Relaxations in thermosets: 5. Dielectric studies of the effects of substitution of amines on curing kinetics and ageing of an epoxide thermoset

M. B. M. Mangion* and G. P. Johari
Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7
(Received 19 March 1990; accepted 13 July 1990)

The dielectric permittivity and loss of thermosets of diglycidyl ether of bisphenol A isothermally cured with pure and mixtures of diaminodiphenylmethane (DDM) and diaminodiphenylsulphone (DDS) have been measured as a function of time during their crosslinking process, after their ageing at 298 K for up to 182 days, and after thermal cycling to 453 K for 8 h. During crosslinking, the dielectric properties of thermosets are determined by two effects, namely: (i) a large decrease in the d.c. conduction at the beginning of the cure, and (ii) the dipolar relaxation process later in the cure. As the curing approaches completion, the time dependence of the complex permittivity follows the formalism $\phi(t)=\exp[-(t/\tau_{\rm cure})^{\gamma}]$ with $\gamma<0.4$. Both the strength of the dipolar relaxation and the value of the curing parameter γ increase with an increase in the amount of DDS in the curing amine. The change in the observed dielectric feature as the molar ratio of DDS in the curing amine mixture is increased are explained semi-quantitatively on the basis of changing kinetics of the crosslinking reactions. Ageing and thermal cycling of cured thermosets cause the strength of both of its sub-T_g relaxations to decrease further, as is generally observed for thermoplastics.

(Keywords: relaxation; thermosets; dielectric properties; curing kinetics; ageing; epoxide)

INTRODUCTION

Isothermal curing of a thermoset involves conversion first from sol to gel state and secondly from gel to glass state[1,2]. The time period required to achieve these states is generally known to vary with the nature of the crosslinking molecule for a given resin[3,4]. This variation is a reflection of the fact that electronic charge distribution, size and steric effects of a molecule all determine the rate at which polyaddition reactions occur. In our earlier studies of the isothermal curing of diglycidyl ether of bisphenol A[5], we had found that for the same curing temperature, the curing period increased by a factor of 40 when diaminodiphenylsulphone (DDS) was replaced by diaminodiphenylmethane (DDM). The study also revealed that the dielectric consequences of the chemical changes that occur with the curing time during the crosslinking of the thermoset were analogous to the frequency dependence of the complex permittivity isothermally measured for an amorphous solid near its T_g and that the curing parameter γ, which was used to describe the stretched exponential behaviour during the later part of the cure, was higher for DDS, a larger molecule, than for DDM. It therefore became important to examine the curing behaviour of an epoxide by systematically substituting one crosslinking molecule by another of a different size and dipole moment and to determine the variation in both the curing kinetics and the ageing behaviour of the thermosets thus formed.

We now report a study of the dielectric behaviour of an epoxide cured by a mixture of diaminodiphenylmethane and diaminodiphenylsulphone with a continuously varied molar ratio of the two components, and we analyse the results in terms of changes in the curing kinetics, sub-T_g relaxation processes, distribution of relaxation times and the effects of ageing on the sub-T_g relaxations of the thermoset formed. The results substantiate our earlier ideas on the theoretical description of the kinetics of curing of thermosets as studied by dielectric methods[5–8], and provide a further confirmation of our earlier views that, in the molecular kinetic behaviour of the glassy thermosets, intermolecular forces play a more important role than intramolecular forces.

EXPERIMENTAL METHODS

Samples of thermosets were prepared by mixing one mole of the mixed amines (x mol diaminodiphenylsulphone (DDS) and $(1-x)$ mol diaminodiphenylmethane (DDM)) with two moles of liquid diglycidyl ether of bisphenol A (DGEBA). An appropriately weighed amount of granular DDS was first mechanically mixed with the required amount of liquid DGEBA for about 2 min at 420 K. The resulting homogeneous liquid was quenched to 360 K and the required amount of granular DDM was added. The mixture was further mechanically mixed for 2 min and allowed to cool to room temperature. It was thereafter directly poured into the dielectric cell at room temperature. DDM and DDS of >99% purity were purchased from Aldrich Chemicals Company, and a commercial sample of DGEBA, under the name of

---

* Present address: G.E.M.P.P.M., Institut National des Sciences Appliquées, Bat. 502, 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France

0032-3861/91/152747–08

Epon 828, was donated to use for our studies by Shell Petroleum. Epon 828 has been carefully characterized by LeMay, Swetlin and Kelley[9] and its properties listed by Choy and Plazek[10]. Its number-average molecular weight is 380, which was used in our sample preparation, and it is assumed that one amine proton reacts with one epoxy group.

The disposable dielectric cell that contained the thermoset sample was constructed from polished aluminium rods and a Nylon spacer. The inner flat bottom of a cylindrical container of about 18 mm diameter and an aluminium disc of about 13 mm diameter served as the two electrodes, which were separated by a 0.5 mm gap. Electrical leads were connected to the electrodes by means of screws. The cell thus prepared was then electrically shielded. The cell constant C_o was determined by measuring the capacitance of the empty cell at the temperature where curing was intended, T_{cure}. The C_o value of the measuring cell was further corrected by assuming the dielectric permittivity ε' value after a long curing time of all thermosets at T_{cure} to be the same, and equal to the limiting high-frequency permittivity of the cured thermosets. Measurements repeated with the various cells gave values within 3% of each other and we regard this to be within the uncertainty of such measurement.

The liquid mixture was poured into the dielectric cell held at room temperature. The cell was electrically connected to the measuring assembly and placed inside a glass jacket preheated to the temperature of cure, T_{cure}. The time at which the temperature of the sample reached $T_{cure}-5$ K was taken as the initial time ($t=0$). The temperature was measured as a function of time for a fixed frequency of 1 kHz. After the dielectric properties of the sample had reached stable values characteristic of the amorphous state, it was stored at room temperature for five months and its sub-T_g relaxations were studied. For this study, each dielectric cell containing the thermoset was cooled to 77 K and thereafter heated at a rate of 1 K min^{-1} during which its ε' and ε'' were measured at 1 K intervals up to 325 K. Each dielectric cell containing the sample was subsequently heated to 453 K, i.e. 18 K above the T_g of the DGEBA-DDM thermoset and 32 K below that of the DGEBA–DDS thermoset, for 8 h to allow the thermoset's cure to reach near-completion, and its sub-T_g relaxations were again studied.

