Re-examination of poly(methyl methacrylate)/poly(epichlorohydrin) blends by small angle neutron scattering and differential scanning calorimetry

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Small angle neutron scattering measurements of deuterated poly(methyl methacrylate) (d-PMMA) and poly(epichlorohydrin) (PECH) blends were used to elucidate differential scanning calorimetry (d.s.c.) measurements previously obtained on similar blends. Debye–Bueche type scattering from the d-PMMA/PECH blends indicated the presence of two phases with correlation lengths of several hundred Ångström. These lengths show a rough compositional correlation with the overall breadth of the glass transition temperature (T_g) events found by d.s.c. The original hypothesis that the broad T_g events were indicative of large scale concentration fluctuations in the blend appears to be incorrect; the broad T_g events are more likely due to separate phases with differing T_gs within the polymer mixture. This interpretation is consistent with a more detailed d.s.c. investigation presented here.

(Keywords: polymer blends; poly(epichlorohydrin); poly(methyl methacrylate); differential scanning calorimetry; small angle neutron scattering)

INTRODUCTION

The most widespread method of determining miscibility is by measuring the glass transition temperature (T_g). A one phase blend will have a single T_g that is usually at some intermediate value between the T_gs of the two components. A two phase blend will display one T_g for each phase as long as the difference between the T_gs of the individual phases is sufficiently great to separately resolve these transitions by the chosen technique. The most common method for measuring T_g is thermal analysis, particularly differential scanning calorimetry (d.s.c.) and thermomechanical analysis (t.m.a.); other methods, including nuclear magnetic resonance (n.m.r.) and dielectric relaxations, can also be used.

Earlier reports[1,2] have suggested that poly(methyl methacrylate) (PMMA) and poly(epichlorohydrin) (PECH) form miscible blends having a single T_g. The miscibility of PMMA/PECH might be attributed to an interaction between the ester groups of PMMA and the hydrogen–carbon–chlorine group of PECH[3]. PECH is also reported to be miscible with a number of other ester-containing polymers; these are listed in *Table 1*.

A systematic study of blends of PECH, poly(ethylene oxide) and poly(epichlorohydrin-*co*-ethylene oxide) with a series of polyacrylates and polymethacrylates (*Table 1*) has been carried out[2,3]. For PECH blends, it was found that increasing the size of the pendant alkyl group of the polymethacrylate or polyacrylate decreased the miscibility of the blend. A rather anomalous feature of the PECH/polymethacrylate blend was the breadth of the T_gs. Although the d.s.c. thermograms seemed to show only one event, for some blend compositions the temperature range of T_g was extremely large (up to 80° between onset and completion of the T_g). The widespread interpretation is that a very broad T_g may be indicative of microphase separation[4]. Paul and co-workers[5,6] have put forward an alternative explanation, suggesting that the broad T_g could be due to equilibrium concentration gradients in an essentially homogeneous, miscible system; the magnitude of these concentration fluctuations was suggested to be related to the difference in the T_gs of the two components[3].

The impetus for this further study of PMMA/PECH blends was to gain additional insight into this issue using small angle neutron scattering (SANS), which should be able to distinguish between microphase separation and concentration fluctuations. In parallel with this, a detailed re-examination of these blends using d.s.c. was also made.

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Table 1 Miscible blends containing PECH

Polymer miscible with PECH	Method	Reference
PMMA	D.s.c. and optical clarity	12
PMMA	Cloud point	3
Poly(ethyl methacrylate)	Cloud point	3
Poly(*n*-propyl methacrylate)	Cloud point	3
Poly(isopropyl methacrylate)	Cloud point	3
Poly(cyclohexyl methacrylate)	Cloud point	3
Poly(methyl acrylate)	Cloud point	1
Poly(ethyl acrylate)	Cloud point	1
Poly(*n*-propyl acrylate)	Cloud point	1

SMALL ANGLE NEUTRON SCATTERING

The absolute coherent elastic scattering cross section, $d\Sigma/d\Omega$, for a one phase mixture of two components (polymer–solvent or polymer–polymer) as a function of scattering vector, Q, may be expressed by:

$$\frac{d\Sigma}{d\Omega} = V_1^{-1}(b_1 - \beta b_2)^2 S(Q) \quad (1)$$

where V_i is the volume of a segment (one repeat unit) of component i; b_i is the coherent scattering length of a segment of component i; β is the ratio, V_1/V_2; Q is the magnitude of the scattering vector, $\boldsymbol{Q}$, $(= 4\pi/\lambda \sin \vartheta/2$; ϑ is the scattering angle); and $S(Q)$ is the molecular structure factor[7].

In practice, to obtain a sufficiently large contrast factor, $(b_1 - \beta b_2)^2$, it is often necessary for one of the components to be deuterium labelled.

The scattering from a single phase blend of two components, 1 and 2, has been shown to have the form (in the Flory–Huggins formulation):

$$S^{-1}(Q) = [\phi_1 S_1(Q)]^{-1} + [\phi_2 S_2(Q)]^{-1} - 2\chi_{12} \quad (2)$$

where χ_{12} is the interaction parameter.

