Phase separation from solutions of poly(ether sulfone) in epoxy resins

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Cloud-point measurements were made on quasi-binary mixtures of diglycidyl ether of bisphenol A (DGEBA) epoxy resin with poly(ether sulfone) (PES). The relative molecular masses of both resin and polymer were varied, and temperature-dependent Flory–Huggins interaction parameters were estimated on the assumption that both components are monodisperse. The data were used to calculate lower critical solution temperatures (*LCST*) and compositions, and to construct coexistence curves. The evolution of two-phase morphology during curing of epoxy–PES blends containing 4,4′-diaminodiphenylmethane (DDM) hardener is related to these results.

(Keywords: poly(ether sulfone); epoxy resin; blends)

INTRODUCTION

Because of their combination of stiffness and toughness, blends of ductile thermoplastics with thermosetting resins are widely used as matrices for high-performance composites. The best-known examples are blends of polysulfones with epoxy resins[1–5], but poly(ether imide)s are also very successful toughening agents for brittle epoxies[6,7], and a recent paper demonstrates the application of this technology to phenolic resins[8]. The main requirements are that the thermoplastic should dissolve initially in the liquid resin–hardener mixture, and that it should form a separate phase during subsequent curing. In addition, reactivity between the resin and functional groups attached to the thermoplastic is desirable, not only to provide adhesion between the phases, but also to generate a limited degree of crosslinking in the thermoplastic phase, in order to resist attack by solvents.

The present paper considers the applicability of quantitative thermodynamic treatments to phase separation in these reactive blends. There are three main problems. First, the polydispersity of the thermoplastic means that blends with liquid epoxy resin are at best quasi-binary mixtures. Secondly, the addition of a hardener turns the system into a quasi-ternary mixture, even before any reaction has taken place. And thirdly, once the curing reaction has begun, the number of distinct molecular species in the solution increases rapidly. Despite these problems, Verchère *et al.*[9] have demonstrated that useful information can be obtained by treating both epoxy resin and carboxyl-terminated butadiene–acrylonitrile (CTBN) rubber as monodisperse, and applying the Flory–Huggins model. The work presented below adopts the same approach for epoxy–poly(ether sulfone) (PES) blends.

EXPERIMENTAL

Materials

Three DGEBA (diglycidyl ether of bisphenol A) epoxy resins were used in this programme: Dow DER332 and DER337, and Ciba-Geigy MY750. Respectively, these have number-average relative molecular masses M_n of 349, 480 and 380, and hydroxy/epoxy ratios of 0.015, 0.245 and 0.075. The hardeners were: DDS (4,4′-diaminodiphenylsulfone), Ciba-Geigy HT976, $M_n = 248$; DDM (4,4′-diaminodiphenylmethane), Ciba-Geigy HT972, $M_n = 198$; and 3DCM (3,3′-dimethyl-4,4′-diaminodicyclohexylmethane), BASF Laromin C260, $M_n = 238$.

The thermoplastics were four grades of ICI Victrex PES, poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene): 3600P, 4100P, 4800P and 5003P. Gel permeation chromatography (g.p.c.) measurements, based on polystyrene (PS) standards, gave $M_n = 14\,500$, $17\,700$, $22\,400$ and $23\,800\ \mathrm{g\,mol^{-1}}$, and polydispersity indices 2.60, 2.66, 2.38 and 2.07, respectively, for these polymers. However, recent work by Eastmond[10] has shown that the use of PS standards for g.p.c. measurements on rigid-chain aromatic polymers such as polyimides (PIs) and polysulfones (PSFs) causes M_n and M_w to be overestimated by a factor of between 2 and 3, depending upon chain structure: hydrodynamic volumes for PIs and PSFs are much larger than for aliphatic macromolecules of similar molar mass. For this reason, it would be more realistic to treat the molar masses listed above as approximating to M_w rather than M_n, a principle that has been applied in the following discussion. From d.s.c., the PES samples had $T_g = 215$,

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216, 222 and 222°C. At 25°C, they had densities of 1370 kg m^{-3}, and refractive indices of 1.65.

Mixing

The PES samples were dried in an oven at 110–120°C for 24 h before being dissolved at 10 wt% in dichloromethane (CH_2CCl_2) at 23°C. The resin was mixed with this solution, which was then heated slowly to 80–90°C in an oil bath to drive off most of the solvent, the remainder being removed overnight at the same temperature under vacuum. At this stage, the solutions were clear, homogeneous, viscous liquids.

Cloud-point measurements were made using an optical microscope equipped with a Linkam THM600 heating stage. One drop of the resin–PES mixture was placed between a glass microscope slide and a cover slip, and cycled between 90 and 160°C at heating rates of 10, 8, 6, 4 and 2 K min^{-1}. Cooling rates were about 10 K min^{-1}, and a period of 3 min was allowed between cycles to allow the blends to homogenize before reheating. The cloud-point temperature was determined by extrapolating to a zero heating rate.

