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REAL TIME DIELECTRIC INVESTIGATIONS OF PHASE SEPARATION AND CURE IN RUBBER MODIFIED EPOXY RESIN SYSTEMS

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Abstract—Real time dielectric and rheological measurements are reported for mixtures of carboxyl-terminated butadiene acrylonitrile in epoxy resins obtained by curing either with diaminodiphelmethane at 80° or triethylenetetramine at 30° with the diglycidylether of bisphenol-A. A good correlation is observed between the time required for gelation determined by the two methods. The mixture is initially homogeneous but soon undergoes phase separation. The occurrence of phase separation is marked by the appearance of a new dielectric feature which is ascribed to the motion of ionic charges in the conducting occluded rubbery phase. This is the *first* time that the dielectric technique has been used as a real time monitor of phase separation processes.

INTRODUCTION

The dielectric technique has in recent years come to a new pre-eminence with its application to the problem of *in situ* monitoring of the cure of polar thermosetting resins [1–6]. Observation of the changes in the dielectric constant and loss can be correlated with the micro-rheology and allows optimization of the cure in composite structures [5, 6]. Incorporation of thermoplastic polymers as a means of toughening of epoxy resins used in structural composite applications [7–10]. Toughening mechanisms in these materials have been extensively investigated [7–9] and structure–property relationships developed. However, these relationships are still at a very empirical level and rely upon understanding of the relationships between chemical and physical structures and mechanical properties. It is generally accepted that the main toughening mechanism involves the formation and growth of plastic shear bands in the matrix resin and cavitation inside the rubber particles [11–13]. Rubber bridging is also accepted as a toughening mechanism, though it is only of relatively minor importance [12]. The possibility of phase separation in carboxyl-terminated butadiene/acetylonitrile (CTNB) modified epoxy resins has been previously recognized [14–16] and shown to influence the mechanical properties of the finally cured materials. The advent of real time dielectric facilities makes it appropriate to re-examine the properties of these systems. In this study, CTBN modified resins obtained by curing the diglycidylether of bisphenol-A (DGEBA) with either diaminodiphelmethane (DDM) or triethylenetetramine (TETA) are discussed.

EXPERIMENTAL PROCEDURES

Materials

The epoxy resin used in this study was DGEBA, supplied by Shell Co. {Epon 828}, $\bar{M}_n \simeq 380$ g/mol. The epoxy resin was cured with either 4,4′-diaminodiphenylmethane (DDM) (Ciba Geigy, U.K.) or TETA (British Drug Houses, Poole, Dorset). The rubber modifier, carboxyl-terminated butadiene/acrylonitrile copolymer (Hycar CTBN 1300 × 15) was obtained from B. F. Goodrich Co., U.S.A.

Sample preparation

DGEBA was mixed with CTBN in a glass vessel to give the required formulation the curing agent, either DDM or TETA, was added in stoichiometric amount. The mixture was placed in a preheated oil bath to lower the viscosity and aid mixing, which was achieved by stirring until a clear fluid was obtained. The conditions used for mixing are shown in Table 1. The mixture was degassed in a vacuum oven to remove trapped air. Curing of the mixtures were either performed in specially designed cells for the dielectric and rheological measurements, or moulded in glass containers. The latter moulds consisted of glass plates (6 cm × 6 cm) separated by resin-coated glass laminate of the required thickness. The glass was cleaned with acetone and water and then dried. The surface was then treated with release agent (Rocal MRS Advanced Non-Silicone Dry Film Spray). The plates were held together by toolmaker's parallel clamps and preheated to the required curing temperature and filled with resin by capillary action. Curing was carried out in an oven for the required period, Table 2. Samples were machined from these cured plaques.

Rheological measurements

The viscosities of the mixtures were determined during the curing process using a Strathclyde Curometer [17]. The apparatus was calibrated using both the temperature dependence of a glass-forming oligomeric poly(phenyleneoxide), SANTOVAC 5 and also a series of silicone oils of various viscosities.

