Relaxations in thermosets: 15. Curing kinetics and dielectric behaviour of butadiene-acrylonitrile-containing epoxide thermosets

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The dielectric permittivity, ε', and loss, ε'', during the crosslinking or curing of diglycidyl ether of bisphenol-A with diamino diphenyl methane and various amounts of an elastomer, amine-terminated butadiene acrylonitrile (ATBN), have been measured from their sol to gel to glass-formation regions. As the elastomer-containing thermoset cures, both ε' and ε'' initially decrease and then increase with time. ε' finally decreases to a value near 3, but ε'' goes through a sharp minimum followed by a peak and ultimately decreases to about 10^{-3}. The initial increase in both ε' and ε'' has been interpreted as an onset of liquid–liquid phase separation, which becomes nearly complete before the monotonic decrease in ε' begins as a result of network formation in the curing thermoset. The time for the onset of phase separation is relatively insensitive to the amount of elastomer in the thermoset, and indicates the time of cure at which the network structure reaches a molecular weight when the elastomer becomes immiscible in it. Both the conductivity and permittivity increase with the increase in the elastomer content, with the consequence that the onset of gelation, which is marked by an approach of conductivity to near zero, is masked by the dipolar relaxation process. Corresponding analysis in the electrical modulus formalism confirms these observations and shows further that the conductivity follows a Maxwell relaxation. The ε'' of the cured thermoset plotted against temperature shows broad peaks and shoulders to these peaks. These are a combination of the sub-T_g relaxations in both the elastomer and the thermoset's network structure and the α-relaxation of the elastomer which appears at 240 K at 1 kHz. The permittivity and dielectric loss of the cured thermoset increase with an increase in the weight fraction of ATBN.

(Keywords: rubber modified epoxy; dielectric permittivity; curing kinetics; butadiene acrylonitrile; epoxide thermosets)

INTRODUCTION

Most high molecular weight polymers are immiscible with each other, but can be dissolved in low molecular weight liquids at elevated temperatures. For cases when the low molecular weight liquid itself polymerizes, the dissolved polymer in it begins to phase separate. This phase separation, which occurs under isothermal conditions, phenomenologically differs from that which occurs at the (upper) critical solution temperature on cooling a polymer solution[1–3]. The dielectric effects of the former type of phase separation are expected to be determined by a variety of sequential processes, which generally involve phase separation in a sol state, gelation and vitrification, and these dielectric effects in turn can be used to investigate phase separation phenomena.

When a polymer is dissolved in a liquid containing components that chemically react, as in the curing of a thermoset[4,5], the phase separation of the dissolved polymer occurs as a result of the increase in the molecular weight of the components, which lowers the solubility or compatibility of the polymer with the network structure of the thermoset[6,7]. This phase separation continues until the viscosity of the liquid reaches values high enough to retard the diffusion of the dissolved polymer, i.e. as the time for gelation, to be followed by vitrification, is approached. The development of the morphology of the phase separated polymer depends upon the rate of growth of the separated phase, its compatibility with the network structure and the rate of curing or crosslinking reactions.

We have been investigating in detail the curing kinetics and the dielectric properties of cured thermosets[8–12]. These studies have led to a description of a curing parameter of a thermoset[9], the effects of substitution of curing agents[10], gelation and vitrification phenomena[11] and the effects of physical and chemical ageing in epoxide-based thermosets[8]. This paper provides the results of a dielectric study of an epoxide-based thermoset containing a third component, namely, an amine-

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terminated butadiene acrylonitrile elastomer, which is capable of chemically reacting with the epoxide groups, albeit at a relatively slow rate.

Elastomer-containing thermosets are used in applications where improved vibration damping efficiency[1] or improved mechanical and fracture toughness is desired. Improved toughness is achieved partly by decreasing the modulus of a thermoset and partly by reducing brittleness through the incorporation of micrometre sized elastomer particles. The electrical properties of elastomer-containing thermosets have scarcely been studied, as evident by their absence from two recent publications[6,7]. It is widely recognized that in their use as thin films for devices where electrical insulation and charge storage capacity are important factors, the electrical properties of elastomer-containing thermosets must be known.

This study has three purposes: first, to improve our understanding of how the curing kinetics of a well-characterized thermoset are affected by the presence of an elastomer (first in the dissolved state and later in a phase-separated state), and whether these dielectric effects could be useful in determining the onset of phase separation in an elastomer-containing thermoset; second, to determine how the electrical properties of a cured thermoset are altered by the presence of a dispersed elastomeric phase; and lastly, to provide data on the electrical properties of a variety of cured thermosets which are useful as adhesives or thin films in electronic applications.

EXPERIMENTAL

The base resin for the rubber-modified thermoset was diglycidyl ether of bisphenol A (DGEBA) obtained from Dow Chemical Company (trade name DER 332) with an epoxy equivalent weight of 190 g. Diaminodiphenyl methane (DDM) 99% pure was obtained from Aldrich Chemicals and used as a curing agent. Amine-terminated butadiene acrylonitrile (ATBN) was obtained from Goodrich Chemical Company (trade name Hycar ATBN16); it had a NH equivalent weight of 850 g, and contained a residual amount of ≈ 3 wt% *N*(2-aminoethyl) piperazine from its synthesis. Its glass transition temperature, T_g, was about 223 K.

A mixture of DGEBA and ATBN was prepared in a glass vial (about 20 mm i.d.) and heated to 363 K. A stoichiometric amount of powdered DDM (1 mol DGEBA to 2 mol DDM) was added to the liquid, which was mechanically stirred, until all DDM was dissolved. A parallel capacitor containing 10 rigid plates was carefully immersed in this solution at 363 K and the absence of air bubbles between the plates was ensured. The glass vial was electrically shielded and transferred to a cavity drilled in a massive aluminium block whose temperature was controlled at 343 K. A copper–constantan thermocouple was immersed into the molten liquid mixture with its junction held above the capacitor.

The capacitance of the parallel plate capacitor was first measured in air prior to its immersion in the liquid mixture. Its value was nominally 14 pF and it changed by less than 0.2% over the temperature range 77–400 K. The capacitance, conductance and the dielectric loss factor of the thermoset containing ATBN were then measured at predetermined time intervals during its isothermal curing at 343 K up to about 10^5 s or about 24 h, when the capacitance and loss factor ceased to change during the time of our observation. The ATBN-containing thermoset was assumed to have been fully cured after this period.

