Delta H_\infty(T_a)$ is treated as an adjustable parameter in this model.

In this study, a more extensive set of enthalpic ageing data for a high molecular weight PMMA sample covering six ageing temperatures is presented. The ageing data will be analysed in terms of the multiparameter phenomenological model and the Cowie–Ferguson model. Another reason for reinvestigating the enthalpic ageing of PMMA was that extensive ageing data for PMMA must be accumulated before one can proceed to investigate the enthalpic ageing of blends of this polymer with styrene/acrylonitrile (SAN) copolymers. This latter work will be reported elsewhere.

EXPERIMENTAL

A Perkin–Elmer DSC2 was used for collecting all heat capacity (C_p) data; it was interfaced to a BBC microcomputer, and was controlled by the computer[9,10]. All C_p data were transferred to an Acorn Archimedes workstation for subsequent data processing and analysis.

A standard sample of poly(methyl methacrylate) with $M_n = 154\,000\ \mathrm{g\,mol^{-1}}$ (Polysciences) was used for all ageing work. The following standard thermal history[9,10] was employed:

(i) The sample was annealed at the upper temperature $T = T_2$ for 10 min, where $T_2 \geqslant T_g + 60$ K.
(ii) The sample was quenched down to the ageing temperature T_a at a cooling rate of 40 K min^{-1}.
(iii) The sample was aged for an ageing time of t_a minutes at the chosen ageing temperature T_a.
(iv) The sample was quenched down to the scan starting temperature T_1, again at 40 K min^{-1}.
(v) Finally, the sample was heated up to the upper temperature limit T_2 at 20 K min^{-1}, and the deflection data collected during this step.

To obtain a measure of how much the sample has aged, one must compare an unaged sample with an aged sample. Deflection data for an unaged sample were collected using the above thermal history with $t_a = 0$, i.e. quench from T_2 to T_1 at 40 K min^{-1}. The enthalpy lost on ageing, $\Delta H(t_a, T_a)$, was obtained by integrating the experimental ΔC_p difference curve over suitable temperature limits[9,10].

In any study of physical ageing, it is important to be consistent in the definition of the glass transition temperature T_g, and in this work the enthalpic glass transition was used. Richardson and Savill[13] have noted that the proper way to describe the glass transition temperature is in terms of an enthalpy temperature diagram. The enthalpic glass transition ($T_{g(en)}$) is then defined as the intersection of the liquid enthalpy curve with the glassy enthalpy curve, and these quantities can be readily obtained from the C_p *versus* T data for the polymer. For the PMMA sample used in this study, $T_{g(en)} = 394.9$ K, and the onset T_g (the extrapolated onset of the baseline shift) was 391.4 K. These temperatures are average values which were taken over the T_g results for all of the unaged PMMA C_p data.

The multiparameter phenomenological model has already been described elsewhere in the literature[4–7], but for the sake of convenience, a brief description will be given. This approach uses the concept of the fictive temperature as first proposed by Tool[14], which is really an attempt to associate an equilibrium state (at the fictive temperature T_f) with a non-equilibrium glassy state (at the temperature T). This concept is best represented diagrammatically, as in *Figure 1*. If one considers the enthalpy difference $H(T_2) - H(T)$, then there are two equivalent ways to define this quantity:

$$H(T_2) - H(T) = \int_T^{T_2} C_p(T')\,\mathrm{d}T' \qquad (2a)$$

and:

$$H(T_2) - H(T) = \int_T^{T_f} C_{p_{\mathrm{glass}}}(T')\,\mathrm{d}T' + \int_{T_f}^{T_2} C_{p_{\mathrm{liquid}}}(T')\,\mathrm{d}T' \qquad (2b)$$

where T' is a dummy variable.

Equating the two equivalent definitions for $H(T_2) - H(T)$ and rearranging gives:

$$\int_T^{T_f} C_p(T') - C_{p_{\mathrm{glass}}}(T')\,\mathrm{d}T' - \int_{T_f}^{T_2} C_{p_{\mathrm{liquid}}}(T') - C_p(T')\,\mathrm{d}T' = 0 \qquad (3)$$