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Table 1. Conditions used in mixing the components

Curing agent	Temperature	Mixing time (min)
TETA	Ambient	3
DDM	80°	10

Real time dielectric measurements

Dielectric measurements were performed using a Solatron 1250 Frequency Response Analyser (FRA) configured as indicated previously [18]. Data were collected between 10^{-1} and 6.3×10^4 Hz in a period of less than 3 min. The system was programmed to store successive sets of data and allowed real time examination of the cure process for all the mixtures. A cell was designed consisting of two pre-etched Cu electrodes mounted on an epoxy glass fibre base. This design generates a three electrode system with an active electrode area of 1 cm^2 and was placed in an Oxford Instruments cryostat (DN1704). The space between the electrodes was maintained constant with a Cu spacer and the electrodes and spacer were soldered together to form a seal around three edges. The resin to be studied was injected as a liquid into the cell, capillary action ensuring the cell was completely filled. The electrodes were in good thermal contact with a Cu block, used to maintain the temperature of the sample at that required for the isothermal cure studies.

RESULTS AND DISCUSSION

Rheological measurements

The cure of the DGEBA/DDM system was investigated using the Strathclyde Curometer as a function of isothermal cure temperature over the range 100–150°, Fig. 1(a). Increasing the cure temperature produces the expected decrease in the curve time. From the measurement of the in-phase and quadrature components of the signal, it is possible to calculate the viscosity profiles and, using the criterion that gelation can be ascribed to a value of *ca* 10^4 Pas, it is possible to determine the variation of the gel time with temperature and hence, assuming a simple Arrhenius type of law, an apparent activation energy. A value of 73 kJ/mol was obtained for the pure system, consistent with other related observations on this system [19]. The main interest in performing this study was to determine a suitable temperature at which to study the cure using the dielectric technique. It is essential that the period before gelation should be sufficient for the collection time used in the experiments to appear to be *instantaneous*. The collection time is *ca* 180 sec, and therefore 5600 sec is a reasonable approximation to this criterion. A second curometer study was performed, Fig. 1(b), in which the concentration of the rubber modifier, CTBN, was varied. Increasing the amount of CTBN in the system leads to progressive shortening of the cure time, Fig. 1(c), and even at 22.6 wt% CTBN the gelation time is *ca* 2400 sec which retains the validity of the approximation used in the dielectric measurements. The gelation time would be expected to decrease with addition of CTBN, there being a smaller volume of material necessary to cure, however these curves do not indicate that there is any abnormality in the rheological changes occurring as a consequence of the presence of CTBN. The

