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Relaxations in Thermosets. 7. Dielectric Effects during the Curing and Postcuring of an Epoxide by Mixed Amines

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ABSTRACT: The dielectric permittivity and loss during the curing of diglycidyl ether of Bisphenol A with a 0.3:0.7 (mole:mole) mixture of diaminodiphenylmethane and diaminodiphenyl sulfone have been measured from their sol to gel to glass formation regions and the effects of physical aging on their sub-T_g relaxations investigated. The permittivity monotonically decreases with the curing, but the loss initially decreases, then increases to a peak value, and finally reaches extremely low values characteristic of a glassy state. The complex permittivity plotted in a complex plane has the shape of a skewed arc similar to that of the Cole–Cole plots, and the dielectric consequences of the chemical changes with time that occur during the cross-linking of the thermoset are phenomenologically analogous to the frequency dependence of the complex permittivity of a chemically stable amorphous solid. The time dependence of the complex permittivity follows a stretched exponential decay, $\phi(t) = \exp[-(t/\tau)^\gamma]$, where $0 < \gamma < 1$. The value of $\gamma = 0.4$ at 377 K. Amongst the two sub-T_g relaxation processes observed here, the low-temperature, or γ, process is initially most prominent, but its strength decreases on physical aging while that of the β-process increases. The strength of the β-process reaches a maximum and then decreases on further aging. The α-relaxation process increasingly separates from the sub-T_g relaxations during the curing of the thermoset, and its strength decreases. Its distribution parameter decreases from 0.60 to a limiting value of 0.40 as curing proceeds. These are discussed in terms of localized segmental motions. A concept of accumulated equivalent curing time is introduced for use in both theoretical and practical investigations of a thermoset's curing, and a method for obtaining the distribution of relaxation times from limited dielectric data is proposed. The low-temperature sub-T_g relaxation is shown to have a distribution of relaxation times which remains unchanged on curing and aging.

Introduction

During the curing process of a thermoset, the reaction of a primary amine (RNH_2) with an epoxide (R'E) first forms a secondary amine (RNHR″) which in turn reacts with another epoxy group to form a tertiary amine (RNR''_2).[1-4] For a given aromatic amine, the two reactions occur concomitantly with two distinct values of chemical rate constants,[5-8] leading to the formation of a fully connected network at the gel point. The reactions continue to occur but become diffusion-controlled when the "internal viscosity" of the gel becomes very large, and this occurrence eventually leads to vitrification or the formation of a glass. The extent of reaction at the time when the mixture becomes a glass depends on the temperature of cure, but its value is found to lie approximately between 80 and 100%.[5] If a mixture of amines is used for curing, the number of rate constants accordingly increases and the extent of reaction for a given time becomes altered.

If the thermoset thus obtained is aged, its amorphous structure relaxes toward a lower energy state as a result

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of slow diffusion of chain segments within the network with a characteristic time known as structural relaxation time. This phenomenon, also known as physical aging, is characteristic of the amorphous nature of all materials, but, in thermosets, the concomitant densification of the structure may in turn facilitate further chemical reactions between the remaining, unreacted components, which is known as "postcure". The postcure further increases the time of thermally activated diffusion of the network segments and raises the T_g of the thermoset. Thus the effects of physical aging become related to curing such that the diffusion of molecules allows the chemical reactions to occur, which in turn retard the diffusion, which retards the chemical reactions until both occur at a prohibitively slow rate.

Choy and Plazek[9] have observed the effects of aging on both the specific volume and compliance of epoxy thermosets; Aherne et al,[10] Plazek et al.,[11] Choy and Plazek,[9] Chai and McCrum,[12] and Mikolajczak et al.[13] have measured the effect of physical aging on the dynamic mechanical behavior of thermosets and Plazek and Frund[14] have recently investigated the calorimetric effects on physical aging of an epoxy thermoset. Both the dielectrically and mechanically observed sub-T_g relaxations are affected by the physical aging of a thermoplastic, for which the effect is removed on heating to $T > T_g$. Similar removal of the effect and the consequent recovery of the properties of an aged thermoset are difficult because its heating above T_g, which could allow such a recovery, causes its postcuring and partial degradation to which dielectric properties are very sensitive. Therefore, the changes caused by aging of the thermosets cannot be examined in the same manner as for thermoplastics, where heating to $T > T_g$ allows the recovery of their physical properties and thus a reinvestigation of the same sample of the polymer.

