Dielectric monitoring of phase separation during cure of blends of epoxy resin with carboxyl-terminated poly(butadiene-*co*-acrylonitrile)

George M. Maïstros, Harry Block, Clive B. Bucknall* and Ivana K. Partridge
School of Industrial and Manufacturing Science, Cranfield Institute of Technology, Cranfield, Bedford MK43 0AL, UK

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Curing experiments were carried out at several temperatures on blends of diglycidyl ether of bisphenol A (DGEBA) epoxy resin with 34.4 phr of 4,4′-diamino-3,3′-dimethyldicyclohexylmethane (3DCM) hardener and 15 wt% carboxyl-terminated poly(butadiene-*co*-acrylonitrile) (CTBN) rubber. Simultaneous measurements were made of turbidity and of dielectric properties over the frequency range 0.1 to 20 kHz. Changes in viscosity, gel fraction and enthalpy were determined in separate experiments. The results were compared with those for the unmodified resin–hardener mixture. In CTBN blends, relative permittivity ε' at low frequencies rose sharply during phase separation, owing to an interfacial polarization process, which can be described by the Maxwell–Wagner–Sillars model: relaxation times τ are in the order of 1 ms. In the neat resin, ε' fell continuously throughout the cure over the whole frequency range, the fall being particularly steep as the resin gelled and began to vitrify. It is concluded that dielectric techniques provide an effective method for monitoring phase separation, gelation and vitrification in resin blends.

(Keywords: epoxy resin; carboxyl-terminated poly(butadiene-*co*-acrylonitrile); CTBN; dielectric monitoring; phase separation; interfacial polarization; Maxwell–Wagner–Sillars model)

INTRODUCTION

Dielectric methods for monitoring cure in thermosetting resins have been developed recently by several research groups, principally as an aid in processing advanced composites[1–11]. The aim is to provide intelligent closed-loop control of presses and autoclaves, based on dielectric monitoring of viscosity changes, gelation and vitrification in the resin, so that pressure can be applied at the optimum time, which is immediately before the gel point.

Apart from two short communications from this laboratory[12,13], published studies of dielectric cure monitoring have to date been restricted to single-phase resins. However, many high-performance thermosets are multiphase materials, made by mixing the resin and hardener with a soluble elastomer or thermoplastic, which undergoes phase separation during cure. Blends of this type can be many times tougher than the parent resin. The present paper considers the application of dielectric monitoring to one such blend system: epoxy resin containing dissolved CTBN (carboxyl-terminated poly(butadiene-*co*-acrylonitrile)) rubber. The aim of the work is to determine whether phase separation can be detected dielectrically, and related to other processes occurring during cure. There are obvious attractions in a technique that can follow phase separation, gelation and vitrification in the same sample.

EXPERIMENTAL

The epoxy resin used was Dow DER332, a DGEBA (diglycidyl ether of bisphenol A) having $MW = 340$ and hydroxy/epoxy ratio = 0.015. The hardener was BASF Laromin C260 (4,4′-diamino-3,3′-dimethyldicyclohexylmethane, 3DCM). The elastomer was BF Goodrich Hycar CTBN 1300X8, of $MW = 3600$ and acrylonitrile (AN) content = 18%; it was pre-reacted at 85°C with an excess of the DGEBA (at 72 phr CTBN) in the presence of 0.32 phr triphenylphosphine catalyst, to give ETBN (epoxy-terminated butadiene–acrylonitrile copolymer)[14]. The resin, hardener and rubber were chosen because curing and phase separation in the system were already well understood as a result of work by Pascault, Sautereau and coworkers[14–18]. Blends were made by dissolving the ETBN–resin solution in additional epoxy resin, removing trapped air over 1–2 h under vacuum, and then adding the stoichiometric amount of hardener, all operations being carried out at the chosen cure temperature.

Unless otherwise stated, the final elastomer content of the blends is equivalent to 15 wt% of CTBN; and the hardener content, based upon the total epoxy resin concentration before reaction with the CTBN, is 34.4 phr. After mixing, the blends were poured into preheated glass moulds, which remained in the curing oven throughout. Dek-Dyne capacitative sensors supplied by Kranbuehl[9] were attached with double-sided adhesive tape to the wall of the mould before it was placed in the oven. A Hewlett–Packard 4276A bridge was used to make

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*To whom correspondence should be addressed

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measurements of relative permittivity ε' and dielectric loss ε'' by scanning 17 frequencies in the range 100–20 000 Hz over 30 s at selected time intervals during the cure. Simultaneous turbidity measurements were made on the same sample, using a tungsten–halogen lamp and a Philip Harris i.r./light detector. Light was transmitted to and from the heated mould via optical fibres. Temperature was measured using an embedded thermocouple.

In separate isothermal experiments, viscosity changes during cure of the resin and its blends were monitored at a fixed shear rate of $100\,\mathrm{s}^{-1}$, using a Contraves Rheomat instrument; and enthalpy changes were recorded by a Perkin–Elmer DSC4 differential scanning calorimeter operating under isothermal conditions. Gel fractions were measured by taking small samples in prepared pans from the curing oven, quenching in liquid nitrogen, grinding to a powder, and weighing before and after extraction with dichloromethane. Gel points were then determined by extrapolation back to zero gel. Similar quenched samples were used in d.s.c. tests at a heating rate of $10\,\mathrm{K\,min}^{-1}$ to measure glass transition temperatures in partly cured resins. Freshly made mixtures of resin and hardener, with and without added rubber, were quenched and then heated from −50 to 300°C at $10\,\mathrm{K\,min}^{-1}$ in the d.s.c. to determine the overall heat of reaction.

After curing at the chosen temperature, resins were post-cured for 14 h at 190°C. Fully cured samples were fractured at liquid-nitrogen temperatures and examined in the scanning electron microscope to determine the size and volume fraction of the CTBN particles. Volume fractions were obtained using a Joyce–Loebl image analyser with Genias software. Dielectric measurements were made on fully cured blends between 40 and 135°C, and dynamic mechanical thermal analysis was carried out in the bending mode at 10 Hz over the temperature range −100 to 250°C, using a Polymer Laboratories d.m.t.a. machine at a heating rate of $3\,\mathrm{K\,min}^{-1}$.

THEORY

In the most general case, the complex relative permittivity ε^* of a resin is the sum of contributions due to electronic, atomic, dipolar, conduction and interfacial responses, which will be represented by the terms ε_e^*, ε_a^*, ε_d^*, ε_c^* and ε_i^*. The first four mechanisms of polarization occur in both liquid epoxy resin and CTBN blends, whereas interfacial polarization is important only in phase-separated blends.