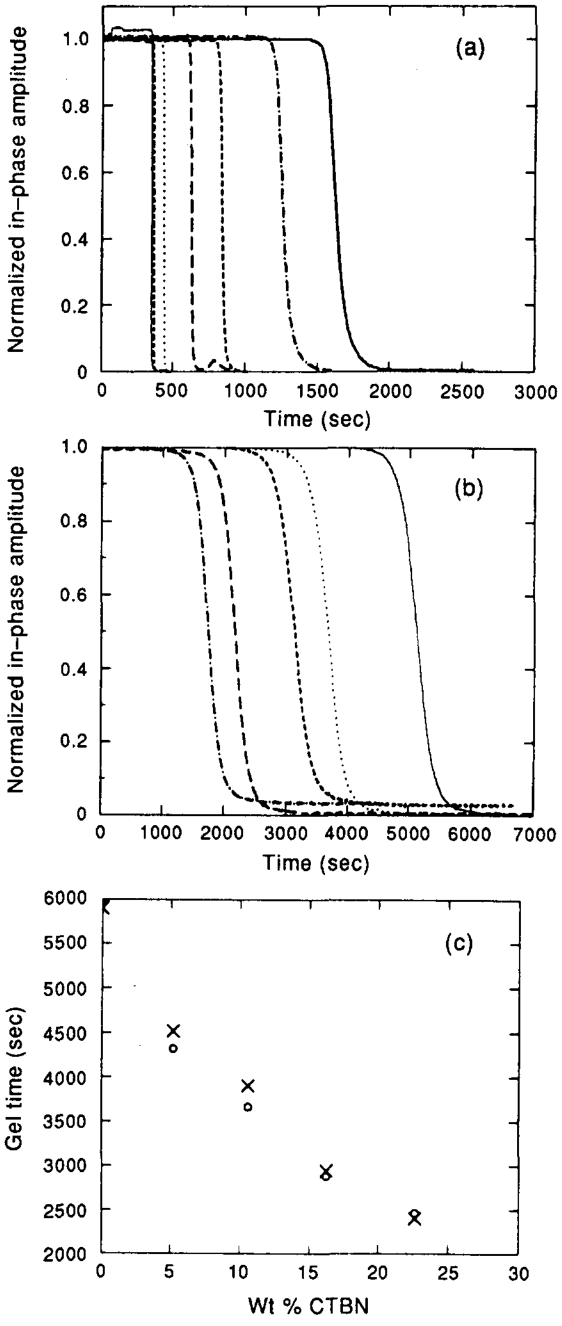

Fig. 1. Rheological studies of cure in DGEBA/DDM/CTBN resins: (a) time amplitude curves at: ——, 150°; —·—·—, 140°; ······, 130°; ———, 120°; --------, 110°; —·—·—, 105°; ——, 100°. (b) Effect of CTBN concentration on cure at 80°: ——, 0 wt%; ······, 5.2 wt%; ———, 10.5 wt%; ————, 16.2 wt%; —·—·—, 22.6 wt%. (c) Gelation time vs CTBN content (wt%). ×, Rheological; ○, dielectric.

Table 2. Curing conditions for resin systems

Resin	Curing agent (phr)	Cure schedule
DGEBA (Epon 828)	TETE (20)	2 hr at 60°
DGEBA (Epon 828)	DDM (HT972) (29.1)	30 min at 100° and 3 hr at 180°

DGEBA/TETA system undergoes cure at ambient temperatures and will rapidly exotherm if heated; therefore it was not possible to perform a temperature dependent study of the rheology on this system.

Real time dielectric measurements of cure

Application of dielectric measurements to the characterization of cure have been reported previously for pure epoxy resins [1–6, 20–23, 29]. In general, the data obtained were restricted to observation of frequencies above 10 Hz and usually focussed on the variation of the dielectric loss and constant at frequencies of the order of 1 kHz. The variations observed in this region are characteristic of the fluid system undergoing a change to a vitrified state and the main peak observed is that associated with the alpha relaxation i.e. the glass transition process of the epoxy resin. The dielectric facilities at Strathclyde allow real time investigation of the frequency range 10^{-1} to 10^5 Hz. This range is much broader than usually available and reveals the presence of important features which are located at lower frequencies [22, 23].

I. Studies of cure in DGEBA/TETA systems. The real time measurements of the cure in DGEBA/TETA were performed at 30°, Fig. 2. The initial high frequency independent value of the dielectric constant reflects the fact that the monomer dipoles are able to undergo facile rotational motion at frequencies *above* those used in this study. The spikes observed at very low frequency are an artefact of these measurements. The large, approximately $1/\omega$ dependence, of the dielectric loss reflects the initial high ionic conductivity of the mixture. As cure proceeds so the amplitude of this component decreases markedly and disappears at the point at which vitrification occurs. The marked drop in the dielectric constant at about 120 min and also the observation of a *peak* which moves to a lower frequency with increasing time, reflects the vitrification of the matrix. The peak corresponds to the main dipolar reorientation process, normally designated the alpha process, is associated with the glass transition at T_g. A small dispersion in the dielectric constant and loss located at around 10^4 Hz is associated with the rotational motion of the pendant OH group, generated as a consequence of the curing reaction. This type of behaviour is consistent with previous observations on this system [14–16].

