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Enthalpy relaxation of styrene–maleic anhydride (SMA) copolymers. 2. Blends with poly(methyl methacrylate) (PMMA)

N.R. Cameron[1], J.M.G. Cowie*, R. Ferguson, I. McEwan

Department of Chemistry, Heriot-Watt University, Riccarton Campus, Edinburgh EH14 4AS, UK

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Abstract

The enthalpy relaxation of miscible blends of styrene–maleic anhydride (SMA) copolymers and poly(methyl methacrylate) (PMMA) has been studied, and the enthalpic data modelled using the Cowie–Ferguson (CF) semi-empirical approach. The blend behaviour in each case was not predictable from the concentration of each component. For the blend with the lower MA content copolymer (SMA2/PMMA), the enthalpy lost by the fully relaxed glass was greater than for either component, whereas the higher MA content copolymer blend (SMA4/PMMA) aged in a manner very similar to PMMA itself. In each case, the blends relaxed more slowly than their components and the distribution of relaxation times was broader. This implies that each blend has a lower free volume than its components; however, this conflicts with the enthalpic data for SMA2/PMMA. Reasons for this apparent contradiction are given. It is likely that concentration fluctuations are present in the SMA4/PMMA blend, suggested by a broad transition range at T_g, which may explain its slower relaxation behaviour.

Keywords: Enthalpy relaxation; Styrene–Maleic anhydride; Poly(methyl methacrylate)

1. Introduction

Physical ageing is the reversible loss of excess thermodynamic properties (volume, enthalpy, entropy) of an amorphous material on annealing at some temperature below T_g, as the system approaches equilibrium. Of the properties listed above, enthalpy loss is arguably the easiest to measure, albeit indirectly [1], using modern differential scanning calorimeters (DSC) [2], and this has been performed with considerable success [3,4]. Several models to describe the enthalpy relaxation process have been developed [5–10], all of which can be classed as Multi-parameter Phenomenological (MP) models since they aim to reproduce the DSC thermograms of aged materials.

Another, more empirical, approach is exemplified by the Cowie–Ferguson (CF) model [11], which aims to determine the enthalpy lost on annealing to equilibrium by curve-fitting data obtained at different ageing temperatures and times. This was developed to overcome the failure of MP models to predict the enthalpy lost on ageing to the equilibrium liquid state. The CF model has been applied to a wide range of polymer systems [11–24] including, most recently, copolymers of styrene and maleic anhydride (SMA) [25]. In this article, we wish to extend this work to their blends with poly(methyl methacrylate) (PMMA).

A considerable volume of work has been published on the enthalpy relaxation of polymer blends, most notably by the group of ten Brinke [26–29] and by ourselves [20,25,30,31]. Blends of polystyrene/poly(vinyl methyl ether) (PS/PVME) aged slower, and the final amount of enthalpy lost was less, than the PVME component at corresponding distances from T_g [30]. This was put down to a retardation of the PVME ageing by the PS component. PS/poly(phenylene oxide) (PPO) blends showed similar behaviour [27,31], which in this case was explained by concentration fluctuations in the blend, producing a range of T_g values and a large transition temperature range (ΔT) at T_g. Other systems that have been investigated include immiscible blends of poly(vinyl chloride) and poly(*iso*-propyl methacrylate) (PVC/PiPMA) [28,29], polycarbonate and poly(styrene–acrylonitrile) (PC/SAN) [32] and a PES-modified epoxy [24], and miscible blends of PMMA/SAN [33,34], poly(ethyleneoxide) and poly(propyleneoxide) (PEO/PPO) [35], polyimides [36,37], a PES-modified epoxy [22] and atactic and syndiotactic PS [23]. In addition, Sartor et al. have investigated the enthalpy relaxation of an interpenetrating polymer network (IPN) of polyurethane

* Corresponding author. Tel.: +44-131-451-3160; fax +44-131-451-3180.

E-mail address: j.m.g.cowie@hw.ac.uk (J.M.G. Cowie).

[1] Present address: Department of Chemistry, University of Durham, South Rd., Durham DH1 3LE, UK.

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and PMMA [38]. Enthalpy relaxation has also been used to determine blend miscibility when the coincidence of individual component T_g values makes this difficult [29,39].