The electronic component of relative permittivity is related to the refractive index μ in the optical region through the relationship:

$$\varepsilon_e' = \mu^2 \tag{1}$$

Allowing for a minor additional term ($\approx \varepsilon_e'/10$) for atomic polarization, the combined contribution of electronic and atomic components to permittivity is therefore $\leqslant 3.0$ units in epoxy resin, which has $\mu = 1.57$ in the liquid state, and 1.59 after curing.

Dipolar relaxations are known to occur in both liquid and solid epoxy resins. Their contribution to permittivity will undoubtedly be enhanced in blends containing a relatively high concentration of $-\mathrm{C{\equiv}N}$ groups. In the simplest case, for a process with a single relaxation time τ, ε_d' and ε_d'' follow the Debye equations:

$$\varepsilon_d' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \tag{2}$$

$$\varepsilon_d'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{3}$$

where ω is angular frequency; ε_0 and ε_∞ are limiting values of permittivity at low ($\omega\tau \ll 1$) and high ($\omega\tau \gg 1$) frequencies. Idealized relaxations of the type represented by equations (2) and (3) are rarely observed in practice, and it is necessary to characterize real systems in terms of a distribution of relaxation times. Nevertheless, the Debye equations provide a useful basis for discussion of the phenomena described in this paper.

Conduction is due to the presence of ionic impurities, which may vary in concentration from sample to sample. Absorbed moisture is one obvious source of mobile ions. For any given resin sample, the conductivity decreases with increasing viscosity during the curing reaction[9]. Because current is out of phase with voltage, the most obvious effect of conduction is to increase ε'':

$$\sigma = \omega\varepsilon\varepsilon_c'' \tag{4}$$

where σ = conductance and ε = permittivity of free space = $8.854\,\mathrm{pF\,m}^{-1}$. However, at low frequencies, conduction also contributes to ε', owing to accumulation of blocked charge at the electrodes. Day *et al.*[19] obtained the following equation for ε_c' in a capacitor with electrode spacing L and blocked layers of thickness b:

$$\varepsilon_c' = \frac{\varepsilon' S^2 (B - 1)}{S^2 + B^2} \tag{5}$$

where $B = L/2b$, $S = \varepsilon''/\varepsilon' = \sigma/\varepsilon\varepsilon'\omega$, and ε' and ε'' are the permittivity and loss of the bulk dielectric.

The difference in character between dipolar and conduction effects is well illustrated in a Cole–Cole plot[20] of ε'' against ε', as will be demonstrated later in the paper. A dipolar relaxation following equations (2) and (3) gives a semicircle, with its centre at $\varepsilon' = (\varepsilon_0 - \varepsilon_\infty)/2$, $\varepsilon'' = 0$. By contrast, conduction causes a steep increase in ε'' with ε', both terms reaching high values, even with quite modest concentrations of mobile ions.

Interfacial effects were first studied by Maxwell[21] and Wagner[22], and the theory was further developed by Sillars[23]. Reviews of the subject have been published by von Hippel[24], van Beek[25] and (with specific reference to multiphase polymers) North *et al.*[26]. Small volume fractions v_2 of semiconducting spheres embedded in a dielectric continuum produce time-dependent redistributions of charge, which may be indistinguishable from a Debye dipolar relaxation. In effect, the spheres behave as macroscopic dipoles, with relaxation times determined by the concentration and mobility of the ionic charge carriers. Provided that $v_2 < 0.2$ and $\sigma_1 \ll \sigma_2$, equations (2) and (3) apply. Relaxation time τ and limiting permittivities (for which by definition $\varepsilon'' = 0$) are given by:

$$\tau = \varepsilon\left(\frac{2\varepsilon_1 + \varepsilon_2 - v_2(\varepsilon_2 - \varepsilon_1)}{2\sigma_1 + \sigma_2 - v_2(\sigma_2 - \sigma_1)}\right) \tag{6}$$

$$\varepsilon_0 = \varepsilon_1\left(\frac{2\sigma_1 + \sigma_2 + 2v_2(\sigma_2 - \sigma_1)}{2\sigma_1 + \sigma_2 - v_2(\sigma_2 - \sigma_1)}\right) + 3v_2\sigma_1\left(\frac{(2\sigma_1+\sigma_2)(2\varepsilon_2-\varepsilon_1)-(2\varepsilon_1+\varepsilon_2)(\sigma_2-\sigma_1)}{[2\sigma_1+\sigma_2-v_2(\sigma_2-\sigma_1)]^2}\right) \tag{7}$$

$$\varepsilon_\infty = \varepsilon_1\left(\frac{2\varepsilon_1 + \varepsilon_2 + 2v_2(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2 - v_2(\varepsilon_2 - \varepsilon_1)}\right) \tag{8}$$

where σ_1 and σ_2 are the conductivities of matrix and spheres respectively. For very small v_2 and σ_1, equations (6)–(8) reduce to[25]:

$$\tau = \frac{\varepsilon(2\varepsilon_1 + \varepsilon_2)}{\sigma_2} \tag{9}$$

$$\varepsilon_0 = \varepsilon_1\left(\frac{1 + 2v_2}{1 - v_2}\right) \tag{10}$$

$$\varepsilon_\infty = \varepsilon_1\left[1 + 3v_2\left(\frac{\varepsilon_2 - \varepsilon_1}{2\varepsilon_1 + \varepsilon_2}\right)\right] \tag{11}$$

These approximate versions of the equations serve to emphasize the point that, for *dilute* dispersions of spheres, the volume fraction of spheres determines ε_0 and ε_∞ but not τ. Because of interactions between neighbouring charged particles, τ is no longer completely independent of v_2 at moderate concentrations of the second phase. There are also problems in applying the Maxwell–Wagner–Sillars model to systems in which ε_1 or ε_2 are frequency-dependent, as they are at certain stages of curing in epoxy resin blends. Nevertheless, the equations given above provide a satisfactory basis for the present discussion.

The principle of Kranbuehl's analysis[9] is that conduction initially dominates the dielectric behaviour of curing resins, especially in the low-frequency region, but decreases in isothermal experiments by about four orders of magnitude between 0 and 50% conversion, at which stage dipolar relaxations are the main feature of the spectra. This change is characterized by plots of $\varepsilon\varepsilon''\omega$ against cure time for frequencies in the range 50 Hz to 1 MHz. From equation (4):

$$\varepsilon\varepsilon''\omega = \varepsilon\varepsilon''_{\mathrm{d}}\omega + \sigma \tag{12}$$

Hence $\varepsilon\varepsilon''\omega$ is independent of frequency when conduction effects predominate. Reductions in σ on curing reflect the increasing viscosity of the resin, and the data can be used to determine whether the system is still sufficiently fluid to flow in a processing operation. When σ is small, dipolar loss peaks can be observed in the frequency plane. These show an increase in relaxation time during cure.