For experiments involving curing, the hardeners were added at the stoichiometric ratio. The epoxy–PES blends were heated before adding the hardeners: to 80°C for 3DCM and DDM, and to 135°C for DDS. In the cases of DDM and DDS, a mixing period of about 10 min was necessary to melt the solid hardeners and disperse them in the PES solution.

Phase separation in these PES blends was monitored by means of optical light transmission measurements in separate isothermal curing experiments, following the procedure described by Verchère *et al.*[9]. Direct observations of phase separation during cure were made using the optical microscope and hot stage mentioned earlier. A Contraves Rheomat viscometer was used in another isothermal curing experiment to follow changes in viscosity at a fixed shear rate of 100 s^{-1}.

The morphology and composition of the cured blends were studied by scanning electron micrography of fracture surfaces formed at liquid-nitrogen temperatures, and etched with dichloromethane. Micrographs were processed with the aid of a Joyce–Loebl Image Analyser.

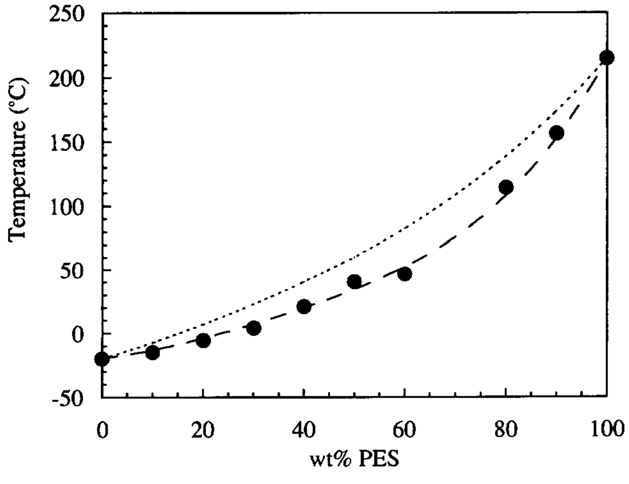

Figure 1 Relationship between T_g (from d.s.c.) and composition in quasi-binary mixtures of PES 3600 with DER332 liquid epoxy resin monomer: (– – –) equation (1) with $\kappa=0.30$; (···) equation (2)

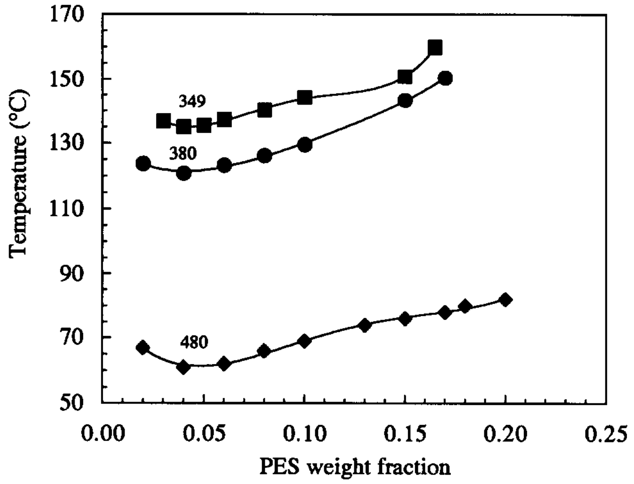

Figure 2 Cloud-point curves for quasi-binary mixtures of PES 3600 with three epoxy resin monomers of relative molecular masses 349, 380 and 480

RESULTS AND DISCUSSION

Binary DGEBA/PES blends

At room temperature, solvent-cast binary blends of PES with DGEBA resin are transparent over the whole composition range, indicating complete miscibility. This conclusion is confirmed by d.s.c. measurements, which show a single T_g that increases with PES concentration as shown in *Figure 1*. The data fit the Gordon–Taylor equation[11]:

$$T_g=\frac{w_1T_{g1}+\kappa w_2T_{g2}}{w_1+\kappa w_2} \tag{1}$$

with a value of 0.30 for the adjustable parameter κ. This result indicates a weak attraction between DGEBA and PES. The same conclusion may be reached after comparing the results with the predictions of the Fox equation[12]:

$$\frac{1}{T_g}=\frac{w_1}{T_{g1}}+\frac{w_2}{T_{g2}} \tag{2}$$

For PES concentrations below about 20 wt%, incipient phase separation is observed on heating the binary blends to temperatures between 60 and 160°C. At higher concentrations, volatilization of DGEBA begins to cause problems before the cloud point is reached.

Cloud-point curves (CPCs) for three blends containing the polymer of lowest molar mass, PES 3600, are shown in *Figure 2*. They are typical of a system exhibiting lower critical solution temperature (*LCST*) behaviour, as previously observed by Yamanaka and Inoue[4] in their study of epoxy–PES blends. The increase in number-average relative molecular mass from 349 to 480 between DER332 and DER337 resins is sufficient to depress the precipitation threshold temperature by 74°C. A related effect has been reported by Verchère *et al.*[9], who observed an increase in the threshold temperature for epoxy–CTBN blends, which show upper critical solution temperature (*UCST*) behaviour.