Changes in the dielectric behavior on the physical aging of an amorphous solid are in general known to be caused by at least four processes,[15,16] namely (i) the contribution to a property from the main or α-relaxation at the temperature and frequency of the sub-T_g relaxation peak decreases,[17,18] (ii) a decrease in the strength of the sub-T_g relaxation peak, which occurs as a consequence of a reduction in the spatial freedom of motion of particular groups contributing to the relaxation and/or reduction in their number (this is the case when a decrease in volume is due partially to the collapse of localized high-volume, high-entropy regions, which remain in an internal thermodynamic equilibrium in an otherwise macroscopically metastable rigid state of a glass[15-18]), (iii) the magnitude of the property associated with the main relaxation, which increases with an increase in the number density of molecular segments; and (iv) the frequency-independent background loss, both electrical and mechanical, over which both the sub-T_g and α-relaxation are superposed, which decreases with a decrease in volume. But, in thermosets, a fifth process, namely, chemical reaction between the epoxide and the resin, as during the curing, also continues to occur as the limited diffusion of the chain segments causes the thermosets' spontaneous densification.[9] Therefore, during the isothermal aging of a thermoset, the occurrence of all five processes causes a change in its properties, but the relative importance of each is expected to depend upon a number of factors, namely (i) the frequency for which the data are collected, (ii) the time and temperature of aging, and (iii) the sensitivity of the relaxation process to a decrease in specific volume. The above-mentioned four effects of the physical aging of an amorphous solid are, of course, a reflection of the persistence of local segmental and/or molecular motions, which also cause spontaneous densification of a thermoset in a fashion similar to that of a thermoplastic during its physical aging but without a change in the chemical structure. This aging effect is generally distinct from the fifth effect, namely the curing, which is specific to a thermoset and which raises its T_g.

In order to investigate in general the effects of curing and postcuring on the dielectric properties of a thermoset, we are studying the curing kinetics as well as the aging effects in thermosets made from diglycidyl ether of Bisphenol A and cured with a variety of pure, and mixtures of, aromatic amines of different molecular sizes, dipole moments, and rates of chemical reactions as cross-linking agents. This paper reports part of this study on a mixed amine-cured thermoset. We analyze the results of this study in terms of the (i) curing kinetics, (ii) origins of the sub-T_g relaxation processes, (iii) distribution of relaxation times, and (iv) effects of physical and chemical aging on the sub-T_g relaxations of the thermoset, and discuss their theoretical aspects.

Experimental Methods

Samples of thermoset were prepared by mixing 1 mol of the mixed amines (30% diaminodiphenylmethane (DDM) and 70% (mole/mole) diaminodiphenyl sulfone (DDS)) with 2 mol of liquid diglycidyl ether of Bisphenol A (DGEBA). An appropriately weighed amount of solid 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 at 360 K, and the required (weighed) amount of solid DDM was added. The mixture was further mechanically mixed for 2 min and allowed to cool to room temperature. Thereafter it was directly poured into the concentric electrode dielectric cell at room temperature. DDM and DDS of 99+% purity were purchased from Aldrich Chemical Co., and a commercial sample of DGEBA, under the name of Epon 828, was donated to us for our studies by Shell Petroleum. Epon 828 has been carefully characterized by LeMay, Swetlin, and Kelley,[19] and its properties were listed by Choy and Plazek.[9] Its number-average molecular weight is 380, which was used in our sample preparation, and it was assumed that one amine proton reacts with one epoxy group.