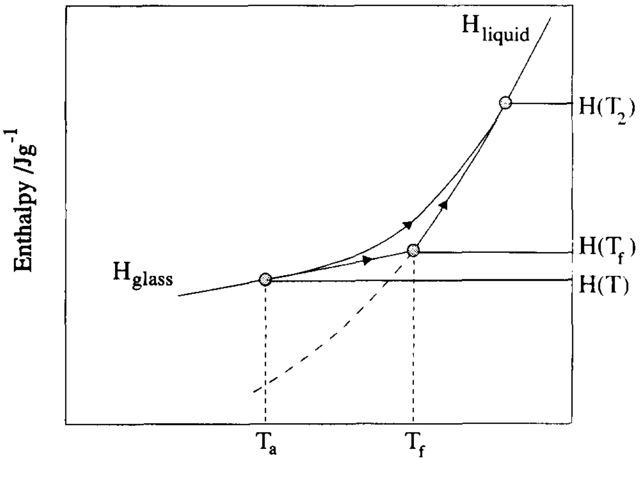

Figure 1 Definition of T_f from enthalpy curves

This equation is of the form $f(T, T_f)=0$, and the normalized heat capacity $(dT_f)/dT$ is obtained from $(dT_f)/dT=-(\partial f/\partial T)/(\partial f/\partial T_f)$, where the quantities $(\partial f/\partial T_f)$ and $(\partial f/\partial T)$ are obtained by partial differentiation of equation (3).

This leads to a definition of the normalized heat capacity in terms of experimental quantities as:

$$\frac{dT_f}{dT}=\left(\frac{C_p(T)-C_{p_{glass}}(T)}{C_{p_{liquid}}(T_f)-C_{p_{glass}}(T_f)}\right) \tag{4a}$$

Several workers have used the following definition for the normalized heat capacity:

$$\frac{dT_f}{dT}=\left(\frac{C_p(T)-C_{p_{glass}}(T)}{C_{p_{liquid}}(T)-C_{p_{glass}}(T)}\right) \tag{4b}$$

However, it should be noted that equation (4b) is identical to equation (4a) *only* if the glassy and liquid state heat capacities are temperature independent. In practice, $C_{p_{liquid}}$ and $C_{p_{glass}}$ are linear functions of temperature on either side of the glass transition region, and one must use equation (4a). The use of equation (4b) would mean that the shape of the normalized C_p curve would be slightly distorted from that given by the correct equation, and that this could also cast some doubt as to the validity of the fitted normalized C_p curve obtained via the MP model.

To evaluate the fictive temperature T_f, when the glassy and liquid C_ps are defined as linear functions of temperature, i.e. $C_{p_{glass}}(T)=G_1+2G_2(T-T_1)$ and $C_{p_{liquid}}(T)=L_1+2L_2(T-T_1)$, and T_1 is a reference temperature, the following set of equations can be used:

$$aT_f^2+bT_f+c=0 \tag{5}$$

$$\begin{aligned} \text{where} \quad & a=(G_2-L_2) \\ & b=2T_1(L_2-G_2)+G_1-L_1 \\ & c=L_1T_2-G_1T+G_2T(2T_1-T) \\ & \quad +L_2T_2(T_2-2T_1)-A \\ \text{and} \quad & A=H(T_2)-H(T) \end{aligned}$$

This follows from equation (3) and the definitions of the glassy and liquid state heat capacities. The quantity $H(T_2)-H(T)$ is obtained by numerical integration, and T_f is the solution of the above quadratic equation. Hence, all of the terms in equation (5) can be evaluated from the experimental $C_p(T)$ data.

The phenomenological multiparameter model takes into account the thermal history used to prepare the polymer glass before ageing, and also predicts what the response will be as the sample is heated. The model is based on equation (6), which takes into account the experimental observations of non-linearity, non-exponentiality, asymmetry and memory effects that have been noted in multiple temperature jump experiments[6,7]:

$$T_f(T)=T_2+\int_{T_2}^{T}\left\{1-\exp\left[-\left(\int_{T'}^{T}\frac{dT''}{Q\tau_0}\right)^{\beta}\right]\right\}dT' \tag{6a}$$

The relaxation time τ_0 is obtained from the equation first proposed by Narayanaswamy[15]:

$$\ln\tau_0=\ln A+\left[\frac{x\Delta h^*}{RT}+\frac{(1-x)\Delta h^*}{RT_f}\right] \tag{6b}$$

where Δh^* is an activation energy parameter, x is the structure parameter, and A is a pre-exponential factor. The integral equation defined by equation (6a) is implicit in T_f because the relaxation time τ_0 is a function of T and T_f via equation (6b), consequently, solutions must be obtained by numerical methods. The MP model parameters $\{\Delta h^*, \ln A, x \text{ and } \beta\}$ are specific to the particular polymer being considered, and by definition should not depend on the thermal history used, i.e. they should *not* depend on ageing time or ageing temperature.