The dielectric cell, which now consisted of a parallel plate capacitor rigidly held inside the solid thermoset, was then cooled to 77 K and its capacitance, conductance and loss factor were measured at intervals of 1 K up to about 340 K.

The capacitance and conductance were measured by means of a GenRad 1869 Digibridge which was interfaced with a personal computer for automatic data acquisition[13]. All connections of the parallel plate capacitor to the bridge were made by coaxial cables. The measured capacitance is accurate to within 0.1%, conductance to within 0.5% and temperatures to within 0.2 K.

RESULTS

The dielectric permittivity, ε', of the pure and ATBN-containing DGEBA–DDM thermosets measured for a fixed frequency of 1 kHz during their curing at 343 K is shown in *Figure 1*. The plot for the pure thermoset is similar to that reported in earlier papers[9–12], but for the ATBN-containing thermosets the plots show at first a small decrease in the permittivity, which is followed by a slow increase and finally a step-wise decrease to a value of about 3.6. The value of ε' of the

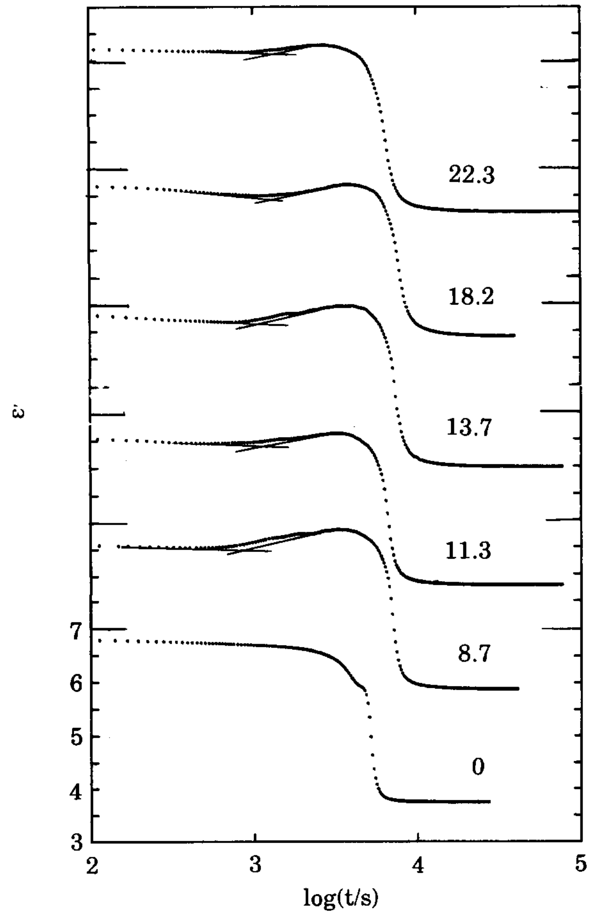

Figure 1 Dielectric permittivity, ε', as a function of curing time for pure and ATBN-containing DGEBA–DDM thermosets at 343 K and a fixed frequency of 1 kHz. Numbers next to the curves refer to the ATBN content (wt%). The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 2 units in ε', except for 18.2% ATBN which has been shifted by 2.5 units

Table 1 Dielectric properties of pure and ATBN-containing thermosets during their curing at 343 K

ATBN (wt%)	$\varepsilon''_{\min}$	$\varepsilon''_{\max}$	t (ks) ($\varepsilon''_{\max}$)	ε' $t = 0$	ε' $t \to \infty$	ε'' $t = 0$	ε'' $t \to \infty$	t_{cure} (ks) ($\sigma_0 = 0.556\,\mu\mathrm{S\,m^{-1}}$)
0.0	0.064	0.323	5.11	6.78	3.72	14.8	0.005	2.84
8.72	0.250	0.356	6.95	6.59	3.85	15.8	0.015	4.24
11.30	0.287	0.345	6.12	6.86	3.88	15.1	0.019	4.20
13.74	0.293	0.355	7.19	6.84	3.97	11.9	0.023	4.13
18.20	0.328	0.329	7.62	6.69	3.99	10.8	0.033	4.11
22.28	0.355	0.364	6.19	7.21	4.17	11.8	0.036	3.43

uncured thermoset is not greatly affected by the amount of ATBN in the sample, but ε' of the cured thermoset increases with increased ATBN concentration (*Table 1*). The time of cure, at which a point of inflexion during the stepwise decrease in ε' appears, increases on the first addition of ATBN to the thermoset and thereafter remains essentially unaltered on further addition of ATBN to the thermoset.

The plots of the dielectric loss, ε'', measured for 1 kHz of the pure DGEBA–DDM thermoset and those containing different amounts of ATBN during their curing, are shown in *Figure 2*. The plots for the ATBN-containing thermoset show a relatively slow increase in ε'', which is followed by a rapid increase before ε'' seems to undergo a step-like decrease with the curing time. This step-like decrease is interrupted by the appearance of a peak in ε''. As the amount of ATBN in the thermoset increases, the peak becomes increasingly obscured, but its position and height remain essentially unaltered. ε'' of the cured thermoset increases with increased ATBN concentration. A summary of these results is given in *Table 1*.

After the pure thermoset and each of the five ATBN-containing thermosets were cured, their dielectric properties were measured over a temperature range of 77–325 K at a fixed frequency of 1 kHz. As *Figure 3* shows, the permittivity increases with temperature from about 2.7 to about 3.7, and this increase becomes greater as the ATBN content of the thermoset is increased. For the pure thermoset, the dielectric loss reaches a peak value at about 235 K (*Figure 4*). Addition of ATBN to the thermoset is accompanied by shoulders on both sides of the ε'' peak and an overall increase in peak heights. A summary of the results shown in *Figures 3* and *4* is given in *Table 2*.

Plots of ε' and ε'' of 100% ATBN measured for a fixed frequency of 1 kHz as a function of temperature are shown in *Figure 5*. The pure ATBN shows an α-relaxation peak in ε'' at 240 K and a broad shoulder to this peak at temperatures below its T_g of 223 K. Its dielectric permittivity increases from 2.1 at 100 K to 8.7 at 300 K, with the major increase occurring near the α-relaxation peak.

