Investigation of thermoplastic-modified thermosets: positron annihilation and related studies of an amine-cured epoxy resin

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Real-time dielectric relaxation and rheological measurements are reported during the course of cure for three thermoplastic-modified thermoset resin blends. Two thermoset resin systems were used, one containing only a difunctional epoxy and the other containing a mixture of tri- and difunctional epoxies. The latter mixture was used to react two reactively terminated polysulfone thermoplastics with slightly different molecular weights. Positron annihilation measurements are reported on one of the thermoplastic–thermoset resin systems as a function of the thermoplastic composition, and indicate that changes in composition lead to variations in the free-volume content. Mechanical properties are presented for all three systems. These data indicate that the phase structure has a significant effect on mechanical performance, but the most dominant effect results from change in the thermoset matrix material.

(Keywords: thermoplastic–thermoset resin; positron annihilation; amine-cured epoxy resin)

INTRODUCTION

Thermoplastic modification of thermoset resins promotes toughening whilst allowing retention of the advantageous mechanical properties of thermoset polymers[1–5]. In two previous papers[6,7], the use of dielectric analysis to monitor the changes at a molecular level during cure has identified the occurrence of phase separation in such blends. At low thermoplastic contents, typically below 20% (w/w), a polysulfone (PS) thermoplastic will separate into approximately spherical domains in epoxy resin systems[8,9]. Above 20% (w/w), the thermoplastic and thermoset form a co-continuous phase, and above approximately 30% (w/w), a phase-inverted morphology is observed. Electron microscopy and dielectric analysis indicate that the microstructure is best represented by a distribution of structures, ranging from chains of fused spheres to single isolated spherical structures[6,7]. These changes have a profound influence on the mechanical properties of the epoxy resin system, and can lead to considerable improvements in toughness, particularly when the thermoplastic-rich phase forms the continuous matrix. The morphological scale size is apparently a function in part of the molecular weight of the thermoplastic, and reflects different thermodynamic constraints present in the mixtures during the initial stages of cure[8].

Positron annihilation lifetime (PAL) measurements have traditionally been used for the investigation of the defect structure in metals and single-crystalline materials[10]. The annihilation of the thermalized ortho-positronium (o-PS) component in an organic material occurs via an electron exchange mechanism, which depends on the overlap integral of the o-PS with that of the surrounding molecular structure[11,12]. The thermalization process in a solid requires the pre-existence of a void, and the lifetime of the o-PS is a direct measure of the mean radius of the cavity. The intensity of the o-PS event is directly related to the probability of finding a suitable void into which the positron can thermalize. Studies in the early 1980s have shown the direct connection between free volume and o-PS annihilation in amorphous polymers. Observations on polycarbonate, poly(ether sulfone) and polysulfone[13] indicate that at room temperature the size of the average free volume is comparable to that found in polystyrene above its glass transition (T_g). The occurrence of a large free-volume density in engineering polymers is consistent with the measurement of high impact strength in these materials. In an attempt to understand what molecular characteristics may be important in determining the mechanical properties of these thermoplastic-modified thermosets, PAL measurements are reported together with dielectric relaxation and related physical properties. The system reported here involves a change of the epoxy matrix from that described in the previous papers[6,7].

EXPERIMENTAL

Materials

The modified thermoset system was based on the cure of a 1:1 (w/w) mixture of diglycidyl ether of bisphenol F (Ciba-Geigy PY306) and triglycidyl aminophenol (Ciba-

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Geigy MY0510) with 4,4′-diaminodiphenylsulfone (4,4′-DDS; Ciba-Geigy HT976). The thermoplastics were both amine-terminated polysulfones, either RT-PS(A) ($M_n = 11\,000$, $R_v = 0.20$ to 0.24) or RT-PS(C) ($M_n = 13\,000$, $R_v = 0.24$ to 0.28) synthesized for this project. The epoxy resin and hardener were used as supplied in the ratio of 2.6:1 (w/w), whilst the thermoplastic was dried before use. Cure samples were made by blending the epoxy resins by heating, and dissolving them in a solution of the thermoplastic in a 95:5 (v/v) mixture of methylene chloride and methanol. The curing agent was added to the solution of this blend before the solvent was boiled off, leaving a homogeneous solution. This blend was poured into an open mould (dimensions 15 cm × 10 cm), which had been preheated to 413 K, and then degassed for 30 min under vacuum to remove residual solvent and trapped air. For dielectric and rheological measurements, the mould was removed from the oven and cooled rapidly to quench the curing reaction, and stored at 253 K until needed. The samples for mechanical and electron microscopic examination, however, were cured at 453 K for a further 120 min, and then allowed to cool slowly to room temperature. A range of samples with varying thermoplastic content were made in each case. Comparison is also made with an epoxy/thermoplastic blend studied in a previous publication[6]. This system is based on the cure of MY0510 with 4,4′-DDS, incorporating RT-PS(A), and will allow for comparisons to be made on the effect of the introduction of a second epoxy, the diglycidyl ether of bisphenol F. The systems are summarized as follows*:

(1) System 1: trifunctional epoxy resin/amine-terminated thermoplastic, MY0510/4,4′-DDS/RT-PS(A)
(2) System 2: di-/trifunctional epoxy resin mixture/amine-terminated thermoplastic, MY0510/PY306/4,4′-DDS/RT-PS(A)
(3) System 3: di-/trifunctional epoxy resin mixture/amine-terminated thermoplastic, MY0510/PY306/4,4′-DDS/RT-PS(C).

Dielectric measurements

Measurements were performed using a Solartron 1250 frequency response analyser operating over a frequency range from 0.1 to 6×10^5 Hz. The frequency range was selected to allow collection of approximately 30 data points within a period of 3 min. Typically, the time taken for cure of the resin after reaching 180°C was 100 min, hence the collection time is sufficiently short for the data to approximate to an instantaneous snapshot of the dielectric properties. A cell was designed that consisted of two pre-etched copper electrodes mounted on an epoxy glass-fibre base, separated by a copper spacer. This configuration generated a three-terminal electrode system with an active area of 1 cm^2. The space between the electrodes was maintained constant by soldering the copper spacer around three edges of the cell. Depending on the viscosity, the initial mixture was either heated and poured into the cell or, alternatively, a section was extracted from the frozen pre-plaque and inserted between the electrodes before soldering was carried out. The cell was attached to a heating block and placed in an Oxford Instruments cryostat (DN1704). The electrodes were in good thermal contact and isothermal conditions were maintained using an Oxford Instruments ITC4 temperature controller. The method used for the dielectric measurements has been described elsewhere[14]. Observations at predetermined times were stored automatically on file for subsequent analysis.

Differential scanning calorimetry measurements

Differential scanning calorimetry (d.s.c.) measurements were conducted using a Du Pont model 9900 calorimeter. In all cases a sample of approximately 10 mg was used at a heating rate of 10°C min^{-1}, over a temperature range of −50 to 300°C. In these experiments the sample was cured during the first temperature scan, allowing evaluation of the heat of reaction. The sample was then cooled slowly to room temperature, and a second scan used to determine the final glass transition temperature.

Rheological measurements

A curometer, designed at Strathclyde[15], was used to monitor changes in the viscosity as a function of time and allow determination of the real and imaginary parts of the shear modulus at 2 Hz. The instrument was calibrated using Santovac-5, which was chosen because it exhibits a very high temperature–viscosity coefficient, and forms a stable supercooled liquid state, which has been studied extensively[16,17].

Mechanical testing

Mechanical properties were assessed at 23°C on moulded plaques, and the following parameters considered: Flexural modulus was determined by a three-point bend test at 5 mm min^{-1}, using a sample size of 50 mm × 10 mm × 3 mm. Yield strength, σ_y, was obtained in compression mode using a sample size of 10 mm × 10 mm × 3 mm. Mode I stress intensity factor, K_{Ic}, was measured at 1 mm min^{-1} using a sample size of 70 mm × 10 mm × 3 mm with a single edge notched on the 10 mm face. Mode I strain energy release rate, G_{Ic}, was also measured under these conditions. Finally, the ductility factor, $(K_{Ic}/\sigma_y)^2$, was derived from these data[8]. The test methods used have been reported fully elsewhere[18].

Positron annihilation measurements

PAL measurements were performed on samples from system 2 with thermoplastic content varying between 0 and 40% (w/w), using a standard fast–slow coincidence configuration. A ^{22}Na-Kapton foil source was sandwiched between two sections of sample of dimensions 20 mm × 10 mm, thickness 2 mm, and was sealed in a Pyrex tube. The PAL measurements were made using two plastic fast scintillators (ME111) coupled to fast photomultipliers (Mullard XP 2230) mounted in line on an Oxford Instruments DC-2 cryostat. This configuration allows measurements to be made over a temperature range from 300 to 400 K with a control of temperature better than 0.1 K. The time resolution of the system was determined from the prompt curve of a ^{60}Co source and was found to be better than 400 ps. The source correction was determined by measuring the positron annihilation lifetimes of benzophenone crystals. Approximately 5×10^6 events were stored for analysis in each spectrum, and the lifetimes were determined using the Positron Fit Extended computer program[19,20].

