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Real-time dielectric studies of polymerizing systems

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Abstract. The use of real-time dielectric relaxation spectroscopy (DRS) for monitoring changes in molecular mobility during reaction for thermosetting systems is described together with phenomenological and molecular theories of the time-dependent relaxation functions that are involved. Reduced molecular mobility normally leads to the diffusion control of a reaction and ultimately to glass formation at the polymerization temperature T_p . We present new DRS results for a boroxine/epoxide system that show glass formation below a 'floor temperature' T_F and very different behaviour above T_F , when the dielectric properties become independent of time and an elastomer is formed.

1. Introduction

When a liquid monomer or monomer mixture is polymerized in the bulk state by a condensation or addition process, there is a continual retardation in the molecular mobility and ion mobility with time which may lead to the diffusion control of the reaction at long times and to the formation of a glassy product. Changes in mobility of dipoles and ions during reaction may be monitored by different physical techniques such as dynamic mechanical relaxation, NMR relaxation and dielectric relaxation spectroscopy (DRS). Examples of bulk polymerization that give glassy products at a polymerization temperature T_p include (i) the condensation reaction of a diepoxide with a diamine and (ii) the addition polymerization of methyl methacrylate monomer. During such bulk polymerizations loss of molecular mobility at high degrees of conversion leads to the onset of diffusion control of the reaction rate and the reaction effectively 'stops' before it reaches chemical completion. The apparent glass transition temperature T_g of the product of such a reaction is approximately equal to the polymerization temperature T_p . Post-curing at $T'_p > T_p$ restores molecular mobility, allowing further reaction to take place until the new T_g of the medium reaches T'_p when the diffusion control of the reaction rate again stops the reaction. Since glassy products obtained in this way are still potentially reactive it is important to understand how molecular mobility and reaction rate are related. Also bulk thermosetting reactions are of considerable importance in practical applications; e.g. epoxide–amine thermosets are widely used as adhesives, as electrical insulators and as precision non-metallic objects, e.g. for aircraft components, both as bulk polymer and as the polymer matrix in high-performance composites. As a result, there is considerable interest in developing reliable physical techniques to study the curing of practical thermosetting systems. In this paper we describe the use of broad-band DRS for the study of curing of thermosetting systems that form glassy products and we shall present new results which show that DRS is able to demonstrate the existence of a 'floor temperature' T_F for a boroxine/epoxide system.

For $T_p < T_F$ the product of reaction is a glass while for $T > T_F$ an elastomer is formed for which the reaction has gone to 'chemical completion' under the reaction conditions.

2. Background literature

There have been many real-time studies of thermosetting systems using dielectric relaxation spectroscopy. As will be explained in section 3 below, measurements of real permittivity $\epsilon'(\omega)$ and dielectric loss factor $\epsilon''(\omega)$ at the frequency $f = \omega/2\pi$ are made as functions of reaction time t_r and give information on the changes of the mobility of dipolar groups and of ions that may be present during a reaction. Changes in mobility with time as a mixture transforms from a liquid to a glass have been determined using single-frequency or multiple-frequency measurements of the dielectric permittivity ϵ' and loss factor ϵ'' in real time. The early reports of the use of DRS for cure monitoring of thermosetting systems were reviewed by Senturia and Sheppard [1, 2] and were extended by them [1–5] to show how changes of permittivity and loss factor of samples contained in parallel-plate cells, or on the surface of specially designed planar dielectric sensors, provided a direct means of monitoring the curing of thermosets. At that time Kranbuehl and co-workers (see references [6–10] and references therein) also developed a continuous dielectric cure-monitoring procedure for epoxide–amine thermosets, polyimide resins and epoxide composites and epoxy laminates. The parameters governing ionic and dipolar mobility changed with time and were used to measure and control the cure-processing parameters under different experimental polymerization conditions including curing in an autoclave. The work of Senturia and Sheppard [1–5] and Kranbuehl and co-workers [6–10] showed that dielectric cure monitoring was of direct value as regards commercial thermosetting systems. Subsequently, Johari and co-workers (see references [11–26] and references therein) made systematic studies of the time evolution of ϵ' and ϵ'' during the polymerization of a wide range of epoxide–amine systems. Data for a range of frequencies, mostly $<10^5$ Hz, and a range of polymerization temperatures T_p were often reported for a system and the dielectric parameters of relaxation strength $\Delta\epsilon$, average relaxation time $\langle\tau\rangle$ for dipole motion and the dielectric relaxation function $\Phi(t)$ were determined during reaction. It was shown how $\langle\tau\rangle$ increased markedly and led to the reaction becoming self-retarding. Plots of ϵ'' versus ϵ' ('Cole–Cole' plots) had a characteristic shape similar to that of the KWW stretched-exponential function [27, 28] (see below). In parallel work, Rolla and co-workers [29–34] made real-time DRS studies of epoxide–amine reactions covering the range 10^3 – $10^{10.3}$ Hz. They showed (see also reference [24] for similar studies) that the $\alpha\beta$ -relaxation, which is due to the micro-Brownian motions of dipoles, occurred at microwave frequencies in the unreacted mixture and, as reaction proceeded, transformed into an α -process (a dynamic glass transition process) and a β -process (a higher frequency process due to motions of low-molar-mass species and to limited local motions of polymer chains in the reaction mixture). The relaxation strength of the α -process increased with time and the process moved rapidly to ultra-low frequencies with time, showing that a glass was formed. Using the information obtained from the DRS studies, Rolla and co-workers [34] and Cassettari *et al* [24] have given a unified description of the changes in dynamics which occur in thermosetting systems that form polymeric glasses (see below). In addition to their studies of polycondensation reactions, Rolla and co-workers [35–39] made extensive DRS studies of free-radical thermosetting and photosetting reactions, notably microwave studies of the polymerization of *n*-butyl acrylate. In further work, Mijovic and co-workers [40–49] made detailed DRS studies of epoxide–amine polymerization reactions in which the electrical behaviour was given as the time-dependent complex impedance $Z(\omega)$ in addition to time-dependent dielectric permittivity. It was shown how data presented as $Z(\omega)$ paralleled data for chemical conversion versus time obtained

from spectroscopic and differential scanning calorimetry measurements. In their systems, $Z(\omega)$ was dominated by the contribution from ion conduction. Information obtained from the behaviour of $Z(\omega)$ complemented that obtained from $\varepsilon(\omega)$ which gave information on the molecular mobility of dipolar groups in the chains. In addition there have been several further DRS studies of the curing of bulk thermosetting systems; e.g. by Deng and Martin [50, 51], Maistros *et al* [52] and Williams and co-workers [53, 54] for epoxide–amine systems, Pethrick and co-workers [55] and Partridge and Maistros [56] for phase-separating epoxide–polymer systems, McGettrick *et al* [57, 58] for anaerobic adhesives and by Williams and co-workers for a photosetting dimethacrylate [59] and a thermosetting diallyl carbonate [60]. Nearly all of these DRS studies [1–60] have been concerned with reactions that become diffusion controlled at long times leading to the formation of glassy products.