2. Experimental

2.1. Materials and Instrumentation

SMA copolymers were obtained courtesy of DSM Research, The Netherlands, and were used as received. The molar mass (M_n) values of each were quoted as 3500 g mol^{-1}. PMMA of $M_n = 1{,}54{,}000$ g mol^{-1} was obtained from Polysciences and was used as received. SMA copolymer compositions and glass transition (T_g) values were reported in a previous article [25], and are reproduced here in Table 1 for convenience. 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 analogue 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. Blend preparation

All polymer blends were prepared by coprecipitation from a 1:1 v/v mixture of THF and dichloromethane into a ten-fold excess of petroleum ether (40–60°). The precipitated solids were collected by suction filtration and dried to constant mass in vacuo.

2.3. Calorimetry

The procedure used for the determination of T_g values by DSC has been reported elsewhere [25]. Of the possible T_g values, the enthalpic T_g (T_g(en)) is used throughout. This is determined from the intersection of liquid and glassy enthalpy lines, and has the advantage of being independent of scanning rate. The thermal history employed in ageing experiments has also been described in detail elsewhere [14].

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

3. Results and discussions

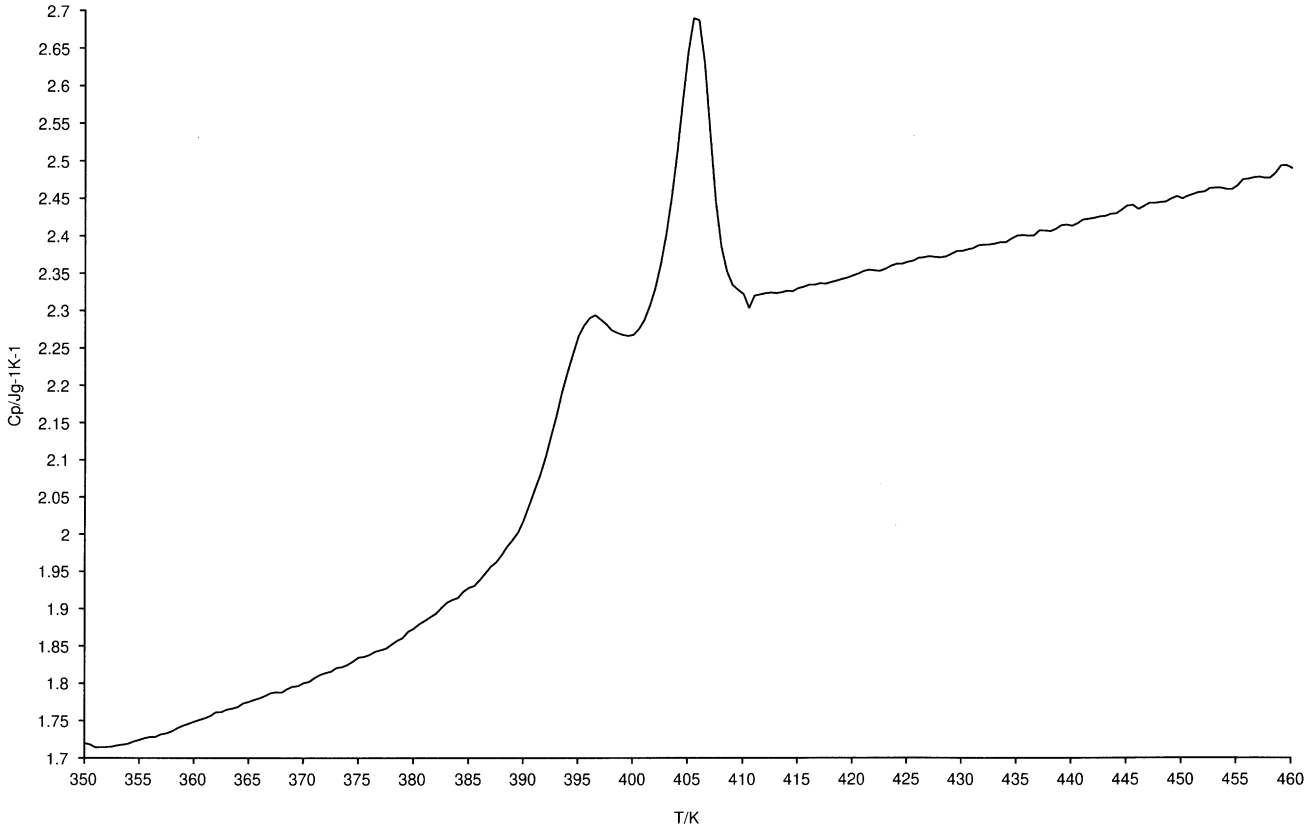
The copolymers SMA1, SMA2 and SMA4 were blended with PMMA, and the miscibility was investigated by DSC. The SMA1 blend appeared to show a single glass transition at 392 K. However, the T_g values of the two components are similar, being 387 K for SMA1 [25] and 395 K for PMMA [14], so it is impossible to determine the miscibility from this observation alone. The miscibility can be determined if the blend is annealed near the T_g of the two components [28]: a miscible blend displays a single enthalpy recovery peak, whereas an immiscible blend has two peaks. The SMA1/PMMA blend was thus annealed at 382K for 24 h and rescanned. Two distinct peaks were observed, as can be seen in Fig. 1a, indicating an immiscible blend. This is not surprising as SMA1 only has 6 mol% MA [25], and PS and PMMA are immiscible.