In the Guinier range, where

$$S^{-1}(Q) = \frac{1}{N}\left(1 + \frac{Q^2 R_g^2}{3}\right) \quad (3)$$

(N is the degree of polymerization and R_g is the radius of gyration), equation (3) becomes:

$$S^{-1}(Q) = G'' + 2KQ^2 \quad (4)$$

where

$$G'' = \frac{\partial^2 \Delta G_m}{\partial \phi^2} = \frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2} - 2\chi_{12} \quad (5)$$

(ΔG_m is the Gibbs free energy of mixing) and

$$K = \frac{1}{6}\left(\frac{R_{g1}^2}{N_1\phi_1} + \frac{R_{g2}^2}{N_2\phi_2}\right) \quad (6)$$

TWO PHASE TWO COMPONENT BLENDS

For homogeneous particles which have sharp boundaries, with surface area A_p and volume V_p, the Porod approximation states[7,8] that the scattered intensity is proportional to the surface-to-volume ratio of the particles, A_p/V_p:

$$I(Q)Q^4 = 2\pi B' \frac{c}{\rho}\left(\frac{A_p}{V_p}\right) \quad (7)$$

where c is the concentration of particles of component 1 in a matrix of component 2 (g cm^{-3}); ρ is the density of the particle (g cm^{-3}), and B' is the scattering contrast per unit volume (cm^{-4}):

$$B' = \left(\frac{b_1 - \beta b_2}{V_1}\right)^2 \quad (8)$$

The $I(Q)Q^4$ term is taken as the ordinate intercept of a Porod plot, $I(Q)Q^4$ against Q^4. If the particles are spherical, then the A_p/V_p ratio is equal to $3/R$, where R is the particle radius.

Debye and co-workers[9,10] developed an expression similar to the Porod approximation, but went on to modify it for the case of perfectly random form and distribution of phases:

$$I(Q) = \frac{k\bar{\eta}^2 a_c^3}{(1 + a_c^2 Q^2)^2} \quad (9)$$

where a_c is known as the Debye–Bueche correlation length, k is a constant and $\bar{\eta}^2$ is the mean square fluctuation in scattering power.

A plot of $I^{-0.5}(Q)$ against Q^2 should yield a straight line where the value of the correlation length, a_c, can be found from the slope/intercept ratio of the line.

In the case where one phase is a dilute component in the second phase, a_c may be taken as a measure of the size of the dilute component. In the case of a more concentrated phase dispersion where it is more difficult to define the particle size, a better estimate of the phase sizes is obtained by converting a_c into the transverse chord lengths of Porod and Kratky[7,11]:

$$\bar{l}_1 = \frac{a_c}{\phi_2} \quad \text{and} \quad \bar{l}_2 = \frac{a_c}{\phi_1} \quad (10)$$

where $\bar{l}_1$ and $\bar{l}_2$ are the average lengths of random chords passing through the two phases (see *Figure 1*).

EXPERIMENTAL

The materials used in this study are described in *Table 2*. The PECH and PMMA are the same commercial materials used previously[3]. The weight average molecular weights of PMMA and PECH were measured by a light scattering photometer (Wyatt Technology Co. Dawn model B). Due to the similarity of the refractive indices of PECH and toluene used for blend preparation, tetrahydrofuran was used for light scattering measurements. The weight average molecular weight of PECH obtained using light scattering is much higher than that

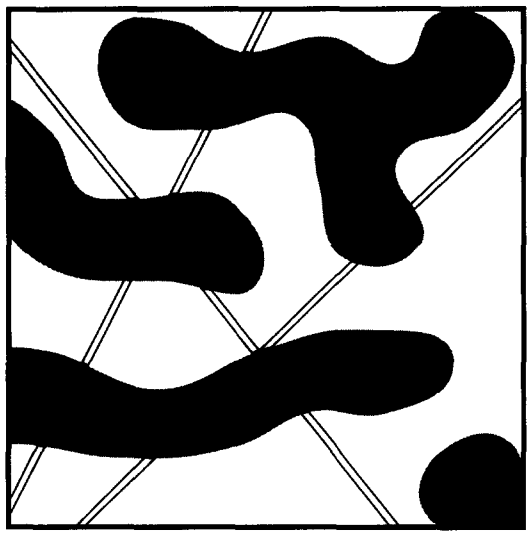

Figure 1 Schematic illustration showing random chords passing through two phases. The intersection lengths for each phase (black and white segments), averaged over many chords, are called the traversal lengths, l[11,19]

Table 2 Characteristics of the component polymers of the d-PMMA/PECH and PMMA/PECH blends

Material	d-PMMA	PMMA	PECH
Monomer mass (g mol^{-1})	108	100	92.5
Scattering length (fm)	98.2	–	16.6
Density (g cm^{-3})	1.28	1.18	1.37
Refractive index	–	1.490	1.495[a]
M_n (kg mol^{-1})	70.4	59.2[b]	283[c]
M_w (kg mol^{-1})	161	130[b]	555[c]
		105[d]	2100[d]

[a]Obtained by group contribution method[18]
[b]Provided by supplier
[c]G.p.c. data[19]
[d]Obtained by light scattering measurements

Table 3 Glass transition temperatures and transition breadths for blends of d-PMMA/PECH

Sample no.	d-PMMA/PECH	T_g (onset, °C)[a]	ΔT_g (°C)[a]
1	0/100	−28	5
2	30/70	−16	18
3	50/50	−6	38
4	70/30	0	85
5	85/15	2	104
	100/0	113	13

[a]Calculated using the method of construction shown in *Figure 4b*

reported by g.p.c.[12]. Blends of PECH with PMMA and with deuterated PMMA (d-PMMA) were prepared at the University of Texas using procedures similar to that employed by Fernandes *et al.*[3]. The blends used for SANS experiments, listed in *Table 3*, were cast from toluene and then hot-pressed into discs, 0.85–1.0 mm thick. Some blends of PECH and PMMA were prepared by variations of this procedure and by melt mixing at 230°C in a Mini-Max moulder in order to determine possible effects of preparation or thermal history on blend phase behaviour.