RESULTS AND DISCUSSION

Phenomenological model and PMMA enthalpic ageing data

First, the phenomenological model was applied to the averaged heat capacity data for the unaged PMMA glass, which was collected using the standard thermal history given in the experimental section. These data were normalized using equations (4a) and (5). The activation energy parameter Δh^* was fixed, and the other three parameters allowed to vary until a best fit to the experimental normalized C_p curve was found. This procedure was repeated with a different Δh^* until the overall best fit to the experimental data was obtained. *Table 1* lists the values of the phenomenological model parameters, together with the sum of squares of the residuals SS for the unaged PMMA glass.

The best fit value of $\Delta h^*=690\,\text{kJ mole}^{-1}$ was used in all subsequent calculations for thermal histories which involved ageing the sample. *Table 2* lists values of the MP model parameters for ageing temperatures of $T_a=375$ K and 387.5 K, and *Figure 2* shows the normalized C_p curves for the longest ageing times at these two ageing temperatures. From inspection of *Table 2*, it can be seen that the MP parameters do indeed vary with ageing time and ageing temperature. The fitted normalized C_p curves shown in *Figures 2a* and *2b* are also narrower than the experimental normalized C_p curves.

However, as was pointed out in the introduction, a much more informative comparison can be made in terms of the values of $\Delta H(t_a, T_a)$ as predicted from the MP model and the experimental $\Delta H(t_a, T_a)$ data. *Figures 3a* and *3b* show such a comparison for the enthalpic ageing data obtained at the two ageing temperatures of 375 K and 387.5 K. It can be seen that whereas the normalized C_p data can be fitted with the MP model (albeit with time and temperature dependent parameters), the same set of parameters completely fail to predict the observed behaviour of the enthalpy lost on ageing. This underlines the danger of merely using the shapes of C_p curves to

Table 1 MP model parameters and sum of squares for unaged PMMA glass

Δh^* (kJ mole^{-1})	ln(A)	x	β	SS
920.5	−275.54	0.294	0.363	0.0145
878.6	−262.90	0.305	0.371	0.0133
836.8	−250.26	0.316	0.379	0.0121
795.0	−237.62	0.331	0.386	0.0112
753.1	−224.99	0.345	0.395	0.0105
732.2	−218.68	0.356	0.398	0.0103
711.3	−212.35	0.362	0.403	0.0101
690.4	−206.04	0.369	0.405	0.0101
669.4	−199.73	0.385	0.411	0.0101
627.6	−187.13	0.415	0.418	0.0107
585.8	−174.52	0.447	0.426	0.0120
543.9	−161.91	0.484	0.435	0.0143

Table 2 MP model parameters, sum of squares and predicted values of $\Delta H(t_a, T_a)$ for PMMA glass aged at (a) $T_a = 375$ K, (b) $T_a = 387.5$ K, with $\Delta h^* = 690.4$ kJ mole^{-1}

$\log_{10}(t_a/\text{min})$	ln A	x	β	SS	$\Delta H(t_a, T_a)$ (Jg^{-1})
a)					
1.0000	−206.18	0.330	0.453	0.130	0.72
1.2304	−206.86	0.333	0.442	0.106	0.93
1.3979	−205.74	0.352	0.456	0.124	0.97
1.6021	−206.04	0.375	0.458	0.101	1.18
1.7993	−206.96	0.586	0.622	0.136	1.00
2.0934	−206.34	0.512	0.598	0.124	1.47
2.2577	−206.22	0.466	0.538	0.142	1.65
2.4997	−205.98	0.528	0.618	0.205	1.80
2.9263	−205.40	0.571	0.674	0.303	2.23
2.9390	−205.34	0.512	0.572	0.292	2.27
3.0073	−205.17	0.499	0.546	0.191	2.38
3.0241	−205.04	0.543	0.625	0.302	2.45
3.3802	−204.92	0.548	0.599	0.534	2.79
3.7428	−203.90	0.601	0.671	0.472	3.37
3.7536	−203.90	0.595	0.655	0.429	3.42
3.9877	−203.29	0.666	0.792	0.414	3.73
b)					
0.6021	−206.02	0.458	0.515	0.010	0.83
0.7782	−205.92	0.458	0.512	0.014	0.95
0.9031	−205.83	0.470	0.518	0.016	1.05
1.0000	−205.77	0.472	0.512	0.018	1.13
1.0792	−205.71	0.479	0.515	0.022	1.20
1.1761	−205.64	0.511	0.532	0.029	1.28
1.3010	−205.49	0.516	0.527	0.014	1.39
1.4771	−205.38	0.531	0.522	0.031	1.53
1.6021	−205.24	0.547	0.521	0.017	1.66
1.7782	−205.14	0.556	0.514	0.019	1.79
1.9031	−205.04	0.567	0.506	0.022	1.90
2.0000	−204.90	0.587	0.507	0.030	2.02
2.0792	−204.83	0.595	0.505	0.019	2.09
2.1761	−204.64	0.625	0.519	0.016	2.23
2.3010	−204.49	0.651	0.524	0.026	2.36
2.4771	−204.30	0.693	0.528	0.020	2.56
2.6021	−204.14	0.722	0.532	0.044	2.75
2.7782	−203.78	0.805	0.596	0.048	2.99
2.9031	−203.69	0.832	0.589	0.054	3.12
3.0000	−203.59	0.866	0.609	0.058	3.20
3.1761	−203.30	0.941	0.671	0.087	3.35
3.3010	−203.03	0.963	0.695	0.114	3.54

