

Phase separation in epoxy resins containing polyethersulphone

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Scanning electron microscopy and dynamic mechanical spectroscopy have been used to study phase separation of dissolved polyethersulphone (PES) from trifunctional and tetrafunctional epoxy resins during curing. No phase separation was observed at high concentrations of the tetrafunctional resin. Observations of nodules on fracture surfaces, and of multiple peaks in the dynamic mechanical spectra provided evidence for a separate, crosslinked, PES-rich phase in the remaining materials. Despite the variety of morphologies obtained in mixtures of PES with different hardeners and resins, modulus and fracture toughness showed little dependence upon composition.

Keywords Polyethersulphone; blends; epoxy; phase separation; microscopy; dynamic mechanical spectroscopy

INTRODUCTION

Phase separation between epoxy resins and dissolved rubbers has been extensively studied, especially in DGEBA (diglycidyl ether of Bisphenol A) resins containing CTBN (carboxyl-terminated butadiene acrylonitrile) rubbers. Rubber particles precipitated during curing increase the fracture toughness of the epoxy resin¹⁻⁶. The degree of crosslinking in DGEBA-based resins is limited by the structure of the DGEBA molecule, which contains two epoxy groups joined by a relatively flexible link. More tightly crosslinked resins are required in high performance composites for use at elevated temperatures. Resins containing three or more epoxy groups have therefore found wide application in advanced carbon- and glass-fibre composites^{7,8}. There appears to be very little published information on phase separation in systems based on these multifunctional resins.

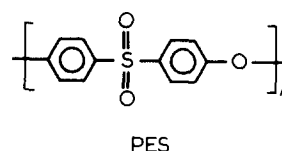
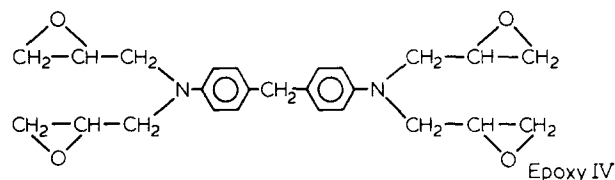
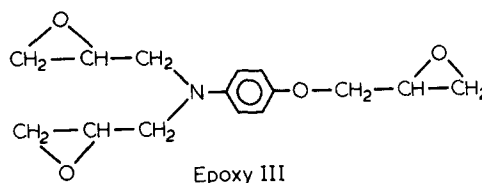
One such system contains dissolved polyethersulphone (PES), which is added to increase viscosity during hot lay-up. The present paper describes the morphology of cured resins containing PES, and discusses the relationship between structure and mechanical properties.

EXPERIMENTAL

Materials

The chemical structures of the two resins used in this study are shown below. The trifunctional resin Epoxy III (Ciba-Geigy ERL 0510) has a low viscosity at room temperature, an epoxy equivalent weight of 100 g mol^{-1} , and a molecular weight of ~ 300 . The tetrafunctional resin Epoxy IV (Ciba-Geigy MY720) has a much higher viscosity at room temperature, an epoxy equivalent weight of $\sim 130 \text{ g mol}^{-1}$, and a molecular weight of ~ 520 . These resins were modified by the addition of Victrex 100P polyethersulphone, a relatively low molecular weight grade manufactured by ICI Ltd. The po-

lymer was micronized to a fine powder with a maximum particle size of $6 \mu\text{m}$.



The resins were cured using one of two hardeners: diaminodiphenylsulphone [DDS] and dicyanodiamide [Dicy].