A General Radio Genrad 1689 Digibridge, which was interfaced with an IBM computer, was used for automatic data collection at a fixed frequency both isothermally as the curing proceeded or with changing temperature.

RESULTS

The data of dielectric permittivity ε', loss ε'' and loss tangent tan δ, which were measured for a fixed frequency of 1 kHz at increasing intervals of time during the isothermal curing of the seven thermosets, are plotted against the time of cure in *Figure 1*. The temperatures of the isothermal cure varied between 375 and 379 K for the different thermosets, mainly because of the difficulties in attaining a fixed temperature, but this variation is considered insignificant for our purposes here and the data are regarded as corresponding to a curing temperature of 377±2 K for all cases. In *Figure 1*, the value of ε' decreases monotonically on the curing of all thermosets, and both ε'' and tan δ initially decrease towards a minimum after a certain period of cure, which is followed by a peak before ε'' and tan δ finally decrease to a low value characteristic of the glassy state of a polymer. The times at which ε'' reaches both its minimum and its peak values for the various thermosets are listed in *Table 1*, along with the values themselves.

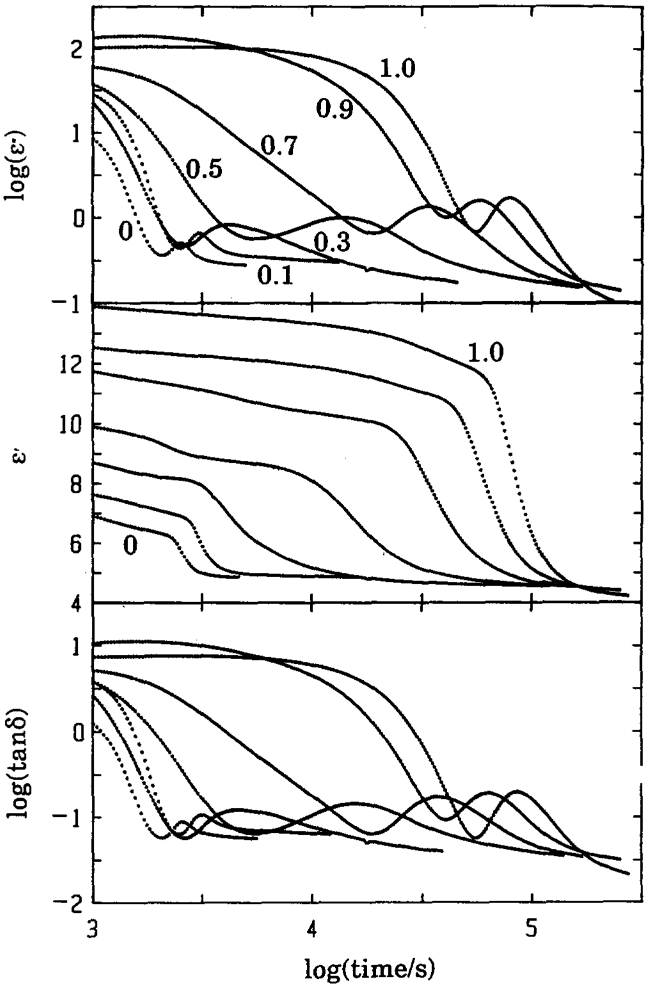

Figure 1 The dielectric permittivity, loss and loss tangent (ε', ε'' and tan δ, respectively) of the DGEBA-based thermosets measured for a fixed frequency of 1 kHz during their curing at 377±2 K. The number next to the curves is the mole fraction x of DDS in the DDM–DDS amine mixture

The ε' and ε'' data shown in *Figure 1* are plotted in a complex plane in *Figure 2*. These plots show changes in ε' and ε'' that occur as the liquid thermoset cures and ultimately becomes rigid. The shape of the plots is skewed at both short and long curing times, with a greater skew at longer times, when ε' approaches its infinite-time limit $\varepsilon'(\infty)$.

The curing times at which ε'' reaches its minimum and its peak values for a fixed frequency of 1 kHz are plotted against the composition of the curing agent, represented by x, the mole fraction of DDS, in *Figure 3a*. The values of ε''_{max} of the seven thermosets are also plotted against x in *Figure 3b*. These plots show an increase in log $t(\varepsilon''_{min})$, log $t(\varepsilon''_{max})$ and ε''_{max} with the increase in the mole fraction of DDS in the DDM–DDS mixtures.

During the isothermal curing, the thermoset samples were kept at T_{cure} for a period of m hours and thereafter

Table 1 The features of the dielectric behaviour during the curing of DGEBA–(xDDS, (1 – x)DDM)

x	T(K)	$\varepsilon''_{\min}$	$t_{\min}$ (ks)	$\varepsilon''_{\max}$	$t_{\max}$ (ks)	m (h)	n (days)	$\Delta\varepsilon$	γ
0	375.0	0.353	2.08	0.495	2.50	49	173	1.59	0.27
0.1	377.3	0.426	2.50	0.636	3.02	96	162	2.20	0.30
0.3	379.7	0.455	2.60	0.807	4.20	49	173	3.80	0.33
0.5	376.4	0.544	6.00	0.978	13.7	45	153	4.32	0.36
0.7	375.6	0.625	18.9	1.297	33.5	47	178	5.60	0.38
0.9	377.8	0.966	40.6	1.526	57.0	69	181	6.60	0.38
1.0	377.3	0.654	55.0	1.560	79.4	75	181	7.50	0.38