follow enthalpic ageing in polymer glasses. It is far more informative to use C_p data to directly monitor the enthalpic ageing process via $\Delta H(t_a, T_a)$.

Cowie–Ferguson model

Six ageing temperatures, which spanned the temperature range $T_g - 20\text{ K} < T_a < T_g - 7$ K, were considered. Non-linear least squares curve fits of the $\Delta H(t_a, T_a)$ *versus* $\log_{10} t_a$ data were obtained using equation (7) (which is a transformation of equation (1) with $\log_{10} t_a$ as the dependent variable) and the Levenberg–Marquhardt algorithm[16]:

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)(1 - \exp(-10^u))$$
$$\text{where } u = \beta(\log_{10} t - \log_{10} t_c) \qquad (7)$$

The Williams–Watts relaxation function parameters β and $\log_{10} t_c$, together with $\Delta H_\infty(T_a)$, the enthalpy lost on ageing after an infinite ageing time, and $\log_{10} t_e$, the time for the sample to approach 0.1% of the equilibrium state (i.e. at $t = t_e$, $\phi(t) = 0.001$) are listed in *Table 3*. *Figures 4a* and *4b* show the enthalpic ageing data, together with the theoretical curve fits obtained from equation (7). In describing the enthalpic ageing data by this equation, one can consider both the thermodynamic and the kinetic aspects of the ageing process. The thermodynamic aspects are embodied in the quantity $\Delta H_\infty(T_a)$, and similarly, the kinetic aspects are embodied in the relaxation function $\phi(t) = \exp[-(t/t_c)^\beta]$. Hence, turning first to the behaviour of the enthalpy parameter $\Delta H_\infty(T_a)$, *Figure 5* is a plot of this quantity against $T_g - T_a$, along with the best fit straight line described by the equation $\Delta H_\infty(T_a) = 0.775 + 0.040$ $(T_g - T_a)$. *Table 4* lists the values of $\Delta H_{\infty\max}(T_a)$ obtained by extrapolating the liquid enthalpy curve down to temperatures less than $T_{g(\text{en})}$ and considering the enthalpy difference $H_{\text{glass}}(T_a) - H_{\text{liquid}}(T_a) = \Delta H_{\infty\max}(T_a)$. This quantity can be obtained from the $C_p(T)$ data from the following integral[9,10]:

$$\Delta H_{\infty\max}(T_a) = \int_{T_a}^{T^*} C_{p_{\text{liquid}}}(T') - C_p(T')\,dT' \qquad (8)$$