The SMA2 blend displayed a single T_g (Table 2) intermediate between those of its components (see Table 1), indicating that a miscible blend had formed. Likewise, SMA4/PMMA formed a miscible blend with a single T_g (Table 2) between the values of its components. Interestingly, the DSC trace of this blend, shown in Fig. 1b, displays a broad endothermic peak above T_g, at a temperature of approximately 460 K, which is reproducible. FTIR spectra of the blend before and after annealing were identical, indicating that this was not the result of any irreversible degradation. It was suggested that phase separation could be manifesting itself as a lower critical solution temperature (LCST), as is known for SMA/PMMA blends [40]. However, quenching from a temperature above the peak and immediate scanning produced the same DSC trace with a single T_g, indicative of a single phase system. Another possibility is that the peak is due to some crystallinity in the blend. To test this hypothesis, the blend was annealed just below the onset of this peak (452 K) for 24 h and the sample was scanned. The peak was slightly larger than before, with a calculated ΔH value of 0.04 J g^{-1}. This may indicate that the peak is indeed due to crystalline regions within the blend. The breadth of the T_g (ΔT) of the SMA4 blend (Table 2) is quite large, indicating that concentration fluctuations may be present in this system [27].

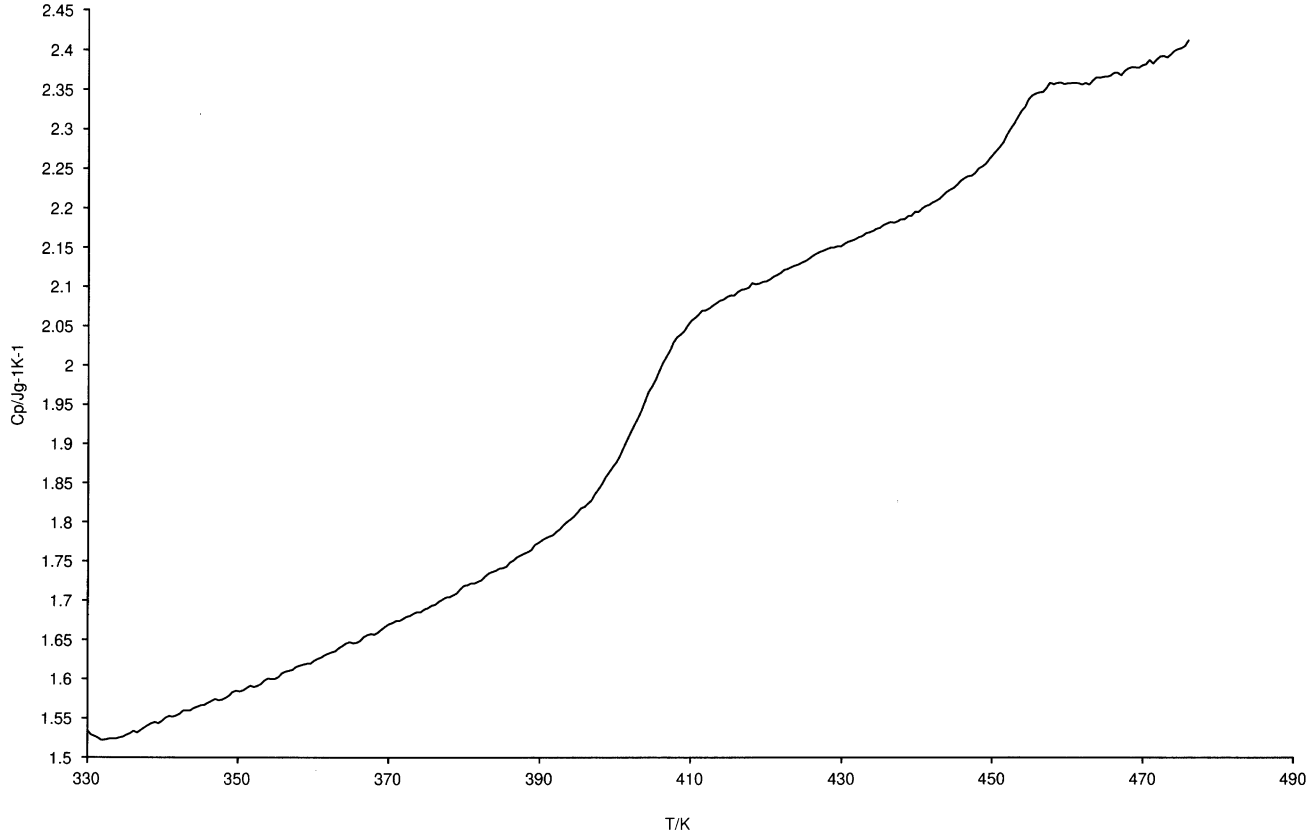
The enthalpy relaxation of the SMA blends with PMMA was investigated by DSC, at temperatures from 5 to 20 K

