Enthalpy relaxation of styrene–maleic anhydride (SMA) copolymers Part 1. Single component systems

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Received 20 September 1999; accepted 12 January 2000

Abstract

The enthalpy relaxation of styrene–maleic anhydride (SMA) copolymers, at various ageing temperatures (T_a) below T_g and for different ageing times (t_a), is described. Values of enthalpy lost ($\Delta H(t_a,T_a)$) were calculated from experimental data, plotted against $\log_{10}(t_a)$ and modelled using the Cowie–Ferguson (CF) semi-empirical approach to give a set of values for three adjustable parameters, $\Delta H_\infty(T_a)$, $\log_{10}(t_c)$ and β. These define the relaxation process, which was found to be sensitive to copolymer composition in a non-linear fashion. Increasing MA content initially causes a faster relaxation with a smaller overall enthalpy loss; further increases in MA levels lead to slower changes to a final state of lower equilibrium enthalpy. All experiments indicate that the enthalpy lost by the fully relaxed glass ($\Delta H_\infty(T_a)$) is less than the theoretical amount possible on reaching the state defined by the liquid enthalpy line extrapolated into the glassy region ($\Delta H_{max}(T_a)$), and that the final enthalpy value is dependent on copolymer composition. The implications of this are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene–maleic anhydride copolymers; Enthalpy relaxation; Physical ageing

1. Introduction

As a direct consequence of the thermodynamic non-equilibrium nature of glasses, an amorphous material in the glassy region will not exhibit long-term stability. Structural relaxations occur, causing a loss in excess thermodynamic properties (volume, enthalpy, entropy). This phenomenon is known as physical ageing. It is a reversible process; the quantity of excess property lost is recovered on returning to the liquid state above T_g. Therefore, physical ageing should not be confused with irreversible chemical ageing, such as degradation.

Physical ageing is of considerable technological importance since changes in thermodynamic properties produce changes in physical and mechanical properties, such as dimensions, brittleness, modulus and dielectric constant. Thermoplastic polymer materials are frequently produced by injection moulding, in which molten polymer is rapidly quenched to below T_g. The resulting products will undoubtedly undergo physical ageing during their lifetimes. Conse-

quently, after a certain period of time, they may not perform to their original specifications. The ability to predict how a material will age with time would therefore be of great benefit to the polymer engineer. This is one of the aims of the present study.

The manifestation of physical ageing studied in this investigation is enthalpy relaxation or recovery, which is conveniently followed by differential scanning calorimetry (DSC). The availability of high-precision calorimeters and the simplicity of experimental procedure have meant that most investigations into physical ageing have focused on enthalpy relaxation. As has been pointed out by Hutchinson [1], however, enthalpy relaxation compares unfavourably with volume relaxation in that the enthalpy is not measured directly by DSC. Rather, it is obtained by integration of heat capacity (C_p) curves, which are in turn calculated from the DSC output signal. Nevertheless, with careful experimental procedures [2], enthalpy relaxation can yield data that are both reliable and informative.

Much effort has been invested into developing expressions which describe the physical ageing process, and a number of models have been developed as a consequence. These can be divided roughly into two categories: the multi-parameter phenomenological (MP) models, including the Narayanaswamy–Moynihan (NM) [3–5], Scherer–Hodge (SH) [6,7] and Kovacs–Aklonis–Hutchinson–Ramos

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(KAHR) [8] models; and the more pragmatic, semi-empirical approaches, of which the Cowie–Ferguson (CF) model is the main example.

Two of the major features of physical ageing, non-linearity and non-exponentiality, are incorporated into the MP models. Non-linearity is dealt with by expressing the average relaxation time as a function of the departure from equilibrium (i.e. the average relaxation time changes as the system progresses towards equilibrium). This departure is measured by the fictive temperature T_f, which is defined as the temperature at which the observed value of the property (i.e. enthalpy) would correspond to the equilibrium value. The enthalpy relaxation is described by a non-exponential decay function, where the degree of non-exponentiality is determined by the term β. A number of reviews on these models have recently been published [1,9,10].

All of the MP models explicitly assume thermorheological simplicity. This means that the shape of the relaxation function is independent of temperature, i.e. the value of β is unchanging. This assumption has been called into question in light of experimental evidence that has indicated that β does indeed vary with temperature [11–13]. Perhaps more importantly, however, the MP models completely fail to predict the enthalpy lost on ageing to the equilibrium liquid state. This has been shown conclusively by Cowie and Ferguson [11]. The role of these models has been to predict the shapes of the C_p curves, and this has been achieved with considerable success in some cases. The discrepancy between calculated and observed $\Delta H_\infty(T_a)$ values, however, demonstrates the unreliability of following ageing by reproducing C_p curves.