The molar mass distribution of the PES component also has a very strong influence upon the CPCs, as shown in *Figure 3*. An increase in molar mass from 14 500 to 23 800 g mol^{-1} results in a 25°C drop in threshold temperature. Because of the problems in calibrating g.p.c.

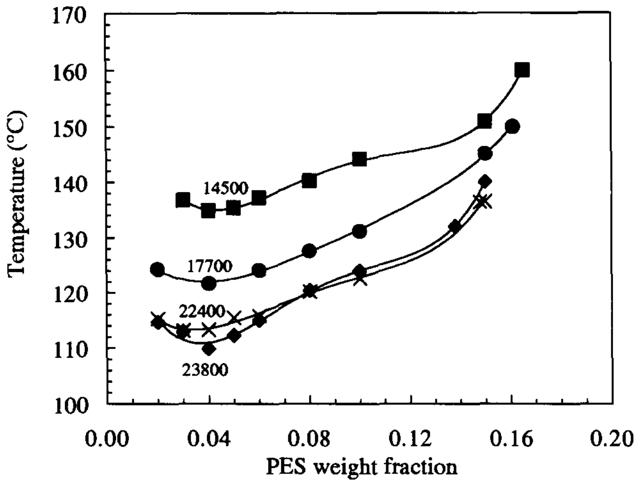

Figure 3 Cloud-point curves for quasi-binary mixtures of epoxy resin DER332 with four PES polymers of differing molar masses (as shown on curves)

columns using PS standards, as discussed earlier, these values are probably closer to weight averages M_w than to number averages M_n, and will be treated as such in the calculations given below.

The polydispersity of the PES samples makes it difficult to give a full thermodynamic description of the blends. This problem is discussed by Verchère *et al.*[9] with reference to epoxy–CTBN mixtures, and the following analysis, using the Flory–Huggins mean-field model, is based on their approach.

The free energy of mixing, ΔG, per unit volume of a binary mixture is related to the molar volumes, V_1 and V_2, and volume fractions, ϕ_1 and ϕ_2, of the two components through the equation:

$$\frac{\Delta G}{RT}=\frac{\phi_1}{V_1}\ln\phi_1+\frac{\phi_2}{V_2}\ln\phi_2+\frac{\Lambda}{RT}\phi_1\phi_2 \qquad (3)$$

where Λ is a variant of the Flory–Huggins interaction parameter χ, expressed in terms of energy per unit volume. In the following discussion, subscripts 1 and 2 refer to resin and PES, respectively. Previous work on blends has shown that χ and Λ are in general not constants, but vary with pressure, temperature and composition[13]. In the analysis given below, variations in Λ with temperature are taken into account, but the interaction parameter is assumed to be independent of concentration. Pressure is not a factor, since all measurements are made at atmospheric pressure.

The spinodal curve for the mixture is defined by the condition that $\partial^2\Delta G_m/\partial\phi_2^2=0$. At the critical temperature, T_c, which in the epoxy–PES system is a *LCST*, the two spinodal points coincide, and $\partial^3\Delta G_m/\partial\phi_2^3=0$. These conditions define ϕ_{2c}, the composition at the critical point, and T_c, the lower critical solution temperature:

$$\phi_{2c}=\frac{V_1^{1/2}}{(V_1^{1/2}+V_2^{1/2})} \qquad (4)$$

$$T_c=\frac{2\Lambda_c}{R(V_1^{-1/2}+V_2^{-1/2})^2} \qquad (5)$$

The molar volumes of the components, obtained from M_w (treated as equal to M_n as determined by g.p.c. with PS standards) and density ($\rho=1170$ and $1370\,\mathrm{kg\,m^{-3}}$ respectively for DGEBA and PES), are first substituted into equation (3), in order to calculate ϕ_{2c} for a binary mixture of DER332 with monodisperse PES having this M_n. The temperature on the experimental cloud-point curve corresponding to this ϕ_2 value then identifies the *LCST*, T_c, which in turn defines the interaction parameter at the critical point, Λ_c, through equation (5).

Figure 4 is a plot of experimentally determined values of Λ_c against calculated *LCST* values T_c for each of the resin–PES combinations. The data give a straight line:

$$\Lambda=\Lambda_0+\lambda_T T \qquad (6)$$

where $\Lambda_0=-11.5\,\mathrm{MJ\,m^{-3}}$, $\lambda_T=45.6\,\mathrm{kJ\,m^{-3}\,K^{-1}}$, and linear regression coefficient = 0.993. For the epoxy–CTBN system, Verchère *et al.*[9] found $\Lambda_0=10.27\,\mathrm{MJ\,m^{-3}}$ and $\lambda_T=-10.42\,\mathrm{kJ\,m^{-3}\,K^{-1}}$. The difference in sign between the two sets of data arises because epoxy–CTBN mixtures exhibit *UCST* behaviour.