All d.s.c. measurements were made at the University of Texas using a Perkin-Elmer DSC Series 7 Thermal Analysis System. The heating rate for these measurements was 20°C min^{-1}.

SANS measurements were made on the five samples listed in *Table 3* as they were received (no annealing after hot pressing). Subsequently samples 4 and 5 were annealed for 100 min at 160°C and then quenched in ice water. Sample 5 cracked during the quench and the resulting crack plane caused a strong neutron reflection at small angles; the offending cells were masked out of the data set before it was radially averaged.

SANS measurements were made on the D17 diffractometer at the Institute Laue-Langevin. A wavelength of 14.5–15 Å was used with a sample-to-detector (S-D) distance of 3.46 m; this gave a working Q range of 5.2×10^{-3} to 0.046 Å^{-1}. The sample holder was a cadmium-covered rack made of aluminium sheeting with eight holes, each 10 mm in diameter. The diameter of the incident neutron beam was defined by the holes in the sample rack and double-sided sticky tape was used to fasten the samples over the holes, on the side of the rack facing the detector.

Water, an empty water cell, an empty sample holder, and the hydrogenous component polymers were all measured in addition to the blend samples of interest. Using the scattering from water, the data were corrected for detector efficiency and the scattering was normalized to absolute units. The parasitic scattering from the sample holder was subtracted from the sample scattering and the incoherent scattering backgrounds were estimated from the scattering of the hydrogenous polymers. The data normalization was checked using a standard blend of h-PMMA/d-PMMA with known molecular weights. Data analysis was then carried out using the standard programs[13].

RESULTS

Differential scanning calorimetry

Table 3 summarizes glass transition information for d-PMMA/PECH blends obtained by d.s.c. The thermograms for these blends (first and second scans) are essentially identical with those for corresponding blends of PMMA with PECH except for the slightly higher T_g of d-PMMA compared to that of PMMA. The following gives a summary of an extended re-examination of the glass transition behaviour of PMMA/PECH blends by d.s.c. which leads to somewhat different conclusions than those reported previously.

Blends of PMMA and PECH prepared here were transparent at room temperature. However, as seen in *Table 2*, the two components are estimated to have very similar refractive indices so it may be difficult to learn much about the phase behaviour of their blends by visual observation. *Figure 2* shows second heat d.s.c. thermograms reported earlier by Fernandes *et al.*[3]. These were measured by a Perkin-Elmer DSC-2. *Figure 3* shows second heat thermograms for selected compositions determined here using a Perkin-Elmer DSC-7. The latter are shown on a more expanded scale and reflect a higher sensitivity than the previous thermograms; however, the two sets of thermograms appear to be essentially the same. The more expanded scale of the current thermograms (*Figure 3*) makes evident some details that we think require re-interpretation of the broad transition regions, especially for blends containing 15, 20 and 30% PECH. The breadth of the glass transition region is the

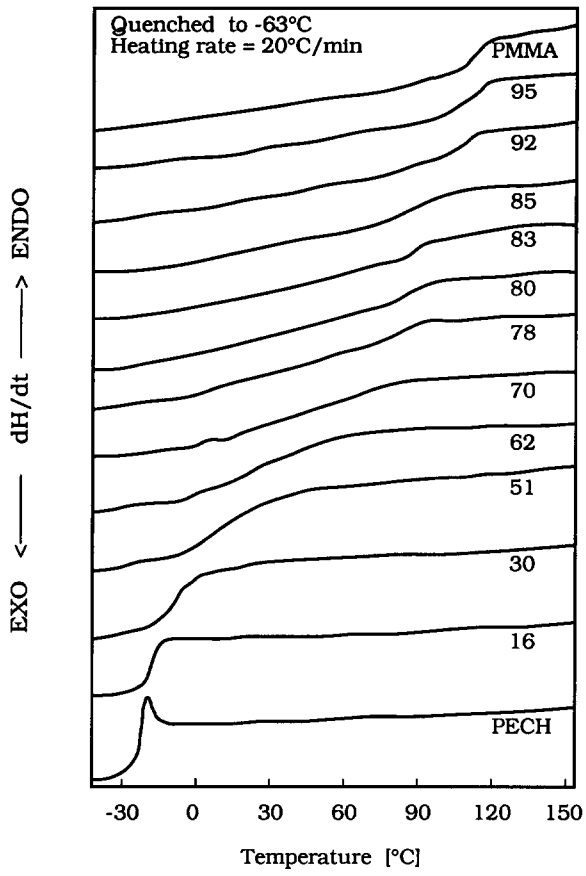

Figure 2 Thermograms of PMMA/PECH blends (second scan) illustrating transition breadths obtained in previous study[3]