Dielectric measurements were performed on resin systems containing CTBN with concentrations up to 22.6 wt%. Several significant changes were observed in the dielectric behaviour compared to the pure resin and are illustrated in the data for 16.2 wt% rubber, Fig. 3. The large peak observed initially at low frequency and short times is associated with blocking electrodes [24]. In the initial system, charges migrating to the electrodes cannot be discharged and a double layer is formed with an associated dielectric dispersion. As cure proceeds, this double layer will thicken ultimately to fill the cell and is marked by the disappearance of the low frequency dielectric feature [29]. The dielectric constant is observed to *increase* slightly, indicative of the generation of an additional dielectric relaxation contribution being formed in the system as the cure proceeds. As in the previous case of the pure resin, the dielectric constant will then fall as vitrification occurs in the system. The dielectric loss contains a component indicative of ionic conduction and obeying a $1/\omega$ relationship. The loss peak associated with the T_g process is not as clearly resolved but disappears into a *new* loss feature which emerges as the cure proceeds. It is well known that CTBN phase separates during the cure process [14–16], and the increase in the dielectric constant at around 30 min is indicative of the generation of heterogeneity in the curing matrix [24–27]. The CTBN which dissolves initially to form a homogeneous mixture, becomes incompatible as the molecular weight of the curing epoxy resin is increased. The resultant morphology conforms to a dispersion of conducting spheres in a non-conducting matrix: this is the classic Maxwell Wagner Sillers (MWS) type of model and will be discussed in detail in a subsequent paper [28]. It is interesting to note that the locus in the frequency–temperature plane of the loss peak associated with the MWS process moves to lower frequency as time proceeds. This would imply that changes are occurring within the occlusions which are influencing the conductivity after the vitrification of the epoxy resin continuum and the reason for these changes is not at present clear.

II. Studies of cure in DGEBA/DDM systems. An investigation similar to that carried out for the DGEBA/TETA system was performed for DGEBA/DDM, Fig. 4. Again, the dielectric traces reflect the initial formation of a blocking electrode system which disappears after about 60 min, a $1/\omega$ dependence of the dielectric loss associated with ionic conduction, and the marked drop in dielectric constant and loss with vitrification after about 80 min. Data were also obtained for a range of concentrations of CTBN; all followed the general trends found in Fig. 5 for the 16.2 wt% composition. The main difference between this system and that of TETA is that the MWS peak does not move with time after the vitrification process. The reason for the difference in behaviour for these systems is not yet clear.

COMPARISON OF RHEOLOGICAL AND DIELECTRIC BEHAVIOUR

In order to compare the rheological and dielectric data, it is important to choose a common time–frequency reference. This has to be that used for the rheological measurements, since in this system the frequency of measurement is fixed at 2 Hz. Inspection of the dielectric plots, Figs 2–5, allows the point at which the dielectric constant and loss become constant to be determined. Analysis of the dielectric and rheological data allows comparison of the values obtained for the *gelation* point in the system, Table 3 and Fig. 1(c). A close correspondence is observed between these data and those reported by other authors [1, 5]. The dielectric data also provide clear indication of the point at which phase separation occurs in this system, Table 3. The variation of the gelation time and point of phase separation with CTBN content both behave according to an equation of the form:

$$t = kV^{-n} \tag{1}$$

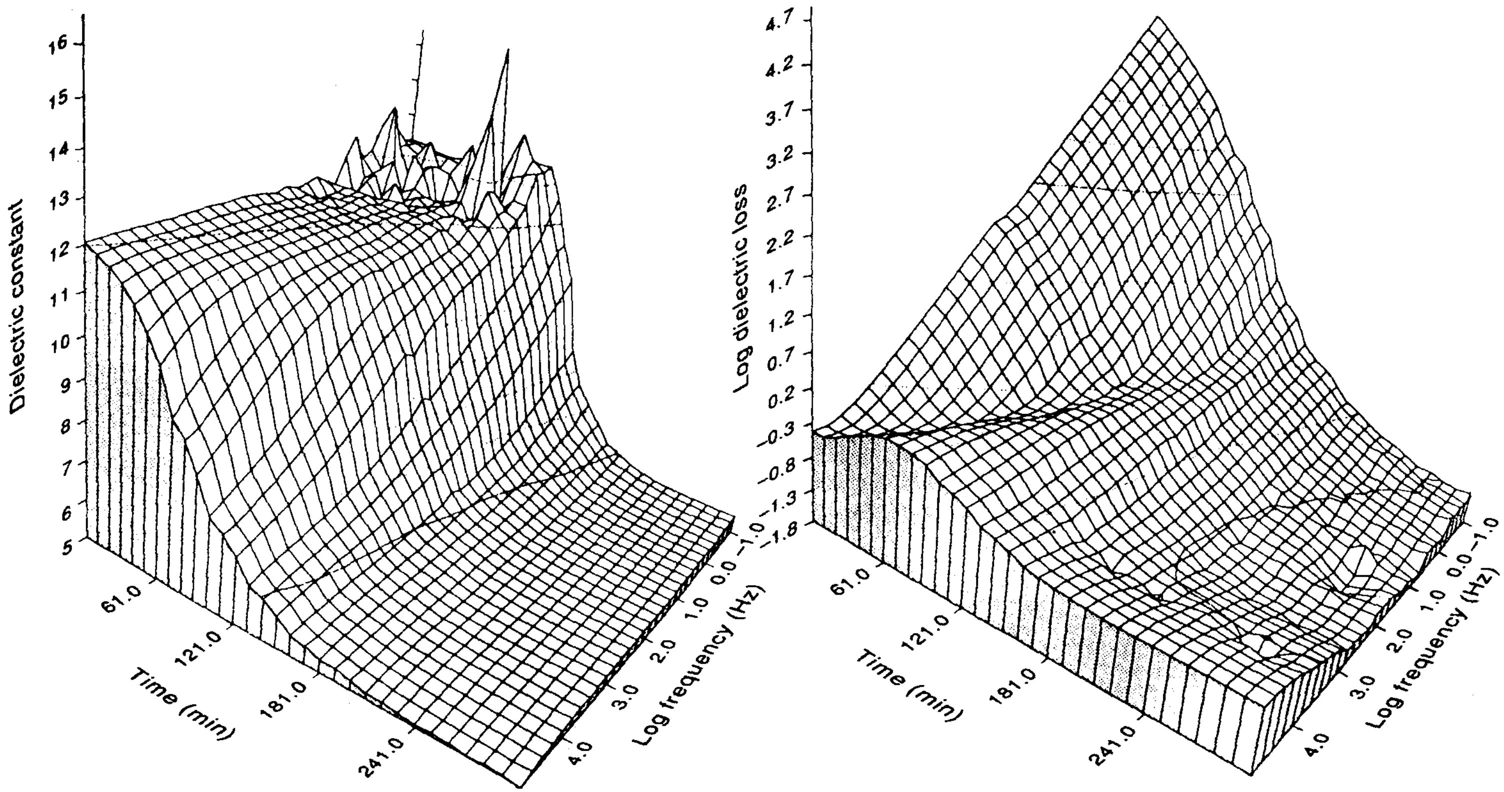

Fig. 2. Dielectric constant and loss for DGEBA/TETA cured at 30°.