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* RT-PS(A) and RT-PS(B) were assigned in a previous publication[7]. RT-PS(C) is assigned in the present work

Table 1 D.s.c. data for epoxy resin systems in the text

	System 1		System 2		System 3	
Thermoplastic (wt%)	$\Delta H_{\text{cure}}{}^a$ (J g^{-1})	T_g (°C)	$\Delta H_{\text{cure}}{}^a$ (J g^{-1})	T_g (°C)	$\Delta H_{\text{cure}}{}^a$ (J g^{-1})	T_g (°C)
0.0	666.7	237.3	599.9	191.3	599.9	191.3
5.4	700.7	227.1	521.8	182.1	507.0	187.3
10.3	555.1	217.6	468.7	185.3	445.0	181.0
15.6	594.8	214.3	458.9	182.4	421.6	188.3
20.6	506.5	188.0	407.7	184.9	358.8	168.9
26.7	415.0	197.3	397.5	179.4	340.1	182.1
30.0	431.2	208.3	395.0	180.9	373.0	183.6
34.6	383.8	199.9	330.0	183.0	323.2	174.8
39.1	396.3	191.5	306.0	183.2	298.8	185.3

Inspection of the matrix of correlation coefficients indicated that a high correlation exists between the two shortest-lifetime components corresponding to the para-positronium and free positron annihilation of $\sigma_1 = 125$ ps and $\tau_2 = 450$ ps, and this was largely indicative of strong interaction in the fitting of these data. Hence this results in an uncertainty in the intensities. The longest-lifetime component was clearly resolved at all temperatures, and exhibited a low correlation coefficient with the other components. The uncertainties of τ_2 and τ_3 were estimated to be 0.01 and 0.02 ns, respectively. Within the precision of these measurements, the shortest lifetimes do not exhibit a defined temperature dependence. The largest lifetime is, however, markedly sensitive to the temperature of observation.

RESULTS AND DISCUSSION

Differential scanning calorimetry measurements

Variations of the heat of cure and the T_g values for the various compositions investigated are presented in *Table 1*. The curing exotherm decreased linearly with increasing thermoplastic content, and no significant deviations from additivity were observed for the three series of blends. For all samples examined, a single T_g is observed owing to the close proximity of the T_g values of the individual components. For system 1, there is a progressive decrease in T_g with the addition of thermoplastic up to ~20% (w/w), which tends to level off above 20% (w/w). For systems 2 and 3, the T_g is lowered significantly by the addition of 5% (w/w) thermoplastic, but does not vary greatly on further increases in thermoplastic content. The depression of T_g initially for all systems is consistent with the dissolution of the thermoplastic to a limited extent in the epoxy resin, leading to an increase in the free volume and a lowering of T_g. The addition of a second epoxy resin to the thermoset component causes a significant reduction in the T_g at corresponding thermoplastic levels, particularly at zero thermoplastic content.

Viscosity data

The time dependence of the viscosity was characterized using the Strathclyde Rheometer at 180°C, and gelation times, designated as the time at which the viscosity reaches 10^4 Pa s, are reported in *Table 2*. As with the previous systems, increasing the concentration of the thermoplastic leads to an increase in the gelation time.

Table 2 Critical point data determined for systems 2 and 3 of the text

Thermoplastic (wt%)	Vitrification time from ε' (min)^a	Gelation time from η (min)^b
System 2		
0.0	136	–
5.4	135	–
11.0	150	–
15.6	136	–
20.5	165	19.8
26.7	150	28.8
30.0	166	40.2
34.6	180	39.3
39.1	220	56.0
System 3		
0.0	136	–
5.4	176	–
11.0	200	–
15.6	166	–
20.5	141	–
26.7	153	23.8
30.0	178	25.8
34.6	220	41.8
39.1	166	58.5

[a] Vitrification point from levelling off of ε' at 10^4 Hz
[b] Gel point from $\eta = 10^4$ Pa s

Dielectric analysis

The dielectric method has been used previously for the characterization of cure in thermoset resin systems, and it has been shown that analysis of the time dependence of the permittivity and loss can allow identification of the gel and vitrification points[21–27]. The real-time dielectric plots obtained for systems 1, 2 and 3 are illustrated in *Figure 1*. The form of the curves is very similar and they show the characteristic marked drop in the low-frequency increment in the dielectric constant on gelation of the material, and the subsequent step down in the dielectric constant on vitrification. As in our earlier studies[6,7], there is a residual low-frequency dielectric process, which can be associated with interfacial polarization effects; however, in this study the process is apparently shifted to a lower frequency. This is clearly indicated in *Figure 2*, which shows the shift in the peak for the three systems studied. The location of the Maxwell–Wagner–Sillars (MWS) process is a function of the conductivity of the occluded phase, its shape and volume fraction. The values of dielectric properties of the finally cured matrix would indicate that the process must occur at lower frequencies than those available in this