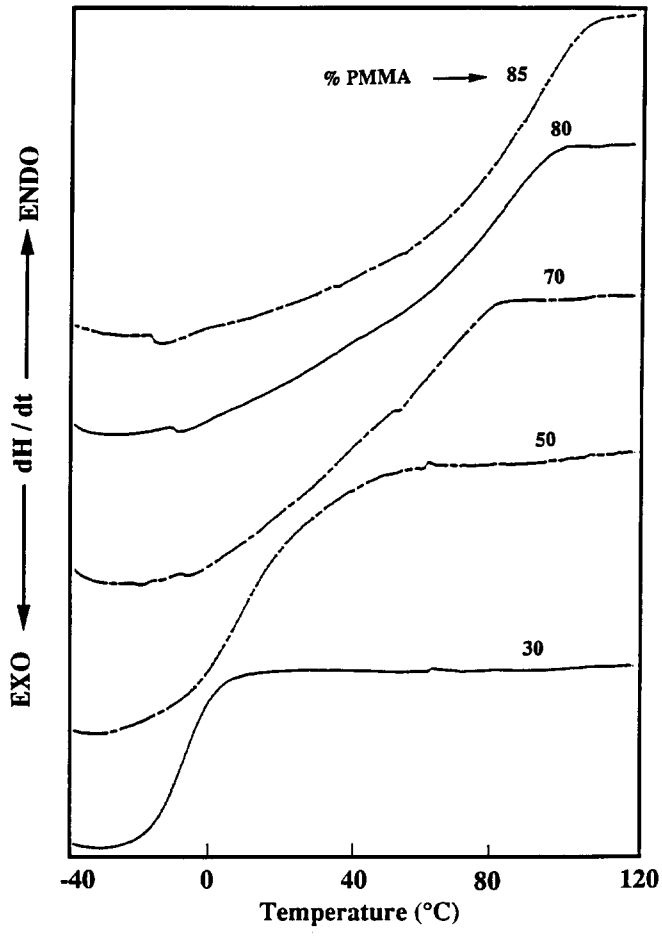

Figure 3 Thermograms for PMMA/PECH blends (second scan) obtained in this study

difference between the completion and onset temperatures that are defined by the intersection of construction lines. Two of these lines are extensions of the base-lines before and after the glass transition region, while the third line is usually drawn as a tangent to the thermogram curve within the transition region. *Figure 4a* shows the method of construction used by Fernandes *et al.*[3]. The middle line was drawn as a tangent to the thermogram at its point of highest slope within the transition region.

However, as seen in *Figure 4a*, this transition region is, at best, highly asymmetrical. An alternative view suggested here is that there are indeed two overlapping transition regions. That is, the completion of the lower transition and the onset of the higher transition cannot be resolved. With this view, we might draw two tangent lines as suggested in *Figure 4b*. The transition breadth shown is an apparent one based on the onset and completion temperatures of two separate transitions. It is not possible to define unambiguously the breadth of the two separate transitions suggested by this interpretation; however, the low slope of the second tangent line drawn in *Figure 4b* suggests that the proposed lower transition region is rather broad. The thermograms shown in *Figure 3* for blends containing 30 and 50% PMMA do not show characteristics like those in *Figure 4* that warrant interpretation in terms of two overlapping transitions.

It is instructive to plot the onset and completion

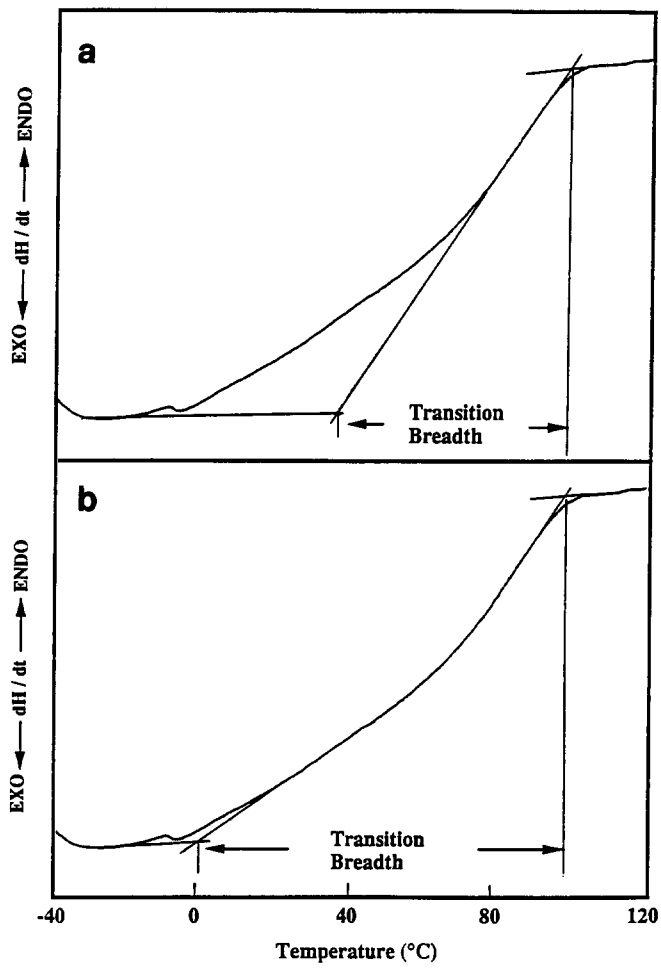

Figure 4 Illustration of construction techniques for defining the transition breadth: (a) Fernandes *et al.*[3]; (b) this study

temperatures for PMMA/PECH blends from second d.s.c. scans obtained in this and the previous investigation. The results are shown in *Figure 5* while the difference, ΔT_g, is shown in *Figure 6*. The results from the two studies are essentially identical for each quantity except for the onset temperature (and therefore ΔT_g) for the 15, 20 and 30% PECH blends. These differences stem entirely from how these quantities were defined or interpreted (see *Figures 4a* and *b*) in the two instances. Use of the interpretation suggested in *Figure 4b* leads to some interesting observations. The completion temperatures (which are identical in the two studies) change uniformly with overall blend composition as one might expect for a single phase blend. However, the onset temperatures (especially those defined by *Figure 4b*) change relatively little, which suggests that perhaps some of the PECH has not mixed to any appreciable extent with the PMMA. That the completion temperature changes more or less in the manner expected for a miscible blend system suggests that most of the PECH does form a mixed phase with PMMA, whose composition varies in direct relation to the overall blend composition.