Another criticism of the MP models is their assumption that the equilibrium state reached after infinite ageing coincides with the equilibrium liquid state extrapolated into the glassy region. This also has been shown to be invalid [11]. Indeed, it will be shown in this article that the experimentally observed $\Delta H_\infty(T_a)$ value is almost always less than the calculated value. The implications of this will be discussed. In addition, the parameters determined by the MP models have been shown to vary with ageing time and temperature [11]. This implies that they are not material parameters, making it difficult to relate them to intrinsic polymer properties with any degree of confidence.

A different approach was introduced recently by Cowie and Ferguson [14]. This attempts to predict the enthalpy lost on annealing to equilibrium ($\Delta H_\infty(T_a)$) by curve-fitting to the experimental enthalpy data accumulated at various ageing temperatures after a range of ageing times ($\Delta H(t_a,T_a)$). These values are determined from experimental C_p data obtained from DSC measurements.

The progression of the system towards equilibrium is described by $\Phi(t)$, given by

$$\Phi(t) = \frac{H_t - H_e}{H_0 - H_e} \tag{1}$$

where H_0, H_t and H_e are the initial, time = t and equilibrium enthalpy values, respectively.

$\Delta H(t_a,T_a)$ can be described by the following empirical equation:

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

where

$$\Phi(ta) = \exp[-(t/tc)^\beta] \tag{3}$$

is the Williams–Watts relaxation function. β gives the width of the relaxation time spectrum ($0 < \beta \leq 1$) and t_c is a characteristic time ($\phi(t_c) = 1/e$) i.e. a kinetic parameter. These expressions are the basis of the CF model. The parameters $\Delta H_\infty(T_a)$, β and $\log_{10}(t_c)$ are obtained from a curve-fitting procedure. Since its inception, this model has been used to investigate the ageing of a number of polymeric systems, including poly(vinyl methyl ether) (PVME) [14,15], plasticised PVC [16], PMMA [11,17], poly(vinyl acetate) (PVAc) [18], polystyrene [19] and several *para*-substituted polystyrenes [20].

Criticisms have been levelled at the CF model for its failure to account for non-linearity in the relaxation process, since it employs a single relaxation time t_c. However, it was shown [17,20] that incorporating non-linearity effects into the CF model has little bearing on its ability to describe the enthalpy changes occurring during ageing. Nevertheless, this does not mean that t_c is time-invariant; simply that $\Delta H(t_a)$ values do not show a time-dependence.

It is important to emphasise that each type of model describes a different aspect of ageing; the MP models follow the structural changes produced by a given thermal history, whereas the CF model looks at the enthalpy changes during annealing only, and tries to determine the quantity of enthalpy lost on attaining equilibrium. It is believed that enthalpy changes in a material are more important technologically than the ability to accurately predict its C_p behaviour.

In this paper, we present our data on the enthalpic recovery of styrene–maleic anhydride (SMA) copolymers. These materials are produced commercially by DSM Research, and have uses as blend compatibilisers [21] and precursors to novel high-temperature foams [22]. Their synthesis [23,24] and blend formation [25–27] have previously been reported. Our aims in this research were to obtain some ageing data on these previously unstudied materials, and to attempt to predict their long-term ageing based on short-term data.

2. Experimental

2.1. Materials and instrumentation

Styrene–maleic anhydride (SMA) copolymers were obtained courtesy of DSM Research, The Netherlands, and were used as received. The molar mass (M_n) values of

Table 1
Composition and T_g data of SMA copolymers

Copolymer	F_{MA} (mol%)	T_g(en) (K)	ΔT (K)
SMA1	6	387	7.1
SMA2	25	410	11.4
SMA3	31	409	12.0
SMA4	45	432	12.4

each were quoted as 3500 g mol^{-1}. Copolymer compositions were determined using quantitative ^{13}C NMR spectroscopy in d$_6$-DMSO at 100 MHz, using a Bruker 400 NMR spectrometer and employing a pulse delay time of 10 s. Glass transition (T_g) determinations and enthalpy relaxation experiments were performed on either a Perkin–Elmer DSC-2 or a Perkin–Elmer Pyris DSC, employing approximately 10 mg of encapsulated sample, with nitrogen as the purge gas. A heating rate of 20 K min^{-1} and a cooling rate of 40 K min^{-1} were employed throughout. The DSC-2 was interfaced to a BBC microcomputer via a 12-bit analog to digital converter, and was controlled via the computer with in-house developed software (© Dr R. Ferguson). The Pyris DSC was interfaced to a PC and was controlled with Perkin–Elmer Pyris software for Windows. Data from both instruments were transferred to an Acorn Risc-PC workstation for analysis and processing, again using in-house developed software (© Dr R. Ferguson).