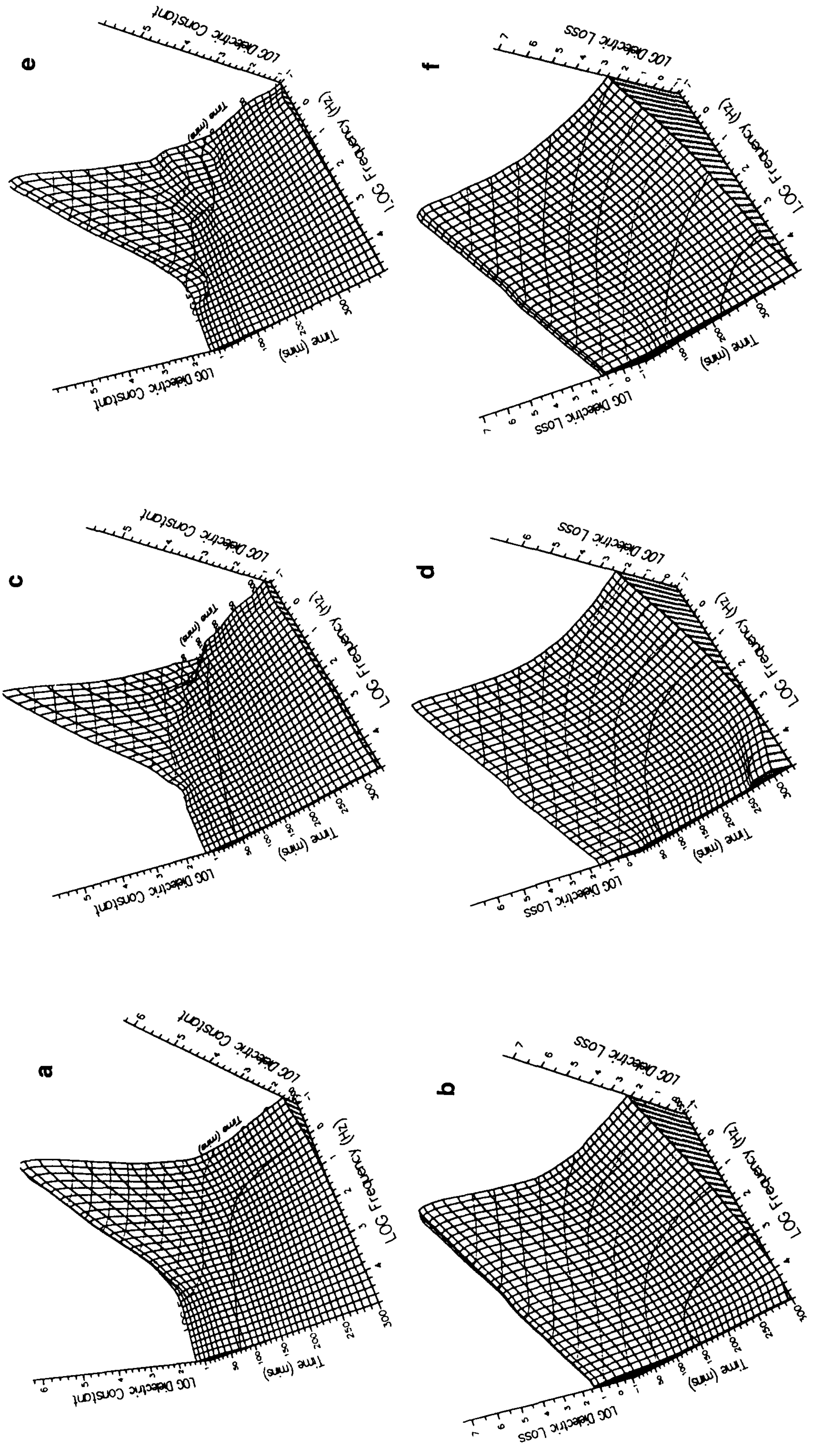


Figure 1 Examples of real-time dielectric traces measured at 180°C. (a) Dielectric constant and (b) dielectric loss for system 1, MY0510/4,4'-DDS/30 wt% RT-PS(A). (c) Dielectric constant and (d) dielectric loss for system 2, MY0510/PY306/4,4'-DDS/30 wt% RT-PS(A). (e) Dielectric constant and (f) dielectric loss for system 3, MY0510/PY306/4,4'-DDS/30 wt% RT-PS(C)