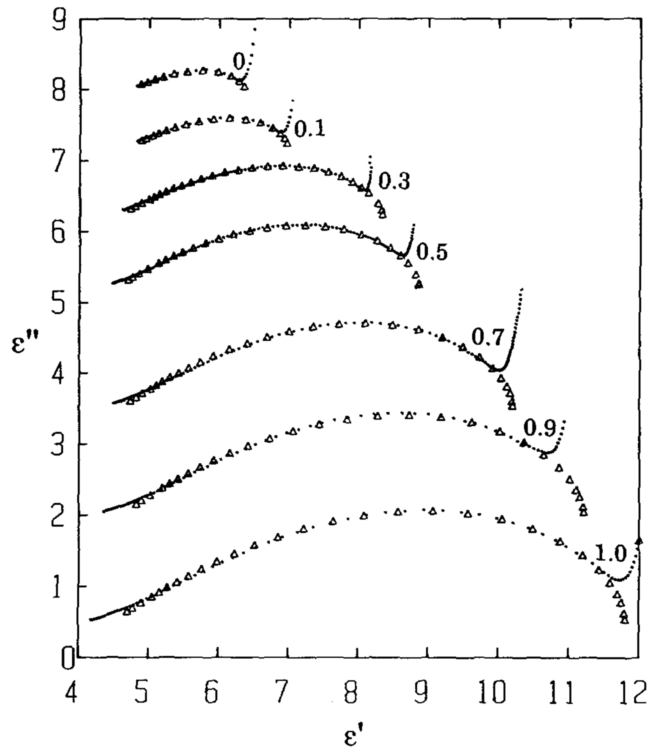

Figure 2 The complex plane plots of ε^* of the DGEBA-based thermosets measured for a fixed frequency of 1 kHz during their curing at 377±2 K. The number next to the plots represents the same as in *Figure 1*. The plots are shifted upwards for clarity

stored at 298±2 K for a period of n days. Numerical values of m and n are listed in *Table 1*. After this period, each sample contained in the cell was cooled to 77 K and its ε' and $\tan\delta$ were measured for a fixed frequency of 1 kHz at 1 K intervals from 80 to 325 K. The $\tan\delta$ values obtained from these measurements on the seven thermosets are plotted against the temperature in *Figure 4a*. These plots show one relaxation or γ peak at low temperatures near 140 K (which, in four of the seven thermosets, remains only partially resolved), and a second better-resolved and more pronounced β relaxation peak near 250 K. The shapes of these peaks are similar to those observed in our earlier studies[6–8].

In order to analyse the features of the sub-T_g relaxation peak, the ε' and ε'' values representing significant features were normalized with respect to the corresponding ε' value at 90 K. These values are represented by subscript N with the temperature in parenthesis. For example, $\varepsilon'_N(320)$ denotes the value of ε' measured at 320 K divided by ε' measured at 90 K, $\varepsilon''_N(\beta)$ the value of ε'' measured at the height of the β peak divided by ε' at 90 K, etc.

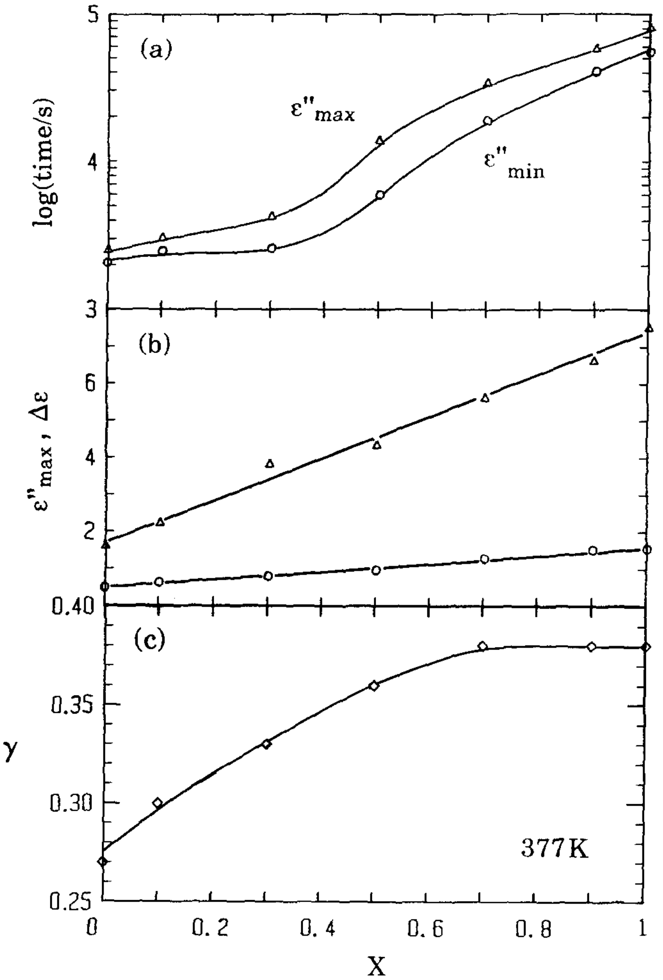

Figure 3 (a) The plots of the time during the curing process when ε'' reaches its minimum value $t(\varepsilon''_{\min})$ and its peak value $t(\varepsilon''_{\max})$ against the composition of the curing agent. (b) The plots of $\Delta\varepsilon$ and $\varepsilon''_{\max}$ at 377±2 K against the composition of the curing agent. (c) The plot of the curing parameter γ against the composition of the curing agent

These values along with the temperature of the β peak, T_β, are listed in *Table 2*.

The data listed in *Table 2* are plotted against the mole fraction of the DDS in the DDM–DDS mixture (used for the curing) in *Figure 5*. The plots clearly show that each of the quantities in *Table 2* varies linearly with the mole fraction of DDS in the thermoset.

After completion of the measurements that are shown in *Figure 4a*, the dielectric cells containing the thermosets were kept at a constant temperature of 453 K for 8 h and cooled to 77 K. The $\tan\delta$ of the thermosets was again measured at 1 K intervals up to 325 K and these data are plotted against temperatures in *Figure 4b*. The ratios

ε'_N and ε''_N were determined from these data in the same manner as for the values listed in *Table 2*, and the corresponding values are provided in *Table 3*.

The data seen in *Figures 4* and *5* and *Tables 2* and *3* indicate that the thermal treatment of the thermosets for 8 h at 453 K substantially alters the features of their sub-T_g relaxations. These changes between the corresponding values of the various quantities listed in *Tables 2* and *3*, and plotted against the mole fraction of DDS in *Figure 5*, clearly show that the strengths of both the γ and β relaxation processes decrease on further curing and/or ageing at 453 K for 8 h, and the temperature of the β relaxation peak increases by about 10 K.