3. Theoretical background

For a thermodynamically stationary system the complex dielectric permittivity $\varepsilon(\omega)$ is related to a macroscopic relaxation function $\Phi(t)$ by the following equation [61, 62]:

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = 1 - i\omega \Im(\Phi(t)) \quad (1)$$

where ε_0 and ε_∞ are the limiting low- and high-frequency real permittivities respectively and \Im indicates a one-sided Fourier transform. For $\Phi(t) = \exp(-t/\tau)$, where τ is the dielectric relaxation time, equation (1) gives the familiar single-relaxation-time equations

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \quad \varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}. \quad (2)$$

Molecular theory for the dielectric behaviour of a stationary isotropic system of dipolar molecules shows that $\Phi(t)$ in equation (1) may be replaced, for approximate work, by the dipole moment time correlation function (TCF) $\Phi_\mu(t)$ where this quantity is given by equation (3) below if cross-correlation terms between dipoles are set to zero and the sum extends over all n dipoles in a macroscopic volume V in the material [61, 63]:

$$\Phi_\mu(t) = \frac{\sum_i^n \langle \mu_i(0)\mu_i(t) \rangle}{\sum_i^n \langle \mu_i^2 \rangle}. \quad (3)$$

Thus for a stationary system, measurements of $\varepsilon(\omega)$ give information on $\Phi_\mu(t)$ which may be calculated from the inverse transform of equation (1) as follows [61]:

$$\Phi_\mu(t) \simeq \Phi(t) = \Im_c \left[\frac{\varepsilon''(\omega)}{\omega(\varepsilon_0 - \varepsilon_\infty)} \right] = \Im_s \left[\frac{\varepsilon_0 - \varepsilon'(\omega)}{\omega(\varepsilon_0 - \varepsilon_\infty)} \right] \quad (4)$$

where \Im_s and \Im_c are the sine and cosine transforms, respectively, with respect to measuring frequency ω [61].

For a non-stationary system, $\varepsilon(\omega)$ is time dependent, so for a chemical reaction we would write $\varepsilon(\omega) \equiv \varepsilon(\omega, t_r)$ where t_r is the reaction time. If a measurement of $\varepsilon(\omega)$ is made to successively lower values of ω during a reaction, then an ω -range will be reached where it is not possible to measure $\varepsilon(\omega, t_r)$ since the value will change during the several cycles required for the measurement. Since $[\varepsilon', \varepsilon'']$ values cannot be obtained at these frequencies, equations (4) will not apply generally to the non-stationary system. If, however, the full relaxation region for $[\varepsilon', \varepsilon'']$ versus $\log f$ is measurable at a given time t_r , then equations (4) will apply. The situation is illustrated schematically in figures 1(a) and 1(b). Equations (4) can be applied to the data in figure 1(a) but not to those in figure 1(b). For figure 1(a) $\Phi(t)$ has the meaning of the relaxation function for the response to a step-on or step-off applied field *at the reaction time*

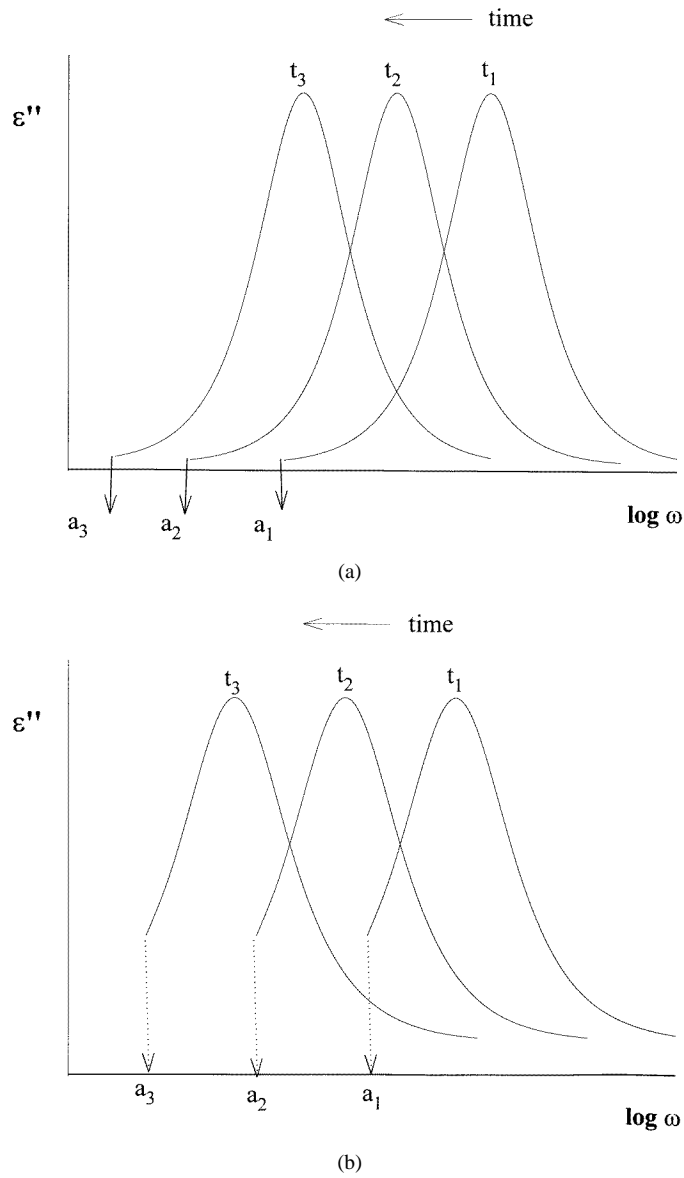


Figure 1. Schematic plots of ϵ'' versus $\log \omega$ for different reaction times. The relaxation process is determined for each time t_i in (a) but this is not the case for (b) due to truncation of the data at low frequencies. Here a_i is the lowest value of $\log \omega$ measured at reaction time t_i .

t_r [61, 62]. This cannot be applied to band-limited data as in figure 1(b) due to the truncation of the Fourier integrals. The question arises of what information is obtainable from the data of figure 1(b). A successful measurement of $[\epsilon', \epsilon'']$ for each frequency for $\omega > \omega_{min}$ implies that $\Phi(t)$ is defined from 0 to a maximum time $t_{max} \sim \omega_{min}^{-1}$, so the steady-state response for $\omega > \omega_{min}$ that allows $[\epsilon', \epsilon'']$ values to be measured is achieved by the measuring instrument. However, without a knowledge of $[\epsilon', \epsilon'']$ values across the entire relaxation range, $\Phi(t)$ cannot be determined from equations (4). We note that Johari and co-workers [16–26] have used a

form of equation (1) together with the KWW stretched-exponential function [27, 28, 64, 65] to analyse real-time DRS data for thermosetting systems. Butta *et al* [31] have pointed out that $[\varepsilon'(\omega), \varepsilon''(\omega)]_{t_r}$ coupled values measured at a fixed frequency but at different times of reaction t_r and which are used to form Cole–Cole arcs are not equivalent to such values taken at a fixed t_r and different frequencies. This presents a difficulty with the analysis used by Johari and co-workers [16–26]. The latter authors have defended their method [25], but this is a matter of continuing debate since equation (1) cannot be applied generally for a non-stationary system when two time variables t and t_r are involved and may overlap.