Electronic, dipolar and conduction effects provide the background against which interfacial polarization is seen in phase-separating blends.

RESULTS AND DISCUSSION

Figure 1 presents results from a range of tests on the neat resin–hardener mixture at a nominal curing temperature of 80°C. The thermocouple readings show that conditions in the dielectric cell are not quite isothermal: the temperature drops to 64°C when the mixture is poured into the mould, and subsequently rises to 88°C as a result of the exotherm, before finally coming to thermal equilibrium with the oven. Also included in *Figure 1* are data on viscosity η, gel content, degree of conversion α and time to vitrification, which were obtained in separate experiments that offered better temperature control, either because the resin was sheared continuously or because smaller quantities were used. The degree of conversion was calculated from d.s.c. measurements of the total enthalpy of reaction, which show that cure is only about 80% complete at the end of an isothermal experiment at 80°C: the remaining 20% occurs during post-curing at 190°C. The enthalpy of reaction for the neat resin was 445 J g^{-1}. The time to vitrification shown in *Figure 1* was determined from T_g measurements in d.s.c. experiments on partly cured resins. Gel time t_{gel} is defined as stated in the 'Experimental' section, by extrapolating the first set of non-zero readings for insoluble gel back to the abscissa.

Dielectric data from the same experiment on the neat resin at 80°C are presented in *Figure 2a*. The curves obtained at frequencies of 100 and 10 000 Hz are very similar: ε' falls relatively slowly during the first 40 min of the cure, while the resin is still liquid, then decreases more rapidly over the following 15 min, as the gel content increases from 0 to 40%. Changes in permittivity cease after about 70 min, when the resin becomes glassy, giving a final value of $\varepsilon' \approx 4.5$ at both frequencies for this stage of cure. Post-cure causes a further decrease in permittivity to 4.1.

At high frequencies, blends containing 15 phr of CTBN exhibit similar dielectric behaviour to that observed under the same test conditions in the neat resin. However, in the lower frequency range, the blends show very different and unusual behaviour, as illustrated in *Figure 2b*. At a certain point in the cure, typically after about 30 min in experiments at 80°C, ε' rises rapidly, reaches a maximum, then falls to a value well above that of the neat resin: towards the end of the curing experiment, the difference between the permittivity readings for 100 Hz and 10 kHz is $\approx$2.5 units. Significantly, the rapid rise in the 100 Hz ε' curve coincides with phase separation,

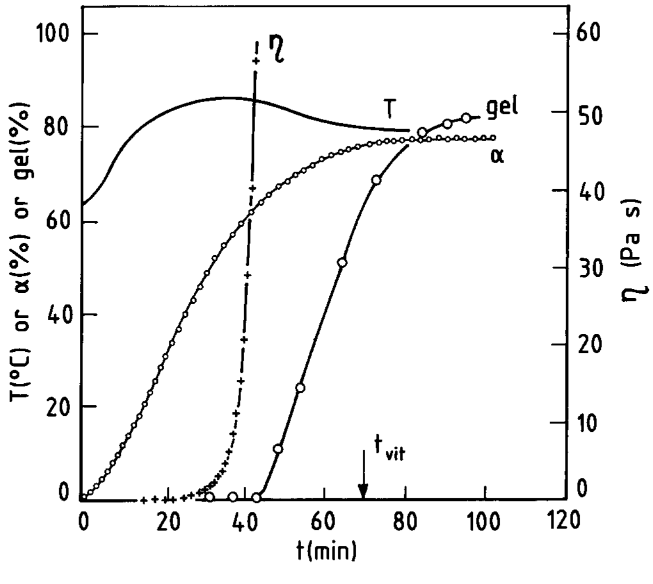

Figure 1 Variation in temperature T of the dielectric sample cell during cure of the neat resin at an oven temperature of 80°C, compared with conversion α, gel fraction and viscosity η for the same system, also at a nominal cure temperature of 80°C. The cure time, t_{vit}, to reach T_g was obtained from a d.s.c. curve

which is marked by the sharp decrease in light transmission.

A more comprehensive picture of the effects of blending on dielectric behaviour is given in *Figures 3* and *4*, which show how dielectric permittivity ε' and loss ε'' vary with cure time t at 80°C, over a range of frequencies f. The key features in the dielectric spectra of the blend are the high initial values of ε' and ε'' at low frequencies, and the appearance of a prominent additional relaxation after about 40 min curing, as already noted in *Figure 2b*. From the position of the ε'' peak at ≈ 300 Hz, the relaxation time τ ($= 1/2\pi f$) is estimated to be 0.5 ms.

The high initial values of ε' and ε'' are characteristic of polar liquids, in which conduction due to trace impurities combined with blocking of charge transfer at the electrodes leads to development of space charges and a high dielectric loss at low frequencies. Equation (4) predicts that in the low-frequency region $\log \varepsilon''$ should be linear with $\log f$, with a slope of -1, during this initial stage of the reaction, when $\varepsilon'' \approx \varepsilon''_c$. Data presented in *Figures 3* and *4* confirm this prediction. However, as the cure proceeds and viscosity increases, dipolar relaxations

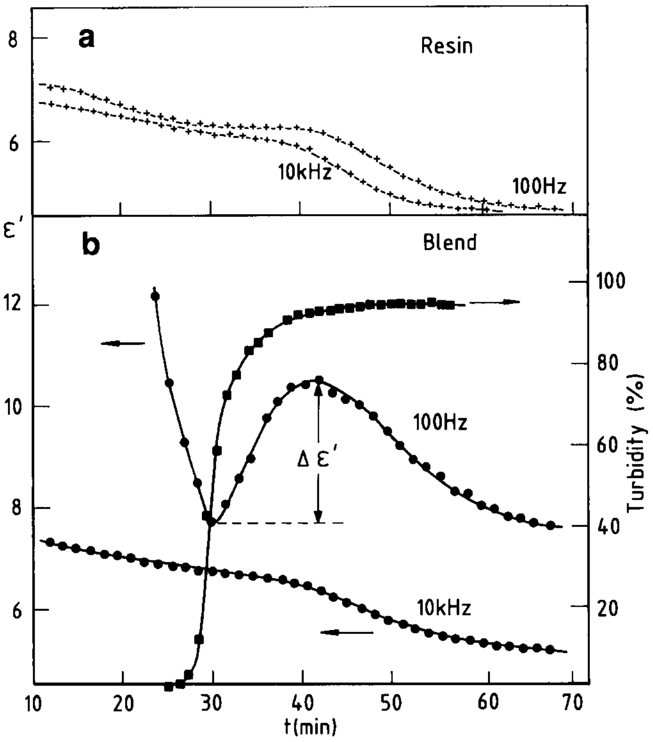

Figure 2 Effects of cure time t on relative permittivity ε' at high and low frequencies in: (a) neat resin, and (b) blend containing 15 wt% CTBN. Cure temperature = 80°C. In the blend, there is a jump $\Delta\varepsilon'$ in the low-frequency curve which coincides with phase separation, as indicated by turbidity