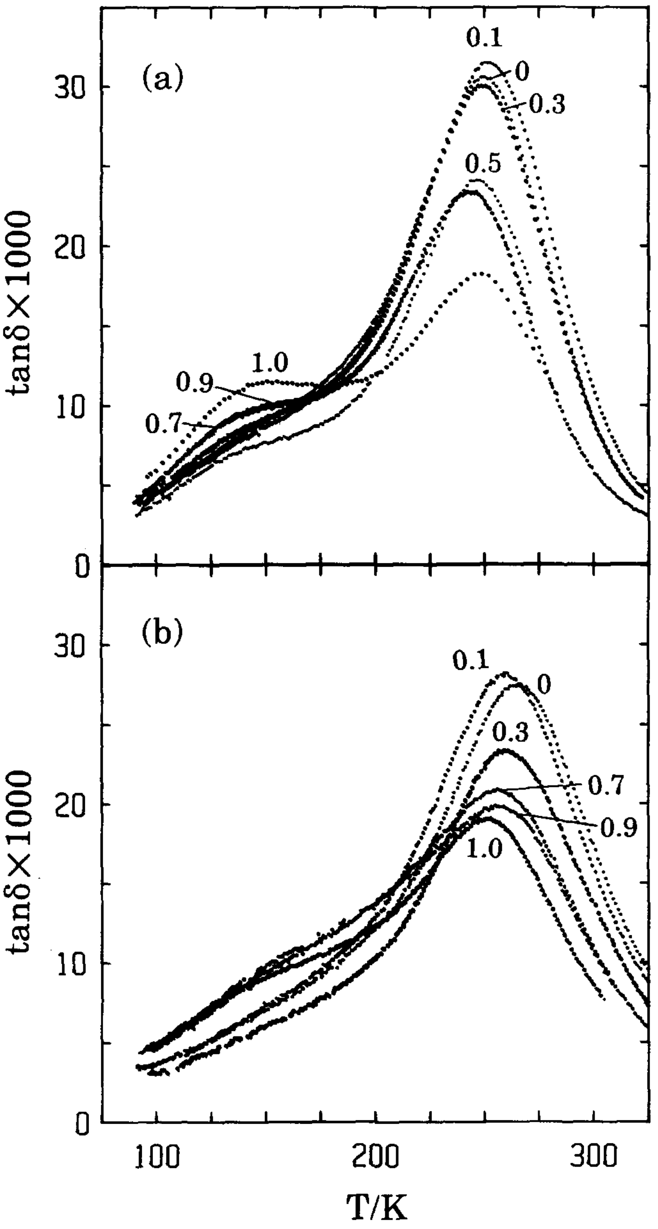

Figure 4 (a) The tan δ for the various thermosets measured after their ageing for n days at 298±2 K; and (b) the corresponding plots after ageing the samples for a further 8 h at 453 K. The data were obtained for a fixed frequency of 1 kHz and are plotted against temperature on a linear scale

DISCUSSION

The dielectric effect during isothermal ageing

The dielectric properties of a thermoset liquid change during the curing of, or crosslinking between, its components as the terminal epoxide group opens to form one OH group and one covalent linkage with the amine[11,12].

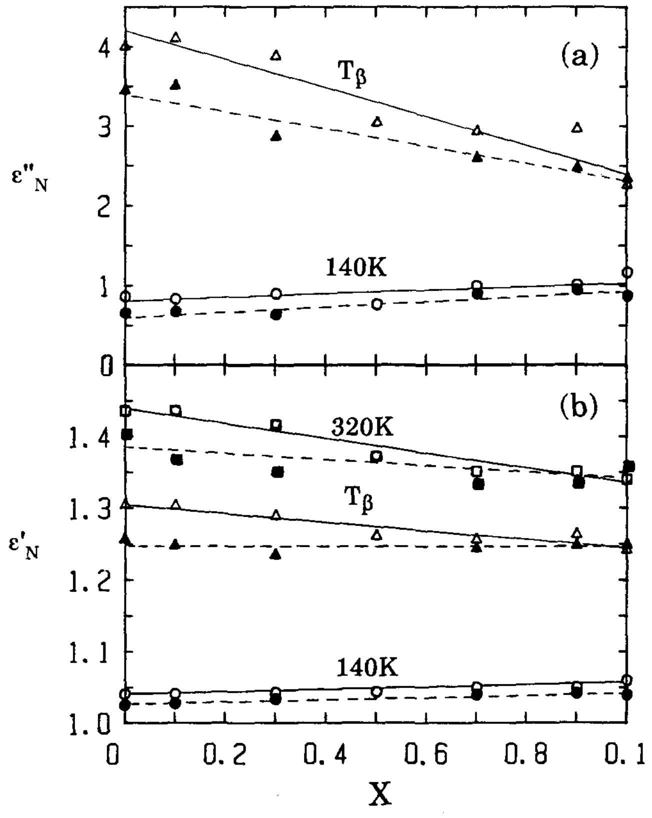

Figure 5 (a) The normalized strengths of the dielectric γ and β relaxation peaks. (b) The corresponding ε' behaviour plotted against the composition of the curing agent. Filled data points and broken lines were measured after the thermoset samples were kept for n days at 298 K and thereafter kept for 8 h at 453 K

Table 2 Features of the dielectric sub-T_g relaxations of DGEBA-(xDDS, $(1-x)$DDM) thermosets after annealing for m hours at 377±2 K and n days at 298 K

x	$\varepsilon'_N(140)$	$\varepsilon'_N(\beta)$	$\varepsilon'_N(320)$	$\varepsilon''_N(140)\times10^2$	$\varepsilon''_N(\beta)\times10^2$	T_β (K)
0	1.041	1.303	1.435	0.863	3.99	252.0
0.1	1.041	1.301	1.435	0.833	4.09	254.5
0.3	1.043	1.287	1.416	0.900	3.87	251.2
0.5	1.044	1.259	1.371	0.767	3.03	249.0
0.7	1.050	1.254	1.350	0.996	2.92	244.5
0.9	1.050	1.261	1.350	1.01	2.95	246.0
1.0	1.060	1.240	1.339	1.16	2.25	249.0