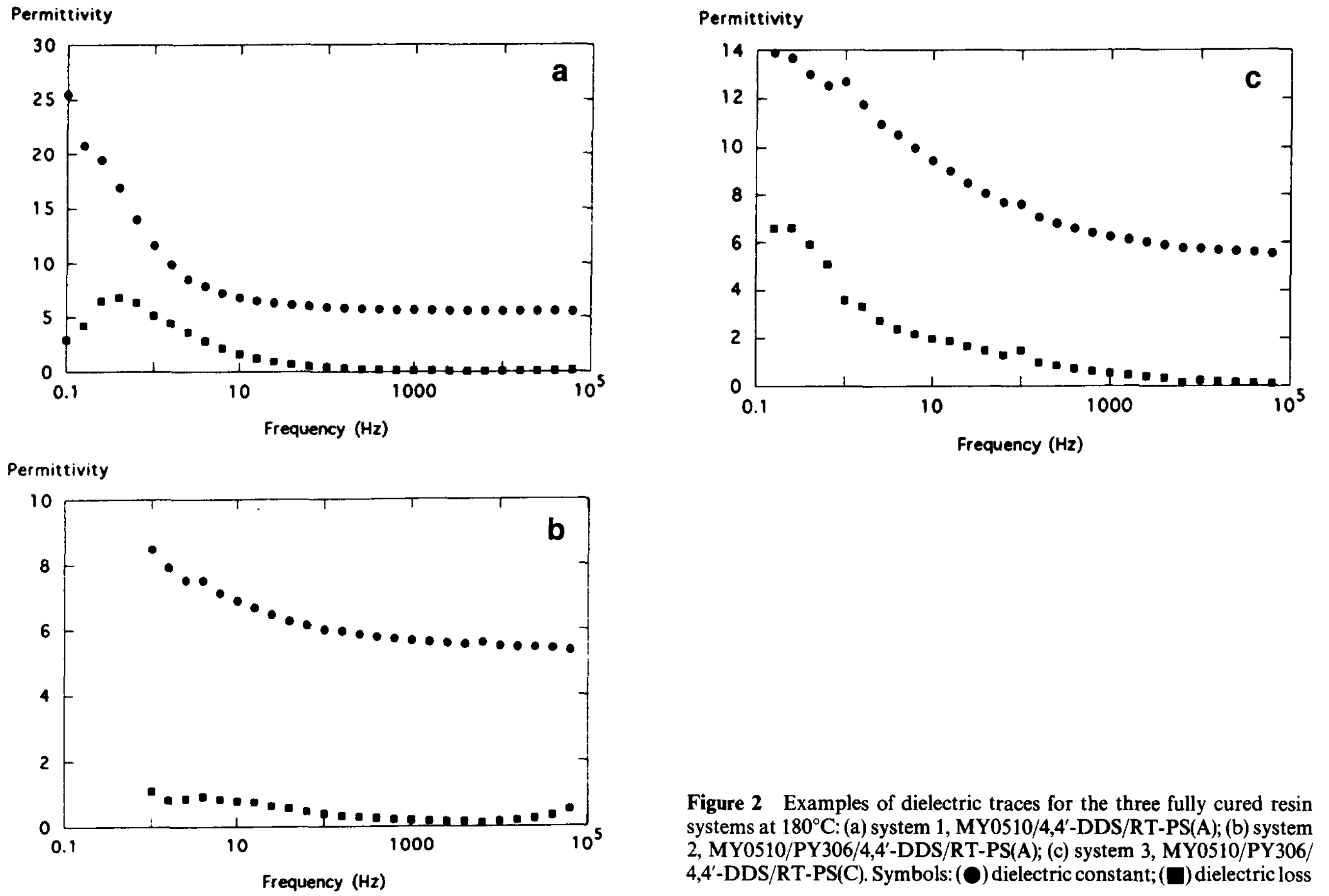
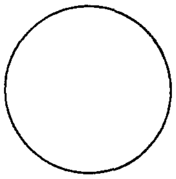
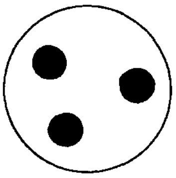
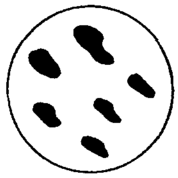
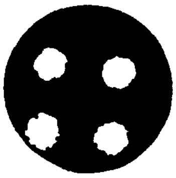


Figure 2 Examples of dielectric traces for the three fully cured resin systems at 180°C: (a) system 1, MY0510/4,4'-DDS/RT-PS(A); (b) system 2, MY0510/PY306/4,4'-DDS/RT-PS(A); (c) system 3, MY0510/PY306/4,4'-DDS/RT-PS(C). Symbols: (●) dielectric constant; (■) dielectric loss