Table 2
T_g data for SMA/PMMA blends

Blend	T_g(en) (K)	ΔT (K)
SMA2/PMMA	406.0	11.4
SMA4/PMMA	414.5	17.5



(a)



(b)

Fig. 1. DSC traces of blends of PMMA with: (a) SMA1; (b) SMA4.

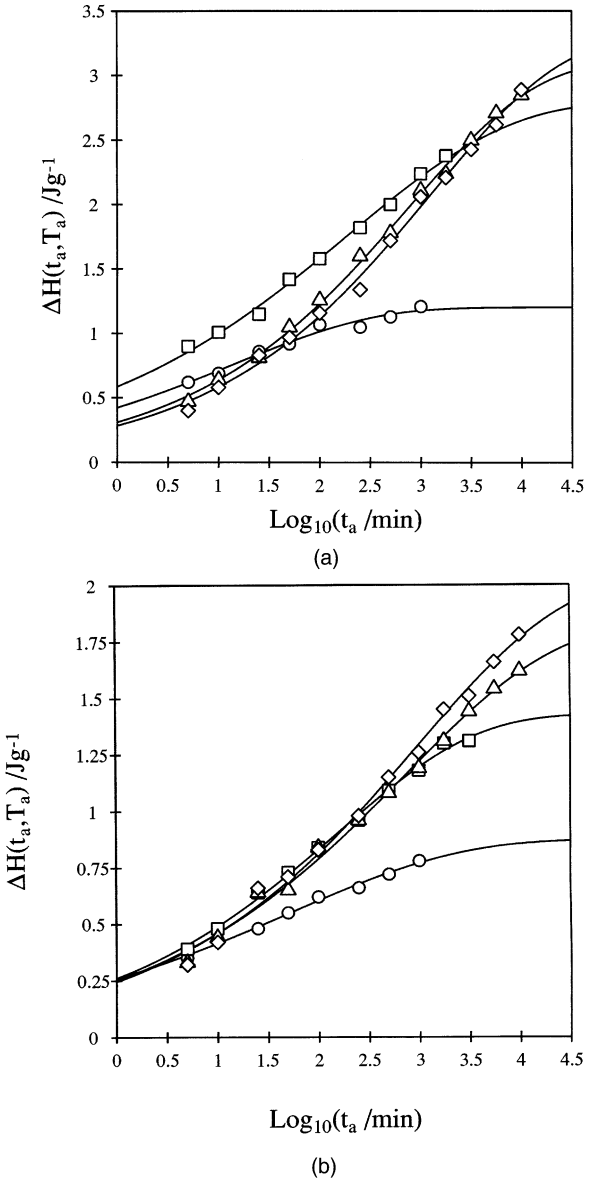


Fig. 2. Enthalpy relaxation of blends: (a) SMA2/PMMA at $T_a = 401$ K (circles), 396 K (squares), 391 K (triangles) and 386 K (diamonds); (b) SMA4/PMMA at $T_a = 409$ K (circles), 404 K (squares), 399 K (triangles), 394 K (diamonds). Solid lines are fits of the experimental data to the CF model.