Table 3 Features of the dielectric sub-T_g relaxations of DGEBA-(xDDS, $(1-x)$DDM) thermosets after annealing for 8 h at 453 K

x	$\varepsilon'_N(140)$	$\varepsilon'_N(\beta)$	$\varepsilon'_N(320)$	$\varepsilon''_N(140)\times 10^2$	$\varepsilon''_N(\beta)\times 10^2$	T_β (K)
0	1.025	1.255	1.402	0.653	3.44	267.5
0.1	1.027	1.247	1.367	0.668	3.50	261.5
0.3	1.033	1.234	1.350	0.631	2.86	263.0
0.7	1.039	1.243	1.332	0.892	2.59	257.3
0.9	1.041	1.247	1.333	0.938	2.47	259.0
1.0	1.039	1.248	1.357	0.865	2.34	253.5

This change is due partly to a concurrent decrease in the net dipole moment per unit of the monomer or per unit volume of the thermoset and partly to an increase in the viscosity and the molecular relaxation time of the thermoset. Thus, the extent of the chemical reactions controls the physical properties of the thermoset. The static dielectric properties examined here are associated with the number and magnitude of the dipole moments of the various segments and the dynamic properties are associated with the ionic transport and molecular chain diffusion. In the plots of *Figure 1*, the ε' and $\tan\delta$ measured for a fixed 1 kHz frequency and fixed 377 K temperature reach with the passage of time a broad minimum followed by a peak with the values ultimately decreasing, albeit slowly, to 10^{-1} or less. The concurrent change in ε' is a monotonic decrease towards a value of about 4.4 with nearly all the decrease occurring during the duration when ε'' and $\tan\delta$ reach 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 measurements, which becomes convincingly evident in the complex plane plots of ε^* shown in *Figure 2*.

In order to develop a theory for the equivalence observed here, we begin by assuming that the value of ε'' of the uncured and ungelled thermoset samples has a relatively large contribution from the d.c. conductivity σ_0. In general, the complex dielectric permittivity can be expressed as:

$$\varepsilon^* = \varepsilon_d^* - i\sigma_0/\omega e_0 \qquad (1)$$

where ε_d^* represents the dipolar contribution to ε^*, ω is the angular frequency of the applied electric field, and e_0 is the permittivity ($=8.854$ pF m^{-1}) of free space. At the early stages of the cure, σ_0 rapidly decreases as curing proceeds to a value where the contribution to ε'' from a.c. conductivity (associated with dipolar relaxation) begins to dominate. (In a subsequent paper[13], this aspect of σ_0 is analysed in terms of gel formation.) This is formally achieved at a curing time equal to or greater than that when ε'' reaches a minimum value in the beginning of the curing process, as is seen in *Figures 1* and *2*. If the contribution to the value of ε'' from σ_0 were considered negligible, the complex permittivity at any instant during the curing process is given by:

$$\varepsilon^*(t_{\mathrm{cure}}) = \varepsilon_\infty(t_{\mathrm{cure}}) + [\varepsilon_0(t_{\mathrm{cure}}) - \varepsilon_\infty(t_{\mathrm{cure}})] \times \int_0^\infty e^{-i\omega t}\left(-\frac{d\phi_{t\,\mathrm{cure}}(t)}{dt}\right)dt \qquad (2)$$

where $\varepsilon_0(t_{\mathrm{cure}})$ and $\varepsilon_\infty(t_{\mathrm{cure}})$ are the limiting low- and high-frequency values of ε' at the instant of t_{cure}, respectively, and $\phi_{t\,\mathrm{cure}}(t)$ is the dielectric relaxation function at the instant of t_{cure}. The function $\phi(t)$ for the decay with time of a measurable quantity is given by an empirical stretched exponential function according to Kohlrausch[14] and Williams and Watts[15], which is modified as[5]:

$$\phi_{t\,\mathrm{cure}}(t) = \exp[-(t/\tau_{t\,\mathrm{cure}})^{\gamma_{t\,\mathrm{cure}}}] \qquad (3)$$

where $\tau_{t\,\mathrm{cure}}$ is the relaxation time of the structural state of the thermoset at a given t_{cure} during its curing period and t is the time (of the order of 1 ms corresponding to 1 kHz) for the observation of the decay of the thermoset's response to an electric field during which the effects on ε^* owing to a change in the state of a thermoset is negligible. It is to be noted that the equivalent Kohlrausch–Williams–Watts function[15] lacks the t_{cure} condition. Therefore, the function $\phi_{t\,\mathrm{cure}}(t)$ of equation (3) is expected to depend on (i) t_{cure}, (ii) $\tau_{t\,\mathrm{cure}}$, and (iii) $\gamma_{t\,\mathrm{cure}}$. This means that for a given fixed value of $\gamma_{t\,\mathrm{cure}}$, the change in $\phi_{t\,\mathrm{cure}}(t)$ during a thermoset's curing process is similar to the change that would be caused by an increase in the molecular weight of a polymer, at least at the initial stage of curing until a gel or a formally infinitely connected network (of infinite molecular weight) is formed. For a chemically stable substance, the parameter γ becomes equivalent to β, the Kohlrausch–Williams–Watts (KWW) parameter[14,15].