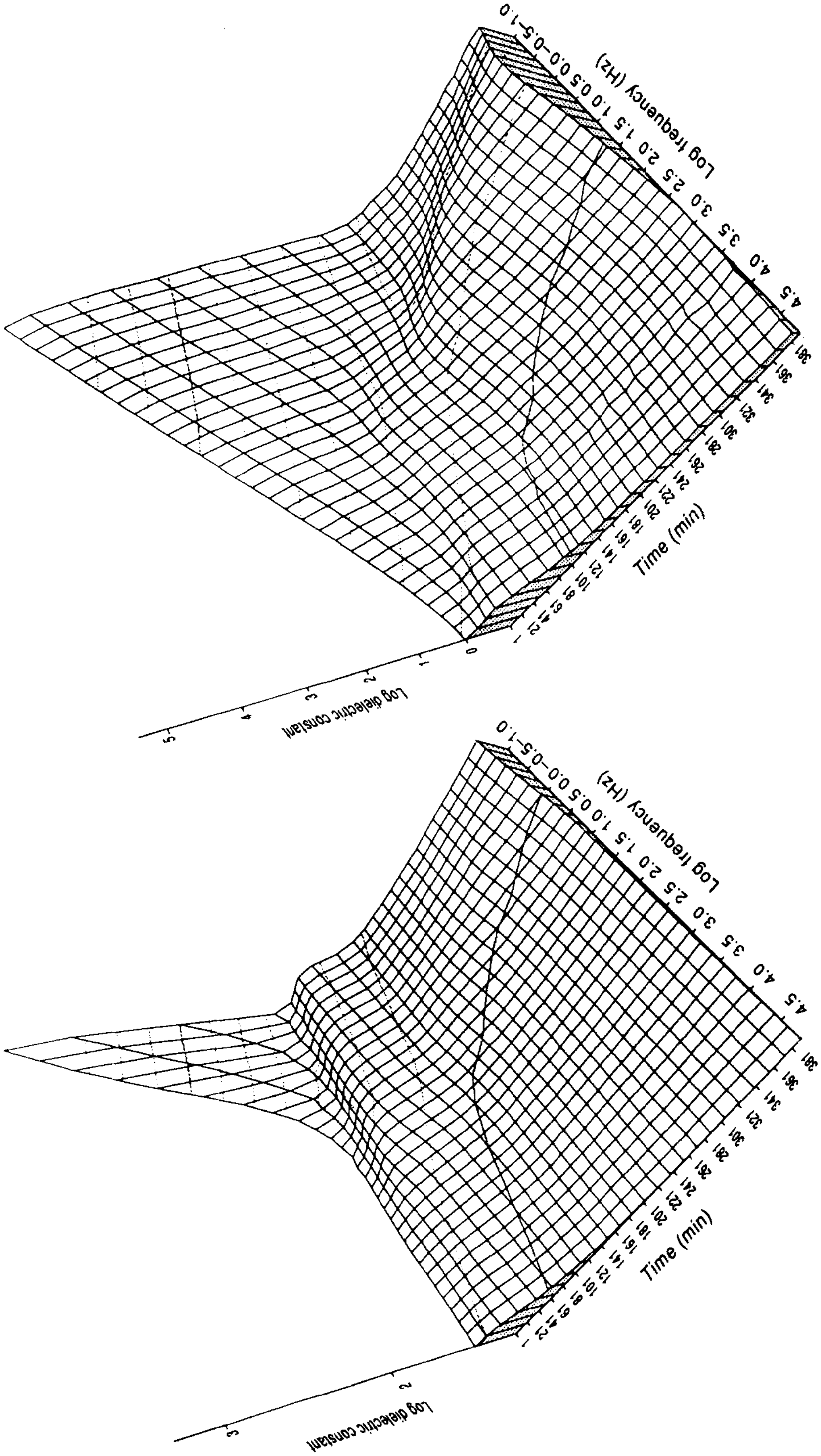

Fig. 3. Dielectric constant and loss for DGEBA/TETA/16.2 wt% CTBN cured at 30°.