DISCUSSION

Curing kinetics

During the curing of a pure thermoset, the terminal epoxide groups of DGEBA open to combine with the primary amine ($-NH_2$) group of the crosslinking agent to form an hydroxy ($-OH$) group and a secondary amine ($-NHR'$) group[4,5], which in turn combines with another epoxide group to form an $-OH$ and a tertiary amine ($-NRR'$) group[4,5]. Thus, the dielectric properties are expected to change as a result of three effects: (1) a decrease in the permittivity owing to a decrease in the orientation polarization, which occurs when the dipole moments of the $-NH_2$ and epoxide groups are replaced by the dipole moment of the $-OH$ group; (2) a decrease of the dipole moment per unit chain segment as the length of the chain and the density of crosslinks increase; and

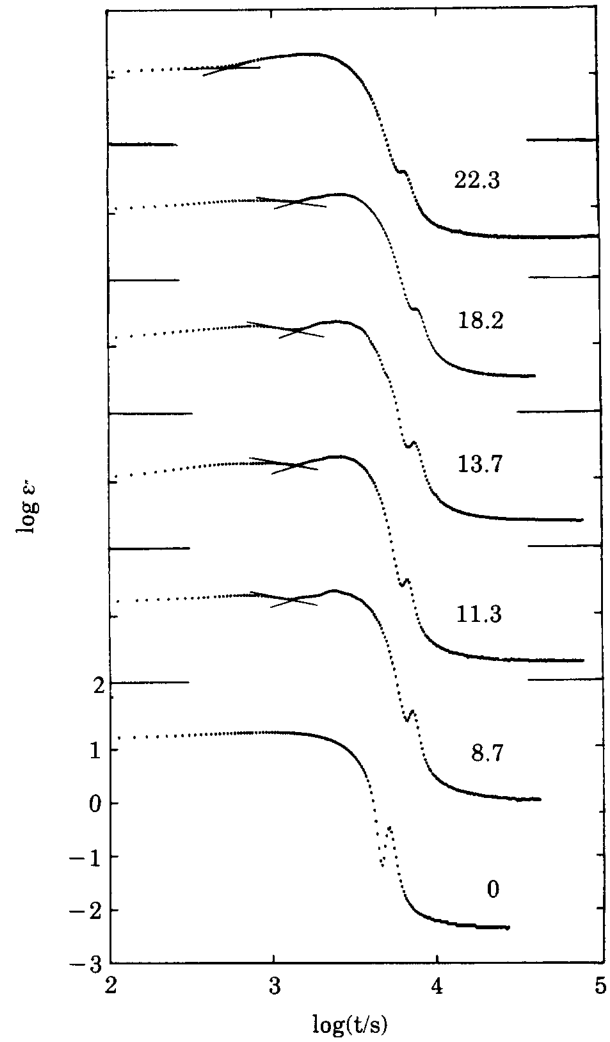

Figure 2 Dielectric loss, ε'', as a function of curing time for pure and ATBN-containing DGEBA–DDM thermosets at 343 K and a fixed frequency of 1 kHz. Numbers next to the curves refer to the ATBN content (wt%). The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 2 units in log ε''

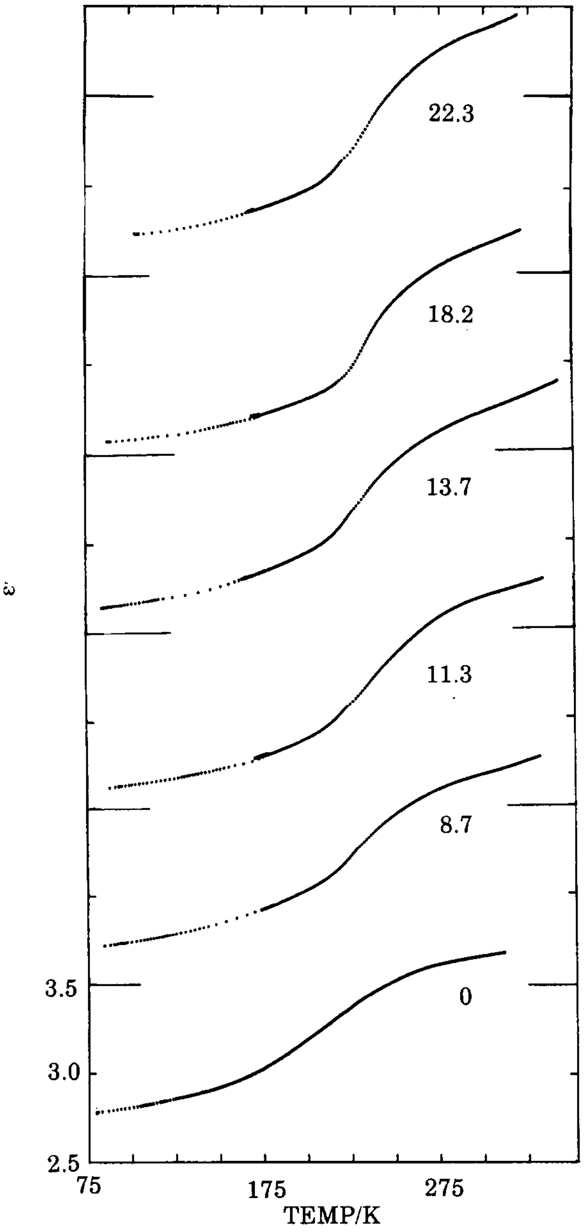

Figure 3 Dielectric permittivity, ε', of cured pure and ATBN-containing thermosets plotted as a function of temperature. Numbers next to the curves refer to the ATBN content (wt%). The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 1 unit in ε'. Measurements were made for a fixed frequency of 1 kHz

(3) a rapid increase in the dipolar reorientation or dielectric relaxation time as the Brownian diffusion of the chain or network segments carrying the dipole becomes progressively slower with the growth of the chain and the network. The relative importance of the three effects depends upon the state of the cure. During the initial stage of cure, the first and second effects on the dielectric properties are relatively small, but the third is expected to be extremely large and its magnitude depends on the time and temperature at which the dielectric properties of the thermoset are measured.