During the cure of thermosets, the value of γ for the α process shown in *Figures 1* and *2* is found to decrease at early curing times and to reach a constant value before the appearance of a minimum in the dielectric loss[7,8]. Alternatively stated, when the contribution to ε^* from σ_0 becomes relatively small, i.e. near the minimum, the value of the parameter γ reaches its limiting value. Since the value of γ could be determined from *Figures 1* and *2* only after the contribution from σ_0 to ε^* has vanished, its value is regarded as constant, and therefore independent of the number of crosslinks and of the curing time t_{cure}. The integral of equation (2) may thus be written as:

$$\int_0^\infty e^{-i\omega t}\left(-\frac{d\phi_{t\,\mathrm{cure}}(t)}{dt}\right)dt = N^*(\omega\tau) = N'(\omega\tau) - iN''(\omega\tau) \qquad (4)$$

where the values of the parameter N^* have been calculated by Moynihan *et al.*[16] for values of γ between 0.3 and 1 (these are expressed as β by Moynihan *et al.*[16]) and values of $z=\omega\tau$ between 10^{-3} and 10^4. For values of γ lower than 0.3, we used the z dependence of N^* derived from the formalism and tables developed by Bendler and coworkers[17–19] as described in the appendix of refs. 8 and 20. A further approximation of a constant value of ε_0 and ε_∞ also needs to be made here, particularly since the two quantities could not be satisfactorily measured during the curing of the thermosets. This approximation is expected to have a negligible effect on our main conclusion, for the changes in ε_0 and ε_∞ with continuously increasing time (after gelation) are relatively small. The values of ε' and ε'' can therefore be calculated from the following two equations, whose various parameters are already defined in equations (2) and (4):

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)N' \quad (5)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)N'' \quad (6)$$

Equations (5) and (6) were fitted to the ε' and ε'' of all the variously cured thermoset samples, and the theoretically calculated points are represented as triangles in *Figure 2*. The equations clearly fit the experimental data satisfactorily, using the values of the stretched exponential decay function parameter γ and $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_\infty)$, which are given in *Table 1* and plotted against x in *Figures 3b* and *3c*.

An important physical 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: (i) increase in the relaxation time of a chemically stable substance by decreasing its temperature, and (ii) increase in the frequency of the electric field for isothermal dielectric measurements on a chemically stable liquid or solid. In both cases, phenomenological equations (5) and (6) yield values of ε' and ε'' that are invariant with respect to one's choice of either ω or τ as a variable. The observations of the shape of skewed arcs in *Figure 2* therefore clearly implies that the average relaxation time increases monotonically during a thermoset's cure. This increase is, of course, caused by the irreversible increase in the chain length and/or in the number density of crosslinks.

Dielectric effects and amine composition

The curves of log ε'' against log t in *Figure 1* show, for each composition, a point of inflection in the initial part, and, as x increases, the rate of decrease of the corresponding slope (d log ε''/d log t) at the point of inflection initially decreases, reaches a minimum value at $x=0.7$ and then increases as x approaches unity. As discussed above, the decrease in ε'' that occurs in the time range of the inflection point is mainly caused by the decrease in the d.c. conductivity, which ultimately reaches zero value at the gel point. The rate of decrease in the d.c. conductivity at the inflection point is expected to be controlled by the rate of increase in the viscosity and of the network formation, which in turn is controlled by the rate of reactions at the corresponding curing time. The extent of reaction at this curing time, i.e. when inflection occurs, is expected to be somewhat less than the extent of reaction α_g at the gelation point. It appears therefore that this point of inflection occurs in the sol state of the thermoset.

Figure 3a further shows that the logarithmic separation in time between the ε'' minimum and maximum initially increases up to $x=0.5$, where it reaches a maximum value, and then decreases. We showed in the preceding section that the appearance of the ε'' peak is caused by an increase in the dipolar relaxation time. Accordingly, a larger logarithmic separation on the time scale between the ε'' minimum and ε'' maximum is due to a slower logarithmic rate of increase in the relaxation time, which is itself, again, controlled by the rate of increase in viscosity and of network formation, and which in turn is controlled by the reaction rates at the corresponding times during the curing stage, from near the gel point to the vitrification point. From the foregoing discussion, it seems that an explanation for the non-monotonic composition dependence of the dielectric features of the DGEBA cured with the mixed amines is related to the manner by which the extent of reaction changes with the curing time in each thermoset. Theoretical consideration and justification for these observations can now be discussed as follows.

In general terms of the fractional degree of conversion α, the curing kinetics of a thermoset is written as[1,21,22]:

$$d\alpha/dt = f(\alpha) \quad (7)$$

where f, the functional form of α, varies with the nature of the thermoset. Barton[22,23] found that the calorimetric data he obtained during the curing of the DGEBA–DDS thermoset could be satisfactorily fitted to the function f in the form:

$$f(\alpha) = (A_0 + A_1\alpha + A_2\alpha^2)(1-\alpha) \quad (8)$$

where the values of the temperature-dependent kinetic constants, A_0, A_1 and A_2, extrapolated to 377 K from Barton's results[23], are $6.40 \times 10^{-6}\ \mathrm{s}^{-1}$, $2.6 \times 10^{-4}\ \mathrm{s}^{-1}$ and $4.86 \times 10^{-4}\ \mathrm{s}^{-1}$, respectively. Equation (8) has been found to account for both the chemically controlled and the diffusion-controlled kinetics for the DGEBA–DDS thermoset. The equivalent expression for the curing kinetics of the DGEBA–DDM thermoset was given by Sourour and Kamal[24] and Huguenin and Klein[25] as:

$$f(\alpha) = (k_1 + k_2\alpha)(1-\alpha)(0.99-\alpha) \quad (9)$$

where the values of the kinetic constants k_1 and k_2 at 377 K are $1.07 \times 10^{-4}\ \mathrm{s}^{-1}$ and $3.35 \times 10^{-3}\ \mathrm{s}^{-1}$, respectively.