The disposable dielectric cell, which contained the thermoset sample, was constructed from cylindrical aluminum electrodes and Delrin spacers. The concentric electrodes were radially separated by a distance of 0.5 mm by means of two Delrin rings, and a polished aluminum rod of 15-mm diameter acted as the central electrode. The Delrin ring spacers at the two ends of the cell ensured the concentric arrangement of the electrodes. A detailed description of the cell is given elsewhere.[20] Because of the stray capacitance from the Delrin spacers, the loss tangent of the empty cell had a maximum value of 0.002 at 200 K for a measurement frequency of 1 kHz but was undetectable or less than 10^{-4} at lower temperatures. This introduces an error of less than 3% in our measured tan δ values at the corresponding temperature. The capacitance of the empty cell varied by less than 5% over the temperature range of 300 K in our study. This introduces an error of less than 17×10^{-4}/K in the permittivity data. Both errors are much less than the overall reproducibility of our data for different samples, which was about 5% for tan δ and 1% for the permittivity. This relatively poor reproducibility of the data for different thermoset samples under study is mainly a reflection of the difference between the extent of their curing and not that of the measurement procedure.

The capacitance of the empty dielectric cell was measured prior to filling it with the thermoset liquid. The cell was electrically shielded and kept inside a sealed glass container, which was also electrically shielded. The assembly was kept inside a hole drilled into a cylindrical brass block, which had a heater wire wound around it and which acted as a thermostat whose temperature could be controlled to within 0.1 K. The temperature of the thermoset sample was measured by means of a copper–constantan thermocouple placed in thermal contact with the outer electrode of the dielectric cell.

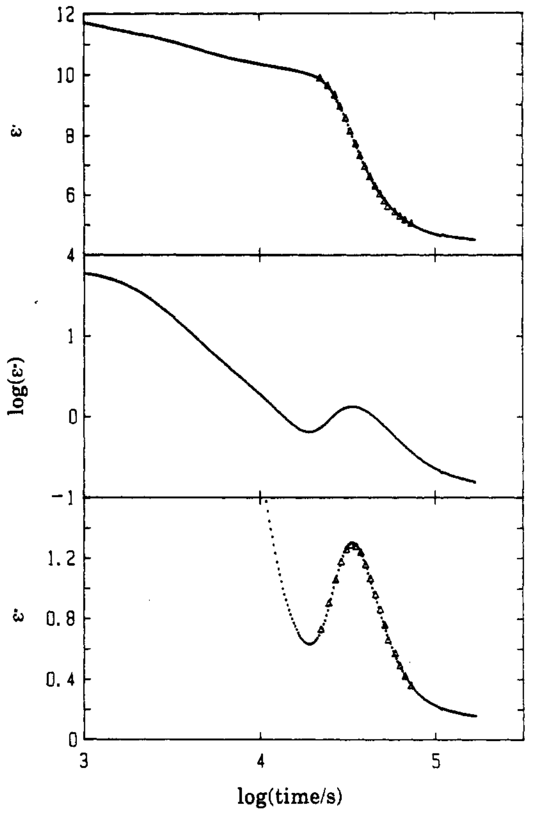

Figure 1. ϵ', dielectric permittivity, and ϵ'', loss of DGEBA-(0.3 DDM-0.7 DDS) plotted against time during the curing, or cross-linking, of the thermoset held isothermally at 377 K. The dielectric properties were measured for a fixed frequency of 1 kHz. The triangles were calculated from eq 2 for $\Delta\epsilon = 5.78$, $\epsilon_\infty = 4.50$, and $\gamma = 0.4$.

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 and with changing temperature as the curing proceeded.

Results

For the first set of measurements of ϵ', ϵ'', and tan δ, i.e., dielectric permittivity, loss, and loss tangent, the sample contained in the dielectric cell immediately after its preparation was heated from room temperature to 377 K. After its thermal stabilization, which took about 10 min, its dielectric properties were measured at this fixed temperature, or T_{cure} (=377 K), as the curing proceeded with time. The plots of the ϵ' and ϵ'', the latter on both linear and logarithmic scales, against logarithmic curing time are shown in Figure 1. The corresponding loss tangent against log (time) plot is shown in Figure 2.

The ϵ' and ϵ'' values measured during the isothermal curing at 377 K are plotted in a complex plane in Figure 3.