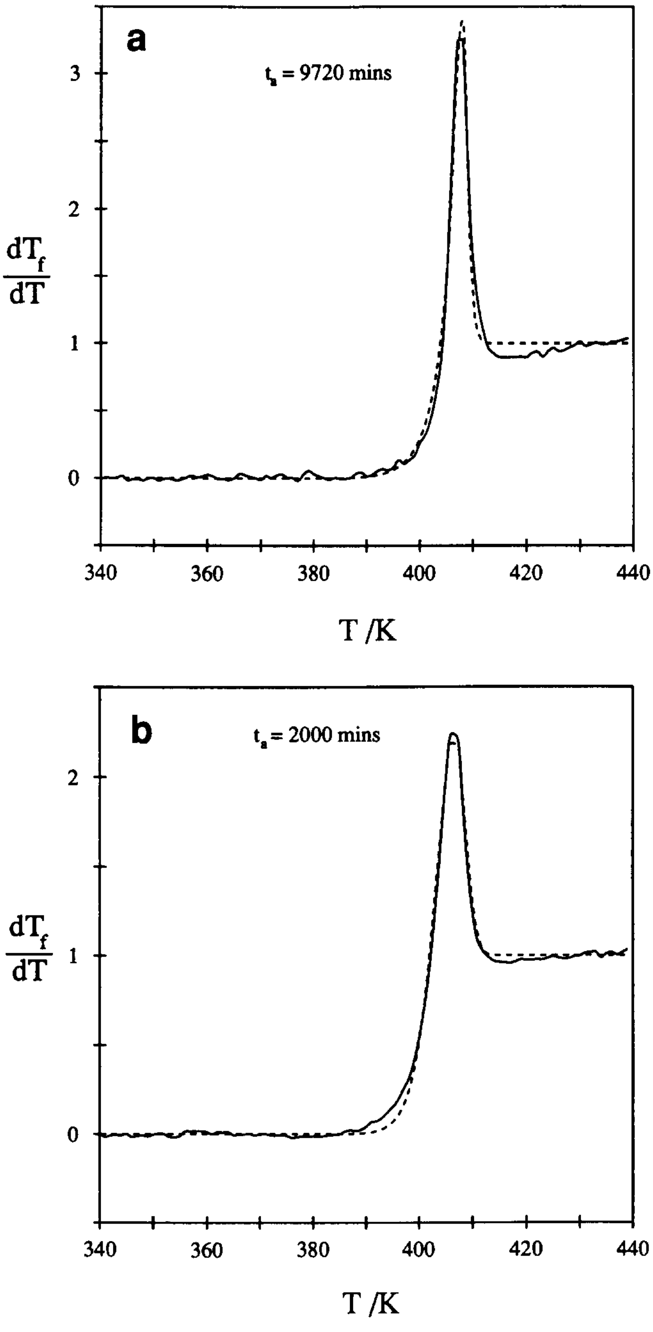

Figure 2 (a) Normalized C_p data (solid line) and MP model fit (dashed line) for PMMA aged at 375 K for 9750 minutes; (b) normalized C_p data (solid line) and MP model fit (dashed line) for PMMA aged at 387.5 K for 2000 minutes

Inspection of *Table 4* shows that for PMMA, the values of $\Delta H_{\infty\max}(T_a)$ obtained by assuming the validity of extrapolating liquid state enthalpy data are significantly larger than those obtained from the experimental $\Delta H(t_a, T_a)$ data via equation (7). *Figure 5* also shows the $\Delta H_{\infty\max}(T_a)$ data together with the best fit straight line described by the equation $\Delta H_{\infty\max}(T_a) = 0.068 + 0.236 (T_g - T_a)$.