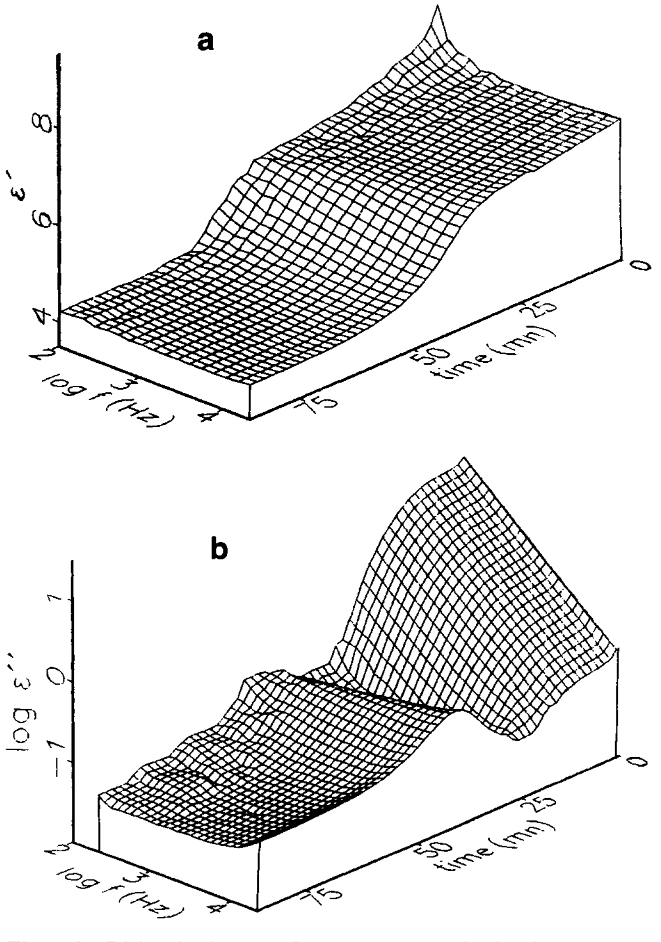

Figure 3 Dielectric data on the neat epoxy resin–hardener system cured at 80°C. Plots of: (a) relative permittivity ε', and (b) dielectric loss ε'', against frequency f and cure time t

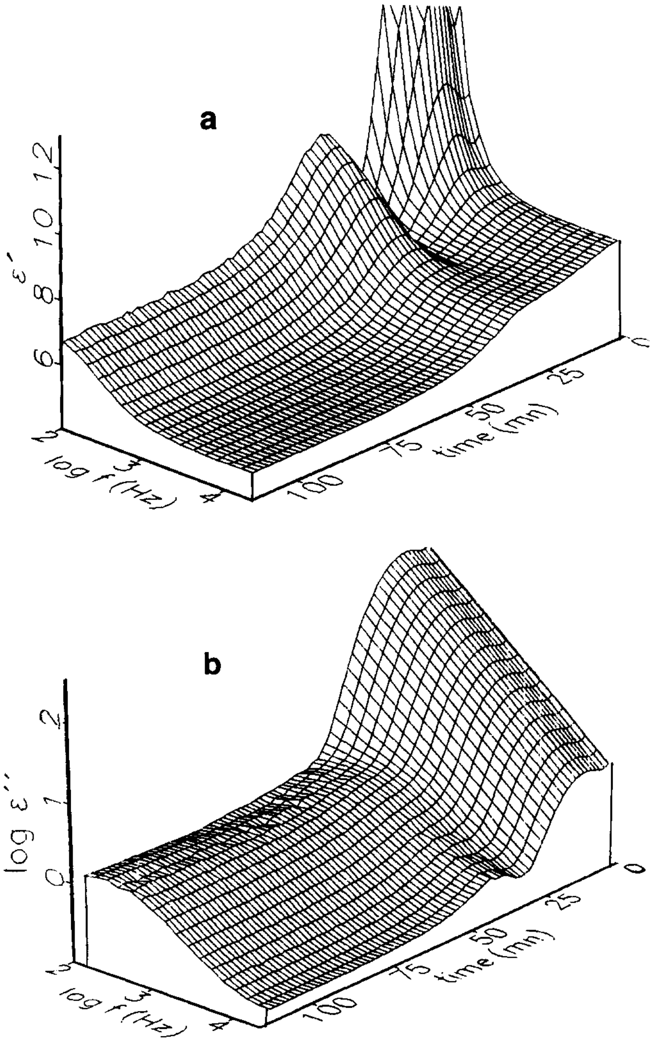

Figure 4 Dielectric data on the blend of epoxy resin and hardener with 15 wt% CTBN rubber, cured at 80°C. Plots of: (a) relative permittivity ε', and (b) dielectric loss ε'', against frequency and cure time. Sample contains highest concentration of adventitious mobile ions (see *Figure 5*). Note that scales for ε' and ε'' are different from *Figure 3*

begin to make a significant contribution to ε'', and $-\mathrm{d}\log\varepsilon''/\mathrm{d}\log f$ falls towards zero.

Because of the dominance of conductance effects, it is not possible to determine whether there are any loss peaks at low frequencies and short cure times. The data show no evidence of loss processes at higher frequencies, although the remnant level of ε' indicates that one or more dipolar relaxations must occur in the liquid resin at frequencies above 20 kHz. Addition of 15% CTBN rubber greatly increases the initial value of ε''. It must therefore be concluded that mixing with CTBN introduces extra charge carriers, which are almost certainly ionic.

The most striking and novel feature of the dielectric data is the large peak that develops in the low-frequency curves of ε' against cure time. Such an increase in permittivity is most unusual, and implies an increase in polarizability during cure, which must be due to a new relaxation process. In the absence of rubber, the permittivity of the resin decreases continuously with cure time, as increasing viscosity, crosslinking and vitrification reduce molecular mobility. The obvious conclusion is that the peak is due to inferfacial polarization resulting from phase separation. This view is supported by the light transmission data given in *Figure 2*, which show that phase separation occurs over the same interval of cure time as the rise in permittivity.