In the ATBN-containing thermosets, the changes in the dielectric properties during curing are also affected by the phase separation of the elastomer at the instant of its occurrence and thereafter by the growth of phase-separated regions, as the crosslinking between the components of a thermoset increases the chain length and the extent of the network. In *Figure 2*, the ε'' values reach a minimum value during curing, which is followed by one or several peaks with the ε'' ultimately decreasing, albeit slowly, to 10^{-2} or less. The concurrent change in ε' shown in *Figure 1* is a monotonic decrease towards a value between 3.6 and 4.0 with nearly all the decrease occurring during the period when ε'' reaches a maximum value.

These changes in ε' and ε'' measured as a function of time, which occur during an irreversible (chemical) kinetic process in a thermoset held at a fixed temperature, remarkably resemble the changes in ε' and ε'' observed when measured as a function of frequency in an isothermal dielectric relaxation experiment on dipolar liquids and solids, where neither chemical nor physical changes occur during the measurement period. This resemblance implies that the chemically and physically irreversible changes in the structure of a thermoset that occur with time during the curing are dielectrically analogous to the effects of an increase in the measurement frequency during the isothermal study of a chemically and physically stable state of a dipolar liquid or solid. The above-mentioned resemblance is, we suggest, a phenomenological equivalence between these two types of measurement, which becomes convincingly evident in the complex plane plots of ε^* shown in *Figure 6*.

An important aspect of the preceding discussion is that the irreversible chemical kinetics during the isothermal curing determines a thermoset's dielectric behaviour in a manner that is qualitatively similar to two unrelated effects: increase in the relaxation time of a chemically stable substance by decreasing its temperature; and increase in the frequency of the electric field for isothermal

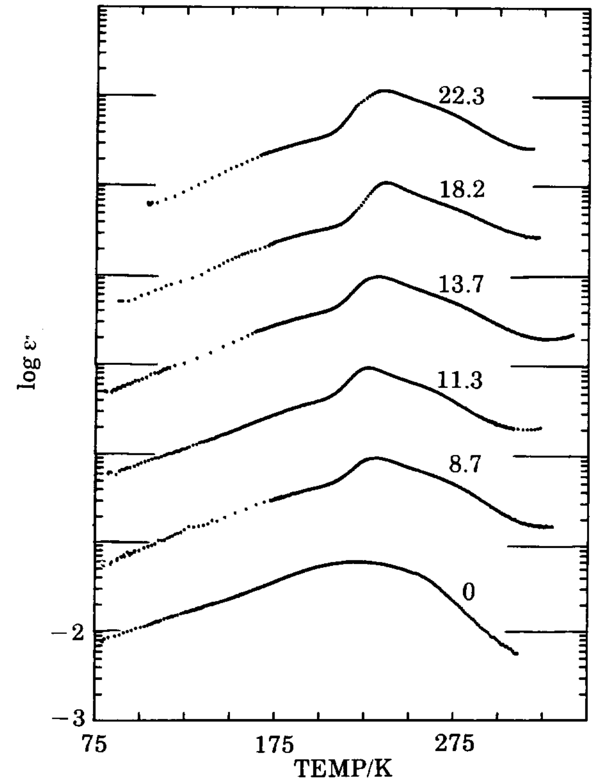

Figure 4 Dielectric loss, ε'', of cured pure and ATBN-containing thermosets plotted as a function of temperature. Numbers next to the curves refer to the ATBN content (wt%). The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 1 unit in log ε''. Measurements were made for a fixed frequency of 1 kHz

Table 2 Dielectric properties of pure ATBN and ATBN-containing thermosets in their cured states

ATBN (wt%)	$T_{\varepsilon''_{\max}}$ (K)	$\varepsilon''_{\max}$	ε'' at 300 K	ε' at 100 K	ε' at 300 K	ε' at $T_{\varepsilon''_{\max}}$
0.0	221.7	0.058	0.007	2.81	3.65	3.34
8.72	232.0	0.083	0.021	2.74	3.68	3.31
11.30	226.4	0.091	0.021	2.72	3.79	3.30
13.74	232.0	0.093	0.027	2.67	3.72	3.25
18.20	235.9	0.104	0.033	2.57	3.64	3.15
22.28	233.3	0.113	0.104	2.73	3.87	3.31
100.0	245.4	1.16	2.07	2.12	8.72	5.77

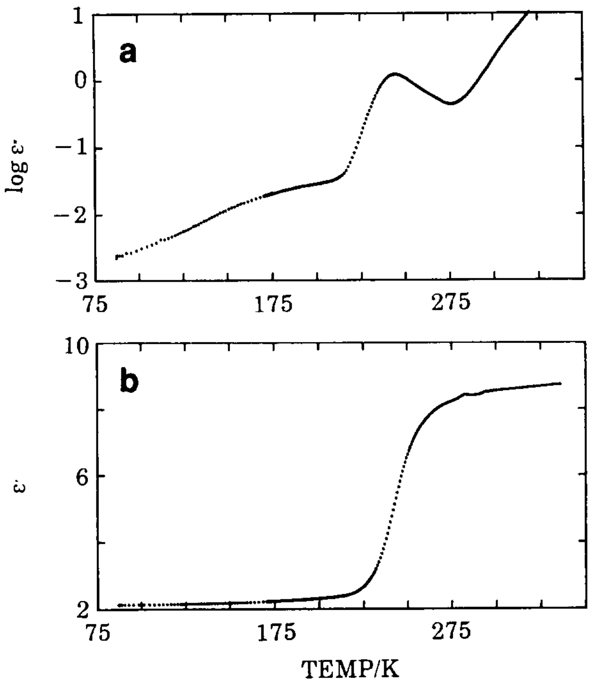

Figure 5 Dielectric loss, ε'' (a) and permittivity, ε' (b) of ATBN plotted as a function of temperature. Measurements were made for a fixed frequency of 1 kHz

measurements on a chemically stable liquid or solid. In both cases, phenomenological equations yield values of ε' and ε'' which are invariant with respect to one's choice of either ω or τ. The latter occurs on irreversible increase in the chain length and/or number of crosslinks in a thermoset. The observation of the shape of skewed arcs in *Figure 6* can be associated with a monotonic increase in the relaxation time[9,10] during the thermoset cure as a result of increase in chain length and the number density of crosslinks[11]. A theory for the dipolar processes during the curing of a thermoset has already been given elsewhere[9,10] and need not be discussed again, but it is important to note that the value of 0.4 for the curing parameter, γ, for the pure thermoset[10,11] remains essentially unchanged with the addition of ATBN. Admittedly, deviations from an arc at the low frequency end, which are caused by the increase in d.c. conductivity, prevent an accurate estimate of the parameter γ.