2.2. Thermal analysis techniques

T_g values were determined by DSC. In each case, a series of 10 scans was taken. The reported T_g values were obtained from an average of the last five scans. Since the glass transition occurs over a *temperature range*, it is possible to quote any of several T_g values; for example, the onset T_g or the mid-point T_g. In this work, and other work from this group, the T_g values given are determined by transforming the C_p curves into enthalpy curves, following the procedure of Richardson and Savill [28]. The point of intersection of the liquid and glassy enthalpy lines extrapolated into the transition region is taken to be the enthalpic T_g (T_g(en)). As this value is independent of scanning rate, it is felt to be more accurate.

The thermal history employed in ageing experiments has been described in detail elsewhere [11].

3. Results and discussion

The compositions of the copolymers were determined by quantitative ^{13}C NMR spectroscopy. This was achieved by comparison of the integrals of the carbonyl and aryl carbon regions in the spectrum of each. The normalised area per carbon from MA units is given by

$$A_{MA}^C = \frac{\text{(total area of carbonyl region)}}{2} \tag{4}$$

and the normalised area per carbon from S units by

$$A_S^C = \frac{\text{(total area of aryl region)}}{6} \tag{5}$$

Therefore, the mole fraction of MA units in the copolymer, F_{MA}, is given by

$$F_{MA} = \frac{A_{MA}^C}{A_{MA}^C + A_S^C} \tag{6}$$

The resulting values are given in Table 1. They are in reasonable agreement with those quoted by the suppliers (6, 26, 34 and 52 mol% for SMA 1–4).

The first stage in performing enthalpy relaxation experiments is to accurately determine the T_g of the material. The T_g values and the T_g temperature ranges (ΔT) of the SMA copolymers are also shown in Table 1. The T_g increases with increasing MA content due to the increased inherent rigidity of the polymer chains. Interestingly, the T_g of SMA2 appears to be comparable with that of SMA3, despite the latter having a higher MA content. This is unlikely to be due to experimental error, as the T_g values were reproducible and the DSC temperature scale was accurate by indium melting point reference (430.9 K, lit. 429.8 K). A recent investigation [29] of free volume in SMA copolymers by positron annihilation lifetime spectroscopy (PALS) found an increase up to 28% MA content, then a decrease. This was ascribed to a change from random to a more alternating copolymer sequence distribution, with concomitant increase in chain packing efficiency. The composition at which this transition occurs falls between the compositions of SMA2 and SMA3, and this may be the source of the apparently anomalous T_g values reported here. In contrast to our findings, the authors observed an almost linear T_g–composition relationship with increasing MA content. However, it should be stressed that materials of considerably higher $(50 - 224 \times 103)$ M_n value were used in that investigation, so comparisons of T_g values may not be appropriate.

Enthalpy relaxation experiments were carried out on each SMA copolymer, at temperatures ranging from 5 to 20 K below T_g. The corresponding plots of $\Delta H(t_a, T_a)$ against $\log_{10}(t_a)$ are shown in Fig. 1a–d. The main point to be taken from these is that the enthalpy lost after a given ageing time increases as T_a decreases. This is always the case, since the distance between the glassy and extrapolated liquid enthalpy lines increases the deeper into the glassy region the system is.

