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Physical ageing of poly(methyl methacrylate): 2. Effects of non-linearity

J. M. G. Cowie* and R. Ferguson
Department of Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, UK

Enthalpic ageing data for poly(methyl methacrylate) are reanalysed in terms of a modified version of the Cowie–Ferguson model which takes account of a time-dependent characteristic time, t_c. In terms of describing the time evolution of enthalpy changes occurring upon ageing, no significant improvement in the fits to the data were found when compared with the original linear model.

(Keywords: physical ageing; enthalpic ageing; poly(methyl methacrylate))

Introduction

The results of a previous study[1] of the enthalpic ageing of poly(methyl methacrylate) (PMMA), as measured by differential scanning calorimetry (d.s.c.) have served to highlight various shortcomings exhibited by different descriptions of the ageing process such as the multi-parameter phenomenological models[2,3]. The enthalpic ageing data obtained were curve fitted using a semi-empirical equation, developed by ourselves, which has successfully described the ageing data in several other systems[4,5]. Moreover, this simple pragmatic approach permitted us to make predictions as to the long-term ageing behaviour of the polymers concerned, a feature that most other approaches are incapable of dealing with, or ignore. It is this aspect of physical ageing which is of interest to material scientists and designers, namely the long-term stability (or otherwise) of polymer glasses. Recently, several workers have questioned our semi-empirical approach[6,7], pointing out that we have neglected to account for the possible time dependence of the characteristic time parameter, t_c. Other workers call this parameter τ, and several possibilities for describing the time dependence of τ have appeared in the literature[2,3,6–8]. We wish to show the results of incorporating two such expressions for τ (or t_c) into our semi-empirical equation (referred to in the past as the Cowie–Ferguson (CF) model).

Experimental

Full details of the PMMA samples used and the experimental methodology for obtaining the enthalpic ageing data for PMMA are described in reference 1. The non-trivial problem of incorporating a time-dependent τ into the CF model will now be addressed.

The original version of the CF model is given in equations (1a) and (1b):

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

$$\phi(t) = \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \quad (1b)$$

* To whom correspondence should be addressed

These equations were then used in the Levenberg Marquhardt non-linear least-squares curve-fitting algorithm[9]. In terms of our computer program, which uses this algorithm, equation (1) is recast as equations (2a) and (2b):

$$F = P_1[1 - \phi(t_a)] \quad (2a)$$

$$\ln \phi = -\exp[P_2 x \ln(10) - \ln \tau] \quad (2b)$$

where, for the sake of convenience, the following substitutions have been made: $F = \Delta H(t_a, T_a), P_1 = \Delta H_\infty(T_a), P_2 = \beta$, and $x = \log_{10} t_a$. In order to use the Levenberg Marquhardt algorithm one also requires the partial derivatives with respect to the various model parameters, i.e. the $(\partial F/\partial P_i)$. To introduce a time/structural dependence into τ, the following expressions for $\ln \tau$ were considered:

$$\ln \tau = \ln A + \frac{E_H}{RT_a} + C[\Delta H_\infty(T_a) - \Delta H(t_a, T_a)] \quad (3a)$$

$$\ln \tau = P_3 + P_4 F \quad (3b)$$

where

$$P_3 = \ln A + \frac{E_H}{RT_a} + C\Delta H_\infty(T_a)$$

and $P_4 = -C$, and

$$\ln \tau = \ln A + \frac{X\Delta h^*}{RT_a} + \frac{(1-X)\Delta h^*}{RT_f} \quad (4a)$$

$$\ln \tau = Q_3 + \frac{Q_4}{T_f} \quad (4b)$$

where

$$Q_3 = \ln A + \frac{X\Delta h^*}{RT_a}$$

and

$$Q_4 = \frac{(1-X)\Delta h^*}{R}$$

Equation (3a) is the Petrie–Marshall (PM)[8] form for $\ln \tau$ which embodies the idea that τ depends on the state of the system, i.e. the structure, in that it depends on the departure of the instantaneous glass from equilibrium. A second way of incorporating a structural dependence into τ is to employ the Narayanaswami–Moynihan (NM) expression[7], equation (4a), which brings in the structural dependence by means of the fictive temperature, T_f. Since both equations (3b) and (4b) include the dependent variable F, either explicitly or implicitly via T_f, $F(=\Delta H(t_a, T_a))$ must now be obtained by solving a non-linear equation in one unknown.