Phase separation during curing

As mentioned earlier, the increase in the polymer's molecular weight, which occurs during the curing, decreases the solubility of the dissolved phase within it.

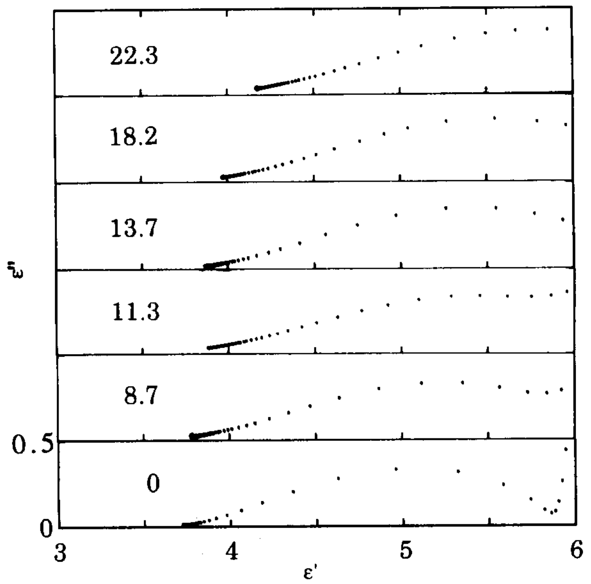

Figure 6 Complex plane plots of ε* of pure and ATBN-containing thermoset measured for a fixed frequency of 1 kHz during their curing. The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 0.5 units in ε''

As a consequence, phase separation of ATBN begins at a certain value of the molecular weight or equivalently after a certain time of isothermal cure when this value of the molecular weight is reached. This of course occurs more readily in the sol state of a thermoset than in its gelled or vitreous state. The phase separation into small spheres of one phase, namely ATBN, dispersed in the second phase, or liquid epoxy, produces a dielectric effect of its own, which is referred to as Maxwell–Wagner[14,15] absorption. The contribution to the dielectric properties arising from this effect has been a subject of several publications[16–21], but a basic discussion relevant to this study may be useful here. When spherical particles of phase 2 of small relative amounts are evenly distributed in phase 1 with volume fraction γ, the resulting permittivity and loss due to the Maxwell–Wagner effect in the phase-separated mixture is given by:

$$\varepsilon'_{\mathrm{MW}} = \varepsilon'_{\gamma}\left(1 + \frac{S}{1+\omega^2 p^2}\right) \qquad (1)$$

$$\varepsilon''_{\mathrm{MW}} = \frac{\varepsilon'_{\gamma} S \omega p}{1+\omega^2 p^2} \qquad (2)$$

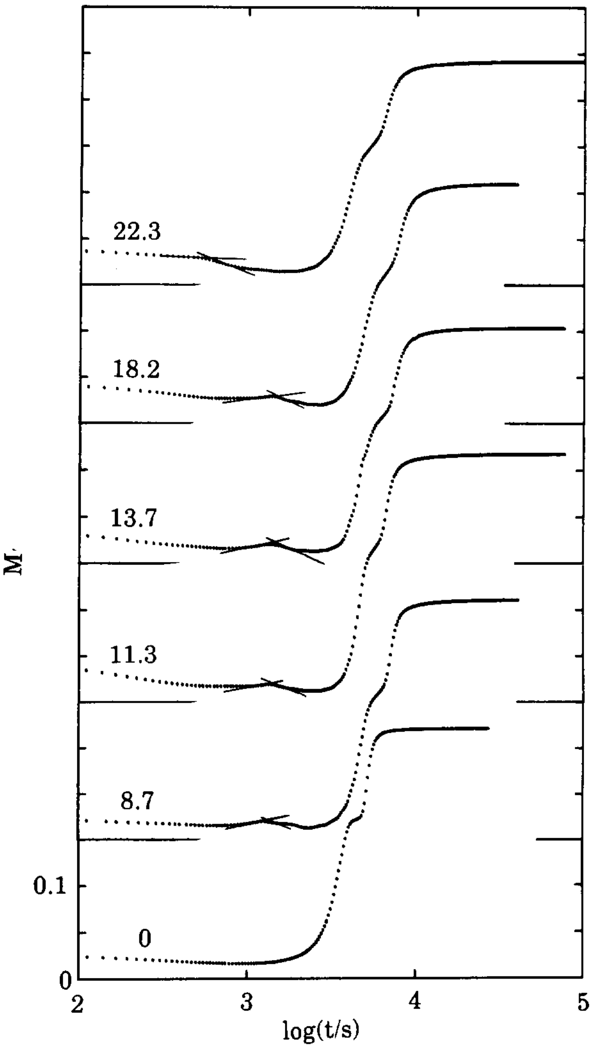

Figure 7 The real component of the electrical modulus, M', of pure and ATBN-containing DGEBA–DDM thermosets during their curing at 343 K and a fixed frequency of 1 kHz. Numbers next to the curves refer to the ATBN content (wt%). The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 0.15 units in M'

where

$$S = \frac{9\gamma\varepsilon'_1}{2\varepsilon'_1 + \varepsilon'_2} \tag{3}$$

$$\varepsilon'_\gamma = 1 + \frac{3\gamma(\varepsilon'_2 - \varepsilon'_1)}{2\varepsilon'_1 + \varepsilon'_2} \tag{4}$$

and

$$p = \frac{2\varepsilon'_1 + \varepsilon'_2}{4\pi(90 \times 10^{12}\sigma_2)} \tag{5}$$

In the above equations, ε'_1, ε'_2, σ_1 and σ_2 are the permittivity and conductivity of phases 1 and 2, respectively.

During the early period of the thermoset's curing, the mixture is homogeneous and $\gamma = 0$. Thus both ε'_{MW} and ε''_{MW} are zero and there is no contribution from the Maxwell–Wagner effect. But, as γ becomes finite, S in equation (3) and ε'_γ in equation (4) increase, because $\varepsilon'_2 = 8.72$ for pure ATBN (*Table 2*) and $\varepsilon'_1 = 6.72$ (*Table 1*) for pure epoxy thermoset remain relatively unchanged during the early stage of curing. In our studies, ω is constant and since the conductivity of ATBN remains constant with the curing time, σ_2 in equation (5) is constant. So, p remains nearly constant as γ increases. When phase separation occurs, both ε'_{MW} and ε''_{MW} therefore become finite and increase as γ increases according to equations (1) and (2), respectively. As further curing increases the viscosity of the mixture and the sol approaches its gel point, the increase in γ progressively slows with the curing time. Thus the magnitude of ε'_{MW} and ε''_{MW} approaches a limiting value with the curing time.