		SYSTEM 1		
0 - 2.5 % wt TP	**5 - 20 % wt TP**	**22.5 % wt TP**	**25 - 30 % wt TP**	**35 - 40 % wt TP**
		Scale size typically µm		
		SYSTEMS 2 and 3		
0 - 5 % wt TP	**5 - 20 % wt TP**	**22.5 % wt TP**	**25 - 35 % wt TP**	**No Phase Inversion**
		Scale size typically 0.1µm		
				
		Microstructure		
Solution	Particulate	Particulate/ Co-continuous	Co-continuous	Phase Inversion

System 1: MY0510/4,4'-DDS/RT-PS(A) Source of data, reference 7
System 2: MY0510/PY306/4,4'-DDS/RT-PS(A) Source of data, reference 28
System 3: MY0510/PY306/4,4'-DDS/RT-PS(C) Source of data, reference 28

Figure 3 Schematic diagram of microstructures of systems 1, 2 and 3 as a function of thermoplastic content

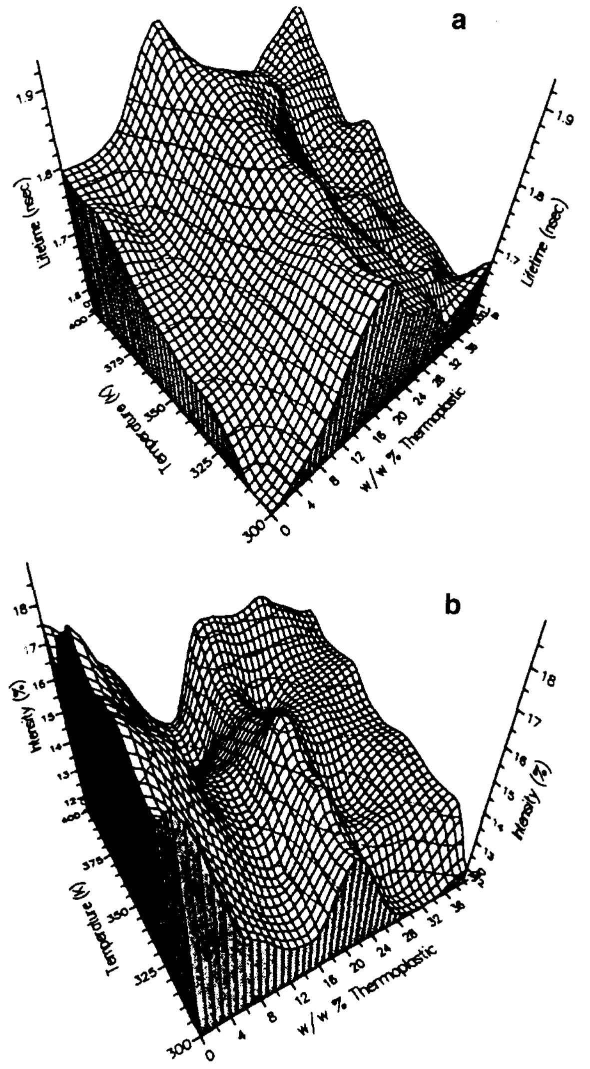


Figure 4 Positron annihilation lifetime and intensity data for system 2: (a) lifetime data and (b) intensity data as a function of temperature and composition

study, consistent with the incorporation of the di-/trifunctional mixture reducing the conductivity of the occluded matrix. The distribution of microstructures obtained is illustrated schematically in *Figure 3*. The scale size in these systems, i.e. systems 2 and 3, is smaller than in those previously investigated as a consequence of the incorporation of the difunctional epoxy resin. This has the effect of successively reducing the frequency position of the maximum in the dielectric loss peak, e.g. the equivalent system to system 1 incorporating Victrex 5003P thermoplastic[6] produces a dielectric loss peak at the highest frequency of all the systems investigated.