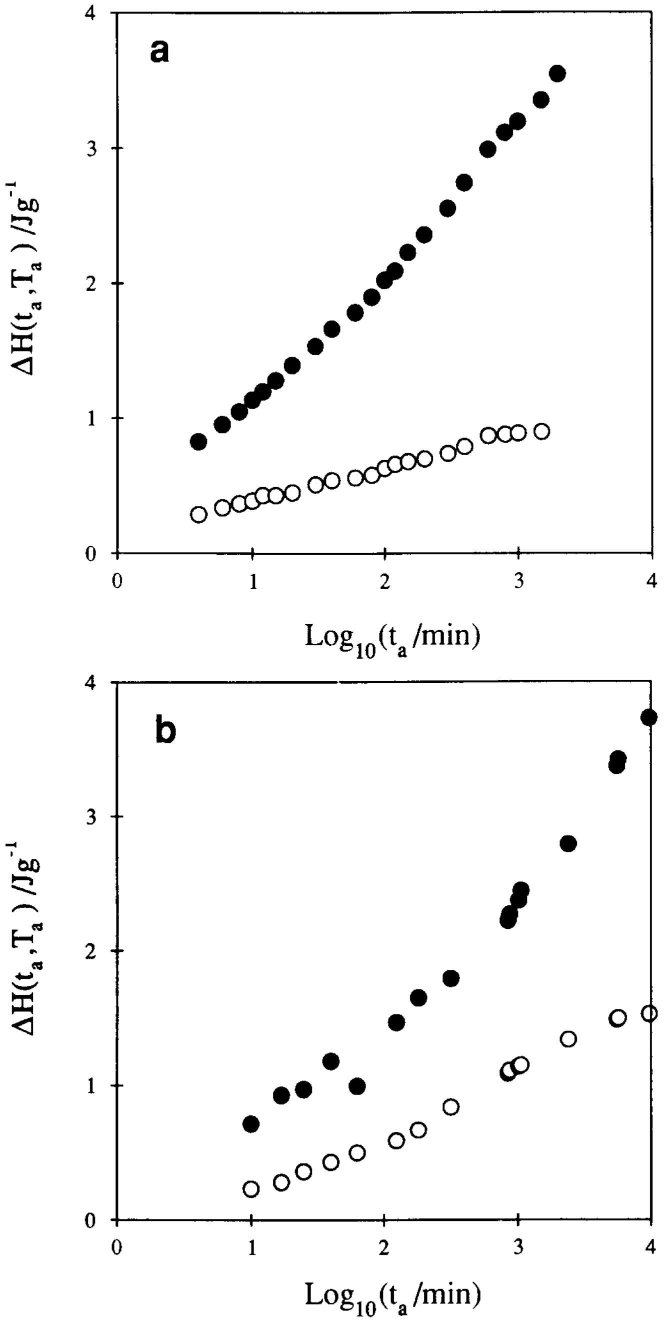

Figure 3 Comparison of enthalpic ageing results for PMMA aged at (a) 375 K and (b) 387.5 K, where open circles = experimental $\Delta H_\infty(T_a)$ data, and filled circles = ΔH_∞ (T_a) calculated from the MP model fit to the normalized C_p data

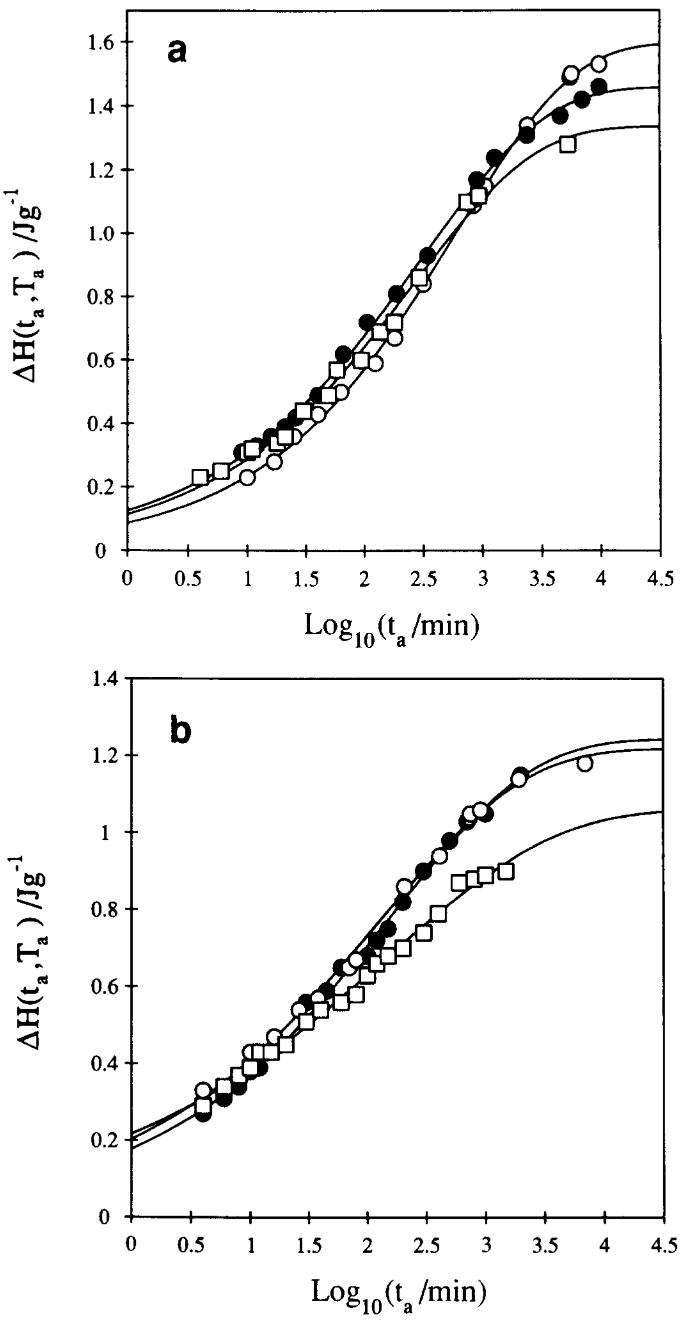

Figure 4 PMMA enthalpic ageing data for (a) $T_a = 375.0$ K (open circles), $T_a = 377.5$ K (filled circles), and $T_a = 380.0$ K (open squares), and (b) for $T_a = 382.5$ K (filled circles), $T_a = 385.0$ K (open circles), and $T_a = 387.5$ K (open squares)