These ideas can now be expressed in terms of dielectric effects during the curing of an elastomer-containing epoxy. At the start of the cure, the dielectric properties of a thermoset have contributions from the d.c. conductivity and the dipolar relaxation process. At the instant phase separation of ATBN occurs, Maxwell–Wagner effects begin to make an additional contribution to the measured ε' and ε''. As the volume fraction of the phase-separated ATBN increases, ε'_{MW} and ε''_{MW} increase, but when the rate of increase of γ with time begins to decrease with the curing time, the contribution from the Maxwell–Wagner effect approaches a limiting value and thereafter any change in the measured ε' and ε'' is caused by the decrease in d.c. conductivity and increase in the relaxation time of the thermoset. On these theoretical grounds, we now expect that ε' and ε'' of the ATBN-containing thermoset would increase at the onset of phase separation, reach a maximum value and thereafter decrease as the epoxy component of the thermoset approaches its gelation and vitrification state.

The increase in ε' and ε'' (or τ) in *Figures 1* and *2*, and M' and M'' in *Figures 7* and *8* after a cure period of about 1 ks indicates the onset of this phase separation. This is supported by the evidence in *Figure 5*, where the extrapolated values of ε' and ε'' to 343 K would appear to be significantly higher than the corresponding values for the pure thermoset. The onset of phase separation is marked by the intersection of the two lines drawn in *Figures 1*, *2*, *7* and *8*, which show that the curing time for the onset of phase separation remains constant at about 1 ks with changing amount of ATBN in the thermoset for all concentrations less than 22 wt%. This observation is remarkable in that it implies that (i) the contributions to ε^* and τ from the pure ATBN or from its phase-separated state are greater than those from its dissolved state in the thermoset sol and (ii) the reactions between ATBN and DGEBA and DDM are too slow and too insignificant to alter the onset of phase separation. For thermosets containing 22 wt% ATBN, the phase separation is not as clearly marked, probably due to the reaction of the ATBN chains with the epoxide groups of DGEBA which becomes more significant as the concentration of ATBN increases. This is expected, since the duration at which ε'' reaches a maximum or peak value depends upon the rates of reactions of primary and secondary amine curing agent in the presence of ATBN, whose amine groups also react with DGEBA.

Properties of the cured thermoset

As is seen in *Table 2* and *Figure 4*, the values of ε'' at 300 K and of ε''_{max}, i.e. ε'' at a temperature where its peak appears, increase with increasing ATBN content of the thermoset and ε''_{max} increases almost linearly with an increase in the ATBN content in the thermoset. In an earlier study[8] where EPON 828 was used as a resin, the sub-T_g broad peak at 250 K of the pure cured thermoset

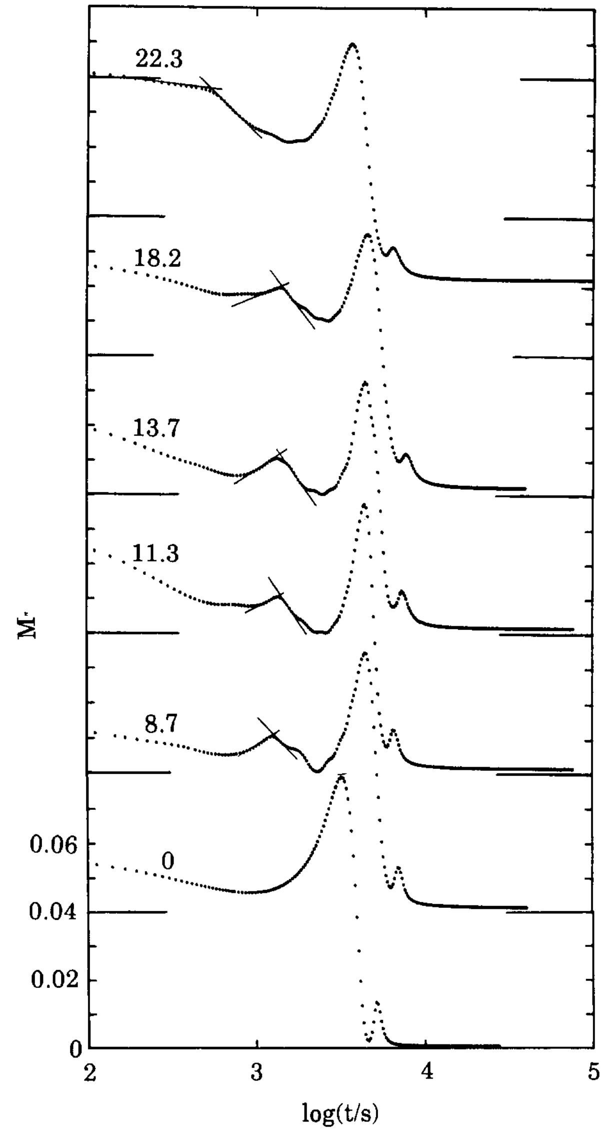

Figure 8 The imaginary component of the electrical modulus, M'', of pure and ATBN-containing DGEBA–DDM thermosets during their curing at 343 K and a fixed frequency of 1 kHz. Numbers next to the curves refer to the ATBN content (wt%). The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 0.04 units in M''

was shown to be a combination of two peaks, namely β and γ peaks. Addition of the ATBN causes the appearance of a new peak, as seen in *Figure 4*. The heights of these new ε'' peaks are superposed over a background loss whose level in turn decreases with increase in the ATBN content of the thermoset. Concomitantly, both the ε'' peaks become relatively more prominent. A comparison of the position of the peaks in *Figure 4* against that in *Figure 7* shows that the temperature at which the peak in ε'' appears in the ATBN-containing thermosets is within 3 K of the temperature at which the α-relaxation peak in the corresponding plots for the pure ATBN appears. This indicates that the ε'' peaks observed for the ATBN-containing thermosets are the α-relaxation peak of pure ATBN which has phase separated in the matrix of the DGEBA–DDM thermoset. The ATBN peak is superposed on the broad background which has resulted from contributions from both the sub-T_g relaxation processes of pure ATBN and the β and γ relaxation processes of the pure thermoset.