The experimental $\Delta H(t_a, T_a)$ data are curve-fitted via a nonlinear least-squares routine [30], employing the expressions in the CF model. This yields a model curve and a set of values for the three CF parameters ($\Delta H_\infty(T_a)$, $\log_{10}(t_c)$ and β). These parameters for the SMA copolymers are reported in Tables 2–5, together with the time taken for the sample to reach 99.9% of the equilibrium state ($\log_{10}(t_e)$) [11] and the theoretical values of the theoretical maximum enthalpy lost
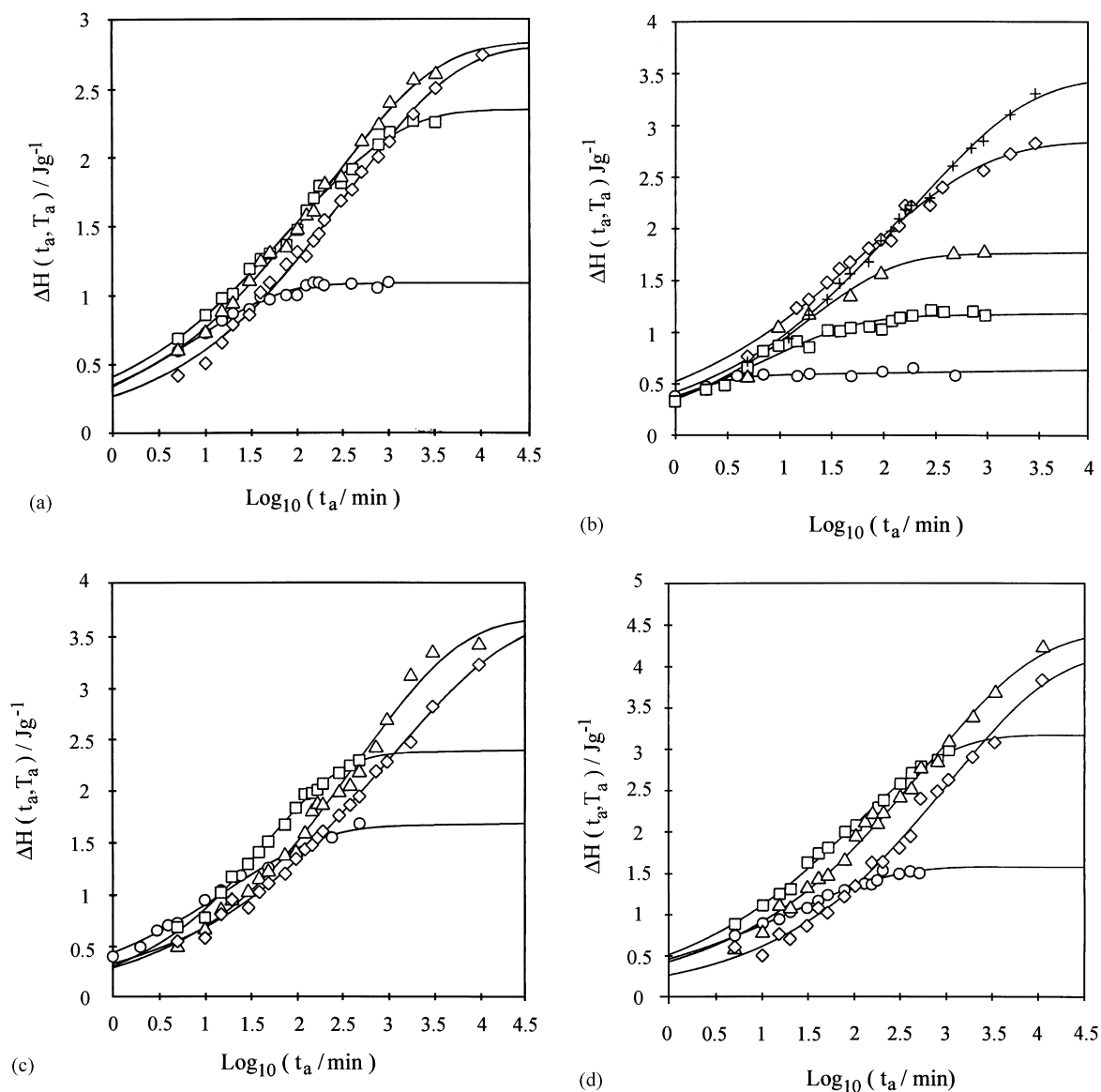
Fig. 1. Enthalpy relaxation of SMA copolymers: (a) SMA1 at $T_a = 382$ K (circles), 377 K (squares), 372 K (triangles) and 367 K (diamonds); (b) SMA2 at $T_a = 405$ K (circles), 403 K (squares), 400 K (triangles), 395 K (diamonds) and 390 K (crosses); (c) SMA3 at $T_a = 404$ K (circles), 399 K (squares), 394 K (triangles) and 389 K (diamonds); (d) SMA4 at $T_a = 429$ K (circles), 424 K (squares), 419 K (triangles) and 414 K (diamonds). Solid lines are fits of the experimental data to the CF model.

on annealing to the extrapolated liquid enthalpy line ($\Delta H_{max}(T_a)$).