The necessary condition for interfacial polarization is that certain regions of the sample have higher conductivity than others. It can occur in the absence of phase separation, for example in polymeric systems when one ion is less mobile than its counterion in regions of higher crosslink density. However, in the present case it is quite clearly the result of phase separation. The charge carriers, which are almost certainly ionic, as in the previous single-phase stage of reaction, are much more mobile in the newly formed CTBN phase than they are in the partly cured resin, and therefore become trapped at the phase boundaries.

The curing experiment on a blend containing 15 wt% of CTBN was performed ten times under identical conditions. A generally similar pattern of behaviour was observed in each case, but there were major variations in initial conductivity, and corresponding variations in relaxation time τ at the end of the cure, in accordance with equations (6) and (9). The peak in ε'' occurred at lower frequencies as the initial conductivity of the blend decreased, and in one case σ was so low that no peak appeared within the frequency range of the experiment. One consequence of the variation in τ is that for certain test frequencies, $\Delta\varepsilon'$, the permittivity jump during phase separation (see *Figure 2*), becomes linear with σ_{cp}, the conductivity at the cloud point, as shown in *Figure 5*. As the curing reaction is being carried out under identical conditions in this series of experiments, the viscosity of the resin blend immediately before phase separation must be approximately the same in each case. Since the nature of the carriers is unlikely to change, it therefore follows that the observed values of σ_{cp} are proportional to the concentration of ionic carriers. The data given in *Figures 2b* and *4* refer to the blend sample with the highest σ_{cp} ($\approx 400\ \mathrm{nS\,m^{-1}}$) and shortest relaxation time ($\tau \approx 0.5$ ms). At the other extreme are samples with $\sigma_{\mathrm{cp}} \approx 60\ \mathrm{nS\,m^{-1}}$. On the assumption that σ_2 is proportional to σ_{cp}, equation (6) predicts that the longest relaxation time for the interfacial polarization process at 80°C should be about 4 ms, which is consistent with the data.

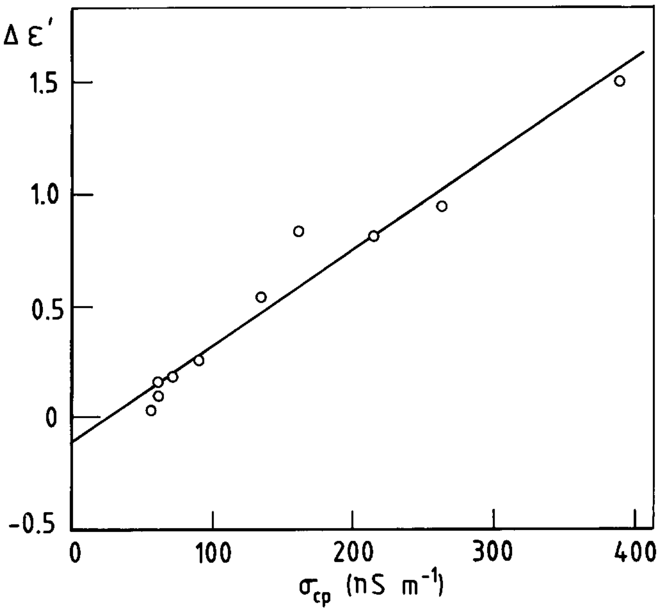

Figure 5 Relationship between σ_{cp}, the conductivity at the cloud point, and $\Delta\varepsilon'$, the jump in relative permittivity at 270 Hz during phase separation, as defined in *Figure 2*. Data for a series of blends containing 15% CTBN but differing in trace impurity content

The identities of the mobile ions, and the reasons for the variations in conductivity, have not been determined with any certainty. However, it was noted that conductivity was a function of the time allowed for degassing the resin–ETBN mixture under vacuum at 80°C before adding the hardener. Accordingly, conductivity measurements were made over 16 h at 80°C under vacuum on a resin solution containing 20 wt% rubber (added as ETBN), without hardener. This solution was the standard starting point for blend experiments, since it gives a final concentration of 15 wt% when the stoichiometric amount of hardener is added. Heating under vacuum was used to eliminate trapped air from all blend samples. The measurements showed that σ increased by a factor of 2 over the first 2 h, and then decreased slowly to its original value during the following 14 h. Water might be involved in these effects, since similar changes do not occur in the open atmosphere.

In a second experiment on the same resin–ETBN blend composition, conductivity measurements were made over the temperature range 40–140°C. The results are presented in *Figure 6*. It was found that σ was essentially independent of frequency over the range of frequencies and temperatures studied. The linearity of the Arrhenius plot confirms that conduction is an activated process, with an activation energy of 64 kJ mol^{-1}. The nature of the activated process is made clear by comparing the conductivity curve with a plot of $\log(\eta^{-1})$ against $1000/T$, which gives an activation energy of 56 kJ mol^{-1}. The agreement is sufficiently good to indicate that there is little, if any, increase in the number of mobile charges with temperature, and that the increase in conductivity is due essentially to the reduction in viscosity of the resin. Similar results on the viscosity of this system have been recorded by Verchère *et al.*[15].

Cole–Cole plots presented in *Figure 7* emphasize the change in dielectric behaviour brought about through

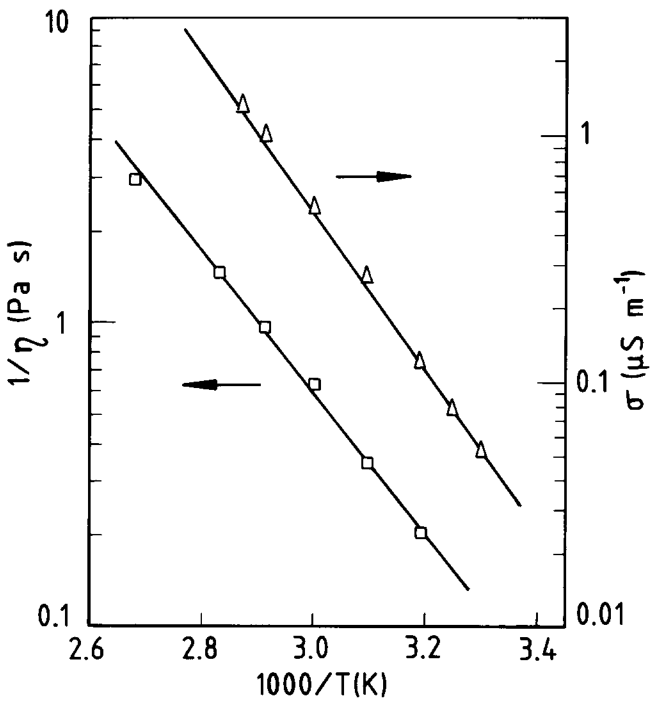

Figure 6 Arrhenius plot of reciprocal viscosity η^{-1} and conductivity σ against reciprocal temperature T^{-1} for blend containing epoxy resin and 20 wt% CTBN rubber with no hardener

curing and phase separation in the CTBN blends. The data are taken from the experiment represented in *Figure 4*, for which $\tau = 0.5$ ms at the end of the curing run, and $\sigma_{cp} = 380$ nS m^{-1}. At the beginning of the reaction, ionic conduction dominates, with the result that blocked charge accumulates at the electrodes, and ε' increases as frequency falls, as predicted by equation (5). However, the more important effect of conduction is to raise ε'', which reaches very high values at low frequencies, following equation (4). Consequently, the Cole–Cole curve is almost vertical.