Most of the materials were made by dissolving PES in Epoxy III at 150°C , cooling to 130°C , and adding hardener plus preheated Epoxy IV. As PES is not readily soluble in Epoxy IV, materials containing no Epoxy III, and some of the mixtures, were made by dissolving the PES in methylene chloride before blending with the hot resin. Mixtures were degassed at 93°C for one hour and cured according to the following schedule, which is based on that used by Bascom⁹:

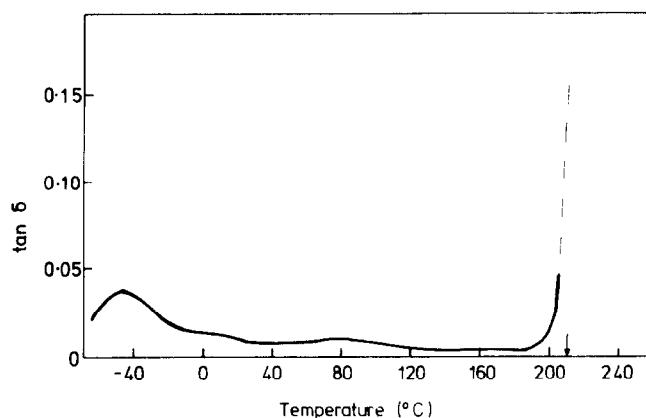


Figure 1 Dynamic mechanical spectrum of pure PES

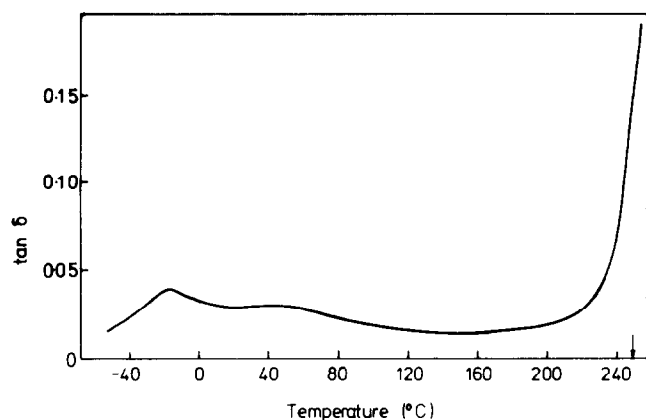


Figure 2 Dynamic mechanical spectrum of 100 Epoxy III, 30 DDS

7 h at 93°C (200°F)
 16 h at 121°C (250°F)
 2 h at 149°F (300°F)
 2 h at 177°C (350°F)
 4 h at 200°C (392°F) (post-cure)

This curing regime reduces the probability of an uncontrolled exotherm. A Barcol indenter was used to check the degree of crosslinking in the cured resins.

Methods

Dynamic mechanical spectroscopy (d.m.s.) measurements were made between -90°C and the glass transition of the matrix resin, at a frequency of 110 Hz using a Rheovibron model DDV-II viscoelastometer fitted with a modified temperature control unit. Specimens were prepared by milling plaques of the resin to a thickness of 1 mm, and then cutting 0.5×1.0 mm strips from the plaque, using a diamond wafering wheel; the sample length was 50 mm between grips. Potential sources of error in Rheovibron measurements have recently been reviewed by Wedgwood and Seferis¹⁰; precautions taken in the present work were in accordance with their recommendations for the accurate determination of $\tan \delta$.

Samples fractured at room temperature were coated with a thin layer of Au-Pd alloy and examined in the scanning electron microscope (SEM). Selected samples were coated with carbon and subjected to energy dispersive X-ray microanalysis for sulphur using the same microscope.

Modulus measurements were made at 20°C and 60% RH using accurate creep rigs. Fracture mechanics data at 23°C were obtained by compact tension and three-point bend tests. The compact tension specimens measured approximately $50 \times 40 \times 3$ mm, and the three-point bend specimens were typically 6×3 mm in cross-section, with a span-to-width ratio of 4.

RESULTS

Dynamic mechanical spectra for the two individual resins and the PES are compared in Figures 1-3. All three materials show a low-temperature beta relaxation, with peaks at -17°C for Epoxy III, -27°C for Epoxy IV, and -47°C for PES. The loss tangent rises rapidly as the temperature approaches the glass transition, and the temperature T_{α} at which $\tan \delta$ reaches 0.15 has been used in the present study to define the onset of the alpha relaxation; values of T_{α} are 252°C for Epoxy III, 242°C for Epoxy IV, and 210°C for PES. A mixture containing equal amounts of the two resins exhibits high and low temperature peaks intermediate between those for the individual resins, indicating that they are mutually compatible.