These functional forms of equations (8) and (9) allow us to calculate the time needed to reach a given conversion during the curing of both the DGEBA–DDM and DGEBA–DDS thermosets by a numerical integration of equation (7), according to:

$$t(\alpha) = \int_0^\alpha d\alpha/f(\alpha) \quad (10)$$

Plots of α against the time of cure of the DGEBA–DDM and DGEBA–DDS thermosets thus calculated are shown in *Figure 6*, where it is evident that, at the same temperature of 377 K, the cure of DGEBA occurs much faster with DDM than with DDS. For example, after 2.6 ks, the extent of reaction is 80% for the DGEBA–DDM thermoset and only 2.5% for the DGEBA–DDS thermoset. Therefore, it is reasonable to assume that, during the cure of DGEBA with a mixture of amines, the addition reaction of the DDM molecule with an epoxide group occurs preferentially and that this reaction reaches

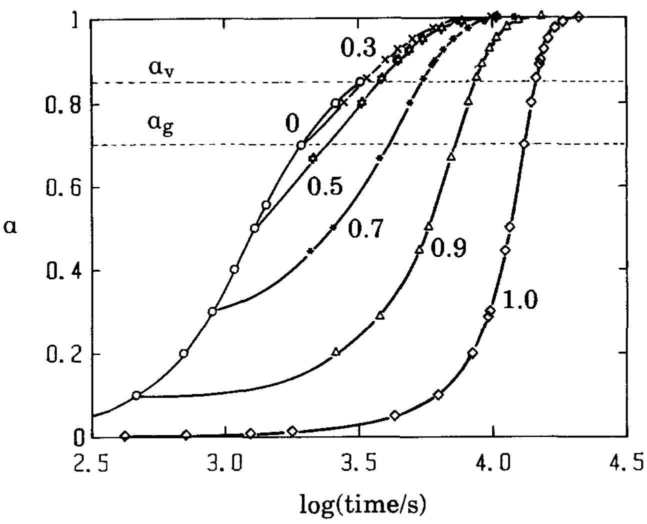

Figure 6 The calculated extent of reaction between DGEBA and a mixture of aromatic amines plotted against the curing time at 377 K. The molar ratio x of DDS in the DDM–DDS amine mixture is shown next to each curve

near-completion before the reaction of the DDS molecule with an epoxide group begins. This allows us to construct the plots of the extent of reaction against the time of cure of the DGEBA–(xDDS, $(1-x)$DDM) thermosets as follows: For a given value of α that is less than the amount $(1-x)$ of DDM in the mixed amine, the plot of α against time would correspond to the one for pure DGEBA–DDM thermoset. For values of α higher than $(1-x)$, such a plot would correspond to that of the pure DGEBA–DDS mixture but would be shifted along the time axis, as is required for the continuity of the addition reactions. Plots of the extent of reaction against the curing time were constructed within these two limits. These plots for all mixed amine thermosets except for the DGEBA–(0.1DDS, 0.9DDM) thermoset, which has been deleted for the sake of clarity, are shown in *Figure 6*. These are only an approximate representation of the reaction kinetics path based on the assumption that no synergistic effects occur. They do, however, provide a general trend with sufficient accuracy for our purpose here, as will become evident in the following: The lower broken horizontal line in *Figure 6* represents the conversion from sol to gel and the upper broken line represents conversion from gel to glass, which we assume to occur at a fixed value of the extent of reaction, i.e. $\alpha_g = 0.7$ and $\alpha_v = 0.85$, respectively, values that were taken from the work of Enns and Gillham[26]. We realize that, since the $T_{g\infty}$ value of the DGEBA–DDM thermoset is about 40 K lower than that of the DGEBA–DDS thermoset, the extent of reaction of DGEBA–(xDDS, $(1-x)$DDM) thermosets reached at the vitrification point during their cure at 377 K is expected to decrease as x increases and that, therefore, the broken lines should be composition-dependent and not horizontal. Since the variation of α_g and α_v with the composition is not to exceed an absolute change of 0.2, the assumption of composition independence of α_g and α_v in *Figure 6* would not alter our conclusions.

The slope of the plots α against $\log t$ curve was measured for each thermoset at the point corresponding to a selected constant value of α. The values of $(d\alpha/d \log t)$ are plotted against x in *Figure 7*, which shows a minimum at about $x=0.7$ for $\alpha=0.5$ and $x=0.5$ for $\alpha=0.7$. The time of cure needed to reach an extent of reaction, or α, of 0.5 is shorter than t_g, the time for gelation. Therefore, as discussed in the beginning of this section, the values of α plotted in *Figure 7* should be related to the rate of the decrease of $\log \sigma_0$ prior to the gel point, which also presents a minimum value at $x=0.7$. Therefore, we conclude that considerations in terms of the curing kinetics of the thermosets alone are sufficient to account for both the occurrence of the minimum in the rate of the decrease in σ_0 with the composition and the position of this minimum in a composition plane. The shift in the position of the minimum from $x=0.7$ for $\alpha=0.5$ to $x=0.5$ for $\alpha=0.7$ is also in agreement with our observation, given in the beginning of this section, that the rate of increase in relaxation time, which corresponds to times near and after the gel point, is minimum for $x=0.5$.

The sub-T_g relaxations and post-cure effects

Earlier investigations of the dielectric sub-T_g and main relaxation processes of thermosets[6] and of their curing time dependence[7,8] showed that, among the two sub-T_g relaxation processes, the low-temperature or γ process is initially prominent and its strength decreases towards a limiting value on curing. The strength of the high-temperature or β process was found to increase initially, reach a maximum value and then decrease on further curing and ageing. It was concluded that the mechanisms for the γ relaxation process involve motions of dipolar entities that are consumed during the curing reaction but those for the β relaxation process involve motions of dipolar entities that are formed.

Ageing of thermosets affects their dielectric behaviour for several reasons[27,28]. Predominant among these is the chemical reactions at the early period of cure. This causes the strength of the β relaxation to increase and its rate to decrease[6]. At long curing times, structural relaxation becomes predominant and, consequently, the strength of the β relaxation decreases as a result of spontaneous densification, as is also generally observed for thermoplastics and other amorphous solids[27–29].