A very different relationship is seen at the end of the cure cycle, when the resin phase is glassy and therefore has a very low conductivity, so that the higher conductivity of the dispersed CTBN phase causes interfacial polarization. The Cole–Cole plot then approximates to the semicircular shape characteristic of a simple Debye relaxation. The intercepts with the abscissa define values of $\varepsilon_\infty = 4.9$ and $\varepsilon_0 = 7.7$. Taking $\varepsilon_1 = 4.5$ for the resin at this stage of the reaction (cf. *Figure 2a*), the value obtained for ε_0 is in excellent agreement with the predictions of equation (10) for this blend, which had a measured $v_2 = 0.19$ from image analysis of scanning electron micrographs. Using the above values of ε_1, ε_∞ and v_2 in equation (11) then gives $\varepsilon_2 = 7.0$ for the CTBN phase at this stage of reaction, before post-cure. Finally, with $\tau = 0.5$ ms, equation (9) gives $\sigma_2 = 280$ nS m^{-1}, which is $\approx 0.75\sigma_{cp}$ for this blend. In a separate test at 80°C, the neat liquid CTBN rubber gave a conductance of 1640 nS m^{-1}. However, a direct comparison is difficult because there are almost certainly differences in ion concentration between the neat CTBN and the blend. In effect, the resin acts as a diluent for the ions.

Prominent interfacial polarization effects in CTBN blends tend to obscure the other changes taking place in dielectric behaviour as a result of gelation and vitrification in the resin phase. These changes are most clearly observed in the neat resin and in blends containing a low concentration of ions. The first sign of gelation is a sharp decrease in $d\varepsilon'/dt$, where t = cure time. As illustrated in *Figure 8* for the case of the neat resin, this change in slope correlates with the steep increase in viscosity that immediately precedes gelation. These data indicate that measurement of $d\varepsilon'/dt$ at a chosen fixed frequency may be useful for controlling the curing process, since it appears to be a good predictor of the gel point.

Shortly after gelation, both the neat resin and the blend exhibit a major dielectric loss peak, which enters from the high-frequency end of the spectrum, and shifts to lower frequencies as the cure proceeds, as illustrated in *Figure 9*, and previously in *Figures 3* and *4*. This process

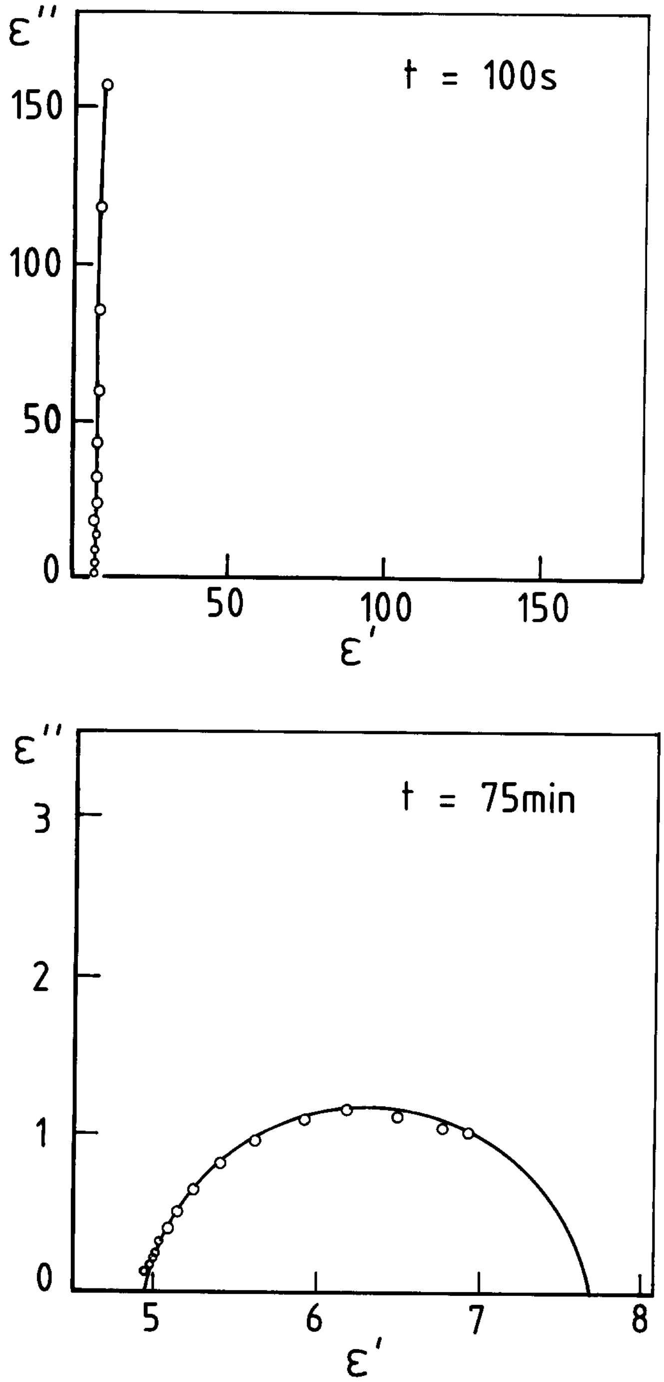

Figure 7 Cole–Cole plots for blend containing 15 wt% CTBN cured at 80°C. Cure times t as indicated