After these measurements were complete, a new sample of the liquid thermoset contained in the dielectric cell was quenched from 360 to 77 K, and after its temperature had stabilized, it was gradually heated at a controlled rate of 1 K/min. The ϵ', ϵ'', and tan δ of the sample were measured for a fixed frequency of 1 kHz at 1 K intervals during this heating, until the sample reached a temperature of 363 K. These values of ϵ', ϵ'', and tan δ measured at 1 kHz are plotted in curve 1 in Figure 4. The sample was then immediately cooled from this T_{cure} (=363 K) to 77 K, allowed to thermally stabilize, and heated at a rate of 1 K/min, and the measurements were repeated. These data are plotted in curve 2 in Figure 4. The sample was then kept for 5 min (t_{cure}) at 363 K (T_{cure}) and quenched to 77 K, and the procedure was repeated. The subsequent procedures including those already described here are listed in the first column of Table I under t_{cure} and T_{cure}, and the curves shown in Figure 5 are identified by the number given in parentheses in the first column of Table I.

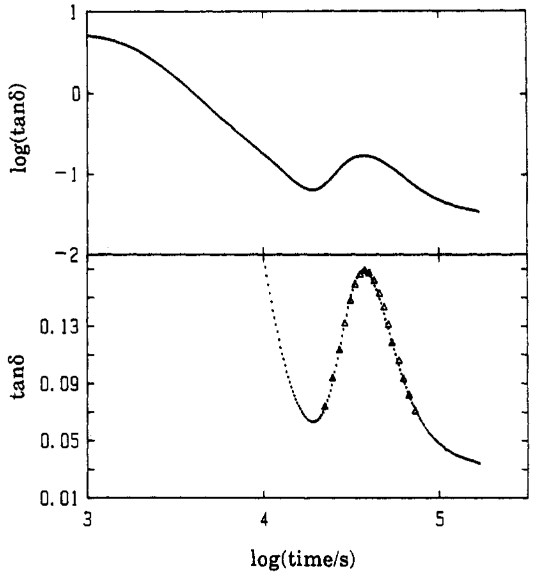

Figure 2. Loss factor (tan δ) plotted linearly and logarithmically against time during the curing or cross-linking of the DGEBA-(0.3 DDM-0.7 DDS) thermoset held at 377 K. The dielectric properties were measured for a fixed frequency of 1 kHz. The triangles were calculated from eq 2.

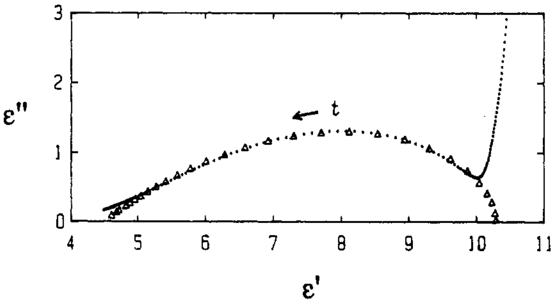

Figure 3. Complex plane plot of ϵ' and ϵ'' measured during the curing or cross-linking of the DGEBA-(0.3 DDM-0.7 DDS) thermoset held at 377 K. The values were measured for a fixed frequency of 1 kHz. Triangles were calculated from eq 2 for $\Delta\epsilon = 5.78$, $\epsilon_\infty = 4.50$, $\gamma = 0.4$. Time increases from right to left.

For the sake of clarity, the magnitudes of the sub-T_g relaxation processes, namely, the γ- and β-processes, are shown on a linear scale plot of ϵ', ϵ'', and tan δ against temperature in Figure 5, where the evolution of the two processes with thermal treatments can be more clearly discerned.