The values of $\log_{10}(t_c)$ are plotted against distance from T_g of the ageing temperature ($T_g - T_a$) for each copolymer (Fig. 2). This parameter gives an idea of the kinetics of the process, in as much as a higher value implies a slower relaxation process. It can, therefore, be seen that the ageing process is slower with decreasing T_a, since the motion of relaxing elements is more restricted with increasing distance from T_g. The kinetics also appear to be influenced by MA content. Further examination of Fig. 2 indicates that the relaxation rate increases (t_c decreases) on increasing the content of maleic anhydride units in the copolymer from 6 to 24 mol%. However, further increase in MA content

beyond this (SMA3 and SMA4) apparently slows the relaxation process. This could signify that the free volume of the copolymers is increasing initially, leading to a faster relaxation, but then decreases towards higher MA content, in accord with the recent PALS data described above [29].

The β parameter gives an idea of the degree of non-exponentiality, in that a value of unity implies an essentially exponential relaxation process with a narrow distribution of relaxation times, whereas a value close to zero suggests extremely non-exponential behaviour and a broad distribution of relaxation times. In terms of actual processes at the molecular level, a small β value indicates that the relaxation process is co-operative, which means that in order for an

Table 2
CF parameters and ΔH_{max} values for SMA1

T_a (K)	$(T_g - T_a)$ (K)	$\Delta H_\infty(T_a)$ (J g^{-1})	$\log_{10}(t_c)$ (min)	β	$\log_{10}(t_c)$ (min)	$\Delta H_\infty(T_a)$ (J g^{-1})
382	5	1.08	0.88	0.47	2.67	0.98
377	10	2.34	1.93	0.37	4.20	2.50
372	15	2.83	2.34	0.37	4.61	4.25
367	20	2.78	2.59	0.38	4.80	6.10

Table 3
CF parameters and ΔH_{max} values for SMA2

T_a (K)	$(T_g - T_a)$ (K)	$\Delta H_\infty(T_a)$ (J g^{-1})	$\log_{10}(t_c)$ (min)	β	$\log_{10}(t_c)$ (min)	$\Delta H_\infty(T_a)$ (J g^{-1})
405	5	0.58	0.42	0.47	2.17	1.83
403	7	1.12	0.84	0.48	2.59	2.50
400	10	1.71	1.73	0.27	4.84	3.59
395	15	2.79	1.87	0.37	4.14	5.57
390	20	3.40	2.30	0.38	4.51	7.67

Table 4
CF parameters and ΔH_{max} values for SMA3

T_a (K)	$(T_g - T_a)$ (K)	$\Delta H_\infty(T_a)$ (J g^{-1})	$\log_{10}(t_c)$ (min)	β	$\log_{10}(t_c)$ (min)	$\Delta H_\infty(T_a)$ (J g^{-1})
404	5	1.63	1.24	0.41	3.29	1.34
399	10	2.33	1.67	0.51	3.32	2.81
394	15	3.55	2.69	0.39	4.84	4.47
389	20	3.63	3.05	0.33	5.59	6.25

Table 5
CF parameters and ΔH_{max} values for SMA4

T_a (K)	$(T_g - T_a)$ (K)	$\Delta H_\infty(T_a)$ (J g^{-1})	$\log_{10}(t_c)$ (min)	β	$\log_{10}(t_c)$ (min)	$\Delta H_\infty(T_a)$ (J g^{-1})
429	5	1.60	1.26	0.37	3.53	1.56
424	10	3.20	1.92	0.39	4.07	3.12
419	15	4.45	2.76	0.36	5.09	4.87
414	20	4.19	3.04	0.39	5.19	6.74

element to relax its neighbours must move to accommodate it. Conversely, a high value of β means that the elements relax independently and the process is non-co-operative [31].

However, assigning a particular significance to the β parameter is not simple. The KAHR model of enthalpy relaxation requires β to be invariant with temperature, since it assumes thermorheological simplicity [32]; this is obviously not the case in the present study, and variation has also been seen in other investigations. However, the variation is not predictable and so it is dubious as to whether anything can be taken from the β values.

Values of $\log_{10}(t_e)$, shown in Tables 2–5, give an indication of the time required to reach the fully relaxed glassy state at each T_a. Similar trends with copolymer composition to those for $\log_{10}(t_c)$ results can be seen; the time initially decreases then increases, on increasing MA content (faster then slower relaxation processes). One point that appears anomalous is for copolymer SMA2 at $T_a = (T_g - 10)$ K;

this is most likely due to the unusually low value of β [2] and may be erroneous due to a curve-fitting error. With the possible exception of this point, these values represent the time taken for each copolymer to reach the equilibrium state (NB: the state determined from experimental data, *not* that defined by the extrapolated liquid enthalpy line) at each ageing temperature; this *long-term ageing data* has been gained from *short-term ageing experiments*.