Figure 4 is a dynamic mechanical spectrum for a sample of Epoxy III containing 25 phr PES. The distinct peak at 225°C , on the shoulder of the main transition, is evidence for phase separation in this material. The size of this secondary peak increases with PES concentration, in-

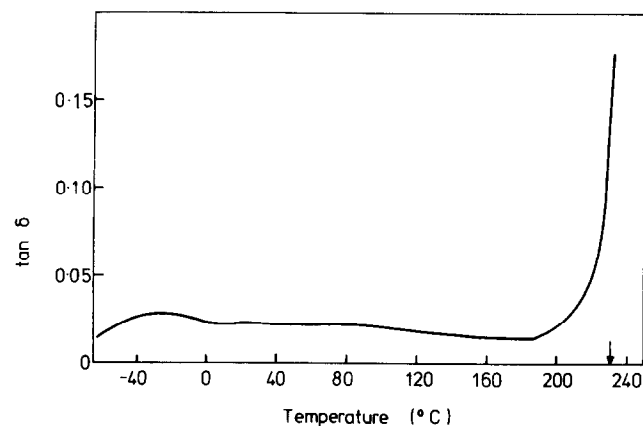


Figure 3 Dynamic mechanical spectrum of 100 Epoxy IV, 30 DDS

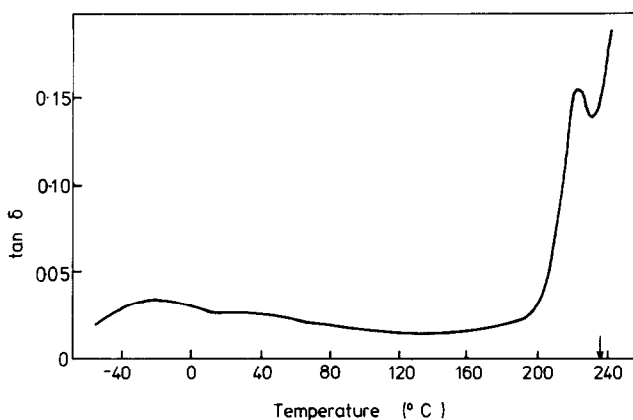


Figure 4 Dynamic mechanical spectrum of 100 Epoxy III, 30 DDS, 25 PES

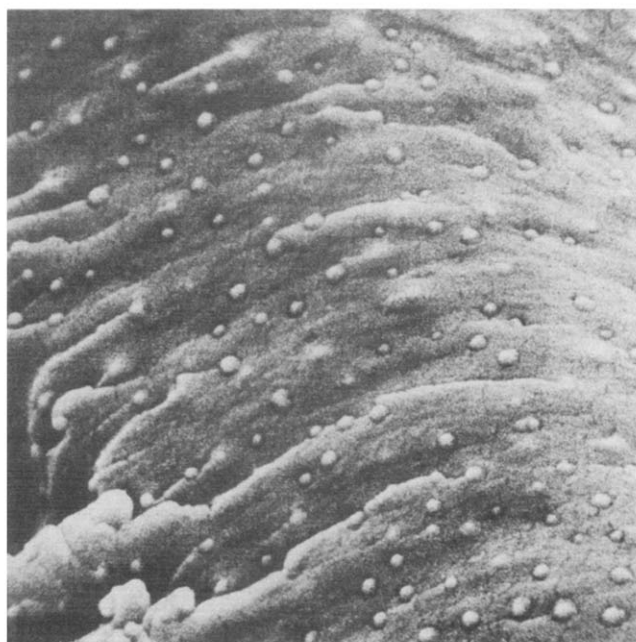


Figure 5 Fracture surface of 100 Epoxy III, 30 DDS, 10 PES at 10000x magnification