Given λ_T as a function of temperature, free-energy curves for quasi-binary mixtures of DER332 with PES can be generated using equation (3). The spinodal curves can then be calculated from the condition $\partial^2\Delta G_m/\partial\phi_2^2=0$, and the binodal curves can be determined by solving equation (3) for the common tangent. In these calculations, the appropriate molar mass is the weight average. *Figure 5* shows the phase diagram obtained in

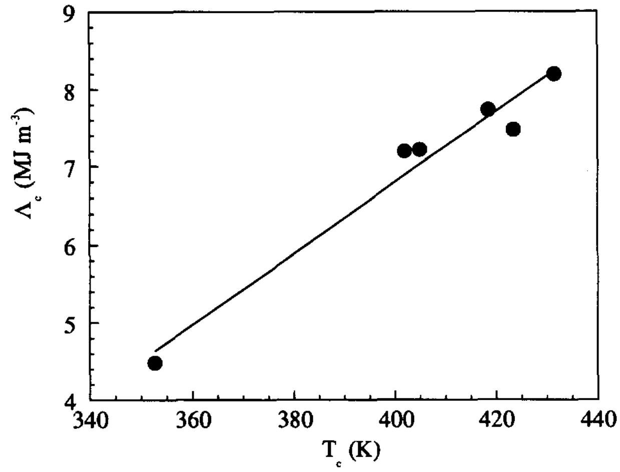

Figure 4 Relationship between calculated Λ_c and *LCST* values, T_c, for mixtures containing PES of different molar mass

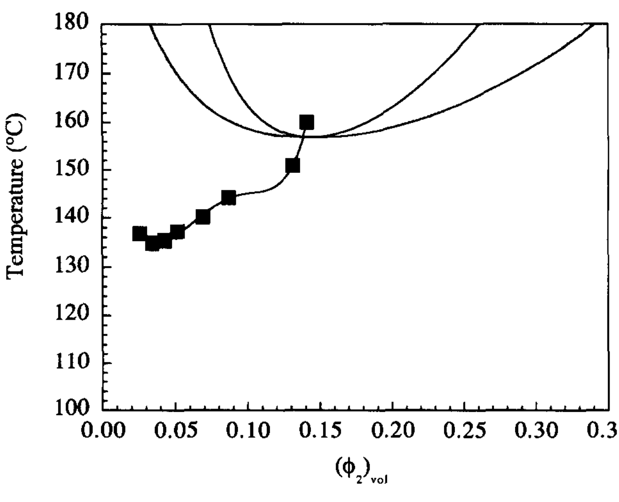

Figure 5 Calculated coexistence curves for binary blends of PES 3600 with DER332 epoxy resin, with cloud-point data (■)

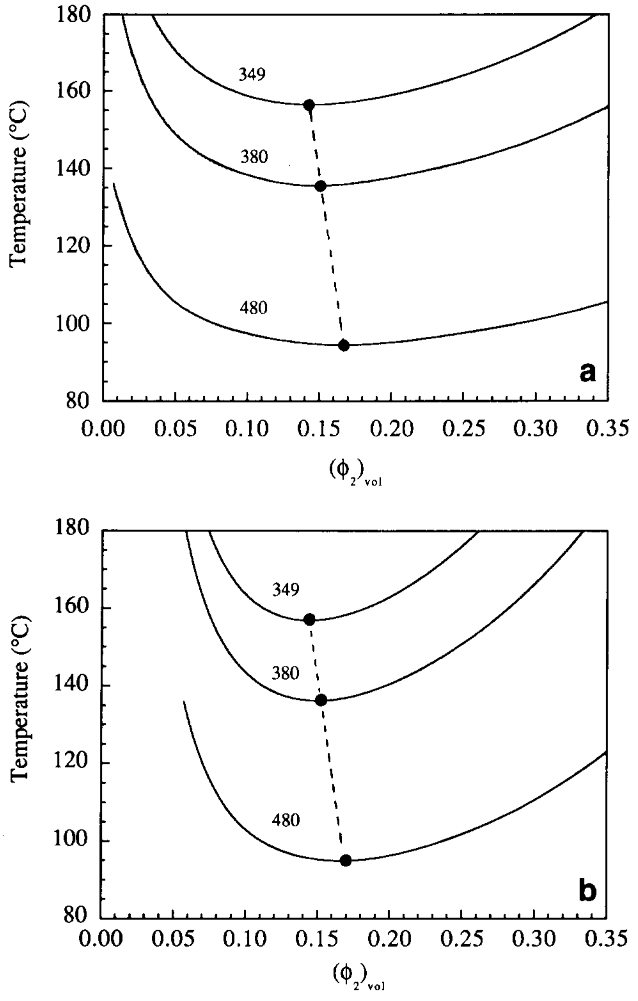

Figure 6 Calculated coexistence curves for binary blends of PES 3600 with DGEBA of various molar masses, as shown on curves: (a) binodal curves; (b) spinodal curves; (●) critical points. Calculations based on cloud-point curves