The dielectric permittivity and loss of the ATBN-containing thermoset at 300 K are of course technically important, in particular for applications as films and adhesives in microelectronics. As seen in *Table 2*, both the permittivity and loss increase with increase in the amount of ATBN in the thermoset and this increase is entirely due to the fact that at ambient temperature the dispersed ATBN phase is in a fluid or rubber state. Further or post-cure of the ATBN-containing thermoset, therefore, is not likely to significantly decrease its ε' and ε'' values which range between 3.68–3.87 and 0.021–0.104, respectively. In comparison, the corresponding values for pure thermoset are 3.65 and 0.007, respectively, and for pure ATBN are 8.72 and 2.07, respectively.

D.c. conductivity and thermoset curing

For a substance whose chemical and physical states irreversibly change with time, as during the curing of a thermoset, the complex permittivity, ε^*, may be written as:

$$\varepsilon^*(t) = \varepsilon'(t) - i\varepsilon''(t) = \varepsilon'(t) - i\left[\frac{\sigma(t)}{\omega e_0}\right] \qquad (6)$$

where ε' and ε'' are the real and imaginary parts of ε^*, σ is the measured electrical conductivity, ω is the angular frequency of measurement and e_0 is the permittivity of free space (= 8.8514 pF m^{-1}). Strictly speaking, σ of an insulator measured at an a.c. frequency ω is equal to the sum of the d.c. conductivity σ_0 and the a.c. conductivity from the reorientation of dipoles, σ_{dip}. Therefore, for thermosets, the conductivity measured at time t is given by:

$$\sigma(t) = \sigma_0(t) + \sigma_{\mathrm{dip}}(t) \qquad (7)$$

$\sigma_0(t)$ arises from the long-range diffusion of ions, including protons, and σ_{dip} from the dipolar reorientation of molecular segments. Earlier studies[10–13,22–29] have shown that during the curing of a thermoset, the magnitudes of $\sigma_0(t)$ relative to $\sigma_{\mathrm{dip}}(t)$ change from a relatively large initial value before curing begins, to a value near zero after the gelation time. This has been attributed to the decrease in the mobility of ions as an infinitely connected network forms and the viscosity increases. Simultaneously, Brownian diffusion of chain segments becomes progressively slower as the network forms, and σ_{dip} begins to progressively increase before the gelation time is reached. Its contribution to $\sigma(t)$ may be written in the form:

$$\sigma_{\mathrm{dip}} = \varepsilon''_{\mathrm{dip}}\omega e_0 = \left[\varepsilon_\infty + \Delta\varepsilon\mathscr{L}\left(-\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)\right]\omega e_0 \qquad (8)$$

$$\phi(t) = \exp[-(t/\tau_{\mathrm{dip}})^\beta] \qquad (9)$$

where $\varepsilon''_{\mathrm{dip}}$ is the contribution to ε'' from dipolar relaxation, ε_∞ is the limiting high frequency permittivity, $\Delta\varepsilon$ is the contribution to permittivity from orientation polarization, τ_{dip} is the dielectric (or dipolar) relaxation time, β is the Kohlrausch–Williams–Watts parameter[30,31] whose value is in the range zero and one, and $\mathscr{L}$ represents a one-sided Laplace transform of a function y. When $\beta = 1$, equation (9) represents a single relaxation time process.

For our analysis, it is necessary to determine the period over which σ_{dip} during the curing process remains insignificant in comparison with σ_0, so that the measured

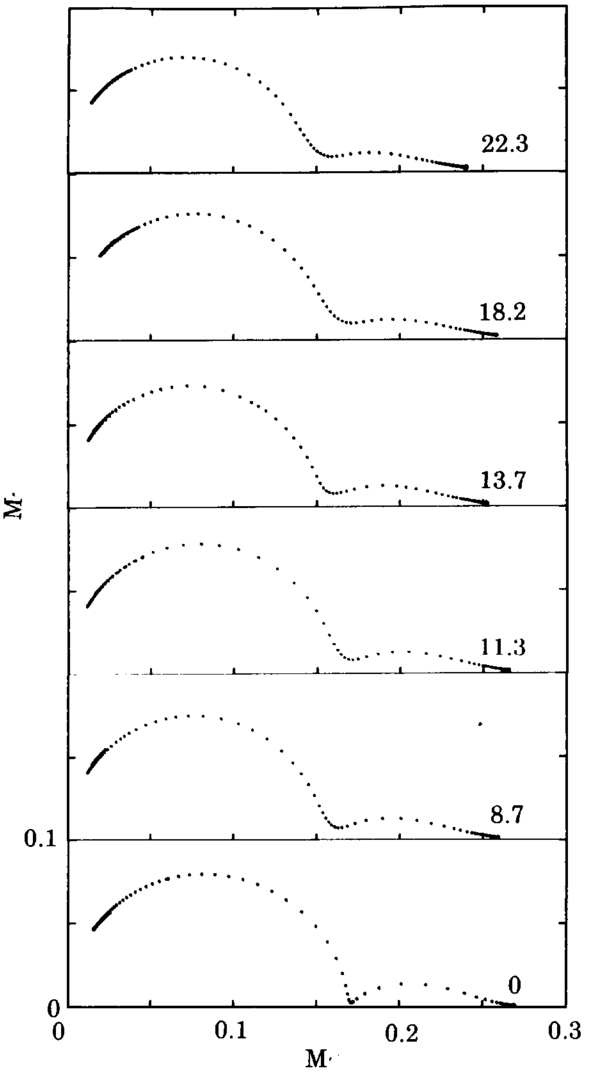

Figure 9 Complex plane plots of M^* of the pure and ATBN-containing thermosets measured during their curing at 343 K and a fixed frequency of 1 kHz. Numbers next to the curves refer to the ATBN content (wt%). The plot for pure epoxy is to scale; all other plots are progressively shifted along the ordinate by 0.1 units in M''