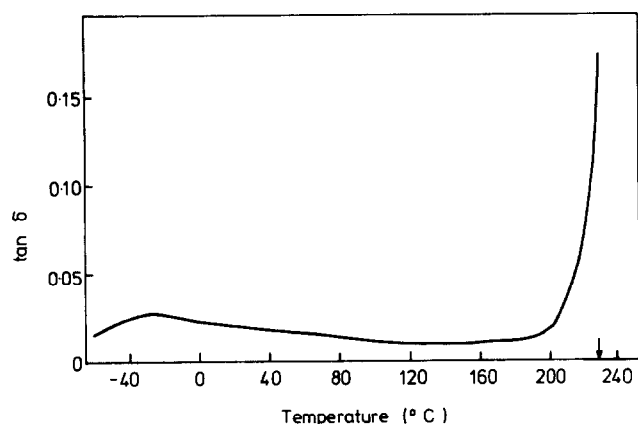


Figure 6 Dynamic mechanical spectrum of 100 Epoxy IV, 30 DDS, 25 PES

dicating that the relaxation is caused by a PES-rich phase. Scanning electron microscopy of fracture surfaces from this series of resins reveals the presence of nodules which increase in diameter with PES concentration, as illustrated in Figure 5. Treatment of the fracture surface with methylene chloride has no effect on the nodules. This procedure would not be expected to cause crystallization of the PES, which can occur as a result of repeated exposure to chlorinated solvents¹¹. On the basis of the SEM evidence, together with the position of the relaxation peak, it is clear that the dispersed phase also contains crosslinked epoxy resin, which has probably reacted with the PES, rendering it insoluble. Such a reaction could be explained by the presence of terminal hydroxyl groups in the PES.

Parallel experiments on Epoxy IV reveal no evidence of phase separation: there is no detectable shoulder on the primary transition peak, as illustrated in Figure 6, nor are

nodules visible on the fracture surfaces, irrespective of PES concentration.

The observation of a double peak is possible only if the glass transitions of the PES phase and of the cured epoxy resin occur at different temperatures. Samples cured with 5 phr of Dicy gave T_g values of 205°–210°C, which obscured any relaxations that might have resulted from a separate PES-rich phase. Examination of fracture surfaces in the SEM showed no sign of nodules in Dicy-cured Epoxy IV compositions containing PES, in contrast to the corresponding compositions based on Epoxy III.

Cured mixtures of Epoxy III with Epoxy IV show no evidence of phase separation, either in dynamic mechanical spectra or in scanning electron microscopy. Addition of PES to mixed resins cured with Dicy produces materials containing spherical nodules, which are usually distributed uniformly throughout the specimen, as shown in Figure 7, but in some cases form clusters, as shown in Figure 8. Unfortunately, for the reasons explained above, it is not possible to obtain evidence for phase separation in these compositions by means of dynamic mechanical spectroscopy.

Dynamic mechanical spectra of equivalent mixtures cured with DDS show evidence of phase separation, as illustrated in Figure 9, but fracture surfaces appeared featureless at all PES concentrations studied. These results suggest that a PES-rich phase is present in these materials, but that the domain sizes are too small to be observed in the SEM. Attempts to prepare thin sections for transmission electron microscopy were unsuccessful.

In order to identify the PES-rich phase, X-ray microanalysis was used to determine the distribution of sulphur in fracture surfaces of Dicy-cured resins. This method is applicable only when nodules are visible, and is unsuitable for DDS-cured materials, which contain sulphur in both phases. The method works best on samples in which the nodules are clustered together. These clusters show a significantly higher concentration of sulphur than the