The convention used in *Figure 4a* suggests that behaviour of the onset temperature is more like that expected of a miscible blend; however, we now believe this may be an overly simplistic interpretation. The SANS information presented later is more consistent with the current interpretation, and indeed it was the SANS results that motivated this more careful d.s.c. re-examination and subsequent re-interpretation. However, further evidence for this view and other useful insights were obtained by the current d.s.c. investigation as discussed next. All of the d.s.c. results discussed thus far have been second scans, which is normal in d.s.c. studies since this procedure eliminates spurious history effects that often appear in the first heats. All first heating runs show peaks which disappear in the second run (see *Figure 7*).

It is well known that sub-T_g annealing leads to enthalpy relaxation that gives rise to certain endothermic peaks near the T_g when such physically aged materials are

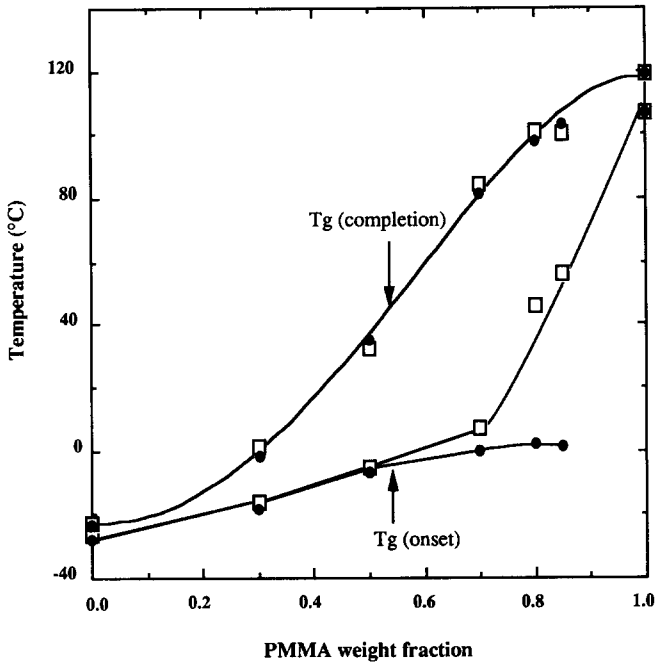

Figure 5 Glass transition onset and completion temperatures for PMMA/PECH blends: □, results of Fernandes *et al.*[3], using method in *Figure 4a* to define the onset temperature; ●, results from this study, using method in *Figure 4b* to define onset temperature

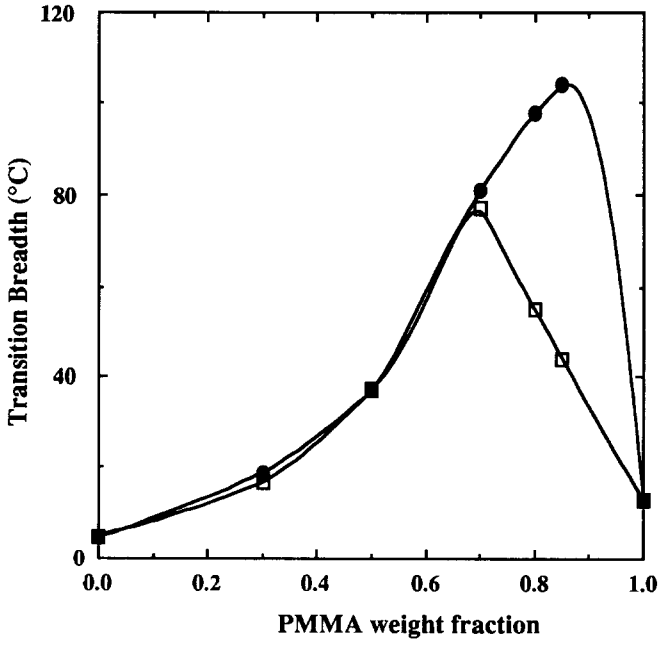

Figure 6 Transition breadths (completion minus onset temperature) of PMMA/PECH blends calculated using the methods of construction shown in *Figure 4*: □, Fernandes *et al.*[3]; ●, this study