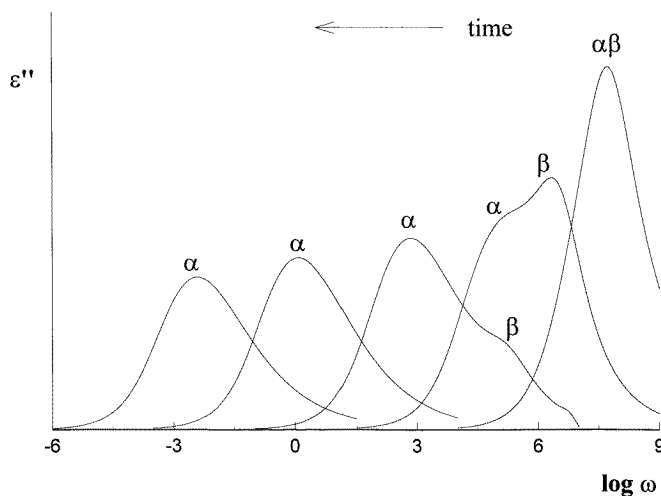


Figure 2. Schematic plots of ε'' versus $\log \omega$ showing how the $\alpha\beta$ -process splits into α - and β -processes as reaction proceeds (after references [24] and [34]).

Cassettari *et al* [24] and Casalini *et al* [34] obtained $[\varepsilon', \varepsilon'']$ data across a wide frequency range for an epoxide–amine system during reaction and found the general pattern of behaviour shown schematically in figure 2. An $\alpha\beta$ -process for the unreacted monomer mixture splits into α - and β -processes (termed ‘a’ and ‘b’ processes by Casalini *et al* [34]); the relaxation strengths $\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_\beta$ increase and decrease with time, respectively, and the overall relaxation strength $\Delta\varepsilon = \Delta\varepsilon_\alpha + \Delta\varepsilon_\beta$ decreases only slightly with time. Since

$$\Delta\varepsilon \propto \sum_i c_i(t_r) \mu_i^2$$

where $c_i(t_r)$ is the concentration of species i at time t_r , its near-constancy over time means that as dipolar groups disappear during reaction, new dipolar groups appear with sufficient dipole moment values to sustain $\Delta\varepsilon$ near its original value. The overall effect is for the total relaxation strength to decrease slightly and for the relaxation frequencies for α - and β -processes to change with time (or overall conversion α_{conv}) as indicated schematically in figure 3. The behaviour shown in figure 3 is similar to that for amorphous polymers [62, 66, 67] and low-molar-mass glass-forming liquids [68] as has been emphasized by Cassettari *et al* [24] and Casalini *et al* [34]. The mechanisms of the different processes were not given explicitly in references [24] and [34] for the reaction system and may be understood as follows.

We regard each loss spectrum in figures 1–3 as a snapshot of the relaxation behaviour at the different times (t_r). Thus $[\Phi_\mu(t)]_{t_r}$ traces that are consistent with such data may be derived *approximately* by taking $\Phi_\mu \sim \Phi(t)$ and performing the inverse cosine transform of the loss data in the frequency domain (see equations (4)). For the behaviour shown in

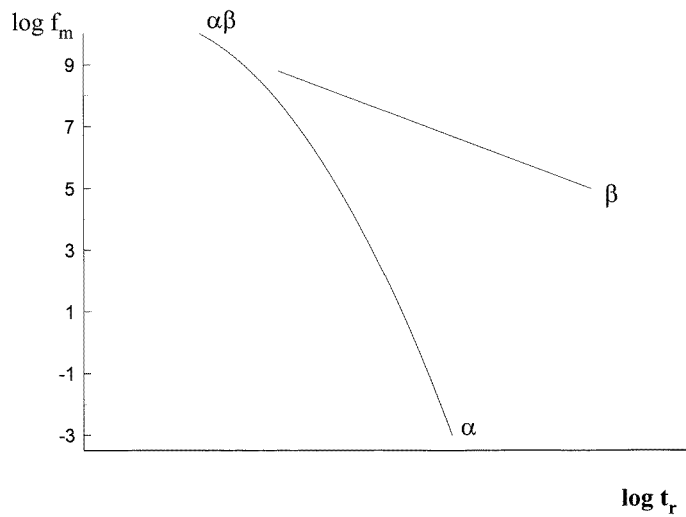


Figure 3. The frequency–temperature locations of the $\alpha\beta$ -, α - and β -processes as functions of the reaction time (after references [24] and [34]).

figure 1(a) the dipole moment correlation functions at different values of t_r are obtained and are shown in figure 4. At short reaction times $\Phi_\mu(t)$ decays as a single $\alpha\beta$ -process. At very long times it loses its meaning since the timescale t and reaction time t_r become comparable. The $\alpha\beta$ -process is due to the cooperative reorientational motions of all dipoles present and this process randomizes all the dipole vectors completely. As t_r increases, the formation of polymeric species makes the dielectric properties of the mixture more complex. Local motions of monomeric species still occur and contribute to the total loss process at short times t , but these motions and the limited local motions of the polymer chains will give only a partial

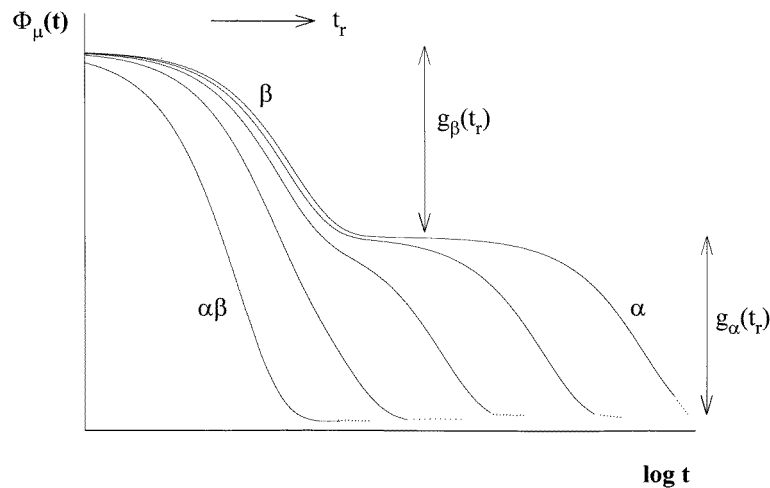


Figure 4. The variation of the dipole moment correlation function $\Phi_\mu(t)$ with time for different reaction times t_r . $g_\alpha(t)$ and $g_\beta(t)$ are the relaxation strengths of the individual processes for a given reaction time.