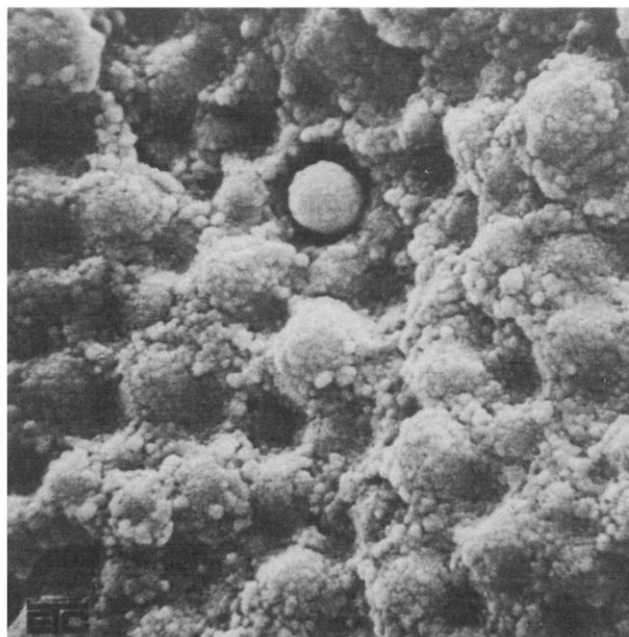


Figure 7 Fracture surface of 80 Epoxy III, 20 Epoxy IV, 5 Dicy, 31 PES, at 10000x magnification

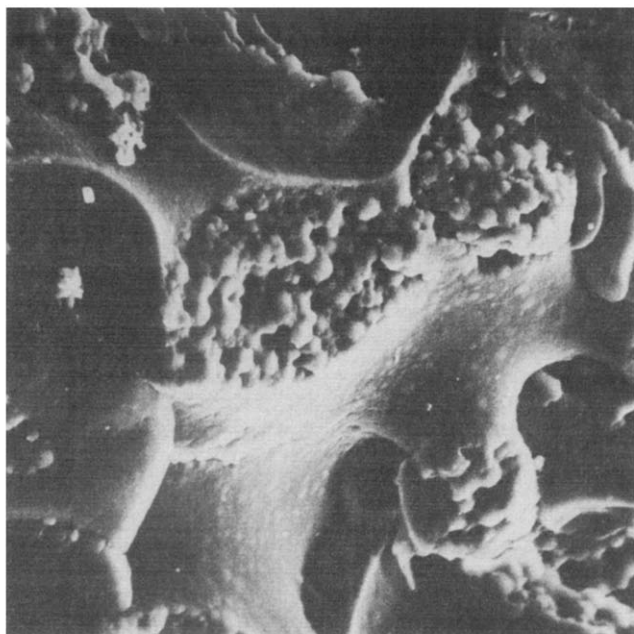


Figure 8 Fracture surface of 50 Epoxy III, 50 Epoxy IV, 5 Dicy, 12 PES, at 2000x magnification

surrounding matrix, identifying them with the PES-rich phase.

Table 1 summarizes the relationships between composition, morphology and mechanical properties in the series of materials studied during this work. Although there are wide variations in morphology and degree of phase separation, the mechanical properties vary only within a very narrow range. There is some scatter in the results from a single plaque of resin, which is probably due to variations in density of crosslinking. In the case of fracture toughness measurements, there is some additional scatter related to the sharpness of the precracks. The estimated errors arising from these sources are ± 0.1 GPa for modulus and $0.1 \text{ MPa}\cdot\text{m}^{1/2}$ for fracture toughness.

The insensitivity of mechanical properties to the presence of PES is further illustrated in Figures 10 and 11, which show creep data over a range of stress levels for PES, Epoxy IV, and a mixture containing 25 phr PES. Although PES has a lower modulus than the resin, it does not have a significant effect upon the creep properties of the mixture, even at a relatively high concentration.

DISCUSSION

The materials prepared for this programme exhibit four categories of behaviour: (a) there is no evidence of phase separation; (b) phase separation is indicated by d.m.s. but not by SEM; (c) loss peaks are not resolved by d.m.s., but nodules are seen by SEM; and (d) both d.m.s. and SEM show clear evidence of phase separation. Only materials containing 80 phr or more of Epoxy IV belonged to category (a). Observation of phase separation by SEM depended in the present work upon the formation of distinct features on the fracture surface, and is therefore limited by the requirement for a difference in fracture response by the two phases and by the ability of the microscope to distinguish small features on an uneven

fracture surface. In practice, this means that domains smaller than about $0.1 \mu\text{m}$ cannot be distinguished with any confidence. Dynamic mechanical spectroscopy complements microscopy, but is restricted in the present case by the proximity of the loss peaks of the components of the mixtures; in particular, resins cured with Dicy show transitions close to those for PES, so that the d.m.s. method is unable to provide evidence of phase separation.