this way for blends of PES3600 with DER332 resin, and *Figure 6* shows the calculated effect of increasing the molar mass of the epoxy monomer continuously, assuming that Λ is independent of resin molar mass: the *LCST* decreases rapidly, but the accompanying shift in ϕ_{2c} in the direction of higher PES concentrations is relatively small. The locus of the T_c–ϕ_c curve marks the approximate boundary between mixtures that form PES-rich particles on phase separation, and those that tend to generate co-continuous morphologies. *Figure 7*, based on similar calculations, shows that increasing the M_w of PES in blends with DER332 also reduces the *LCST*, but shifts ϕ_{2c} to *lower* PES concentrations.

Ternary epoxy/hardener/PES blends

The main reason for studying miscibility in epoxy–PES blends is to understand phase separation during the curing reaction, in the presence of a hardener. In the present programme, three hardeners were evaluated: one aliphatic diamine, 3DCM; and two aromatic diamines, DDS and DDM. It was found that 3DCM gave immediate demixing when blended with epoxy–PES solutions at room temperature, and that blends containing DDS showed no sign of phase separation at any stage of mixing and subsequent cure. Of the three hardeners studied, only DDM gave controlled phase separation during the reaction. Solubility parameters δ throw some light upon these differences in miscibility, but must be treated with some caution. Using Fedors' method[14], calculated δ values (in $(\mathrm{MJ\,m^{-3}})^{1/2}$) are 21.5 for DER332 epoxy resin, 23.1 for PES, 19.4 for 3DCM, 22.3 for DDM, and 23.3 for DDS.

Light transmission experiments show the expected decrease in signal as the blend undergoes phase separation. However, for blends containing less than about 12% PES, there is an unexpected increase in the amount of light transmitted during the later stages of phase separation, as illustrated in *Figure 8*. Examination of the specimens revealed a semi-transparent green region coinciding with the path of the light beam, whilst the remainder of the specimen was densely cloudy. Subsequent exposure of the cured blend to sunlight on the laboratory bench caused the whole specimen to turn green and semi-transparent. The green colour also formed in the absence of PES: similar effects have been observed in DGEBA–DDM resins by Bellenger and Verdu[15], who concluded that the colour arises from photo-oxidation of the diamine bridge. In the present work, the oxidation of the epoxy resin appears to raise its refractive index (initially 1.57) sufficiently to approach that of the PES (1.65 for the neat polymer). The effects on

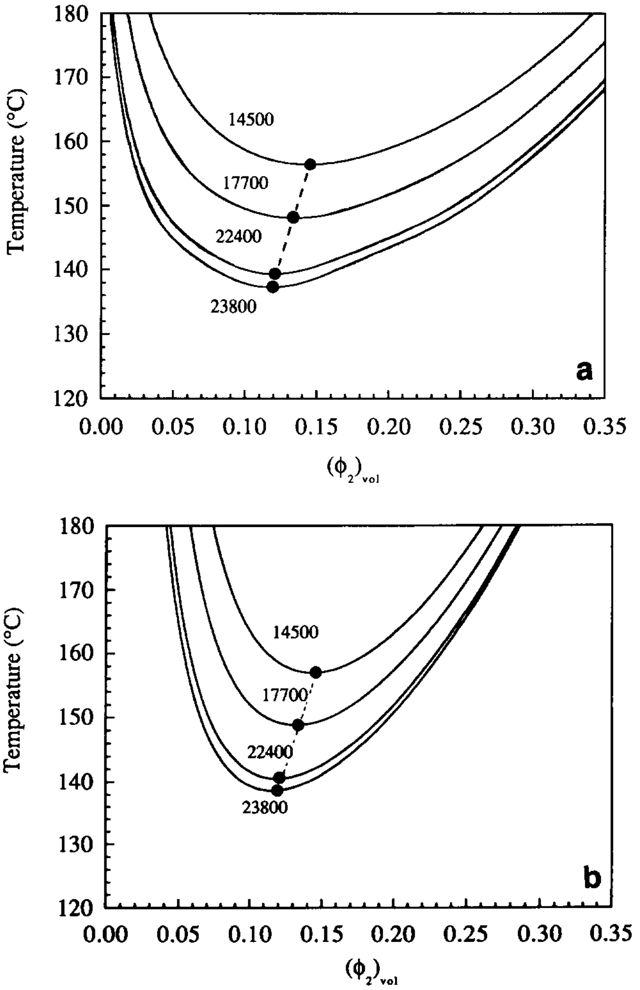

Figure 7 Calculated coexistence curves for binary blends of DER332 DGEBA with PES of various molar masses, as shown on curves: (a) binodal curves; (b) spinodal curves; (●) critical points. Calculations based on cloud-point curves