randomization of the dipole vectors in the system at t_r (whether the system is cross-linked or otherwise) and a weighted sum of these processes gives rise to an overall β -relaxation process. At longer times t for a fixed value of t_r , micro-Brownian motions (the dynamic glass transition process) relax the remainder of $\Phi_\mu(t)$ as shown in figure 4. So $[\Phi_\mu(t)]_{t_r}$ falls in two stages, as β - and α -processes (of relative magnitudes g_β and g_α), and their timescales separate (in t) as reaction time t_r increases, as is shown in figures 2, 3 and 4. $[\Phi_\mu(t)]_{t_r}$ may be expressed as a generalization of our original equations [67, 69, 70] for α -, β - and $\alpha\beta$ -processes in glass-forming liquids and polymers. We write

$$[\Phi_\mu(t)]_{t_r} = \sum_i c_i(t_r) [\Phi_{\mu_i}(t)]_{t_r} \quad (5)$$

where $[\Phi_{\mu_i}(t)]_{t_r}$ is the dipole TCF for species i at time t_r and this function decays essentially to zero well within the timescale required for the dielectric properties of the system to change significantly as a result of reaction. So

$$[\Phi_{\mu_i}(t)]_{t_r} = \left\{ \left[\varphi_{\alpha_i}(t) \left[\sum_r^0 p_{r_i} q_{r_i} + \sum_r^0 p_{r_i} (1 - q_{r_i}) \varphi_{\beta_{r_i}}(t) \right] \right] \right\}_{t_r} \quad (6)$$

where all factors on the r.h.s. of equation (6) refer to time t_r , $\varphi_{\beta_{r_i}}(t)$ are the relaxation functions for the α - and β -processes for species i , $^0 p_{r_i}$ is the probability of species i being in environment r and $q_{r_i} = \langle \mu_{r_i}^2 \rangle / \langle \mu_i^2 \rangle$ where $\langle \mu_{r_i} \rangle$ is the net dipole moment (a vector quantity) residing in environment r when the β_{r_i} -process is completed for species i . In equation (6) the sum extends over all possible environments for the dipole i at time t_r . According to equations (5) and (6), when all of the $\varphi_{\alpha_i}(t)$ decay much faster than all of the $\varphi_{\beta_i}(t)$, an $\alpha\beta$ -process is obtained with

$$[\Phi_\alpha(t)]_{t_r} \simeq \sum_i [\Phi_{\alpha_i}(t)]_{t_r}.$$

For the case where all of the $\Phi_{\alpha_i}(t)$ decay more slowly than all of the $\varphi_{\beta_i}(t)$, two processes are obtained as expressed by equation (6). Motions of low-molar-mass species and limited motions of chain dipoles give the faster β -process, of relaxation strength

$$\sum_i c_i(t_r) \left[\sum_r^0 p_{r_i} (1 - q_{r_i}) \right]_{t_r}$$

and the slower, residual relaxation occurs as a result of the α -process having a relaxation strength

$$\sum_i c_i(t_r) \left[\sum_r^0 p_{r_i} q_{r_i} \right]_{t_r}.$$

When the α -process becomes extremely slow at the later stages of reaction, a glass is formed and the β -process remains observable at medium frequencies. Thus equations (5) and (6) are able to rationalize the complex pattern of DRS behaviour shown in figures 2 and 3, established experimentally by Cassettari *et al* [24] and Casalini *et al* [34] for thermosetting systems, in terms of the limited and the more extensive reorientational motions of dipolar species.

As indicated above, most DRS studies of thermosetting systems have been concerned with mixtures that form a glass at the polymerization temperature T_p . In the following sections we present new results where either a glass or an elastomer is formed, depending on the choice of T_p .

4. Experimental procedure

We studied a three-component mixture consisting of (i) a commercially available diepoxide Ciba–Geigy PY306, which is a very pure form of the diglycidyl ether of bisphenol A (DGEBA)—which is the diepoxide used in most DRS studies of epoxide–amine studies, (ii) a cyclic boroxine hardener trimethoxy boroxine (TMB) and (iii) benzyl alcohol (BA) which is an inhibitor for the reaction. Reaction proceeds by an ionic mechanism and the trifunctionality of TMB and bifunctionality of DGEBA leads to a highly cross-linked 3D-network polymer being formed. Dielectric measurements of $[\varepsilon', \varepsilon'']$ were made using a Novocontrol dielectric spectrometer with the sample contained in a parallel-plate dielectric cell. Temperature control of the sample and programmed measurements at 26 frequencies in the range 1 to 10^4 Hz were made as we described previously for the bulk polymerization of the DGEBA–diaminodicyclohexylmethane system [53] and for diethylene glycol bis(allyl carbonate) [60]. A frequency sweep in intervals of 0.2 in units of $\log_{10}(f/\text{Hz})$ took approximately 3.5 min. In order to achieve an almost continuous recording, the sweep was initiated every 4 min. This is to be compared with the multi-frequency DRS studies of Johari and co-workers [20, 21] in which one sweep of 26 frequencies in the range 12 to 10^5 Hz [21] and of 24 frequencies in the range 15 to 10^5 Hz [20] took 21 min and 18 min respectively. A sample containing PY306, TMB and BA in the ratio 14.0:3.0:1.0 by weight was prepared by stirring the components together for ~ 5 min at 50°C to ensure homogeneity. Prior to stirring, the mixture was a white liquid, but on stirring at 50°C , it became a clear liquid of low viscosity. The sample was poured into the cell which was placed in the Novocontrol BDS 1200 sample holder that had been pre-heated to T_p . The act of opening and positioning the sample cell in the cryostat/heater chamber of the instrument lowered the temperature of the chamber momentarily from T_p . Thus dielectric measurements were started (i.e. $t_r = 0$) at the point at which the chamber re-registered T_p , which was after only a matter of minutes.

5. Results and discussion

A total of eleven separate experiments, for values of T_p ranging from 60°C to 120°C , have been made for reaction mixtures of the given composition. Each experiment started with a freshly made mixture and real-time DRS measurements were performed across the entire f -range. We show here only the results for two polymerization temperatures; one for $T_p < T_F$ for which diffusion control leads to glass formation and the other for $T_p > T_F$ for which an elastomer product is formed in which molecular mobility is retained at the longest values of t_r . The full study and its quantitative analysis will be published separately [71].

Figures 5(a) and 5(b) show plots of real permittivity ε' and loss factor ε'' versus $\log(\text{time/s})$ for fixed frequencies for $T_p = 60^\circ\text{C}$. At short times, ionic conduction, due to extraneous ions, gives rise to large values of ε' and to the large conductivity ‘tail’ in ε'' . This behaviour is well known for polymerizing systems [1, 12, 29, 40]. The specific conductivity $\sigma_{ion}(t_r)$, and hence also the loss factor, decrease rapidly with increasing t_r . Johari and co-workers (see e.g. references [12, 13, 16, 26, 72]) extrapolated the values of $\sigma_{ion}(t_r) \rightarrow 0$ using two empirical formulae to yield apparent gel times t_{gel} or t_0 . They have compared such values with gel points predicted using the statistical theories of gel formation by Stockmayer [73] and Flory [74]. Zukas [75] has criticized the determination of gel points from DRS data for $\sigma_{ion}(t_r)$. Parthun and Johari have defended their procedure [76]. The determination of gel points from dynamic measurements made during a reaction is a subject of some confusion. Winter [77] has described an empirical method based on the instant at which the real modulus G' and loss modulus G'' cross each other, but we take the view that gelation in the thermodynamic sense