Phase separation is controlled by both thermodynamic and kinetic factors. As the resin cures, the resulting increase in molecular weight causes a decrease in the configurational entropy of mixing, so that the enthalpy term, which is usually positive (endothermic), becomes increasingly more important in determining the free energy of mixing¹². At the same time, opening of the epoxy ring, with the formation of polar hydroxyl groups, alters the enthalpy of mixing. Calculations of solubility parameters, using Small's method¹³, indicate that this factor alone is sufficient to cause the PES to separate from solution. On the other hand, reaction between epoxy groups and the terminal hydroxyls on the PES molecules produces a block copolymer, which will be more soluble than PES itself in the resin. It is not clearly established that this reaction occurs to a significant extent before the gel point, beyond which phase separation becomes very difficult, but it might explain why some of the mixtures, notably those containing a high proportion of Epoxy IV, show no evidence of phase separation.

Differences in reaction kinetics must also be taken into account. The choice of resin and of hardener will determine the rate of reaction at any given temperature, and hence the period during which phase separation can take place. Rates of diffusion decrease as the curing reaction proceeds, and therefore depend directly upon the kinetics of cure.

In comparing Epoxy III with Epoxy IV, or DDS hardener with Dicy, it must be recognized that there are differences in both thermodynamic and kinetic influences on phase separation, since the groups formed during reaction are different in each case, and the rates of reaction, which depend particularly upon the choice of hardener, are also different.

As the PES and the two resins have comparable moduli, it is not entirely unexpected that the presence of a separate PES-rich, crosslinked phase has relatively little effect

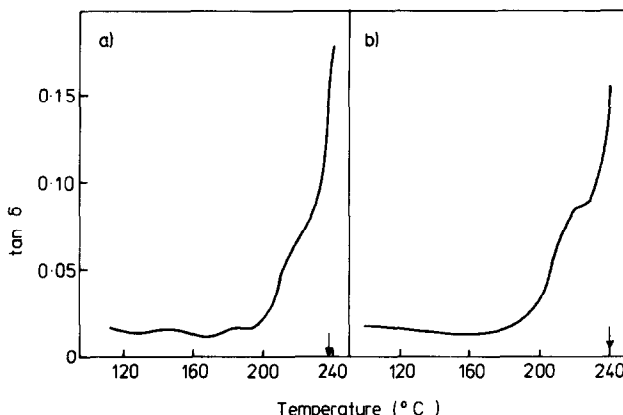


Figure 9 High temperature dynamic mechanical spectra for (a) 50 Epoxy III, 50 Epoxy IV, 30 DDS, 15 PES; and (b) 80 Epoxy III, 20 Epoxy IV, 30 DDS, 18 PES

Table 1 Summary of sample composition and properties

Composition (pbw)					Relaxation temperatures (°C)			Average nodule diameter (μm) SEM of fracture surfaces	Young's modulus (GPa) E (at 100 s)	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$) K_{IC}
Epoxy III	Epoxy IV	Dicy	DDS	PES	T_{α}	T_{α}'	T_{β}			
100	—	—	30	0	252	none	-15	none	3.7	0.6
100	—	—	30	10	246	215	-25	0.2	3.5	0.7
100	—	—	30	25	239	225	-25	0.8	3.5	—
100	—	5	—	40	—	—	—	1.1	3.6	0.8
80	20	—	30	18	242	225	—	none	3.7	0.6
80	20	5	—	14	—	—	—	5.5	3.5	0.9
80	20	5	—	31	—	—	—	1.0	3.9	0.8
50	50	—	30	0	241	none	-21	none	3.8	0.6
50	50	—	30	15	240	220	—	none	3.6	0.8
50	50	—	30	25	234	217	-25	none	3.7	0.9
50	50	5	—	12	—	—	—	1.6	3.9	0.8
50	50	5	—	25	206	—	-30	0.8	3.6	0.7
20	80	—	30	10	239	—	—	none	3.6	—
20	80	5	—	10	—	—	—	0.2	3.7	0.7
—	100	—	30	0	236	none	-27	none	3.9	0.7
—	100	—	30	4	—	—	—	none	4.1	0.6
—	100	—	30	10	239	—	—	none	3.7	0.6
—	100	—	30	25	232	—	-25	none	3.8	0.6
—	100	5	—	25	200	—	—	none	—	0.9
—	—	—	—	100	210	none	-47	none	2.8	~2.5