The maximum value of ϵ'' or ϵ''_{m} and the temperatures for the peaks due to the γ-, β-, and α-processes have been listed in Table I. For the purpose of our discussion of aging effects, we have also listed in Table I the values of $\epsilon'_{\mathrm{m}} - \epsilon_\infty$ for the γ-process, $\epsilon_0 - \epsilon'_{\mathrm{m}}$ for the β-process, and $\epsilon_0 - \epsilon_\infty$ for the α-process, where ϵ'_{m} is the value of ϵ' at a temperature where ϵ'' due to that process is maximum (or $\epsilon'_{\mathrm{m}} = \epsilon'$, when $\epsilon'' = \epsilon''_{\mathrm{m}}$) and ϵ_0 and ϵ_∞ are, respectively, the limiting low- and high-frequency permittivities for a given relaxation process. In our analysis, ϵ_∞ for the γ-process was taken as the value of ϵ' at 90 K, and ϵ_0 for the β-process, as the value of ϵ' at a temperature where ϵ'' was minimum between the β- and α-relaxation peaks.

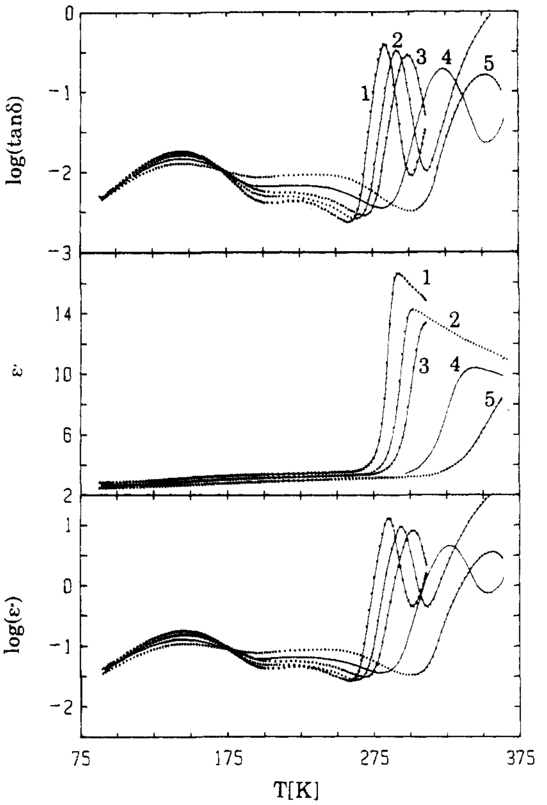

Figure 4. Evolution of γ-, β-, and α-relaxation processes during the aging of the DGEBA-(0.3 DDM-0.7 DDS) thermoset shown in the tan δ, ϵ', and ϵ'' data measured for a fixed frequency of 1 kHz. The accumulated equivalent curing time for curves 1-5 are 0.32, 1.6, 3.2, 11.0, and 33.0 ks in numerical order.

Discussion

(a) Dielectric Effects during Isothermal Curing. During the curing of, or cross-linking between, the components of a thermoset, dielectric properties change as the epoxide group opens to form a linkage with the amine.[21,22] These changes are partially due to a concurrent decrease in the net dipole moment per unit of the monomer or per unit volume of the thermoset and partly due to an increase in the viscosity, or the molecular relaxation time, of the thermoset. Thus, the extent of chemical reactions controls the physical properties of the thermoset. Most of the properties examined here are associated with ionic transport and molecular or chain diffusion, and the magnitude of these properties depends on the variety of ways in which changes in the temperature, curing time, extent of cross-linking, and densification altogether affect the mechanisms of dipolar reorientation and ion transport by creating steric hindrance to the chain diffusion. In the plots of Figures 1 and 2, the ϵ'' and tan δ measured for a frequency of 1 kHz with the passage of time but at a fixed temperature reach a broad minimum followed by a peak, with the values ultimately decreasing, albeit slowly, to 10^{-2} or less. The concurrent change in ϵ' is a monotonic decrease from 12 to 4.2, with nearly all the decrease occurring during the time when ϵ'' and tan δ 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 measurements are made as a function of frequency, in an isothermal dielectric relaxation experiment on dipolar liquids and solids, where no chemical or physical changes occur during the measurement period. This resemblance, which implies that the chemically and physically irreversible changes that occur with the passage of time in the structure of a thermoset 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, is in fact a phenomenological equivalence which becomes convincingly evident in the complex plane plot of ϵ^* shown in Figure 3.