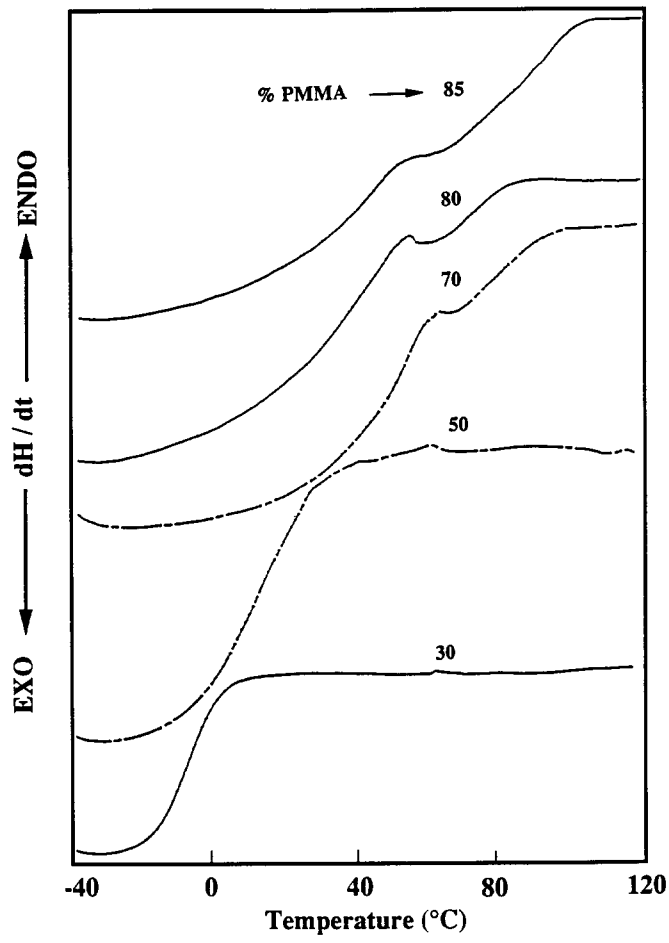

Figure 7 First scan thermogram of PMMA/PECH blends

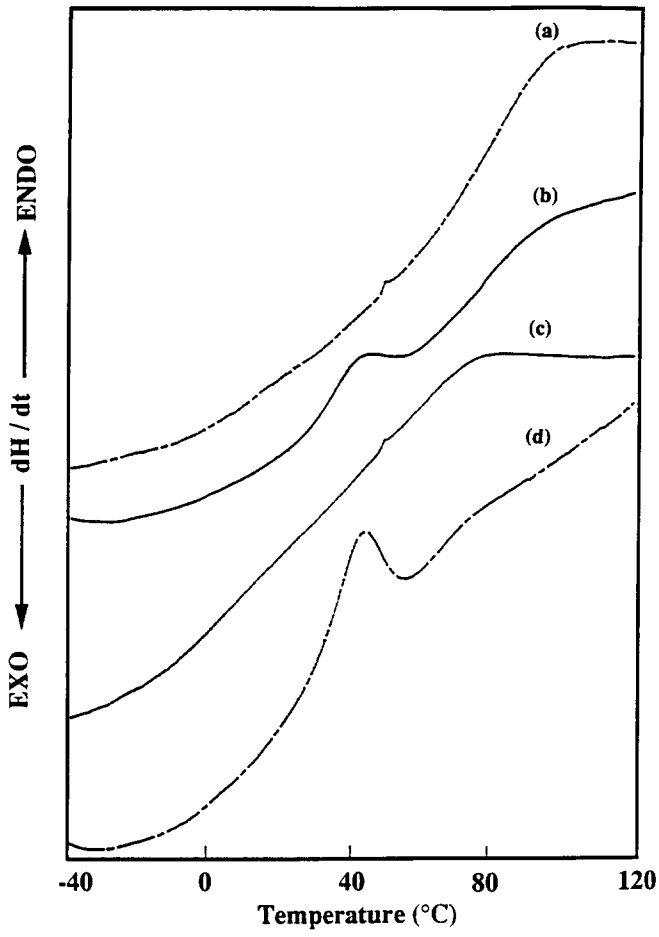

Figure 8 Effect of annealing at 25°C for 5 days on d.s.c. thermograms for PMMA/PECH blends. (a) Second scan for PMMA/PECH = 80/20; (b) first scan for PMMA/PECH = 80/20; (c) second scan for PMMA/PECH = 70/30; (d) first scan for PMMA/PECH = 70/30

subsequently heated during d.s.c. Each polymer has its own specific ageing behaviour characterized by the position and magnitude of the enthalpy recovery peak. This has been used recently[14] to aid in deciding whether certain blends have one or two T_gs. This is especially useful when the transitions of the component polymers are not sufficiently separated to obtain confident resolution in their blends *Figure 8* shows thermograms for blends containing 20 and 30% PECH following carefully controlled thermal histories. The samples were annealed at 150°C for 5 min to erase prior sub-T_g history, quenched into liquid nitrogen, and then aged at 25°C for 5 days. The strong endothermic peak seen in the first heat at about 55°C for each sample is not present in the second heat which immediately followed the first. We believe this peak is a heat capacity overshoot of a phase capable of substantial ageing at 25°C. Since the overshoot occurs well below the completion temperature, defined in *Figure 4b*, it must involve a phase other than the one associated with this event. These results provide some evidence for a multiphase nature of these blends. There is no second endothermic peak associated with the higher T_g phase and this is probably because this postulated phase would not undergo significant enthalpic relaxation at 25°C owing to its much higher T_g.

One possibility is that the PMMA/PECH blends are one phase at equilibrium but that the solvent casting procedure used results in some degree of non-equilibrium phase separation induced by the well known $\Delta\chi$ effect[15,16]. Several experiments were conducted to examine this possibility. A series of blends were annealed at 170°C for 3 days and then examined by d.s.c. It was felt that this procedure would allow the blends to reach spatial homogeneity by diffusion, if this is the equilibrium state. However, the d.s.c. thermograms obtained after this treatment were not different from those described already. As a second test of this hypothesis, blends were prepared by melt mixing at 230°C as described earlier. Again, the resulting blends had d.s.c. thermograms entirely comparable to those described above. The previous study[3] suggested visual evidence for a cloud point at high temperature (~270°C) implying the existence of a lower critical solution temperature (*LCST*) phase boundary and, therefore, complete thermodynamic miscibility at lower temperatures. Because of the similarity of the refractive indices of PMMA and PECH (see *Table 2*), we now feel that this visual indication of a cloud point may have been in error. An alternative way to test for *LCST* behaviour is to heat the blends to a temperature above the suspected cloud point, quench them, and then to examine their T_g behaviour[17]. D.s.c. thermograms of samples treated at 300°C for 5 min were not significantly different from those obtained from samples not heated to this temperature. Thus, there appears to be no evidence for an *LCST* phase boundary for this blend system. A final possibility considered was that the system has a very low *LCST* and phase separates during solvent evaporation at 110°C. To explore this, blends were dried at 50°C for 3 days. The transition behaviour for these blends was essentially similar to those prepared using other drying conditions or by melt blending except, of course, for slightly lower T_gs owing to incomplete solvent removal.