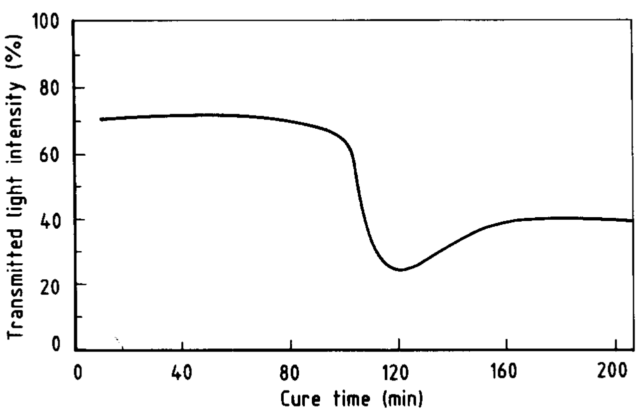

Figure 8 Changes in light transmission with curing time at 80°C for DER332 resin–DDM hardener combination blended with 7% PES 3600, showing phase separation followed by an increase in transparency

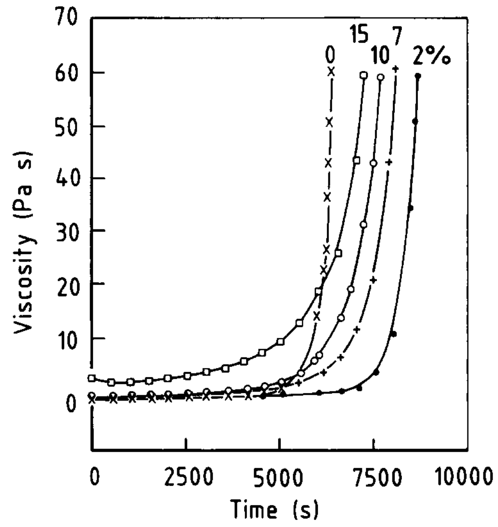

Figure 9 Changes in viscosity with cure time at 80°C for DER332–DDM blends containing 0 to 15 wt% of PES 3600

transparency of reducing PES concentration are due primarily to the reduction in particle size.

Whilst the PES remains in solution, it raises the viscosity of the resin, as expected, and also reduces the rate of curing. This effect is clearly shown in *Figure 9* for blends cured at 80°C: the upturn in viscosity as the system approaches gelation is delayed from 100 to 140 min on addition of only 2 wt% PES. Further addition of PES reduces the time to reach the upturn, but this can be related directly to the raised viscosities of blends containing a PES-rich second phase. Verchère *et al.* reported a reduced rate of cure in epoxy resins on addition of 6.5% CTBN rubber[16], but the rate was thereafter essentially independent of CTBN concentration over the composition range studied (up to 15% CTBN).

Since the identities and concentrations of the species present in reacting mixtures are changing continuously, it is difficult to make a complete thermodynamic analysis of resin–hardener–PES blends. In order to resolve this problem, the interaction parameter for DDM/PES mixtures is treated here as being equal to that for DGEBA/PES mixtures, and changes in Λ due to formation of –OH groups on the epoxy molecule are neglected. Curing can then be treated simply as an increase in average molar mass of the epoxy component, so that the critical point for the quasi-ternary mixture follows a locus close to that given in *Figure 6*. The solubility parameter values quoted earlier suggest that PES might in fact be a little more miscible with DDM than with DGEBA.

Development of morphology

The morphology of resin–thermoplastic blends is typically complex, as illustrated in *Figure 10*, which shows the fracture surface of a DER332–DDM resin containing 15 wt% PES and cured at 140°C, with post-cure at 200°C. It can be seen from *Figure 6* that this combination of PES concentration and temperature lies close to the calculated *LCST* point for PES–MY750 blends. In other words, a relatively small increase in the molar mass of the resin, from 349 to 380 g mol^{-1}, is required to take the system into the region of spinodal decomposition. Furthermore, the composition is close to the boundary at which formation of co-continuous morphology is to be expected. The electron micrographs, and observations made in the hot-stage optical microscope, support the conclusions reached on the basis of the very approximate thermodynamic analysis given above: that