Positron annihilation data

The intensity and lifetime of the longest-lifetime component for system 2 vary with composition and temperature as illustrated in *Figure 4*. The uncertainty in the values of t does not justify attempting to use other than a simple exponential fit of the data. It can be argued that it would be more appropriate to fit a distribution of relaxation times; however, the quality of the data does not justify an extension of the analysis to a distribution of exponential decays[29,30]. Although there are uncertainties in the analysis, the overall variation in both the lifetime and the intensity with change in composition are an order of magnitude larger, and hence conclusions can be drawn. At any given thermoplastic content, the lifetime increases with increasing temperature, consistent with expansion of the sample through heating. Addition of the thermoplastic causes a reduction in the intensity of the longest component, which is consistent with part of the epoxy matrix being replaced by a second phase. In a system comprising two phases, the positronium will be formed in the phase with the lowest ionization constant and largest number of voids. The expected variation with composition would be a linear extrapolation between the values for pure epoxy and thermoplastic. The observed increase and then decrease is not consistent with a simple additivity relationship and therefore must be interpreted as a real effect of the changes in void size in the matrix. The loss in intensity might be inferred as being a consequence of the reduction in the number of ortho-positroniums formed with reduction in epoxy phase. However, further addition leads to the intensity of the longest component being regained. Once the morphology becomes co-continuous at approximately 30% w/w PS for systems 2 and 3, the thermoplastic phase becomes dominant, reflected in a decrease in the o-PS intensity. There is a further increase of this intensity being observed for higher thermoplastic contents, however. The intensity of the o-PS component is a measure in these systems of the mean free volume of the total matrix, and will reflect the state of both the thermoplastic and thermoset phases. The o-PS lifetime increases with thermoplastic content, reaching a maximum at the point at which the co-continuous phase will be expected to form, and then decreasing as the thermoplastic becomes the dominant phase. The value of the lifetime increases with temperature, as would be expected for an increase in the size of voids with temperature. Around the point at which the co-continuous phase is being formed, there will be the highest probability of co-solution of the thermoset and thermoplastic components. The mixture starts as being homogeneous, and it is only when it is raised to the cure temperature that phase separation is initiated. The precise path that the system will follow as it demixes will depend on a number of factors, and will be frozen at the point at which gelation takes place. Co-solution of the thermoplastic in the epoxy appears to lead to a reduction in the number of voids, but creates voids with a larger mean radius. Beyond the maximum in the lifetime component with composition, co-continuous phase separation occurs. There is a corresponding minimum in the intensity. A sub-maximum is observed to coincide with the occurrence of the co-continuous phase, and a slight shoulder in the lifetime composition plot is observed at this point. The lifetime becomes less composition-dependent at highest RT-PS(A) contents and the intensity dips through a minimum and then increases slightly. The o-PS data indicate that the distribution of free volume in these systems is a reflection of the delicate balance of factors that control the final phase structure and does not lend itself to a simple interpretation.

Mechanical testing

Results of mechanical tests are presented in *Figure 5*. The yield strength of system 1 falls dramatically with increasing thermoplastic content. System 1 contains a trifunctional epoxy with a tetrafunctional amine chain