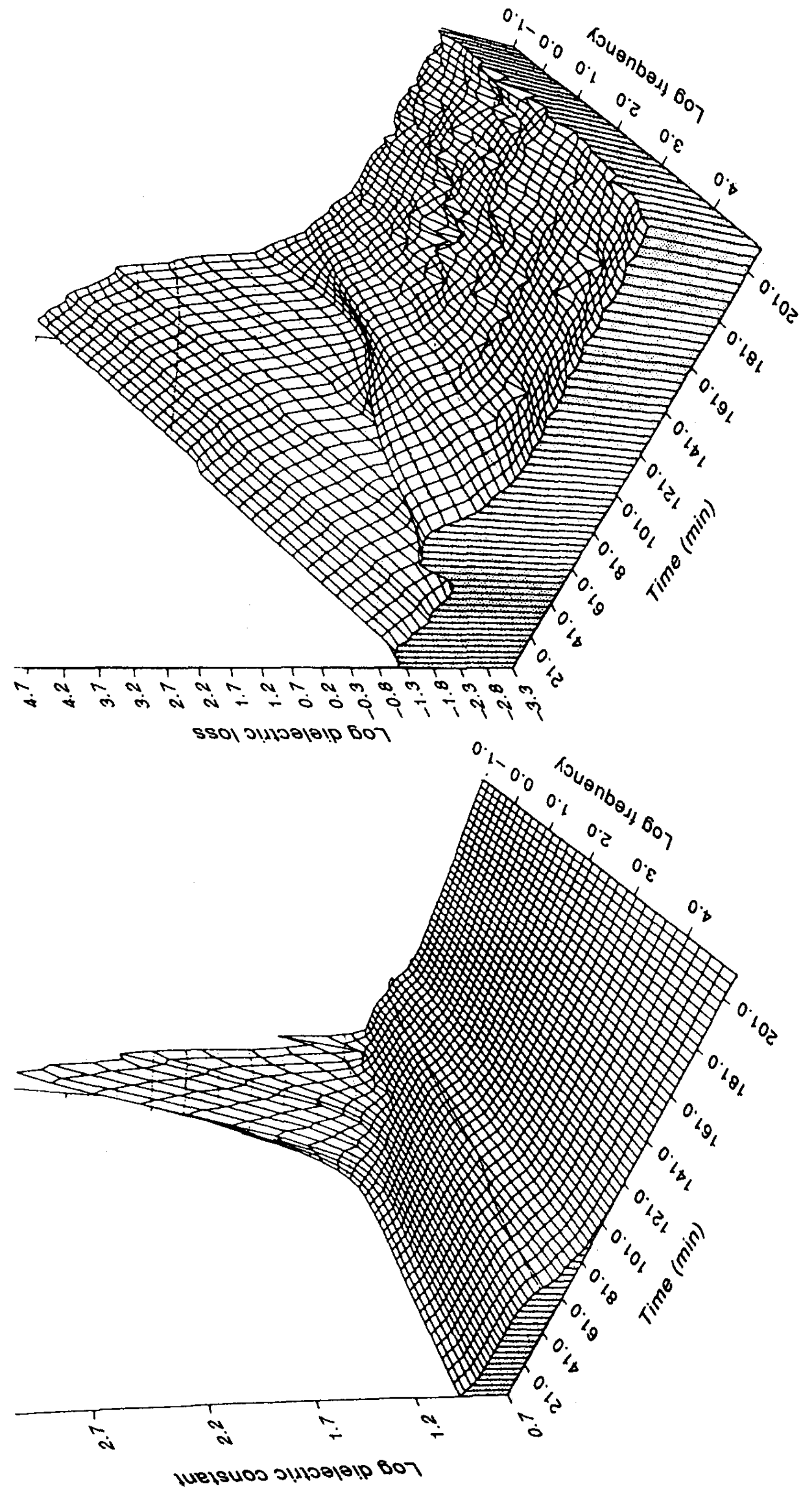

Fig. 4. Dielectric constant and loss for DGEBA/DDM cured at 80°.