In order to develop a theory for the phenomenological equivalence observed here, we begin by assuming that the value of ϵ'' of the uncured and ungelled thermoset sample has a relatively large contribution from σ_0, the dc conductivity. In such a general case, the complex dielectric permittivity can be written as

$$\epsilon^* = \epsilon^*_{\mathrm{d}} - i\frac{\sigma_0}{\omega e_0} \qquad (1)$$

where ϵ^*_{d} represents the dipolar contribution to ϵ^*, ω the angular frequency, and e_0 (=8.85 pF/m) the permittivity of free space. At the initial stages of the cure, σ_0, and therefore its contribution to ϵ'' (=$\sigma_0/\omega e_0$), rapidly decreases as the curing proceeds, and at a certain time during the cure its contributions become so small that the contribution to ϵ'' due to ac conductivity (associated with dipolar relaxation) begins to dominate. This is formally achieved at times equal to or greater than that when ϵ'' reaches a minimum value in the beginning of the cure, as is seen in Figures 1-3. 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

$$\epsilon^*(t_{\mathrm{cure}}) = \epsilon_\infty(t_{\mathrm{cure}}) + [\epsilon_0(t_{\mathrm{cure}}) - \epsilon_\infty(t_{\mathrm{cure}})]\int_0^\infty e^{-i\omega t} \times \left(-\frac{\mathrm{d}\phi_{t_{\mathrm{cure}}}(t)}{\mathrm{d}t}\right)\mathrm{d}t \qquad (2)$$

where $\epsilon_0(t_{\mathrm{cure}})$ and $\epsilon_\infty(t_{\mathrm{cure}})$ are the limiting low- and high-frequency values of $\epsilon'(t_{\mathrm{cure}})$ at the instant of t_{cure}, respectively, and $\phi_{t_{\mathrm{cure}}}(t)$ is the dielectric decay 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 according to Kohlrausch[23] and Williams and Watts,[24-27] which is written as

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

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, are negligible. It is to be noted that the equivalent Kohlrausch-Williams-Watts function[23,24] lacks the t_{cure} condition. Therefore, the function $\phi_{t_{\mathrm{cure}}}(t)$ of eq 3 is expected to depend on t_{cure} as well as on $\tau_{t_{\mathrm{cure}}}$ and on $\gamma_{t_{\mathrm{cure}}}$. 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 that change that would be caused by an increase in the molecular weight of a polymer at least in the initial stage of the curing until a gel or a formally infinitely connected network of infinite molecular weight is formed. The value of γ, which for a chemically stable substance becomes equal to β, the Kohlrausch-Williams-Watts[23,24] parameter is generally found to depend on both the temperature and molecular weight of a specific polymer.[25] It is here regarded, as a first approximation, to remain independent of both the chain length and the number of cross-links and therefore of the t_{cure} value. The integral of eq 2 may be

Table I
Curing and Aging Conditions of the DGEBA-(0.3 DDM-0.7 DDS) Thermoset and the Features of Their Observed Dielectric Behavior

			$100 \times \epsilon''_m$			T_m, K					
t_c, S	T_{cure}, K	AECT (s) at 363 K	γ	β	α	γ	β	α	$\epsilon'_m - \epsilon_\infty$: γ	$\epsilon_0 - \epsilon'_m$: β	$\epsilon_0 - \epsilon_\infty$: α
0	0 (1)	3.2×10^2	5.37	1.42	403	145	223	285	0.30	0.11	12.9
0	363 (2)	1.6×10^3	4.91	1.58	306	147	223	294	0.29	0.12	10.8
3.0×10^2	363 (3)	3.2×10^3	4.86	1.78	255	147	223	302	0.28	0.17	9.9
6.0×10^2	363	7.2×10^3	4.45	1.85	167	144	223	319	0.25	0.17	7.8
2.1×10^3	363 (4)	1.1×10^4	4.14	2.12	146	145	223	327	0.24	0.18	7.1
3.6×10^3	363	1.8×10^4	3.74	2.25	132	146	228	334	0.19	0.19	6.5
1.08×10^4	363 (5)	3.3×10^4	3.50	2.85	114	147	241	356	0.21	0.18	5.1
2.16×10^4	363 (6)	5.8×10^4	3.24	3.60		151	247		0.21	0.21	
5.40×10^4	363 (7)	1.16×10^5	2.95	4.49		150	247		0.19	0.24	
7.92×10^4	363 (8)	1.99×10^5	2.77	5.40			251		0.17	0.28	
1.19×105	363	3.11×10^5	2.70	5.37			252		0.17	0.24	
2.88×10^5	363 (9)	6.13×10^5	2.68	5.34			252		0.17	0.26	