Table 3 Cowie–Ferguson model parameters (errors in brackets) and $\log t_e$ for PMMA

T_a(K)	$(T_g - T_a)$(K)	$\Delta H_\infty(T_a)$(Jg^{-1})	$\log_{10}(t_c)$	β	$\log_{10}(t_e)$
375.0	19.9	1.597 (0.012)	2.791 (0.017)	0.447 (0.006)	4.669 (0.059)
377.5	17.4	1.460 (0.009)	2.490 (0.016)	0.418 (0.005)	4.498 (0.057)
380.0	14.9	1.338 (0.014)	2.428 (0.023)	0.431 (0.006)	4.376 (0.071)
382.5	12.4	1.244 (0.022)	2.208 (0.042)	0.368 (0.008)	4.489 (0.129)
385.0	9.9	1.219 (0.012)	2.103 (0.028)	0.352 (0.007)	4.488 (0.107)
387.5	7.4	1.062 (0.034)	2.149 (0.088)	0.299 (0.010)	4.959 (0.257)

Considering the kinetic aspects of the ageing process, *Figure 6* is an Arrhenius plot of $\ln t_c$ *versus* $1000/T_a$ together with a linear least squares fit to the first five points of this data set. The apparent activation energy is $182\,\mathrm{kJ\,mole^{-1}}$. The mechanical β relaxation process in PMMA has an apparent activation energy of $75\,\mathrm{kJ\,mole^{-1}}$ (ref. 17), hence it can be concluded that the molecular rearrangements which occur during enthalpic ageing only involve a small number of segments.

Table 4 Comparison between fitted and 'extrapolated' $\Delta H_{\infty}(T_a)$ values for PMMA

T_a(K)	(T_g-T_a)(K)	$\Delta H_{\infty}(T_a)(\mathrm{Jg^{-1}})$	$\Delta H_{\infty\max}(T_a)(\mathrm{Jg^{-1}})$
375.0	19.9	1.60	4.79
377.5	17.4	1.46	4.16
380.0	14.9	1.34	3.55
382.5	12.4	1.24	2.96
385.0	9.9	1.22	2.39
387.5	7.4	1.06	1.85

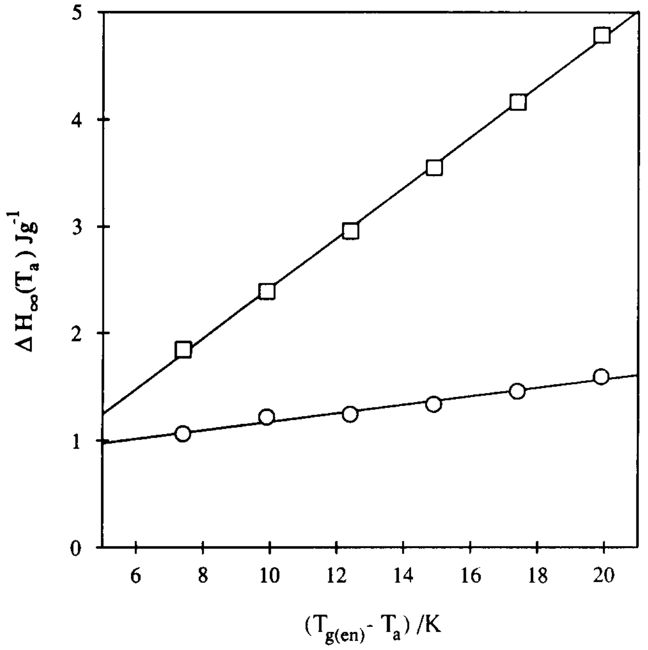

Figure 5 Variation of $\Delta H_{\infty}(T_a)$ with T_g-T_a for PMMA, where open circles $=\Delta H_{\infty}(T_a)$, and open squares $=\Delta H_{\infty\max}(T_a)$