below T_g. The data are presented as plots of the enthalpy lost after ageing for time t_a at temperature T_a ($\Delta H(t_a,T_a)$) against $\log_{10}(t_a)$ (see Fig. 2). These plots show the characteristic behaviour of increasing enthalpy lost after a given t_a as T_a decreases. This is due to the increasing distance between the glassy and extrapolated liquid enthalpy lines as the system moves deeper into the glassy region. The experimental $\Delta H(t_a,T_a)$ data are curve-fitted via a nonlinear least-squares routine [41], employing the expressions in the CF model. These are given below

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

$$\Phi(t_a) = \exp[-(t/t_c)^\beta], \quad (2)$$

where $\Delta H_\infty(T_a)$ is the enthalpy lost on annealing to the equilibrium liquid state, t_c is a characteristic time such that $\phi(t_c) = 1/e$ and β indicates the width of the relaxation time function ($0 < \beta \leq 1$). Eq. (2) is the well known Williams–Watts stretched exponential relaxation function. Further details of the CF model and some discussion on its suggested shortcomings have been documented elsewhere [14,17,25].

The curve fitting routine produces values for $\Delta H_\infty(T_a)$, t_c and β together with a model curve for the enthalpy lost at each ageing temperature (lines in Fig. 2). These data for the SMA2/PMMA blend are reported in Table 3, together with the time taken for the sample to relax to within 99.9% of the equilibrium state ($\log_{10}(t_e)$) [14] and the values of the theoretical maximum enthalpy lost on annealing to the liquid enthalpy line extrapolated into the glassy region ($\Delta H_{max}(T_a)$). The $\Delta H_\infty(T_a)$ values for the SMA2 blend at different ageing temperatures, together with those of each individual component for the sake of comparison, are shown in Fig. 3a. Interestingly, the blend appears to lose more enthalpy than either of its components. This implies that the blend has more free volume than either individual component, which could arise from a disruption of chain packing of each polymer by the other's presence. Similar behaviour for PEO/PPO and polyimide blends was reported by Morales and Acosta [35] and Goodwin [37], respectively.

$\log_{10}(t_c)$ values for SMA2/PMMA are shown in Fig. 3b and are higher than for both the SMA2 and PMMA components (also shown in Fig. 3b) at corresponding distances from T_g, indicating that the overall relaxation process of the blend is slower. This behaviour was seen for polyimide blends by Goodwin [37], who suggested this was caused by densification on blending; however this contradicts our enthalpy data (Fig. 3a), which indicate that the free volume increases in the blend. A longer time to achieve equilibrium, i.e. $\log_{10}(t_e)$ higher for the blend (see Table 3), would be correct if the free volume for the blend is higher than for its

Table 3
CF parameters and $\Delta H_{max}(T_a)$ for the SMA2/PMMA blend

T_a (K)	$(T_g - T_a)$ (K)	$\Delta H_\infty(T_a)$ (J g^{-1})	$\log_{10}(t_c$ (min))	β	$\log_{10}(t_e$ (min))	$\Delta H_{max}(T_a)$ (J g^{-1})
401	5	1.20	1.15	0.32	3.77	1.76
396	10	2.80	2.29	0.27	5.40	3.44
391	15	3.12	2.88	0.34	5.35	5.32
386	20	3.31	3.12	0.34	5.59	7.34