In order to obtain the required partial derivatives, one has to resort to the technique of implicit differentiation. For the PM expression for $\ln\tau$, the results are:

$$\left(\frac{\partial F}{\partial P_1}\right)=\frac{-F/P_1}{[1+(P_1-F)P_2P_4U]}$$
$$\left(\frac{\partial F}{\partial P_2}\right)=\frac{(F-P_1)[x\ln(10)-\ln\tau]U}{[1+(P_1-F)P_2P_4U]}$$
$$\left(\frac{\partial F}{\partial P_3}\right)=\frac{(P_1-F)P_2U}{[1+(P_1-F)P_2P_4U]} \qquad (5)$$
$$\left(\frac{\partial F}{\partial P_4}\right)=\frac{(P_1-F)P_2UF}{[1+(P_1-F)P_2P_4U]}$$

and for the NM expression for $\ln\tau$ one has:

$$\left(\frac{\partial F}{\partial P_1}\right)=\frac{-F/P_1}{\left[1+(F-P_1)P_2Q_4U\left(\frac{\partial T_f}{\partial F}\right)/T_f^2\right]}$$
$$\left(\frac{\partial F}{\partial P_2}\right)=\frac{(F-P_1)(x\ln(10)-\ln\tau)U}{\left[1+(F-P_1)P_2Q_4U\left(\frac{\partial T_f}{\partial F}\right)/T_f^2\right]}$$
$$\left(\frac{\partial F}{\partial Q_3}\right)=\frac{(P_1-F)P_2U}{\left[1+(F-P_1)P_2Q_4U\left(\frac{\partial T_f}{\partial F}\right)/T_f^2\right]} \qquad (6)$$
$$\left(\frac{\partial F}{\partial Q_4}\right)=\frac{(P_1-F)P_2U/T_f}{\left[1+(F-P_1)P_2Q_4U\left(\frac{\partial T_f}{\partial F}\right)/T_f^2\right]}$$

where $U=\exp[P_2(x\ln(10)-\ln\tau)]$.

Finally, the fictive temperature and its partial derivative with respect to F are given by:

$$T_f=\frac{-2c}{\left[b+\frac{|b|}{b}\sqrt{b^2-4ac}\right]} \qquad (7)$$
$$\frac{\partial T_f}{\partial F}=\frac{1}{[2aT_f+b]}$$

where $a=G_2-L_2, b=G_1-L_1-2aT_1$ and $c=-F-aT_g^2-bT_g$. Here, T_g is the enthalpic glass transition temperature, and the constants G_1, G_2, L_1, L_2 and T_1 are used to define the glassy and liquid state heat capacities, as was discussed before in reference 1.

Discussion

Figures 1 and *2* show the ageing data for PMMA at $T_a = 375$ and 387.5 K together with the corresponding curve fits from the three versions of the CF empirical equation. It is apparent that, over the range of ageing times spanned by the experimental ΔH data, the three versions of the CF equation generate nearly identical curves. In other words, when curve fitting the enthalpic ageing data, there is little or nothing to be gained by invoking a structural dependence for $\ln\tau$. *Table 1* lists the results of applying all three versions of the CF empirical equation to the PMMA ageing data, and there are two main points to be noted. First, inspection of the $\ln\tau$ parameter values (P_3, P_4 or Q_3, Q_4) for the two non-linear cases (PM and NM) reveals that no discernible

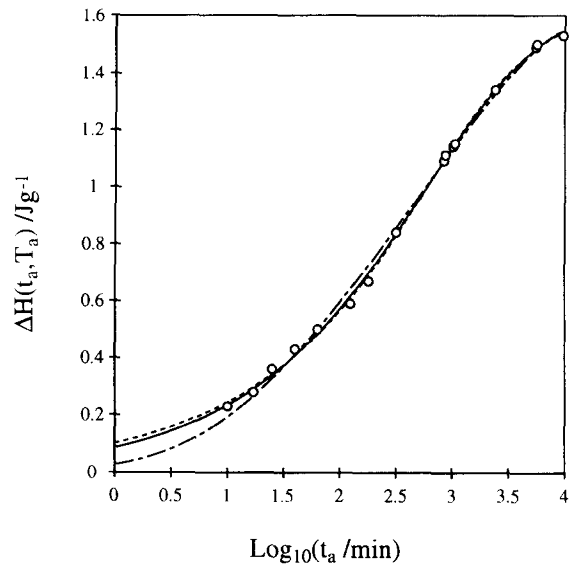

Figure 1 Curve fits to enthalpic ageing data for PMMA with $T_a = 375$ K. The fitted curves are from the three versions of the CF empirical equation with $\ln\tau$ = constant (——), $\ln\tau = P_3 + P_4F$ (– – –) and $\ln\tau = Q_3 + Q_4/T_f$ (- - -)

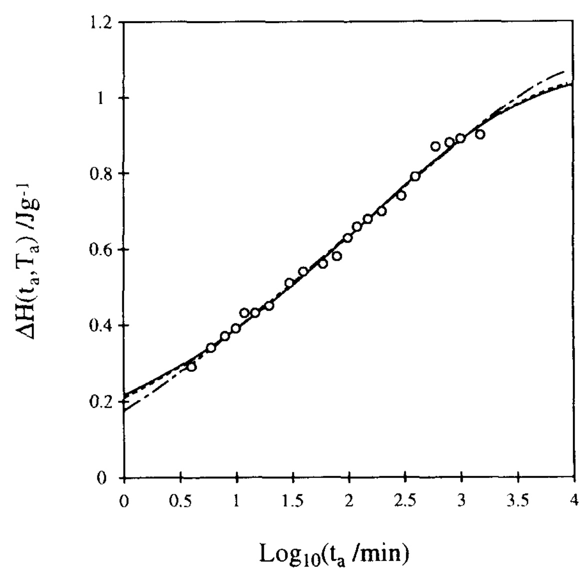

Figure 2 Curve fits to enthalpic ageing data for PMMA with $T_a = 387.5$ K. The fitted curve are from the three versions of the CF empirical equation with $\ln\tau$ = constant (——), $\ln\tau = P_3 + P_4F$ (– – –) and $\ln\tau = Q_3 + Q_4/T_f$ (- - - -)