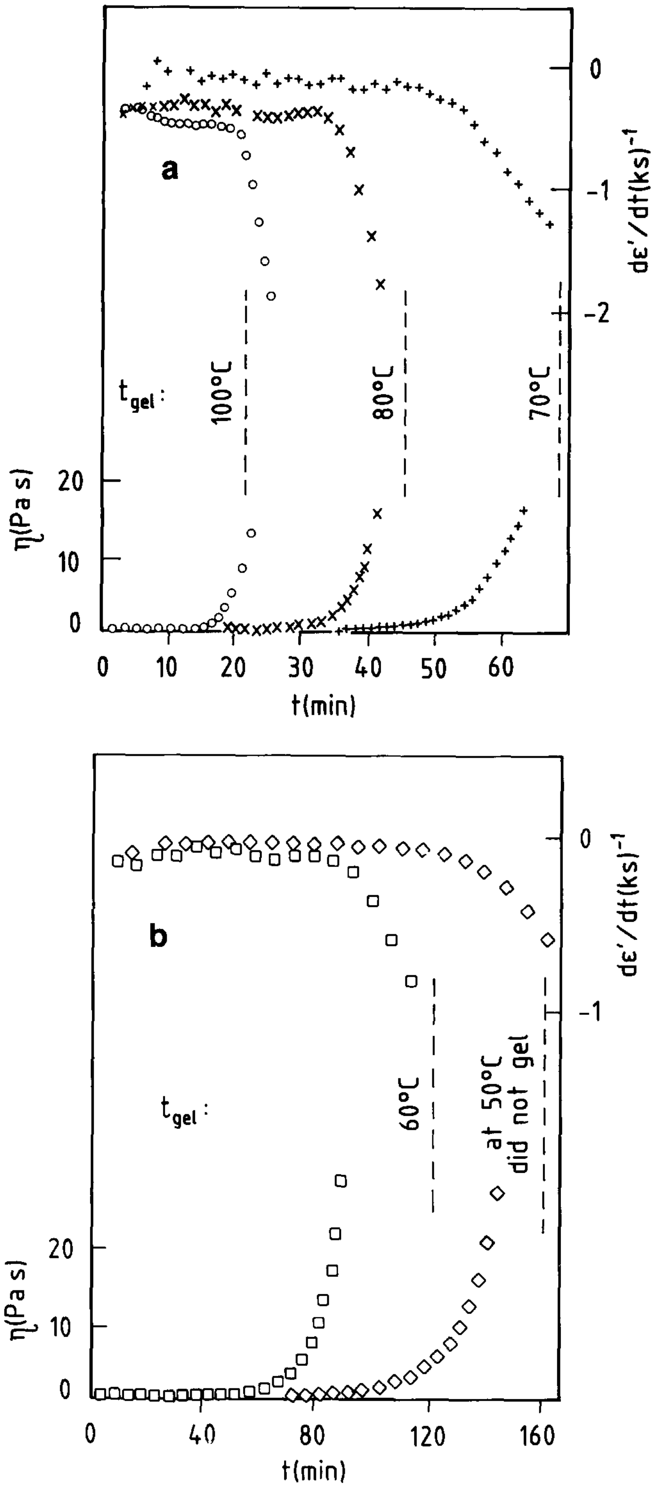

Figure 8 Comparison of viscosity η for the neat resin at 100 s^{-1} during cure with the corresponding rate of change of permittivity dε'/dt at 10 kHz over two temperature ranges: (a) 100 to 70°C, and (b) 60 to 50°C. The gel times specified for each temperature were determined by solvent extraction

has its origins in micro-Brownian motion of the chain. During the early stages of reaction it occurs at frequencies well above 20 kHz, beyond the scope of the equipment used in the present study. Restrictions upon these responses of the free chain, as the resin begins to cure and interactions and entanglements between neighbouring chains become significant, are the principal cause of the drop in the high-frequency values of ε' at the onset of gelation.

Figure 10 shows the relationship between f_{max}, the frequency of the observed dielectric loss maximum, and cure time for four cases: neat resin cured at 70, 80 and 100°C, and a CTBN blend cured at 80°C. The α peak occurs at a later stage in the blend because overall reaction rates are reduced slightly on addition of 15%

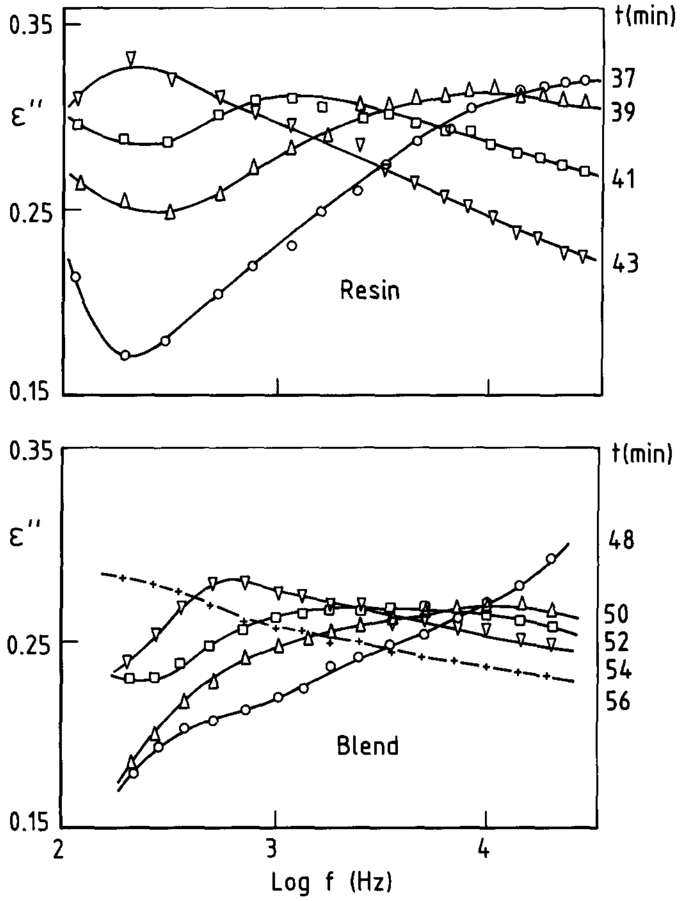

Figure 9 Shift in the α transition during cure at 80°C in the neat resin and in a blend containing 15% CTBN. Curves show frequency dependence of dielectric loss ε'' at cure times indicated