In summary, the d.s.c. data shown here suggest that the previously reported broad T_g regions for certain PMMA/PECH blends might alternatively be interpreted as arising from incomplete mixing. This incomplete mixing does not appear to be altered by the method of blend preparation nor by thermal treatments. By this analysis PECH blends with d-PMMA are similar to those with PMMA, although the deuterated blends used in the SANS experiments described next were not studied by d.s.c. in as much detail, in order to conserve the limited supply of d-PMMA.

Small angle neutron scattering

In *Figure 9*, a set of scattering curves for four blend compositions is presented. The curves are very similar; there is no obvious trend in scattered intensity with composition. None of the data from these blends could be fitted over the whole Q range by a scattering law of the form in equation (2). The high Q data gave a satisfactory fit, but there was always excess scattering at low Q. On the other hand, neither of the two forms for phase separated samples (equation (7) or (9)) could be fitted at low and high Q.

The data were therefore fitted by a two function scattering law of the form:

$$I_{expt} = I_1 + I_2 \qquad (11)$$

where I_2 is of the form of equation (7) or (9) and I_1 has the form of equation (1), i.e. assuming that the sample is phase separated but that within the domains, single phase scattering laws prevail. Equation (9) gave a better

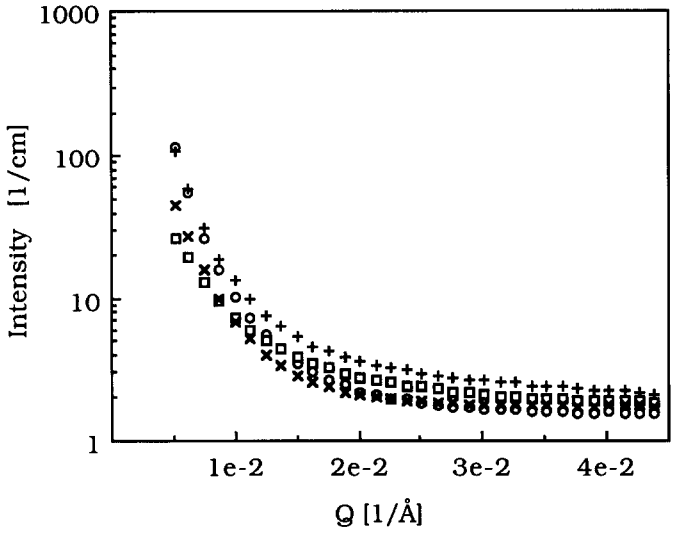

Figure 9 SANS for four blend compositions of d-PMMA/PECH: □, 30/70 (sample 2); ×, 50/50 (sample 3); ○, 70/30 (sample 4); +, 85/15 (sample 5)

fit to the low Q data, therefore:

$$I_1 \propto (aQ^2 + b)^{-1}$$
$$I_2 \propto (cQ^2 + d)^{-2} \qquad (12)$$

I_1 was obtained by first fitting the data at high Q where $I^{-1} \propto Q^2$, and then I_2 was found by difference $(I_{expt} - I_1)$. The fitting parameters can then be identified in terms of equations (4) and (9), $\{a \rightarrow K,\ b \rightarrow G'',\ c \rightarrow a_c\}$. Clearly, if the blend is two phase, G'' is not the true G'' of a phase but represents an average of the value in the two phases. One such fit for I_{expt} is shown for the 30/70 blend, sample 2, in *Figure 10*. The results of the two component fits for all samples are listed in *Table 4*.

One problem with these measurements (especially the $\partial^2 \Delta G_{mix}/\partial\phi^2$ measurements) is that they were not made 'at temperature'. It is difficult to estimate the effective thermodynamic temperature of these blends because the samples could not be truly quenched. This problem is partially related to our lack of full understanding of the glass transition events of PMMA/PECH measured by d.s.c. The ambient temperature at which SANS of these blends was measured is within the large onset-to-completion T_g range of all four blend compositions studied. This suggests that part of the blend may be mobile and in equilibrium above T_g, while other areas of the blend may be 'frozen' at some above-ambient, fictive temperature, a sort of local T_g. Since the relative amounts of mobile and 'frozen' material will vary according to the composition of the blend, the values of $\partial^2 \Delta G_{mix}/\partial\phi^2$ in *Table 4* cannot be compared as if the different blends were all at the same temperature. The tabulated values of $\partial^2 \Delta G_{mix}/\partial\phi^2$ here represent the thermodynamic state of a material between its ambient temperature and the completion temperature of the T_g event, which will be different for each composition.