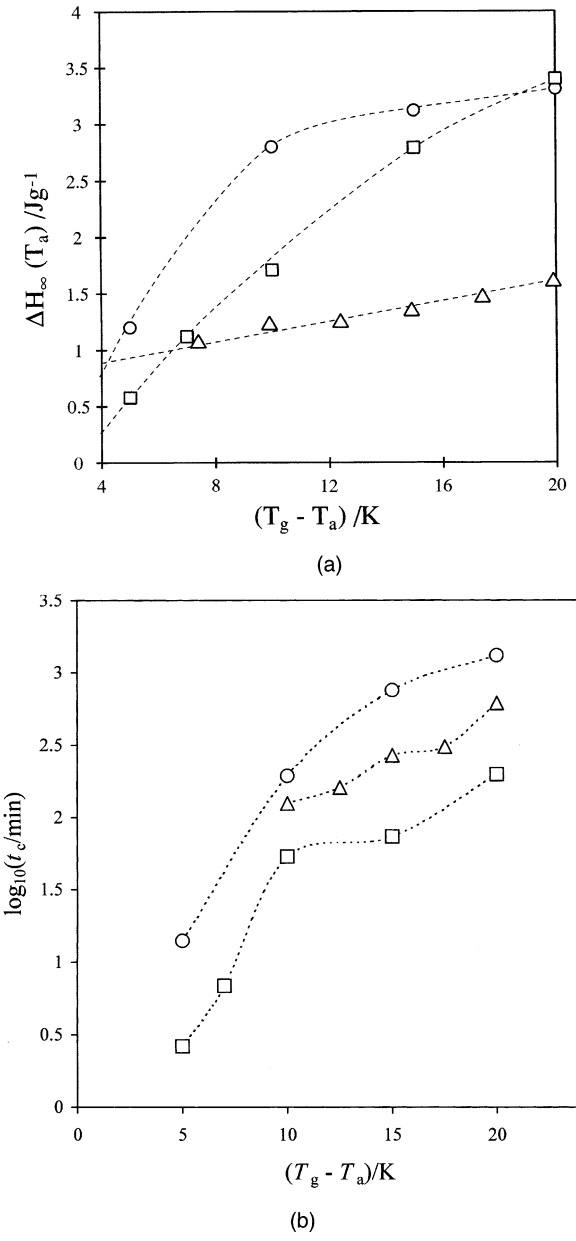


Fig. 3. Variation of CF parameters with $(T_g - T_a)$ for SMA2/PMMA (circles), SMA2 (squares; data from Ref. [25]) and PMMA (triangles; data from Ref. [14]): (a) $\Delta H_\infty(T_a)$; (b) $\log_{10}(t_c)$. Lines are a guide to the eye only.

individual components. This is because the relaxation processes would have more free volume to work in and so take longer to reach equilibrium. For this reason, we believe that Goodwin is mistaken in suggesting that densification is the cause of the slower kinetics.

Values of β for the SMA2 blend are listed in Table 3 and show more or less no variation with ageing temperature. Comparison with β for each of the blend components indicates that the distribution of relaxation times in the blend is broader (i.e. relaxation is more non-exponential). This feature of ageing in miscible polymer blends has been

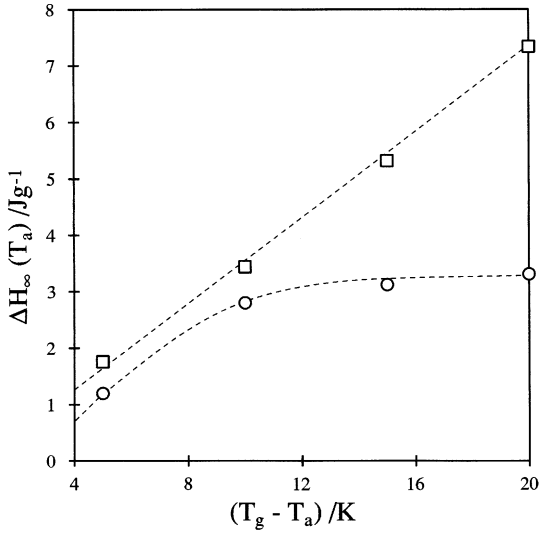


Fig. 4. Comparison of $\Delta H_{max}(T_a)$ (squares) and $\Delta H_\infty(T_a)$ (circles) with $(T_g - T_a)$ for SMA2/PMMA. Lines are a guide to the eye only.

observed previously and was ascribed to two possible features: greater coupling between relaxing elements in blends, possibly as a result of a reduction in free volume [20]; or concentration fluctuations within the blend that have individual characteristic relaxation times [31]. We believe that the latter is more likely here as the blend has a higher free volume than the components.

The $\Delta H_\infty(T_a)$ and $\Delta H_{max}(T_a)$ values are compared in Fig. 4 for the SMA2 blend. As we have found previously, the experimentally determined equilibrium enthalpy values fall well below those calculated by extrapolating the liquid enthalpy curve into the glassy region. The implications of this have been discussed in detail elsewhere [25] for single polymer components and the same arguments pertain to the blends. In amorphous polymer systems, chain entanglements and the random coil conformations will preclude the possibility of perfect packing in the glassy state. Consequently, in physical ageing, which is a reflection of the drive by an amorphous polymer in a non-equilibrium state to improve the chain packing and reach a more ordered state, there must be a physical limit to this process. As the free volume reduces with ageing time, there will come a stage where no further densification is possible. This is represented by $\Delta H_\infty(T_a)$, which usually falls short of the theoretical value $\Delta H_{max}(T_a)$ obtained by a linear extrapolation of the liquid enthalpy curve below T_g. Thus $\Delta H_\infty(T_a)$ is normally less than $\Delta H_{max}(T_a)$ except perhaps when T_a is close to T_g and the two values approach one another. This difference is clearly the case for both blends as shown in Figs. 4 and 6.