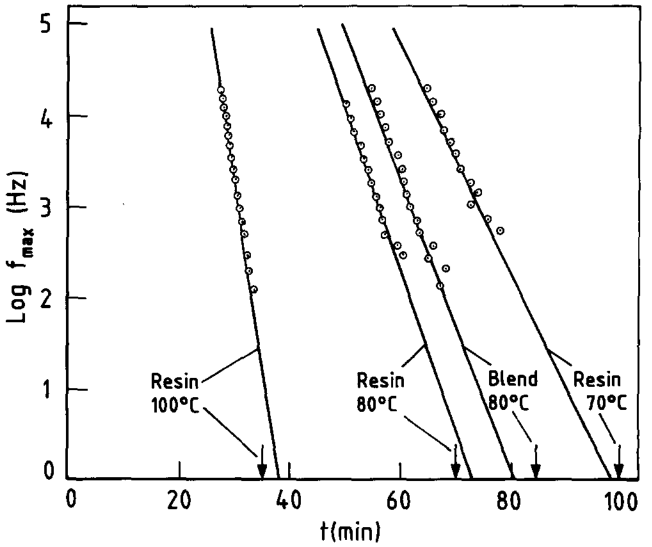

Figure 10 Effects of increasing cure time t on f_{max}, the frequency of the dielectric loss maximum in neat resin cured at 70, 80 and 100°C, and in a 15% CTBN blend cured at 80°C. The arrows indicate vitrification times obtained from d.s.c. experiments, including one value for the blend from ref. 15

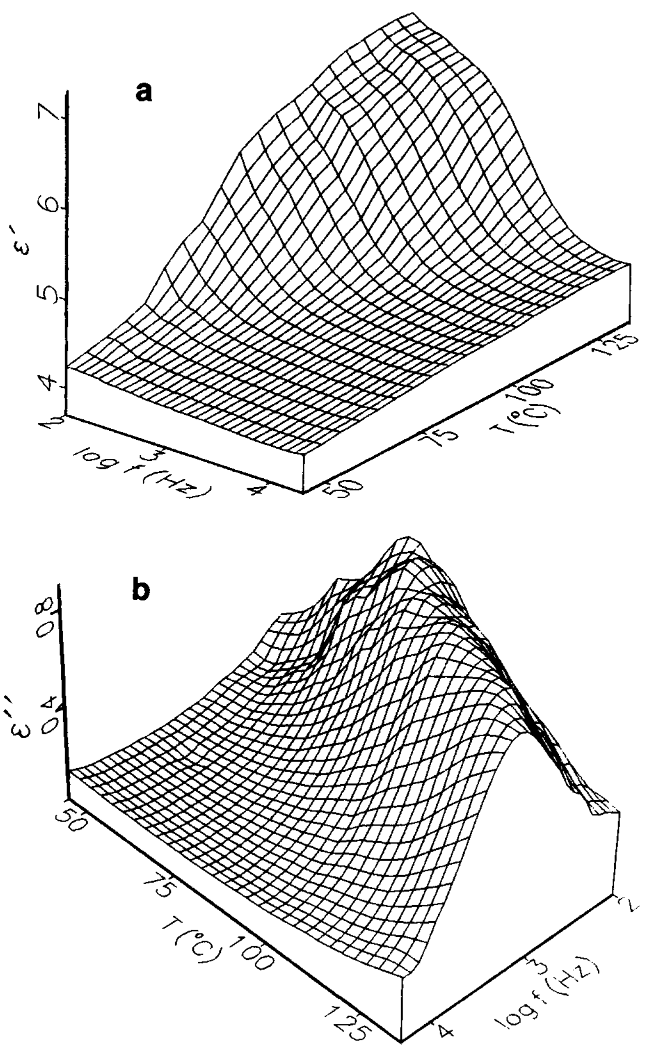

Figure 11 Temperature and frequency maps of relative permittivity and dielectric loss for fully cured blend containing 15% CTBN, over the temperature range 40–140°C

CTBN[15]. Extrapolation of these curves to $f_{max} = 1$ Hz provides an estimate, albeit somewhat arbitrary, of the times at which the resins reach vitrification. These times are compared in *Figure 10* with cure times at which vitrification is observed in independent d.s.c. experiments. The estimated and measured vitrification times are in reasonably satisfactory agreement.

Electron microscopy of blends cured at 80°C reveals that the CTBN forms particles approximately 0.5 μm in diameter, within the range previously reported for this system by Verchère *et al.*[15]. Particle sizes are governed by the viscosity of the solution during phase separation[15,16], which in the present case was ≈ 10 Pa s. As stated earlier, the volume fraction of the CTBN-rich phase was ≈ 0.19. The rubber phase of the post-cured blend had a dynamic mechanical loss peak at −45°C, about 10°C above the T_g of unreacted CTBN, while the principal resin loss peak occurs at 173°C. The corresponding peak for the neat resin is at 192°C. This shift in the T_g of the resin has been related to incomplete phase separation[14].

Dielectric data on the cured blend are presented in *Figure 11*. They show a shift in the interfacial polarization peak to higher frequencies with increasing temperature, reflecting the higher ionic mobility in the rubber phase. As shown in equation (9), the Maxwell–Wagner–Sillars theory predicts a decrease in relaxation time with increasing conductivity of the second phase. An Arrhenius plot of data from *Figure 11* gives an activation energy of 50 kJ mol^{-1} for the relaxation.

The high-frequency relative permittivity of the blend, measured at the Cole–Cole limit at 80°C, is 4.9 at the end of the isothermal run, and falls further, to 4.5, on post-curing. Atomic and electronic relaxations account for a maximum probable contribution to ε' of ≈ 3.0, as already noted. The remainder must be attributed to dipolar relaxations at frequencies above 20 kHz, perhaps associated with rotations of hydroxy side-groups in the resin, and nitrile groups in the rubber.

CONCLUSIONS

This work has shown that, in addition to monitoring viscosity changes and vitrification in epoxy resins, dielectric methods can be used to follow phase separation in blends of the resin with a soluble rubber. The key observation is that, as the second phase forms, a strong interfacial relaxation appears in the low-frequency region of the dielectric spectrum. The relaxation time is dependent upon the concentration of ionic impurities.

The significance of these observations is that a single monitoring technique can follow all of the major changes taking place in the resin during cure: (a) viscosity increases in the liquid resin; (b) phase separation; (c) onset of gelation; and (d) vitrification. Previous authors[1–11] have discussed the applicability of the technique in controlling processing of fibre composites based either on unmodified resins or on blends in which the effects of phase separation were not apparent in the dielectric spectra. The present study extends the principle to blends containing elastomers, which produce marked changes in dielectric behaviour. Where it is possible to measure turbidity, the main advantage of using a dielectric method is the convenience in monitoring the signal, with the associated possibility of using dielectric data as a basis for automation of process control. Where, on the other hand, it is difficult or impossible to measure turbidity, dielectric monitoring provides a valuable alternative. The rate of change of permittivity, $d\varepsilon'/dt$, appears to be a good indicator of imminent gelation.

It should be recognized that a high concentration of mobile ions, giving strong interfacial polarization effects in a phase-separating system, can obscure other features of the dielectric signal, especially at frequencies below 1 kHz, and may thereby limit the usefulness of the dielectric monitoring technique under some circumstances.

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