On the other hand, the correlation length measurements do corroborate, to some extent, the d.s.c. measurements and may help to answer questions about the relationship between the broad T_g measured by d.s.c. and the blend microstructure. It is unlikely that the excessively broad T_g events are due to simple concentration fluctuations in a one phase mixture, which, according to the SANS results, are small in these samples. It is more probable that the very large concentration fluctuations which give rise to the Debye–Bueche neutron scattering are also responsible for the extraordinarily broad T_gs seen in this blend. *Figure 11* suggests that there is some correlation between the ΔT_g

Table 4 The second derivative of the Gibbs free energy, $\partial^2 \Delta G_{mix}/\partial\phi^2$, and correlation length, a_c, for blends of d-PMMA/PECH

Sample	d-PMMA/PECH	$\frac{\partial^2 \Delta G_{mix}}{\partial \phi^2}$	Correlation length, a_c (Å)
2	30/70	0.24	140
3	50/50	0.31	370
4	70/30	0.31	470 (360)[a]
5	85/15	0.14	340 (600)[a]

[a] Values in parentheses were obtained using samples annealed at 160°C for 100 min

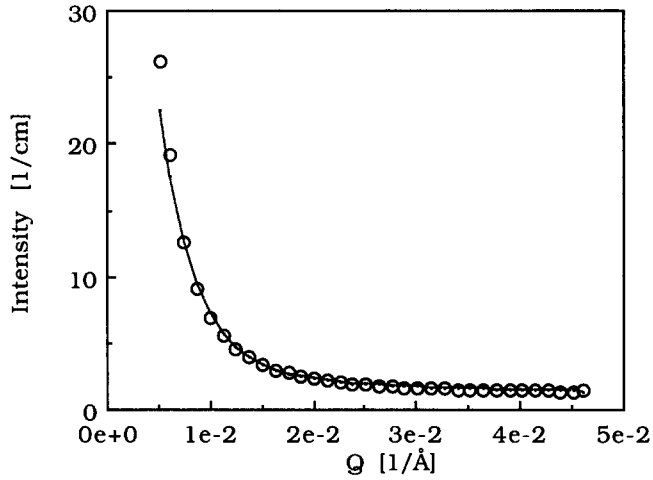

Figure 10 SANS for 30/70 d-PMMA/PECH blend (○) data points (---) combination fit using Zimm and Debye–Bueche scattering models

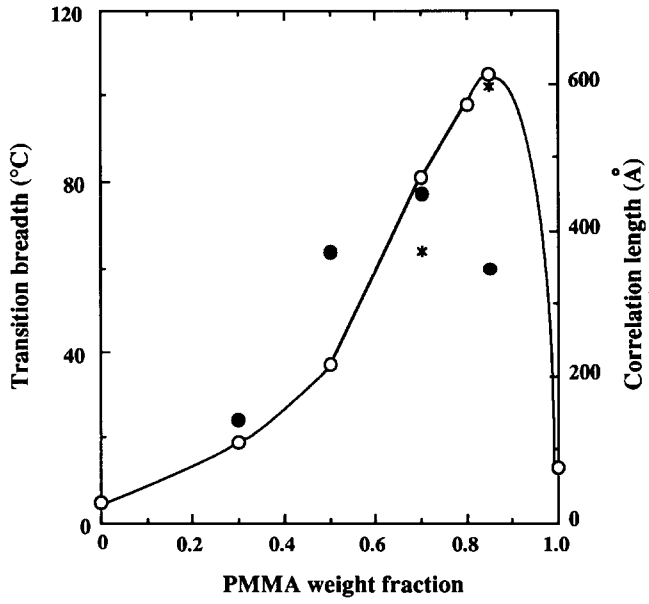

Figure 11 Superimposed plot of SANS correlation length before annealing (●) and after annealing (*), and transition breadth (○), as defined in *Figure 4b*, *versus* PMMA weight fraction for PMMA/PECH blends

measured by d.s.c. and the correlation lengths, a_c, measured by SANS. It seems clear that these fluctuations are introduced by the thermodynamic situation in the multiphase polymer–polymer system and do not necessarily reflect the true equilibrium state of the polymer–polymer system.

In *Figure 11*, both the pre-annealing and the post-annealing a_c values for samples 4 and 5 are shown on the plot. It is difficult to say which fits more appropriately in the set. On one hand the unannealed samples 4 and 5 may best complete the unannealed series. On the other hand, perhaps a stronger argument may be made for including the annealed values, because samples 1 to 3 are already in an annealed-like state because their T_g values are close to or below ambient temperature and because annealed samples may be better compared with second scan d.s.c. measurements since the first d.s.c. scan affects annealing.

SUMMARY

The glass transition behaviour of the PMMA/PECH blends by d.s.c. has been extensively re-examined and re-interpreted. Blends rich in PECH have rather normal symmetrical heat capacity increases at what appear to be single glass transitions. For PMMA-rich blends this event is both broader and asymmetrical. For these blends, we believe there is some justification for interpreting this as two overlapping transitions arising from separate phases. Blend preparation procedure or thermal history did not alter the nature of the thermograms obtained. The temperature at which the glass transition of these blends is completed correlates with the overall blend composition (*Figure 5*) in a manner that one might expect for a completely miscible blend system. However, the onset temperature does not shift with overall composition to the extent expected. This is the origin of the observed nature of the transition region and its extraordinary breadth for blends rich in PMMA. It is as if some fraction of the PECH does not participate in the mixing. A potential cause for such behaviour could be a gel fraction in the PECH material. Some attempts to determine whether this PECH has a crosslinked fraction that could not mix with PMMA using light scattering and g.p.c. were made but the results were inconclusive.

The work presented here was a first attempt to examine a complex problem and more work is obviously needed to reach a full understanding of the phase diagram of PMMA/PECH blends. However, this work does add some definitive cautionary information about blend systems that show unusually broad glass transitions.

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