The results of curve-fitting the SMA4/PMMA enthalpy relaxation data (Fig. 2b) to the CF equation, along with calculated $\log_{10}(t_e)$ and $\Delta H_{max}(T_a)$ values, are shown in Table 4. For comparison, the data in Table 4 are plotted with those for SMA4 and PMMA at the corresponding

Table 4
CF parameters and $\Delta H_{max}(T_a)$ for the SMA4/PMMA blend

T_a (K)	$(T_g - T_a)$ (K)	$\Delta H_\infty(T_a)$ (J g^{-1})	$\log_{10}(t_c$ (min))	β	$\log_{10}(t_e$ (min))	$\Delta H_{max}(T_a)$ (J g^{-1})
409	5	0.87	1.73	0.26	4.96	1.41
404	10	1.43	2.18	0.32	4.80	2.45
399	15	1.83	2.86	0.29	5.75	3.22
394	20	2.03	2.98	0.30	5.78	4.53

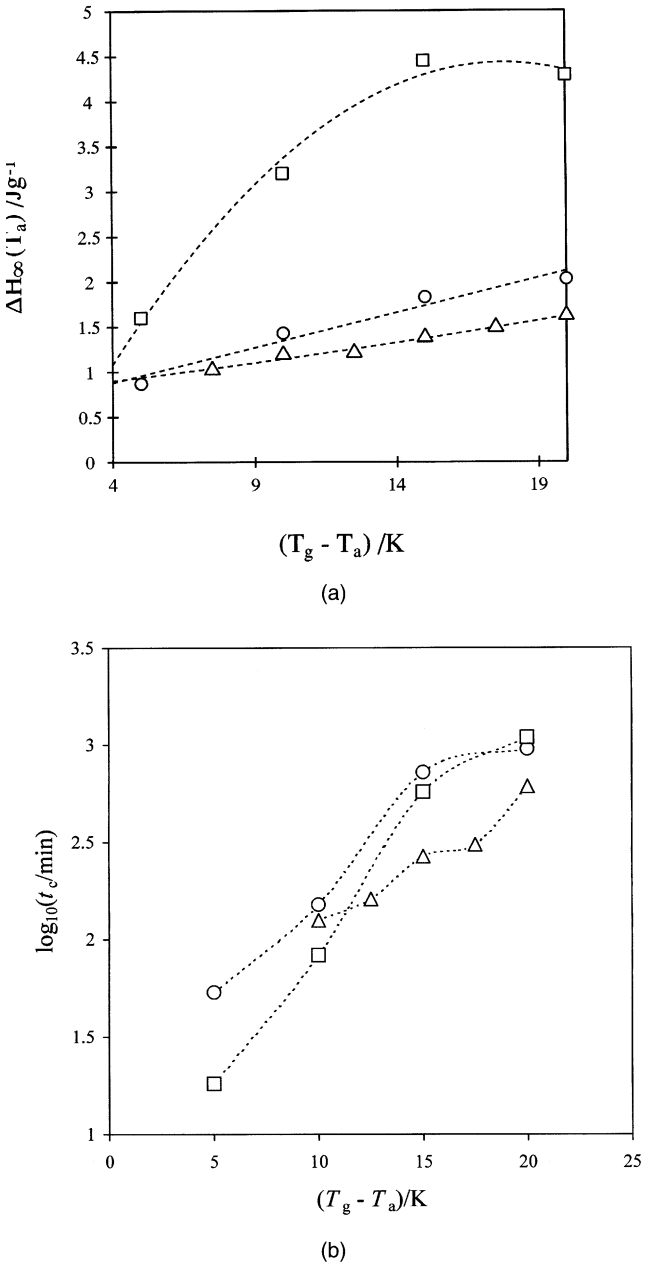


Fig. 5. Variation of CF parameters with $(T_g - T_a)$ for SMA4/PMMA (circles), SMA4 (squares; data from Ref. [25]) and PMMA (triangles; data from Ref. [14]): (a) $\Delta H_\infty(T_a)$; (b) $\log_{10}(t_c)$. Lines are a guide to the eye only.

distances from T_g; see Fig. 5a, b. The $\Delta H_\infty(T_a)$ values for SMA4, PMMA and the blend (Fig. 5a) indicate that the blend values coincide with those of the PMMA component, suggesting that the SMA component is not participating significantly in the relaxation process. Similar observations were made previously for PS/PVME blends [30]. The kinetics of the process, shown in Fig. 5b, demonstrate that the blend relaxation is again slower than that of the SMA component, however in this case it is comparable with that of PMMA. These results also suggest that the PMMA component is mainly responsible for the ageing of the blend. However, β values for the blend (Table 4) are well below those of PMMA itself (especially at higher T_a), indicating that the SMA component is influencing the distribution of relaxation times in the blend.