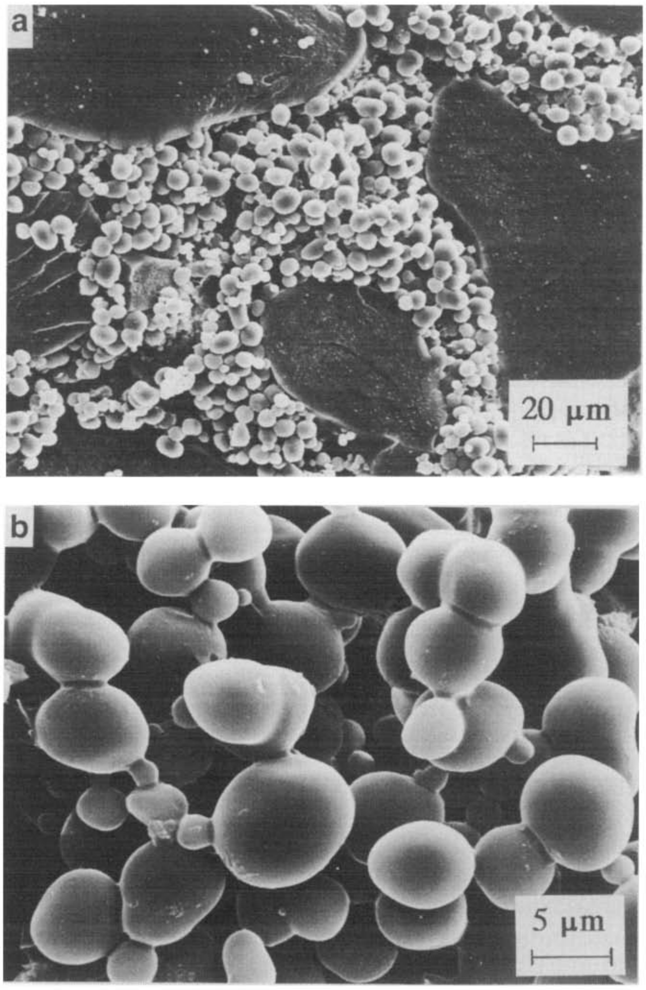

Figure 10 Fracture surface of DER332–DDM resin blended with 15 wt% PES 3600 and cured at 140°C. Surface etched with methylene chloride. (a) General view showing continuous domains in which epoxy sub-inclusions are embedded in a PES matrix. (b) Close-up of nodular epoxy sub-inclusions

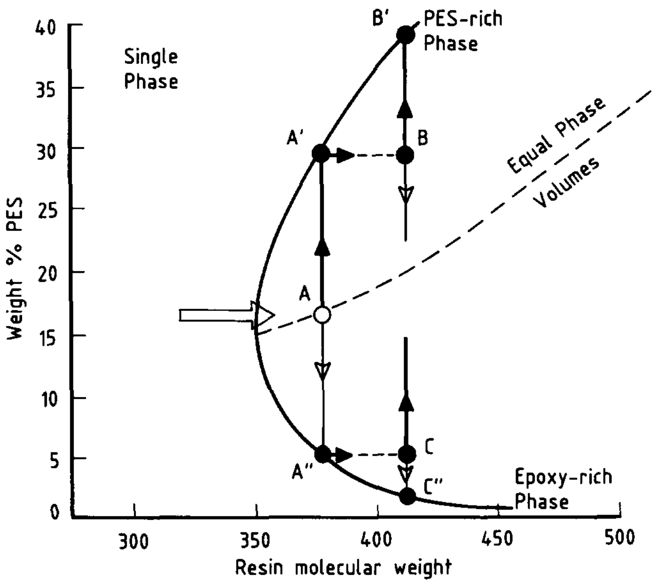

Figure 11 Schematic diagram showing effects of epoxy resin molar mass upon binodal points for PES blends, based on data for 140°C cure

the concentration of PES is just sufficient to give the co-continuous morphology that is evident in *Figure 10.*

Figure 11 is a schematic diagram based on *Figure 6*, showing the evolution of the binodal curve with increasing relative molecular mass of the epoxy resin. This curve represents the limiting compositions formed as the mixture undergoes phase separation. In practice, because of the increasingly high viscosities and the continuous chemical changes, the blend will never fully reach equilibrium. Nevertheless, the diagram provides a helpful basis for discussing the evolution of two-phase morphology. In epoxy–PES blends, raising the molar mass of the resin by chemical reaction has a similar effect to increasing the temperature of the mixture whilst keeping the molar masses constant: both types of change establish conditions under which phase separation can take place. By analogy with thermally induced transformations in alloys, Inoue has used the term 'chemical quenching' to describe demixing brought about by polymerization of the resin[4].

The arrows on *Figure 11* show schematically how the compositions of the PES-rich and resin-rich phases would be expected to develop in a blend containing ≈ 16 wt% (14 vol%) of PES, as the resin cures at 140°C. An initial increase in molar mass brings the blend to point A on the diagram, exactly halfway between the binodal points A′ and A″. If the blend were able to reach equilibrium instantaneously, compositions A′ and A″ would then form in equal volumes, according to the lever rule, since the lengths AA′ and AA″ are equal. It should be noted that at this stage of demixing the 'PES-rich' phase (composition A′) actually contains only 30 wt% PES. At the PES concentration chosen in *Figure 11*, the system enters directly into the spinodal region, so that arguments about possible contributions from nucleation and growth processes during the early stages of phase separation are not applicable. Demixing is spontaneous and, as the curing reaction proceeds, is driven by an increasing free-energy difference between mixed and phase-separated states.