Table 1 PMMA ageing parameters obtained from the modified CF empirical equation

T_a(K)	P_1[a]	P_2[b]	P_3	P_4	$\ln\tau$	χ^2	No. of parameters	No. of points
$\ln\tau$ = constant								
387.5	1.062	0.299	–	–	4.948	48.37	3	21
385.0	1.219	0.352	–	–	4.842	39.06	3	14
382.5	1.244	0.368	–	–	5.085	54.07	3	19
380.0	1.337	0.431	–	–	5.591	99.37	3	16
377.5	1.460	0.418	–	–	5.733	47.90	3	18
375.0	1.597	0.447	–	–	6.426	35.46	3	16
$\ln\tau = P_3 + P_4F$								
387.5	1.064	0.355	3.961	1.480	–	48.18	4	21
385.0	1.256	0.150	12.015	–8.803	–	21.00	4	14
382.5	1.252	0.598	3.062	2.599	–	48.79	4	19
380.0	1.340	0.244	9.178	–4.237	–	55.32	4	16
377.5	1.458	0.443	5.470	0.278	–	47.64	4	18
375.0	1.599	0.376	7.286	–0.840	–	31.66	4	16
$\ln\tau = Q_3 + Q_4/T_f$								
387.5	1.064	0.355	–129.605	52745	–	48.18	4	21
385.0	1.256	0.150	806.281	–313655	–	21.00	4	14
382.5	1.252	0.598	–231.458	92611	–	48.79	4	19
380.0	1.340	0.244	391.42	–150947	–	55.32	4	16
377.5	1.458	0.443	–19.656	9922	–	47.64	4	18
375.0	1.599	0.376	83.028	–29911	–	31.66	4	16

[a] $P_1 = \Delta H_\infty(T_a)$
[b] $P_2 = \beta$

Table 2 Results of applying the statistical F-test to the modified CF model results

T_a(K)	χ^2	No. of points	χ^2(CF)	Significance level
Petrie Marshall form for $\ln\tau = P_3 + P_4F$, no. of parameters used = 4				
387.5	48.1806	21	48.3687	0.411
385.0	21.0004	14	39.0650	0.091
382.5	48.7872	19	54.0680	0.458
380.0	55.3157	16	99.3689	0.064
377.5	47.6413	18	47.9022	0.442
375.0	31.6563	16	35.4595	0.518
Narayanaswami form for $\ln\tau = Q_3 + Q_4/T_f$, no. of parameters used = 4				
387.5	48.1804	21	48.3687	0.412
385.0	21.0008	14	39.0650	0.091
382.5	48.7871	19	54.0680	0.458
380.0	55.3157	16	99.3689	0.064
377.5	47.6413	18	47.9022	0.442
375.0	31.6563	16	35.4595	0.518

trends can be seen for these parameters, as might otherwise be expected. For example, in the PM model, the P_4 parameter should be constant with respect to the ageing temperature, and this is clearly not the case. In addition, the P_3 parameter values appear to be random. Secondly, it was also found that the errors in the $\ln\tau$ parameters were unacceptably large.

Another method of assessing whether the modified CF equation provides an improved description of the enthalpic ageing process in PMMA is to consider the goodness of fit parameter, χ^2. While this parameter does have lower values for the PM and NM versions of the CF equation, this improvement is only apparent, an observation confirmed using the statistical F-test[4] to test the null hypothesis that 'the PM and NM versions of the CF model were not significantly better at fitting the data than the original model'.

The results obtained after applying the F-test are shown in *Table 2*. If the significance level is less than 0.01 then one can conclude that the null hypothesis is false and that both the PM and NM versions of the CF equation are better at describing the enthalpic ageing data when compared with the original equation. Inspection of *Table 2* shows that, at best, there are only one or two entries where a slight improvement could be possible but that overall there is no improvement (significance levels >0.05). Thus, again, it can be concluded that in terms of a description of the enthalpy data, there is nothing to be gained by allowing τ to depend on the structure of the polymer glass.

It should be remembered that the CF equation was employed as a means for obtaining information about the long-time behaviour of polymer glasses, and this is something which most of the other, more theoretical approaches (such as the Hodge model) do not consider. Indeed, most of the other theoretical approaches consider the shapes of the heat capacity curves for aged and unaged polymer glasses rather than the enthalpy changes involved during the ageing process. Our reason for focusing on the enthalpy lost on ageing was so that one could attempt to correlate enthalpic, volumetric and mechanical ageing, and already some success has been met in this regard[10].

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