Previously, the ageing of PS/PVME blends was found to come mainly from the PVME component [30]. Oudhuis and ten Brinke [27] argued that these results, and those for PS/PPO blends, were due to concentration fluctuations in the blends, identified indirectly by a broad ΔT at T_g (38 K for PS/PVME) and a lower $\Delta H_\infty(T_a)$ for the blend compared to the PVME component. These fluctuations give rise to a range of T_g values for the blend, which result in the ageing of only those regions of the blend whose T_g values are close to the particular T_a. In our case, ΔT at T_g is also quite large

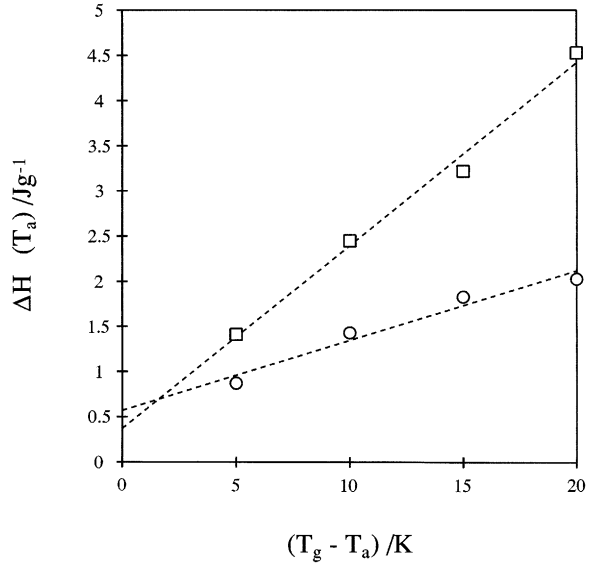


Fig. 6. Comparison of $\Delta H_{max}(T_a)$ (squares) and $\Delta H_\infty(T_a)$ (circles) with $(T_g - T_a)$ for SMA4/PMMA. Lines are a guide to the eye only.

(17.5 K, see Table 1) but the blend $\Delta H_\infty(T_a)$ is almost exactly the same as for PMMA (Fig. 5a). This suggests that concentration fluctuations may be present but that only those regions very rich in PMMA are relaxing significantly at the ageing temperatures investigated. The lower values of β for the blend compared to either component (Table 4) could be another indication of these concentration fluctuations.

The comparison between $\Delta H_\infty(T_a)$ and $\Delta H_{max}(T_a)$ for the SMA4 blend is shown in Fig. 6. As before, the calculated values of equilibrium enthalpy are significantly higher than those determined from experimental data. The appearance of Fig. 6 is very similar to that for the ageing of pure PMMA [14], which again implies that the overall ageing behaviour of the SMA4 blend is very similar to that of the PMMA component alone.

4. Conclusions

The enthalpy relaxation behaviour of miscible blends of SMA copolymers with PMMA has been investigated and modelled using the CF approach. For the blend with the copolymer containing 25 mol% MA (SMA2), a positive deviation of maximum enthalpy lost for the fully relaxed glass ($\Delta H_\infty(T_a)$) was observed for the blend compared to either individual component. In addition, the relaxation kinetics were slower for the blend, as indicated by a larger t_c value. These results are interpreted in terms of a higher free volume in the blend, caused by the disruption in chain packing, which leads to a longer relaxation time for the blend to age to equilibrium. The lower values of β for the blend also indicate a slower relaxation process and a broader distribution of relaxation times, whereas the better coincidence (at higher T_a) between $\Delta H_\infty(T_a)$ and the theoretical maximum enthalpy lost on annealing to the extrapolated liquid curve ($\Delta H_{max}(T_a)$) supports the suggestion that the blend can relax further into the glassy state than SMA2 itself.

For the blend with the higher MA content copolymer (SMA4), different behaviour was observed. In this case it appeared that most of the blend relaxation was accounted for by the lower T_g PMMA component. However, the broader distribution of relaxation times (indicated by a lower β) demonstrates that the SMA component is involved in the relaxation to some extent. This behaviour may be due to concentration fluctuations in the blend, as implied by a broad transition range at T_g, in accordance with findings by other workers.

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