As is seen in *Tables 2* and *3* and *Figure 5*, the post-curing for 8 h at 453 K consistently decreases the strength of both the β and γ relaxations. The decrease observed in *Figure 5* is larger in the pure DGEBA–DDM thermoset than in the pure DGEBA–DDS thermoset and

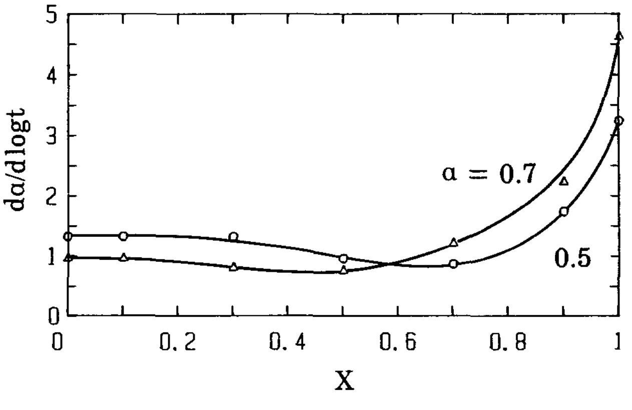

Figure 7 The tangent to the curves of *Figure 6* ($d\alpha/d \log t$) measured for $\alpha=0.5$ and 0.7 plotted against the molar ratio x of DDS in the curing amine mixture

this is due to the lower $T_{g\infty}$ value of 435 K of the DGEBA–DDM thermoset as compared with that of 485 K of the DGEBA–DDS thermoset. This implies that, when subjected to the same heat treatment, the curing reactions will reach a further extent in the DGEBA–DDM thermoset, and therefore have a greater effect on its dielectric properties than in the DGEBA–DDS thermoset.

CONCLUSIONS

The dielectric properties of thermosets of diglycidyl ether of bisphenol A isothermally cured with pure and mixtures of DDM and DDS are determined by two factors, namely: (i) a large decrease in the d.c. conductivity at the beginning of the cure, and (ii) the dipolar relaxation process later in the cure.

As curing approaches completion, the complex plane plots of the dielectric permittivity acquire the shape of an arc that is skewed at both the limiting short- and long-time intercepts, which demonstrates that the crosslinking of thermosets causes the relaxation time to increase. The isothermal spectra of dielectric permittivity at any instant of cure is given by:

$$(\varepsilon^* - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_\infty) = \mathscr{L}(-\mathrm{d}\phi(t)/\mathrm{d}t)$$

where $\phi(t) = \exp[-(t/\tau)^\gamma]$, where $\mathscr{L}$ represents a one-sided Laplace transform and γ is the KWW parameter in the chemically stable phases. The value of γ initially decreases and reaches a limiting value before the time of the appearance of a minimum in ε''. The values of the curing parameter γ and of $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_\infty)$ are found to increase with an increase in the DDS content in the curing amine mixture.

The non-monotonic trends observed in the various features of the dielectric properties of the DGEBA-based thermosets cured with mixed amines, with one amine being replaced by the other, are caused by the large difference in the kinetics of the crosslinking reactions of DGEBA with each of the two amines, which we suggest is a reflection of the effects of steric hindrance and intermolecular forces on the rates of chemical reactions.

REFERENCES

1 Williams, R. J. J. in 'Development of Plastics Technology' (Eds. A. Whelan and J. L. Craft), Elsevier, London, 1985, Vol. 2, p. 339
2 Gillham, J. K. *Polym. Eng. Sci.* 1986, **26**, 1429
3 Aronhime, M. T. and Gillham, J. K. *Adv. Polym. Sci.* 1986, **78**, 83
4 Kaiser, T. *Prog. Polym. Sci.* 1989, **14**, 373
5 Mangion, M. B. M. and Johari, G. P. *J. Polym. Sci., Polym. Phys. Edn.* 1990, **28**, 1621
6 Mangion, M. B. M. and Johari, G. P. *J. Polym. Sci., Polym. Phys. Edn.* 1990, **28**, 71
7 Mangion, M. B. M. and Johari, G. P. *Macromolecules* 1990, **23**, 3687
8 Mangion, M. B. M. and Johari, G. P. *J. Polym. Sci., Polym. Phys. Edn.* 1991, **29**, 437
9 LeMay, J. D., Swetlin, B. J. and Kelley, F. N. in 'Characterization of Highly Crosslinked Polymers', ACS Symp. Ser. 243 (Eds. S. S. Labana and R. S. Dickie), American Chemical Society, Washington DC, 1984, p. 65
10 Choy, I.-C. and Plazek, D. J. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 1033
11 May, C. A. and Tanaka, Y. (Eds.) 'Epoxy Resins, Chemistry and Technology', Marcel Dekker, New York, 1973
12 Candauy, S., Bastide, J. and Delsanti, M. *Adv. Polym. Sci.* (*Polym. Networks*) 1982, **44**, 27
13 Mangion, M. B. M. and Johari, G. P. *J. Polym. Sci., Polym. Phys. Edn.* in press
14 Kohlrausch, R. *Ann. Phys.* (*Leipzig*) 1854, **91**, 179
15 Williams, G. and Watts, D. C. *Trans. Faraday Soc.* 1970, **66**, 80
16 Moynihan, C. T., Boesch, L. P. and Laberge, N. L. *Phys. Chem. Glasses* 1973, **14**, 122
17 Montroll, E. W. and Bendler, J. T. *J. Stat. Phys.* 1984, **34**, 129
18 Dishon, M., Weiss, G. H. and Bendler, J. T. *J. Res. Natl. Bur. Stand.* 1985, **90**, 27
19 Weiss, G. H., Bendler, J. T. and Dishon, M. *J. Chem. Phys.* 1985, **83**, 1424
20 Mangion, M. B. M. Ph.D. Thesis, McMaster University, 1990
21 Prime, R. B. in 'Thermal Characterization of Polymeric Materials' (Ed. E. A. Turi), Academic Press, New York, 1981, p. 435
22 Barton, J. M. *Adv. Polym. Sci.* 1985, **72**, 111
23 Barton, J. M. *Polymer* 1980, **21**, 603
24 Sourour, S. and Kamal, M. R. *Thermochim. Acta* 1976, **14**, 41
25 Huguenin, F. G. A. E. and Klein, M. T. *Ind. Eng. Chem., Prod. Res. Dev.* 1985, **24**, 166
26 Enns, J. B. and Gillham, J. K. *J. Appl. Polym. Sci.* 1983, **28**, 2567
27 Johari, G. P. *Ann. NY Acad. Sci.* 1976, **279**, 117
28 Pathmanathan, K., Cavaillé, J. Y. and Johari, G. P. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 1519
29 Diaz-Calleja, R., Ribes-Greus, A. and Gomez-Ribelles, J. L. *Polymer* 1989, **30**, 1433