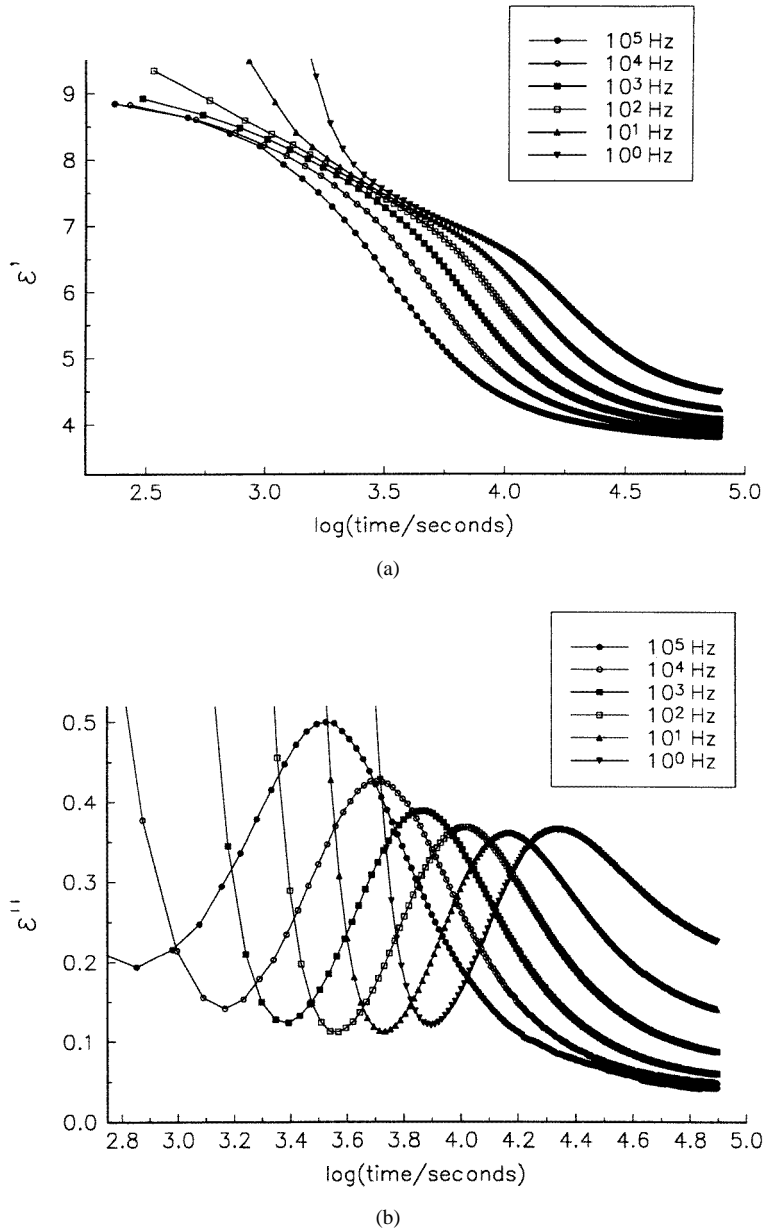


Figure 5. Plots of (a) ϵ' and (b) ϵ'' versus $\log(\text{time/seconds})$, measured at each decade of frequency in the range 1 to 10^5 Hz, during the curing of PY306/TMB/BA at 60°C .

has no corresponding feature in the DRS behaviour for thermosetting systems, in accord with Zukas [75]. The marked decrease of $\sigma_{ion}(t)$ will occur as the medium becomes increasingly immobile and forms a glass, and this occurs independently of the formation of a gel at any stage of the reaction. At longer times, a well-defined dispersion region and an absorption region are seen in figure 5 which show the dielectric α -process (see figure 2) which moves rapidly to low frequencies as t_r is increased. The cross-plots from figure 5, which include all

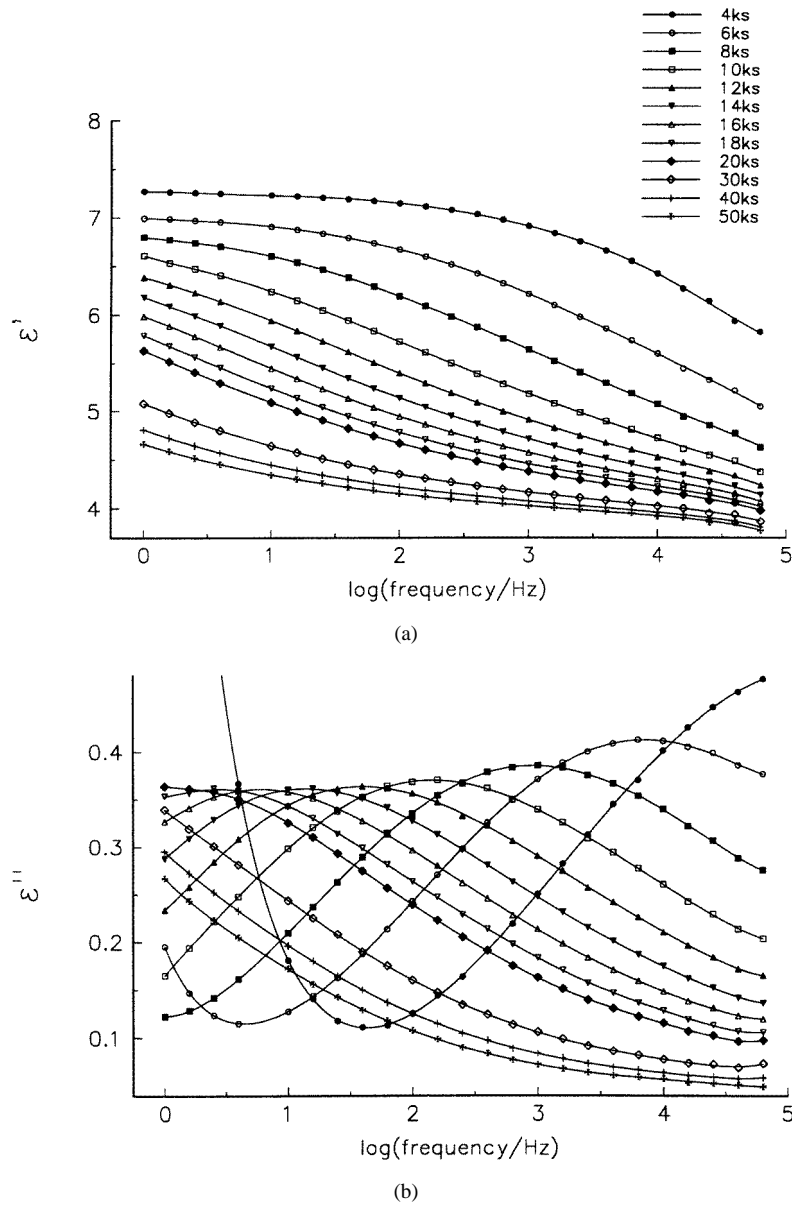


Figure 6. Plots of (a) ε' and (b) ε'' versus $\log(f/\text{Hz})$ for different reaction times during the curing of PY306/TMB/BA at 60 °C. The reaction times in (b) are the same as those in (a).