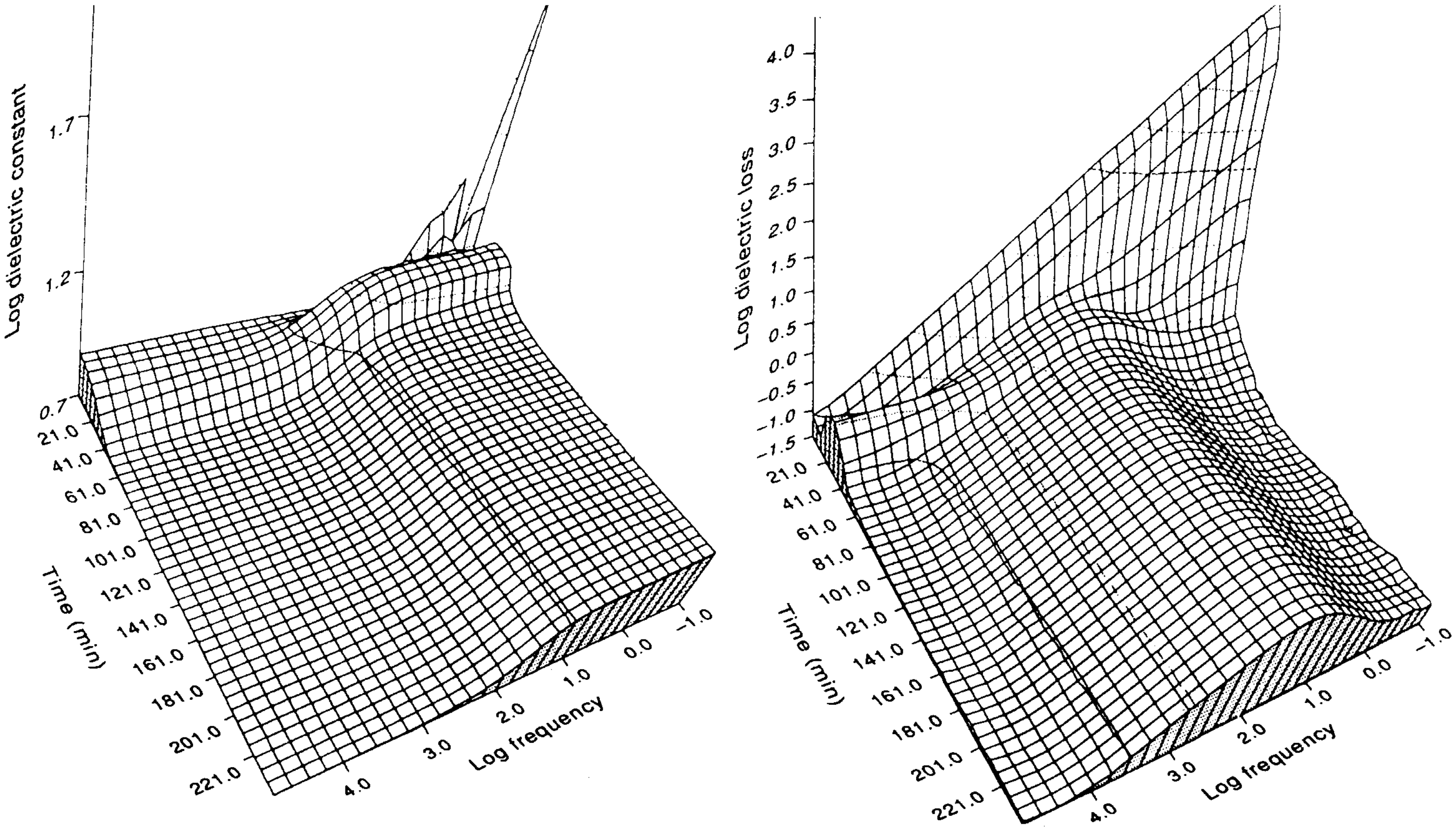

Fig. 5. Dielectric constant and loss for DGEBA/DDM/16.2 wt% CTBN cured at 80°.

Table 3. Gelation and phase separation times for DGEBA/TETA/CTBN and DGEBA/DDM/CTBN

Resin: DGEBA/	CTBN (wt%)	Gelation time t_{gel} (sec) Rheological	Gelation time t_{gel} (sec) Dielectric
TETA	0		15600
	5.2		10820
	10.6		10200
	16.2		9800
	22.6		10200
DDM	0	5900	6000
	5.2	4520	4320
	10.6	3900	3660
	16.2	2940	2880
	22.6	2400	2460

Resin: DGEBA/	CTBN (wt%)	Phase separation time (sec) Dielectric (sec)
TETA	0	
	5.2	6400
	10.6	4980
	16.2	4080
	22.6	4200
DDM	0	
	5.2	2640
	10.6	1560
	16.2	1260
	22.6	1020

where t is the gelation time, k and n are constants characteristic of the system and V is the volume fraction of the rubbery phase. The coefficients obtained from fitting the data of Table 3 are presented in Table 4. The process of phase separation in these systems may be associated with the change in the entropic contribution to the free energy as a consequence of increase in the molecular weight and also with the generation of branched chain structures on curing the resin.

CONCLUSIONS

Comparison of the gelation times obtained using both dielectric and rheological measurements indicated that there is a close correspondence between these processes. The fact that these times are similar may be purely coincidental; gelation rheologically is associated with the generation of long range structure, whereas dielectric relaxation is associated with cooperative local motion of the matrix. Observation of this apparent correlation reflects the fact that cure only leads to an infinite matrix structure towards the end of the reaction. In the later stages of reaction, the molecular weight has increased sufficiently that it becomes viscoelastic and large increases in viscosity are observed. The build-up of the matrix structure will also lead to the generation of significant chain branching which will also restrict the motion of the pendant molecular dipoles and lead to the observed changes in the dielectric spectrum.

This paper reports the first observations using real time dielectric measurements of the phase separation process. The simplicity of the correlation equation, indicating that the presence of the rubbery phase reduces the cure time but does not significantly modify the mechanism of the curing process, shows that the underlying phenomenon is one of a reduction in the total volume required to be cured.

Table 4. The best fit values for k and n calculated using equation (1)

Resin: DGEBA/	Process	Coefficients k (sec)	Coefficients n
DDM	Phase separation	426	0.674
	Gelation	1396	0.431

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