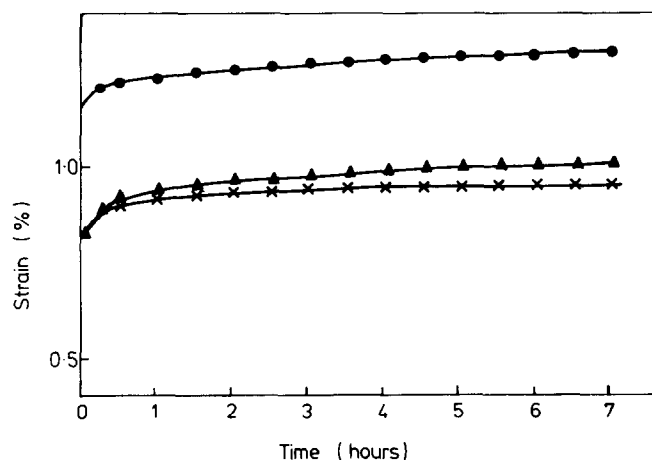


Figure 10 Creep curves at 20°C for PES (●), Epoxy IV (▲), and Epoxy IV containing 25 phr PES (x), all at a tensile stress of 30 MPa

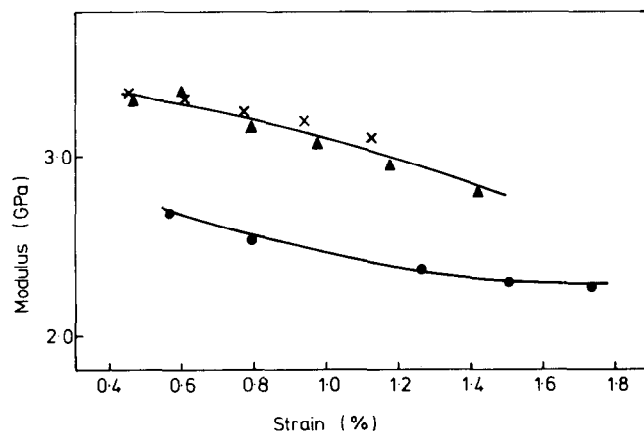


Figure 11 Relationship between 10 000 s isochronous tensile creep modulus and strain for PES (●), Epoxy IV (▲), and Epoxy IV containing 25 phr PES (x)

upon creep behaviour. In this respect, these materials are quite different from the more familiar rubber-modified polymers, which consist of a rigid matrix incorporating particles of much lower modulus. Addition of PES might perhaps have been expected to have a greater effect upon K_{IC} , since the thermoplastic is substantially tougher than either of the resins. However, the only observable effect of the PES-rich phase upon fracture behaviour is seen in the deviation of the crack front around the nodules. In this respect, the PES acts in a very similar way to elastomeric inclusions in samples fractured at low temperatures.

CONCLUSIONS

The following conclusions may be drawn from the results of this programme: (a) dynamic mechanical spectra and scanning electron microscopy may be used to study the phase separation of PES from solution in epoxy resin; (b) the two methods are complementary, as d.m.s. is of little value when the phases being examined exhibit similar relaxation temperatures, whilst SEM is able to detect particles only when they produce a recognizable feature on the fracture surface and are sufficiently large to be resolved; (c) the type and concentration of resin and hardener affect the morphology of the PES-rich phase; and (d) addition of PES has little effect upon the creep and fracture toughness of the resin mixtures, irrespective of the degree of phase separation or the morphology.

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