The variation of $\Delta H_\infty(T_a)$ with MA content is shown in Fig. 3. Once again, this demonstrates the possibility of obtaining data on long-term ageing behaviour from short-term experiments. An interesting trend can be seen; equilibrium enthalpy generally increases with increasing MA content, with the exception of copolymer SMA2, which at lower ageing temperatures equilibrates at the lowest enthalpy values. This suggests that free volume also increases with increasing MA content, apart from SMA2,

[2] $\log_{10}(t_e) = \log_{10}(t_c) + 1/\beta \log_{10}(\ln(1000))$.
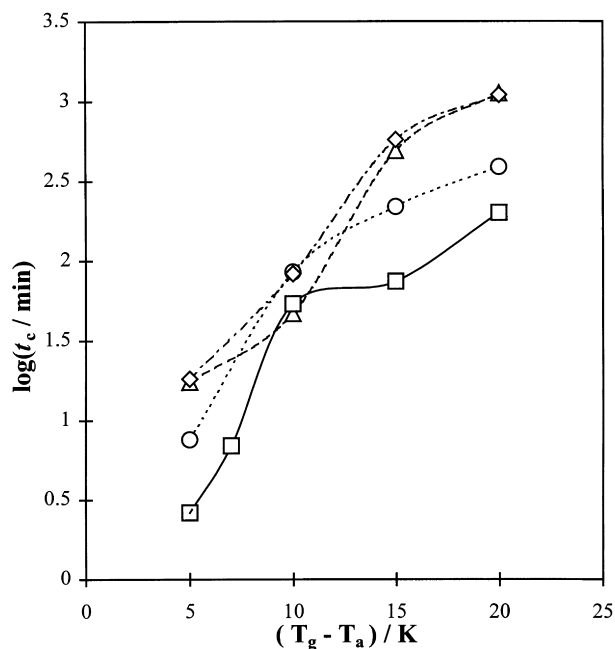
Fig. 2. Variation of $\log_{10}(t_c)$ with $(T_g - T_a)$ for SMA1 (circles), SMA2 (squares), SMA3 (triangles) and SMA4 (diamonds). Lines are a guide to the eye only.
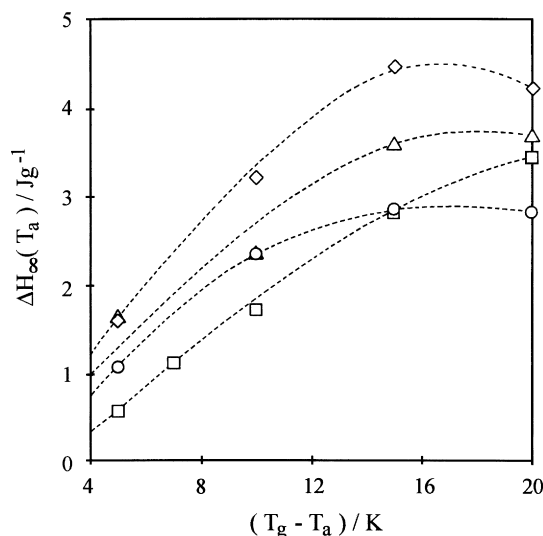

Fig. 3. Variation of $\Delta H_\infty(T_a)$ with $(T_g - T_a)$ for SMA1 (circles), SMA2 (squares), SMA3 (triangles) and SMA4 (diamonds). Lines are a guide to the eye only.

which has a lower free volume. These conclusions are in direct conflict with those from the kinetic results and literature PALS data [29], both of which suggest the opposite trend—free volume increases initially, then decreases with increasing MA content. We shall come back to this apparent contradiction at a later stage.

Fig. 3 also shows that the values obtained at $T_a = (T_g - 20)$ K are quite often lower than those at $T_a = (T_g - 15)$ K. This may reflect an inherent problem with the ability of the CF model to predict the equilibrium enthalpy difference at low values of T_a. The plots of $\Delta H(t_a, T_a)$ against $\log_{10}(t_a)$ must go through an inflection point before an accurate prediction of $\Delta H_\infty(T_a)$ can be made. Looking at the data for the lowest value of T_a in Fig. 1d, it is difficult to say conclusively that this has occurred. Collecting data beyond $\log_{10}(t_a) = 4$ (10 000 min, approximately 6.5 days) is difficult within reasonable experimental time scale and, in any case, may not be justifiable in terms of the aim of *predicting long-term ageing from short-term data*. Therefore, it may not be possible to make accurate predictions of $\Delta H_\infty(T_a)$ values at the low ageing temperatures.