26 frequencies, are shown in figure 6 as $[\varepsilon', \varepsilon'']$ versus $\log f$. The α -process moves rapidly to ultra-low frequencies with time, showing that a glassy product is formed at 60 °C. Such behaviour is entirely similar to that observed in the related DRS studies that we summarized above [1–60]. The average relaxation time $\langle\tau\rangle = (2\pi f_{max})^{-1}$ where f_{max} is the frequency of maximum loss obeys the empirical relaxation

$$\langle\tau(t_r)\rangle = \tau_0 \exp bt_r \quad (7)$$

as found previously (see e.g. references [11–26] and [53] for detailed accounts). The loss

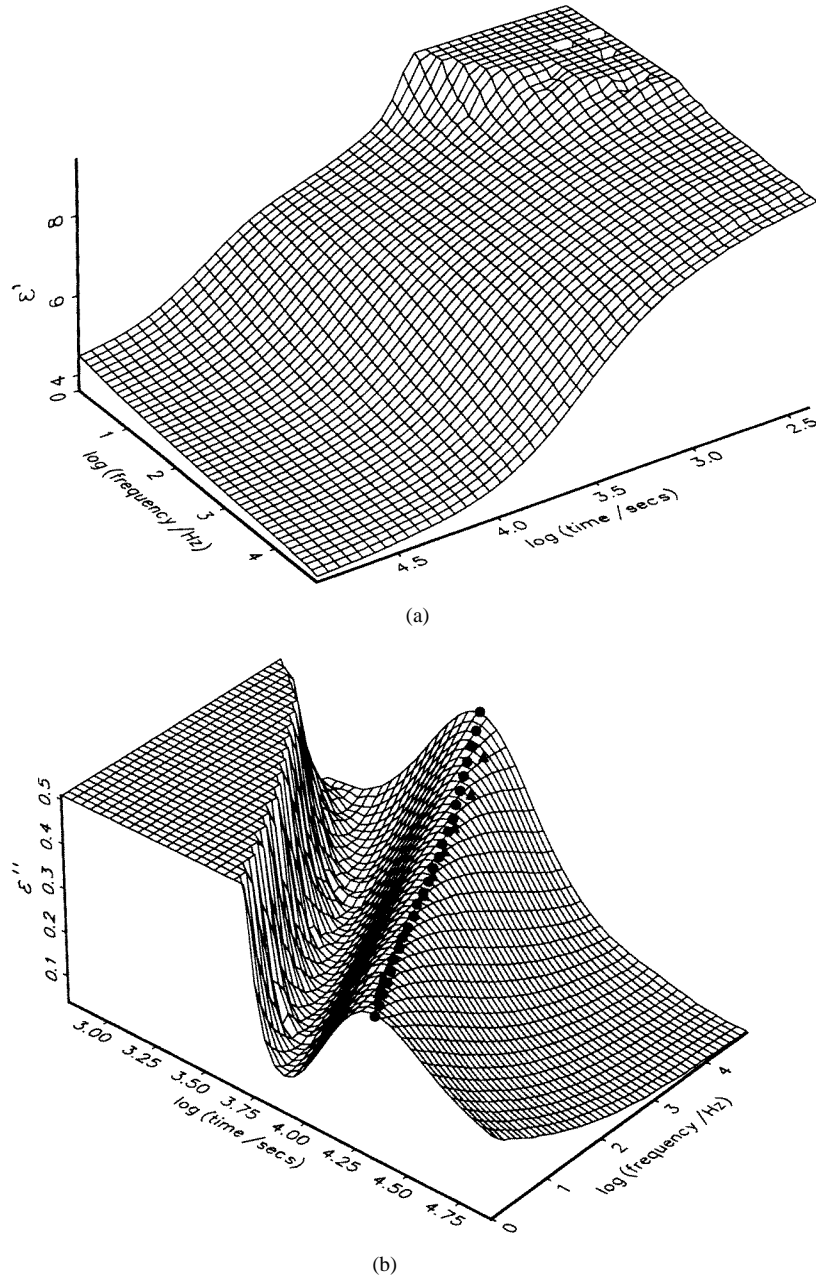


Figure 7. 3D plots of (a) ϵ' and (b) ϵ'' versus $(\log(\text{time/s}), \log(f/\text{Hz}))$ during the curing of PT306/TMB/BA at 60 °C. The values of $\log f_{\max}$ are indicated as ● and their locus shows that a glass is formed at long times.

curves for the α -process are extremely broad with half-widths $\Delta_{1/2} \sim 3.5$ compared with 1.14 for a single-relaxation-time process and 1.7–2.5 for α -relaxations in amorphous polymers [67]. It seems likely that the enhanced broadening of the loss curves is associated with the presence of cross-linking. Glatz-Reichenbach *et al* [78] have examined the influence of cross-linking

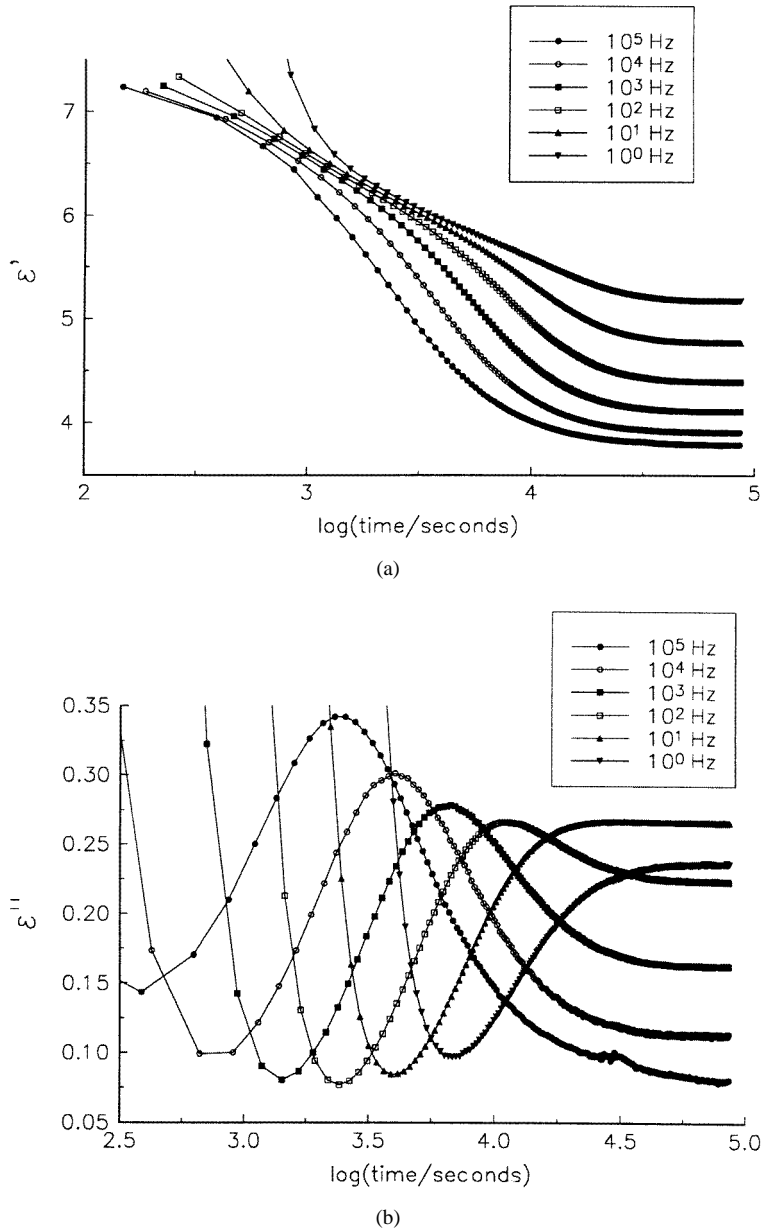


Figure 8. Plots of (a) ϵ' and (b) ϵ'' versus $\log(\text{time}/\text{s})$, measured at each decade of frequency in the range 1 to 10^5 Hz, during the curing of PY306/TMB/BA at 80°C .