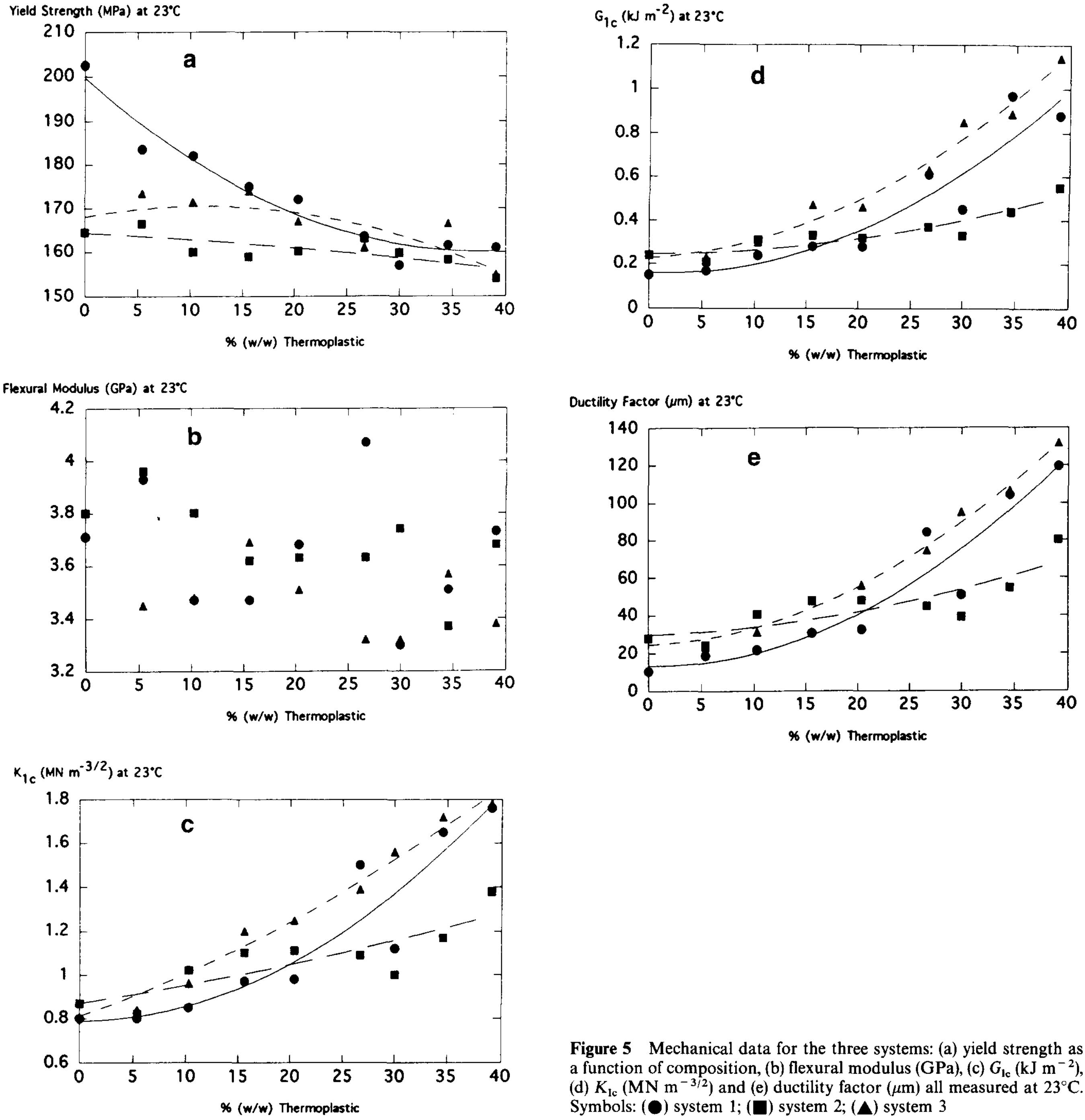


Figure 5 Mechanical data for the three systems: (a) yield strength as a function of composition, (b) flexural modulus (GPa), (c) G_{Ic} (kJ m^{-2}), (d) K_{Ic} (MN $\mathrm{m}^{-3/2}$) and (e) ductility factor (μm) all measured at 23°C. Symbols: (●) system 1; (■) system 2; (▲) system 3

extender. Systems 2 and 3 contain a proportion of tri- and difunctional epoxy resins; they have initial yield strengths that are lower and the subsequent variation with thermoplastic composition is smaller. The flexural modulus in all three systems varies unpredictably with the thermoplastic content, but no significant decreases are observed. The G_{Ic} and K_{Ic} values both show similar behaviour, increasing with thermoplastic content. Systems 1 and 3 show similar values, with system 2 showing consistently lower values above approximately 10–15% (w/w) thermoplastic. System 3, which contains the slightly higher-molecular-weight thermoplastic, shows higher G_{Ic} and K_{Ic} values when compared to the corresponding thermoset system containing RT-PS(A), i.e. system 2. The introduction of the difunctional epoxy, PY306, to system 1 to produce system 2 causes a significant decrease in the G_{Ic} and K_{Ic} values. Similar trends were observed for the ductility factor. The overall trends that emerge are as follows:

(i) The incorporation of thermoplastic causes a decrease in the yield strength of the blends but an increase in the toughness.

(ii) The change of tri- to incorporation of a difunctional epoxy resin has a larger effect than changing the molecular weight of the thermoplastic resin.

(iii) The influence of changing the molecular weight of the thermoplastic is most marked on the values and variation with composition of K_{Ic} and G_{Ic}.

CONCLUSIONS

The positron annihilation data indicate the complexity of the free-volume distribution that exists in these thermoplastic–thermoset systems and indicate the way in which the phase-separation process is influencing the properties of the matrix. A more detailed analysis is not possible with this system because of the similarity of the two components. In systems where there are significant differences in the dynamic properties of the matrix components, as in the case of a styrene–butadiene–styrene block copolymer, a more detailed analysis is possible from the temperature dependence of the Ps data. However, since the components have similar T_g values and constants, such analysis did not appear justified. However, there is no obvious parallel between these free-volume data and the mechanical measurements, reflecting the importance of the interfacial region on the measured properties. The dielectric data do not show any evidence for a Maxwell–Wagner–Sillars process in the cured material for systems 2 and 3, which is a result of the lower conductivity of the epoxy resin blend used. The relaxation process occurs at lower frequencies than those considered in this study, reflecting a combination of morphological and matrix topological effects. Significant changes are observed in the mechanical properties with incorporation of thermoplastic, reflecting the generation of the co-continuous and phase-inverted structures. This indicates the effects of both the molecular-weight properties.

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