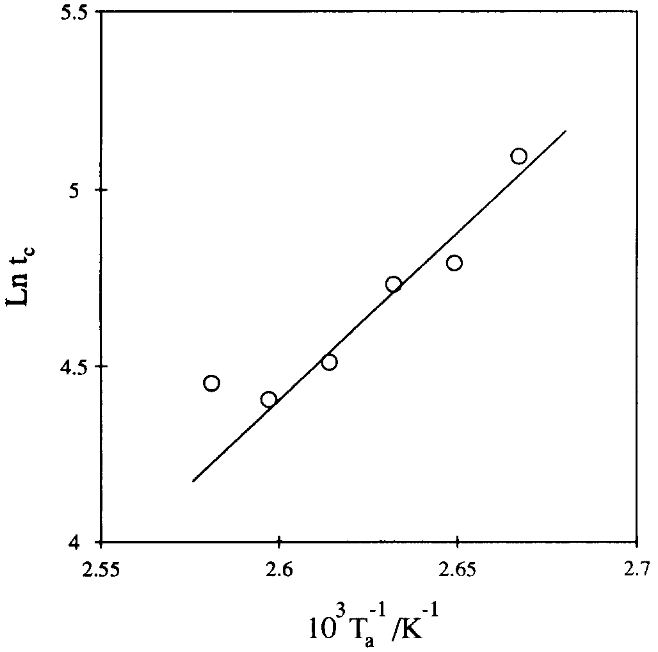

Figure 6 Variation of $\ln t_c$ with $1000/T_a$ for PMMA

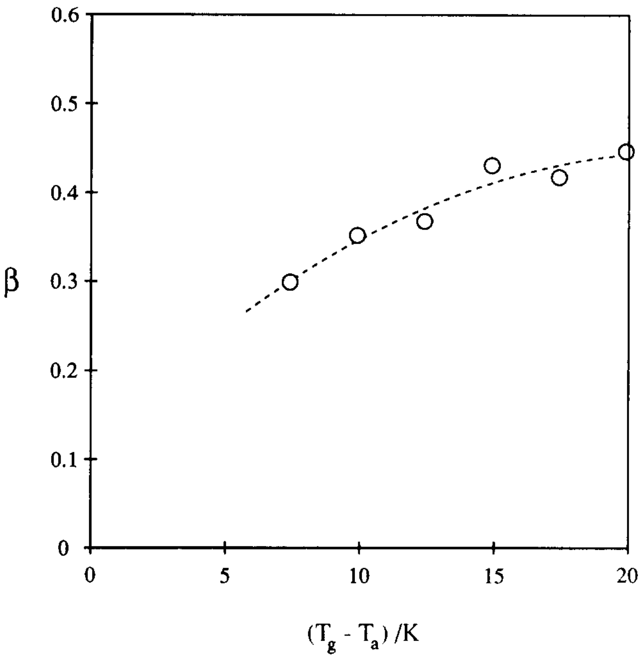

Figure 7 Variation of β with T_g-T_a for PMMA

Figure 7 is a plot of β *versus* T_g-T_a. Previous studies have shown that as one approaches the polymer glass transition, β approached unity[9,10]; however, this is not true for PMMA. The Williams–Watts β parameter is associated with the distribution of relaxation times, a small value of β implies a broad distribution, and β close to unity implies a narrow distribution. Thus, for PMMA as one approaches the polymer glass transition, the underlying relaxation time distribution of the ageing process(es) is broadening, i.e. the ageing process is not 'thermorheologically simple'. Dielectric and photon correlation spectroscopic studies of PMMA have shown that at the glass transition of PMMA, the α and β relaxation processes merge[18,19], hence if enthalpic ageing is envisaged as probing limited segmental motions of the polymer backbone, then the broadening of the relaxation time distribution could result from the added effects of the β relaxation process.

CONCLUSIONS

Enthalpic ageing in poly(methyl methacrylate) has been studied for several ageing temperatures in the range $T_g-20<T_a<T_g-7$ K and the results discussed in terms of the MP and the CF models. The analysis of enthalpic ageing via the shapes of heat capacity curves (the multiparameter phenomenological model) has been shown to (a) not satisfy some of the original assumptions of this model in that the MP parameters do depend on ageing time and temperature, and (b) not predict the actual values of the enthalpy lost on ageing.

The results presented here also call into question the validity of extrapolating liquid enthalpy curves to temperatures below the glass transition to obtain $\Delta H_{\infty\max}(T_a)$.

ACKNOWLEDGEMENTS

R.F. acknowledges support from the SERC received during the course of this project via a postdoctoral fellowship. We also thank Dr I. M. Hodge for kindly supplying us with the Fortran source code for his version of the multiparameter phenomenological model.

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