on the dielectric α -relaxation in styrene-butyl acrylate copolymers. They showed that the α -process broadened from $\Delta_{1/2} \sim 3$ to ~ 4.5 on going from 0 to 10 wt% cross-linking agent and showed further that the loss curves were more symmetrical (and of Cole-Cole type) for the 10% cross-linked material than those for the non-cross-linked material (which were of KWW type). This suggests that in the cross-linked materials there is contribution to the α -process from low-frequency modes of motion of chains in close proximity to the cross-links. We note

that for simple organic glass-forming liquids, e.g. isoamyl chloride and isoamyl bromide [70], a single unstructured narrow α -relaxation is obtained for the mixtures although the pure liquids have very different T_g -values and hence very different relaxation behaviours. In those cases the dipole TCFs for the individual components in the mixture are approximately the same, as we have discussed [70]—i.e. there is no difference between the tumbling behaviours of the individual molecules. However, heterogeneity in the motional behaviour in cross-linked polymers such as the reacting system studied here (figure 6) and the materials studied by Glatz-Reichenbach *et al* [78] is evident from the considerable broadening of the α -relaxation. We have shown above (equation (6)) that the strength of the α -process is proportional to

$$\sum_i c_i(t_r) \left[\sum_r^0 p_i q_{ri} \right]_{t_r}.$$

This is the contribution from the net dipole vectors $[\langle \mu_{ri} \rangle]_{t_r}$ for dipoles i residing in environment r at reaction time t_r to the overall relaxation, after the β -relaxation is completed. For the results shown in figures 5 and 6 these motions (the α -process) become increasingly retarded at long times, diffusion control of the reaction sets in and the reaction effectively ‘stops’ when the glass is formed. For completeness and for comparison with our results at 80 °C to be described below, figure 7 shows 3D plots of the permittivity and loss data for $T_r = 60$ °C. The short-time low-frequency behaviour of the loss factor is dominated by ionic conduction and the α -process is seen to move steadily to ultra-low frequencies as the material forms a glass.

In figure 8 we show plots of $[\varepsilon', \varepsilon'']$ versus $\log(\text{time/s})$ at fixed frequencies for $T_p = 80$ °C. The ion conductivity affects the ε' -values at short times but the dispersion due to the α -process is evident at longer times. The ε'' -curves exhibit the conductivity tails at short times and then the α -process is seen as a well-defined peak for 10^5 and 10^4 Hz. As frequency is decreased an increasingly pronounced tail occurs at *long* times but the peak is still seen for 10^3 and 10^2 Hz. At 10 and 1 Hz no peak is observed; the ε'' -values simply increase to a plateau level with time and the ε' -values are constant in figure 8(a) at long times, with plateau values increasing with decreasing frequency. The contrast with the data of figure 5 is apparent. When the data of figure 8 were obtained they were unexpected, since they were qualitatively different from the previous DRS curing data for thermosetting systems (see however reference [79]). The reason for the unusual behaviour is apparent when the cross-plots of $[\varepsilon', \varepsilon'']$ versus $\log f$ for fixed values of t_r were constructed, as shown in figure 9. As time increases the α -process initially moves steadily from high frequencies to lower frequencies but shows no further movement for $t_r > 40$ ks. This behaviour is seen more clearly in the 3D plots of $[\varepsilon', \varepsilon'']$ versus $[\log f, \log t_r]$ shown in figure 10. The α -process initially moves steadily to low frequencies and then the ε' - and ε'' -values become independent of time at long times with $\log(f_{max}/\text{Hz}) \sim 0.8$. Thus at long times the system becomes stationary in its dielectric properties and this strongly implies that the reaction has gone to chemical completion at 80 °C [80]. Also since the limiting value of f_{max} for the α -process is ~ 7 Hz the molecules are mobile at this temperature and the product is a cross-linked elastomer. Subsequent cooling of this material gives a chemically stable glass at room temperature. Clearly our data for T_p equal to 60 °C and 80 °C for a mixture of this initial composition point to the existence of a ‘critical temperature’ of curing which we shall call the *floor temperature*, T_F . Isothermal curing below T_F at T_{p1} , say, leads to diffusion control of reaction and glass formation at long times, where the product is chemically unstable since further reaction occurs if the sample is heated above T_{p1} . Isothermal curing of the initial mixture at T_{p2} above T_F gives a thermodynamically stable cross-linked elastomer whose glass transition temperature T_g is below T_{p2} .

In a further publication [71] we shall present our DRS data for the eleven separate experiments conducted with the PY306:TMB:BA system of this composition in the range