$\sigma(t)$ can be taken, within an upper error limit, as the value of $\sigma_0(t)$. The value of $\sigma_0(t)$ is thus directly proportional to $\varepsilon''(t)$ in cases where measurements are made at a fixed a.c. frequency during the curing process of the thermosets. We transform first the measured $\varepsilon'(t)$ and $\varepsilon''(t)$ into the complex electrical modulus, $M^*(t)$, a formalism which was originally developed by Moynihan and co-workers[32,33]:

$$M^*(t) = 1/e^*(t) = M'(t) + iM''(t) \qquad (10)$$

where

$$M'(t) = \frac{\varepsilon'(t)}{\varepsilon'(t)^2 + \varepsilon''(t)^2} \qquad (11)$$

and

$$M''(t) = \frac{\varepsilon''(t)}{\varepsilon'(t)^2 + \varepsilon''(t)^2} \qquad (12)$$

where M' and M'' are the real and imaginary components of M^*, and ε' and ε'' are as defined in equation (6), all at a time t during the curing process. If M^* was entirely due to d.c. conduction and had no contribution from σ_{dip} or $\varepsilon''_{\text{dip}}$, as discussed earlier, it is represented by:

$$M^*(t) = M_s(t)\frac{i\omega\tau_\sigma(t)}{1 + i\omega\tau_\sigma(t)} \qquad (13)$$

where τ_σ is the conductivity relaxation time formally given by the Maxwell equation:

$$\tau_\sigma = \frac{e_0\varepsilon_s}{\sigma_0} = \frac{1}{\omega \tan\delta} \qquad (14)$$

and

$$M_s = 1/\varepsilon_s \qquad (15)$$

where ε_s is the limiting low frequency permittivity. $M^*(t)$ in equation (13) is clearly invariant with respect to one's choice of ω or τ_σ as a variable. Therefore, according to equations (13) and (14), a decrease in $\sigma(t)$ during the curing process, when measured for a fixed value of ω, gives a complex plane plot of $M'(t)$ and $M''(t)$, whose shape is a semicircle, with a radius equal to $(M_s/2)$ and centre on the $M'(t)$ axis, provided the measured $\sigma(t)$ was entirely due to the d.c. conductance, and $\varepsilon_s = (1/M_s)$ remained unchanged on curing. But if $\sigma(t)$ also included contributions from σ_{dip}, then, as shown previously[12,13], the complex plane plot of M^* deviates from a semicircle, and this deviation is much larger than that caused by a decrease in ε_s. The complex plane plots of M^* for the various thermosets, measured at a fixed frequency of 1 kHz, are shown in *Figure 9*.

In *Figure 9*, the semicircle at short times during the cure, which appears at the extreme left of *Figure 9*, has its centre on the M' axis. Therefore, it indicates a single relaxation time process. The arc due to dipolar relaxation is skewed and follows the M^* representation of a stretched exponential decay function similar to that of equation (9). For the conductivity's single relaxation time, the frequency (1 kHz) of the M'' peak or $f(M''_{\max})$ is related to d.c. conductivity, σ_0, by:

$$\sigma_0 = 2\pi e_0 \varepsilon_\infty f(M''_{\max}) \qquad (16)$$

where e_0 is as defined in equation (6), and ε_∞ is the limiting high frequency permittivity for the conductivity relaxation process ($\varepsilon_\infty = M_\infty^{-1}$). According to equation (16), the time when M'' reaches its peak value during the curing in *Figures 8* and *9*, the physically and chemically arrested state of a thermoset would show in its isothermal spectrum at 343 K an M'' peak for a measurement frequency of 1 kHz. Since the d.c. conductivity is characterized here by a single relaxation process, $\varepsilon'(\omega) = \varepsilon_s = \varepsilon_\infty$ during the conductivity relaxation process and therefore ε_∞ in equation (16) is equal to ε' for 1 kHz when $M'' = M''_{\max}$. Alternatively, at any time during the cure when M' and M'' data lie on a semicircle, as in *Figure 9*, $\sigma(t)$ is equal to $\sigma_0(t)$. Thus either $\sigma_0(t)$ can be calculated from ε' data in *Figure 1* and equation (16) but at a time t when M'' reaches a peak value, or alternatively, and directly, the time t at which $\sigma_0(t)$ of the thermoset reaches a fixed value can be determined from *Figure 2*, where $\sigma(t) = e_0\varepsilon''(t)\omega$ is plotted against the time of curing. We determine the time of cure required to reach a fixed value of $\sigma_0(t)$ of 0.556 μS m^{-1}. These values are also listed in *Table 1*. The data clearly show that the time of cure required to reach a fixed value of d.c. conductivity is increased on the initial addition of ATBN to the thermoset and that further addition decreases this time. This is evidently due to an increase in the conductivity on the phase separation of ATBN, a phenomenon to which the complex plane plots of $M^*(t)$ are relatively insensitive.

CONCLUSIONS

A detailed dielectric study of pure ATBN, pure thermoset and ATBN-containing thermosets during their sol to gel to glass transformation and phase separation in the sol states shows time-dependent changes that can be understood in terms of the d.c. conductivity, orientation polarization and liquid–liquid phase separation.

During the curing of the ATBN-containing thermosets studied here, their electrical properties change first when phase separation of ATBN occurs in the sol state, and thereafter when a decrease in conductivity occurs as the gelation is approached and when an increase in the relaxation time occurs as the network gradually reaches the mechanical modulus characteristic of the glassy state. The complex plane plots of the permittivity and electrical modulus have the shape of an arc which is skewed at both the limiting short- and long-time intercepts for dipolar process. The shape of these plots can be fitted to a stretched exponential function with the value of the cure parameter $\gamma = 0.4$.

The onset of phase separation in the ATBN-containing thermosets is marked by both an increase in the permittivity and loss and in the real and imaginary components of the electrical modulus. This may provide a useful procedure for determining the time at which liquid–liquid phase separation begins and thereby for controlling the morphology of an elastomer-containing thermoset.

The main relaxation peaks in the cured thermosets are due to the α-relaxation of the phase-separated ATBN and its sub-T_g relaxation process which are observed in the pure ATBN. But this peak is superposed on a broad shoulder which has contributions from both the γ and β relaxations in the pure DGEBA thermoset. Both the permittivity and loss of the thermoset increase on addition of ATBN.

The complex plane plots of the electrical modulus show that the d.c. conductivity in the thermosets follows a single relaxation time, or Maxwell behaviour, and the time to reach a fixed value of d.c. conductivity decreases with increasing the amount of ATBN in the thermoset.

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