As the cure continues, the two phases represented by A′ and A″ undergo further demixing. For example, phase separation from point B on the diagram results in the formation of compositions B′ and C″, in the volume ratio BC″/BB′, whilst at the same stage in the reaction, point C gives a small amount of composition B′ and a preponderance of C″, which is quite close in composition to pure epoxy resin. It is clear from the diagram that the main changes taking place after the initial phase separation consist of the expulsion of epoxy resin from the 'PES-rich' phase, leading eventually to the formation of a true PES-rich phase containing almost no epoxy resin. Optical microscopy shows that during the early stages the epoxy molecules migrate to existing resin-rich areas, but that, as the curing reaction advances, there is an increasing tendency to form sub-inclusions within the PES phase, to form the morphology illustrated in *Figure 10.*

In practice, demixing is even more complicated than is suggested by the schematic diagram. The viscosities of both phases increase throughout the cure, reducing diffusion coefficients, so that deviations from equilibrium become larger with increasing cure time. In addition, the blends are far from being binary mixtures, and in the period immediately before gelation they contain epoxy resins with a very wide spread of molecular weights, typical of condensation polymerization. Nevertheless, this qualitative treatment does help to explain the main features of the morphology. First, compositions equivalent to only 14 vol% PES can give co-continuous structure because the phases formed initially are approximately equal in volume, and are generated by spinodal decomposition, as discussed by Yamanaka and Inoue[4]. Secondly, demixing of epoxy from the PES-rich phase formed in the early stages results in the extensive formation of epoxy sub-inclusions. Thirdly, the size of these sub-inclusions increases with increasing cure temperature, because diffusion coefficients are reduced on heating. Fourthly, in the compositions under discussion, relatively small concentrations of PES-rich particles form in the epoxy-rich phase, and the sizes of these PES particles become smaller with increasing cure time.

Diffusion of small molecules occurs more rapidly when the host material is well above its glass transition temperature. In epoxy–PES blends, vitrification takes place in the two phases at different times and for different reasons: the epoxy becomes glassy as a result of crosslinking, whilst the T_g of the 'PES-rich' phase increases as it expels dissolved epoxy and hardener molecules, which act as plasticizers. If all of these low-molar-mass molecules were expelled, the T_g would reach that of the neat PES. In practice, some residual small molecules usually remain even after a post-cure at ≈ 200°C.

The diffusion coefficient at the point of phase separation increases with increasing temperature, leading to an increase in PES particle size, as shown in *Figure 12.* Increasing the PES concentration from 2 to 10% also increases particle size, essentially because phase separation begins at an earlier stage of the reaction, when the diffusion coefficient of the resin is relatively low. Similar effects have been seen in CTBN blends[17], but the opposite trend, with particle size decreasing as cure temperature increases, has been observed during the present research programme in blends of epoxy resin with poly(methyl methacrylate) (PMMA)[18].

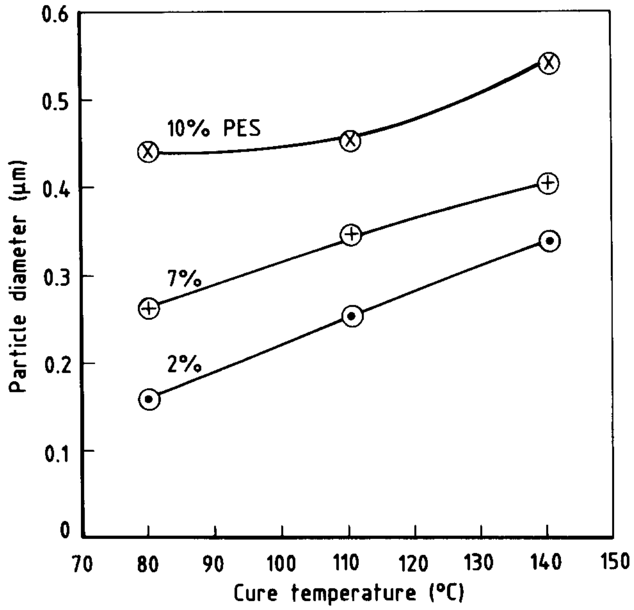

Figure 12 Effects of cure temperature and polymer content on PES particle diameter

CONCLUSIONS

This study has shown that resin molar mass is the main factor controlling phase separation in epoxy–PES blends. Calculations based on cloud-point data show that the composition at the critical point is only weakly affected by the M_n of the DGEBA. Phase separation from blends containing about 15 wt% of PES results in a complex morphology, with large PES domains containing a high proportion of resin sub-inclusions. This morphology can be related to the evolution of the phase diagram with degree of cure in the resin.

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