The equilibrium enthalpy difference ($\Delta H_\infty(T_a)$) can be compared with the calculated maximum enthalpy lost on relaxing to the extrapolated liquid enthalpy curve ($\Delta H_{max}(T_a)$) for copolymers SMA1–4 (Fig. 4a–d). The latter values are determined from the C_p–temperature plots of unaged material by integrating the region between the curve and the linear extrapolation of its liquid portion to below T_g, using T_a as an integration limit. It can be seen that the value of $\Delta H_\infty(T_a)$ calculated by the CF equation from fits to experimentally determined data is lower than

the theoretical value in every case. Furthermore, it has been consistently lower in every system studied by this group, where it has been determined [11,18]. The CF model is the only approach to consider $\Delta H_\infty(T_a)$ as an adjustable parameter; other models of enthalpy relaxation assume that $\Delta H_\infty(T_a)$ is equal to $\Delta H_{max}(T_a)$. The validity of this assumption is obviously questionable.

A closer look at of Fig. 4a–d also allows some trends with varying MA content to be seen. SMA1 and particularly SMA2 fall well below the calculated maximum enthalpy, while equilibrium enthalpy values for SMA3 and SMA4 increasingly approach the theoretical values. Relating this to the kinetic and enthalpic data described earlier allows a picture of the relaxation processes occurring in the copolymers to be tentatively drawn. Increasing MA content up to (in this study) 24 mol% causes an increase in free volume that results in a faster relaxation process but a decreasing ability to reach the equilibrium structure defined by the extrapolated liquid enthalpy curve ($\Delta H_\infty(T_a)$ well below $\Delta H_{max}(T_a)$). Beyond this MA content, the copolymer sequence distribution changes to a more alternating pattern, allowing greater chain packing density. This, in turn, results in lower free volume, slower relaxation and yet an ability to achieve a structure closer to equilibrium ($\Delta H_\infty(T_a)$ nearer to $\Delta H_{max}(T_a)$). The values of $\Delta H_{max}(T_a)$ shown in Fig. 4a–d support these conclusions; SMA2 has the greatest values at a given distance from T_g, implying that it has the most free volume. However, for as yet undetermined structural reasons, not all of this free volume is readily accessible to the relaxing copolymer chains.

These conclusions imply an inability of the SMA copolymers to relax completely to the structure defined by the extrapolated equilibrium liquid enthalpy line. We believe that this is a general phenomenon peculiar to
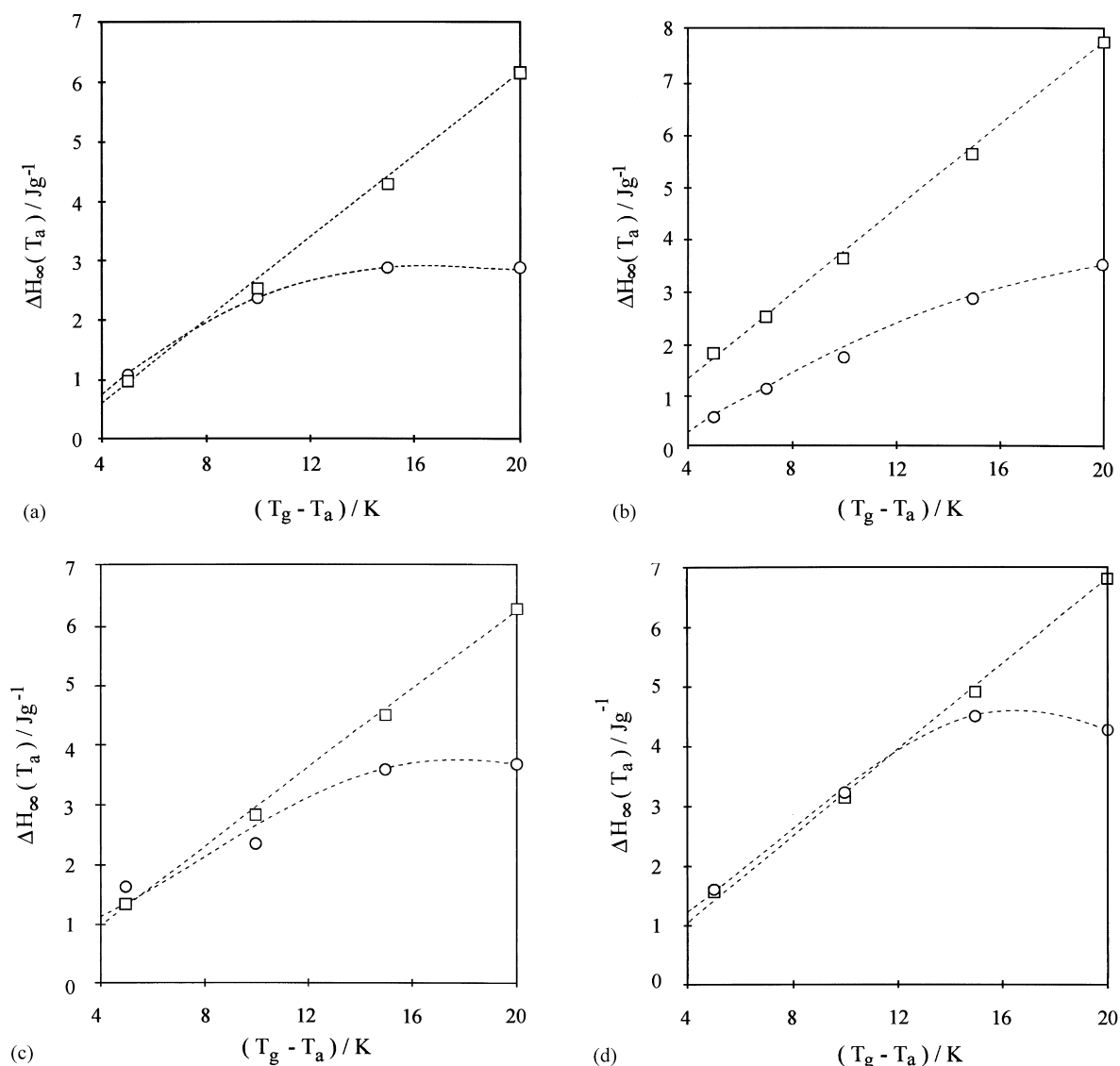
Fig. 4. Comparison of $\Delta H_{max}(T_a)$ (squares) and $\Delta H_\infty(T_a)$ (circles) with $(T_g - T_a)$ for: (a) SMA1; (b) SMA2; (c) SMA3; and (d) SMA4. Lines are a guide to the eye only.