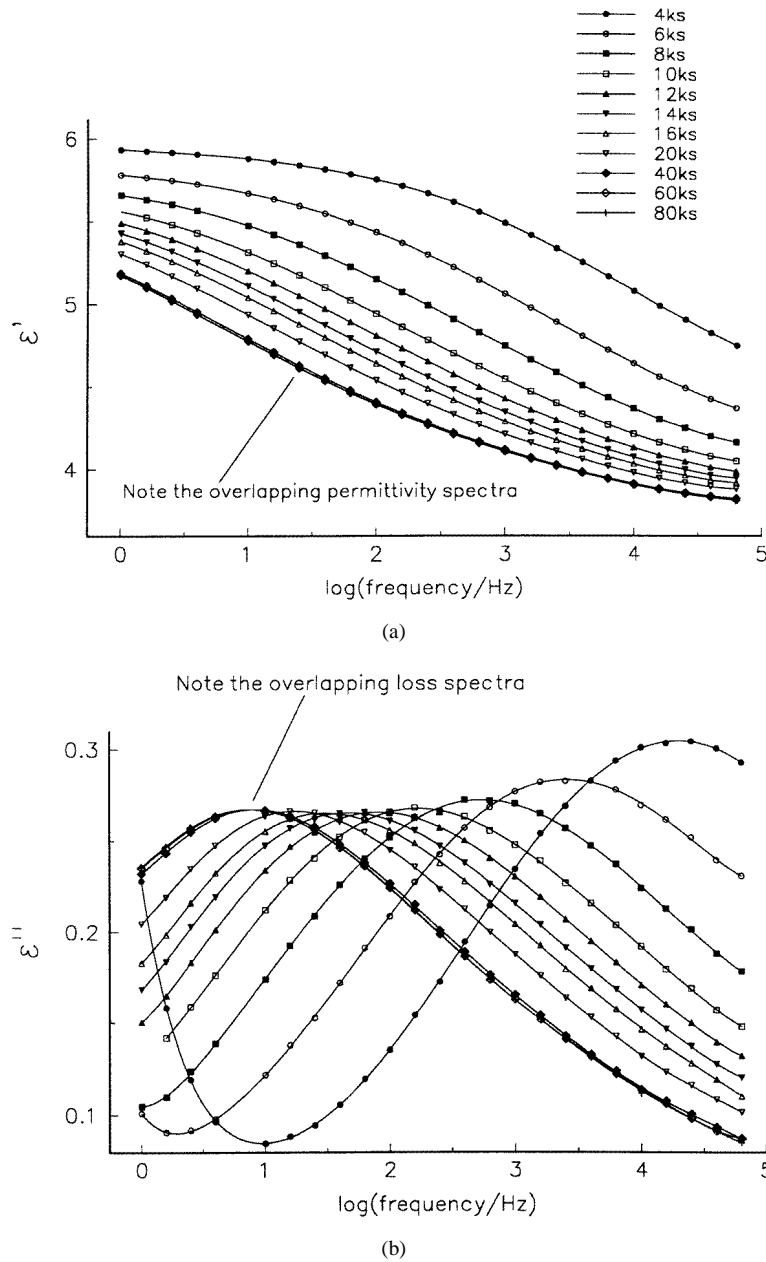
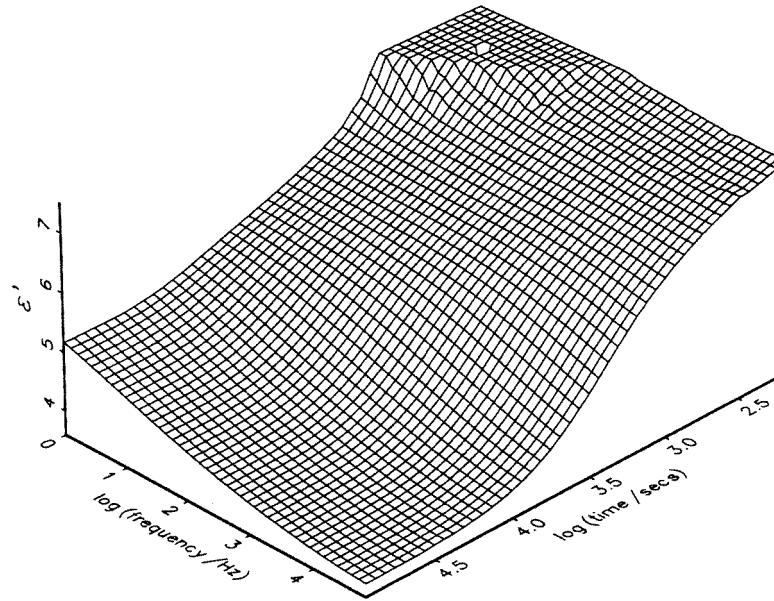
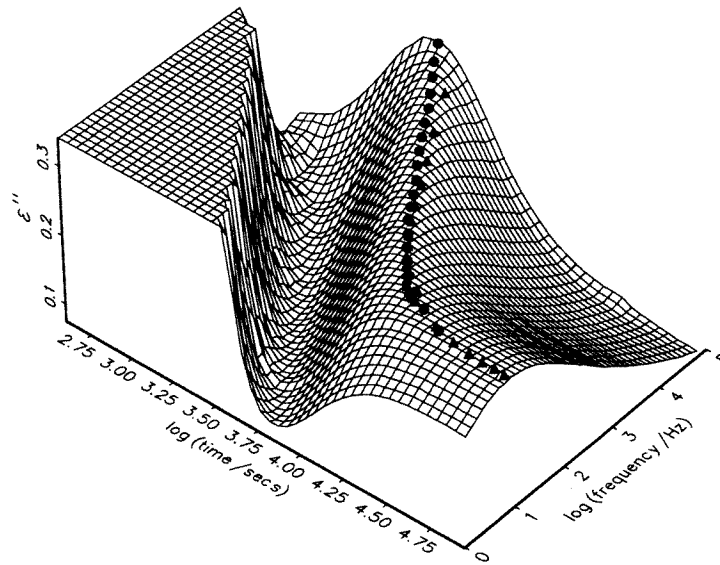


Figure 9. Plots of (a) ϵ' and (b) ϵ'' versus $\log(f/\text{Hz})$ for different reaction times during the curing of PY306/TMB/BA at 80 °C. The reaction times in (b) are the same as those in (a).

$60 \leq T_p \leq 120$ °C. In that paper a full analysis of the DRS data will be presented including comparisons with the studies of thermosetting systems by Gillham and co-workers [81, 82] using dynamic mechanical relaxation and Montserrat [83] using differential scanning calorimetry. The meaning of T_F will be discussed [71] in relation to the apparent glass transition temperatures T_g of products formed for $T < T_F$ and $T > T_F$.



(a)



(b)

Figure 10. 3D plots of (a) ϵ' and (b) ϵ'' versus $(\log(\text{time/s}), \log(f/\text{Hz}))$ during the curing of PT306/TMB/BA at 80°C . The values of $\log f_{\max}$ are indicated as ● and their locus shows that the system becomes stationary at long times.

6. Summary

In the present paper, we have summarized briefly the previous DRS studies of the curing behaviour of thermosetting systems and have given a theoretical framework for rationalizing

the behaviour of the α -, β - and $\alpha\beta$ -processes with reaction time. In most previous studies the product at a fixed reaction temperature was a chemically unstable glass. We have presented new DRS data for a PY306/TMB/BA system of a particular composition that show two classes of behaviour. For this system, at $T_p = 60^\circ\text{C}$ a glass is formed but at $T_p = 80^\circ\text{C}$ a chemically stable elastomer is formed. This implies that a floor temperature T_F exists between 60 and 80°C for this reaction. Below T_F a glass forms and above T_F an elastomer forms, as will be considered in greater detail in a future publication [71]. Finally, we note that we chose to present our DRS data as $[\epsilon', \epsilon'']$. DRS data may also be presented as electrical moduli $M (=1/\epsilon)$, electrical conductivities (σ) or electrical impedances (Z), admittances $Y = 1/Z$ or resistivities $\rho = 1/\sigma$, all being complex quantities. Johari used M , Kranbuehl used σ and Mijovic used Z , in addition to ϵ , for the curing of thermosets. A comparison of these different presentations for thermosetting systems and their relationships to the motional behaviour of dipolar groups and ions will be presented in a further paper [84]. It is clear from that work that changes in the molecular dynamics of chain dipoles with curing time are expressed directly using ϵ as we have done for the present system.

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- [80] By 'chemical completion' we do not mean 100% conversion of monomeric species to polymeric species. For the cross-linked elastomer at $T_p = 80$ °C, reactive groups will be present at long times but the topological constraints of the network will prevent them from reaching each other.
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