macromolecules. Recently, a new MP model has been developed, based on configurational entropy, which takes into consideration this hypothesis [33–39]. The authors propose that there exists a limiting state, lying somewhere above the theoretical equilibrium state, beyond which a polymer will not relax. This could be due to chain entanglement, or other entropic effects peculiar to macromolecules. The authors employ a new adjustable parameter that defines this limiting state and have consistently found that this leads to improved fits of modelled C_p curves to experimental data. We believe that the results presented herein, together with others from this group, also support the presence of a limiting state for polymers. The location of this state is likely to be dependent on structural factors, as suggested by the variation in $\Delta H_\infty(T_a)$ with MA content reported in the present study.

It is appropriate to remember that the original work on physical ageing, which has been used as the basis for all MP models that are now routinely applied to polymers, involved low molecular weight (organic and inorganic) glasses [3]. These are entirely different from amorphous polymers, and it would indeed be remarkable if the two classes of material were described adequately by the same expressions. Recent evidence suggesting that polymers relax more slowly and have a greater degree of non-exponentiality than low molecular weight glasses lends support to this hypothesis [40].

4. Conclusions

The enthalpy relaxation of SMA copolymers has been investigated at different ageing temperatures, and useful data on their long-term ageing behaviour has been gained from short-term experiments. The relaxation of these

systems is not a simple function of the copolymer composition; up to 24 mol% MA there was seen to be an increase in relaxation rate, which then decreased as MA content increased to 52 mol%. This was ascribed to an increase then decrease in free volume, due to a change in microstructure from random to more alternating sequence distribution. However, the enthalpic behaviour was found to be opposite to that expected from such a free volume variation. Copolymer SMA2 was found to have the lowest equilibrium enthalpy value, which implies that it has the lowest free volume. Comparison of $\Delta H_\infty(T_a)$ values with the calculated maximum enthalpy on relaxing to the extrapolated liquid enthalpy line ($\Delta H_{max}(T_a)$) shows that none of the copolymers achieve this theoretical equilibrium state, and that SMA2 in particular equilibrates at significantly higher enthalpy values. The $\Delta H_{max}(T_a)$ values of this copolymer are the highest, suggesting that it indeed has the most free volume. These results are in keeping with previous observations by ourselves and others that polymers in general do not relax fully to equilibrium, and suggest that copolymer structure has an influence on the limiting state accessible to a given material.

Acknowledgements

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