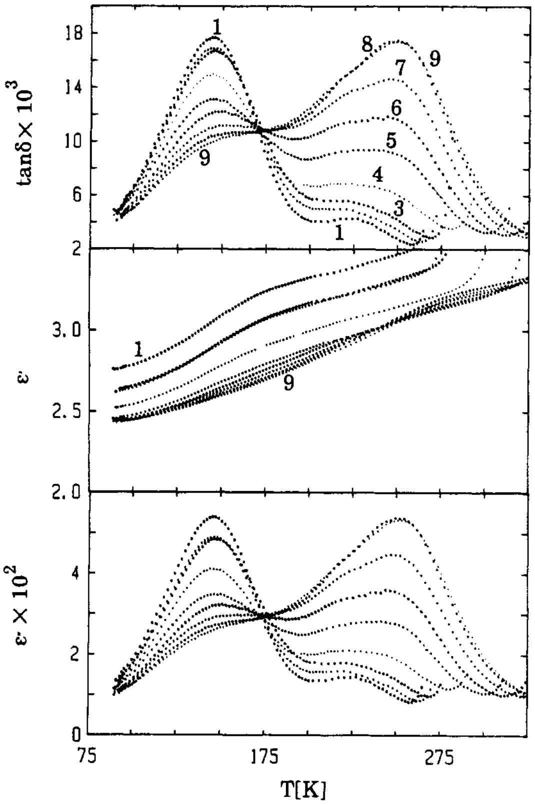

Figure 5. Evolution of γ- and β-relaxation processes during the curing and postcuring of the DGEBA-(0.3 DDM-0.7 DDS) thermoset shown in the tan δ, ϵ', and ϵ'' data measured for a fixed frequency of 1 kHz. The accumulated equivalent curing time for curves 1-9 are 0.32, 1.6, 3.2, 11.0, 33.0, 58, 116, 199, and 613 ks, in numerical order.

written as

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

where the values of the parameter N^* have been calculated by Moynihan et al.[26] for the various values of γ (Moynihan et al. express it as β for a relaxation process) and $\omega\tau$. A further approximation of a constant value of ϵ_0 and ϵ_∞ needs to be made here, particularly since the two quantities could not be satisfactorily measured during the curing time of the thermoset. This approximation is expected to have negligible effect on our main conclusion, for the changes in ϵ_0 and ϵ_∞ with the continuously increasing time are relatively small. The values of ϵ' and ϵ'' can therefore be calculated from the following two equations, in which the various parameters are defined in eqs 2 and 4.

$$\epsilon' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)N' \quad (5)$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)N'' \quad (6)$$

Equations 5 and 6 were fitted to the ϵ', ϵ'', and tan δ data for the DGEBA-(0.3 DDM-0.7 DDS) measured during its curing at 377 K, and some of the values are shown by data points in Figures 1-3. The equations fit the experimental data satisfactorily with the values of $\gamma = 0.4$ in our formalism given above.

An important physical aspect of the preceding discussion is that the irreversible chemical kinetics during the isothermal curing controls a thermoset's physical behavior in a manner that is qualitatively similar to two unrelated effects: (i) increasing the relaxation time of a chemically stable substance by decreasing its temperature or increasing its pressure, and (ii) increasing the frequency of the electric field in isothermal dielectric measurements of a chemically stable liquid or solid. In both cases the phenomenological eqs 4-6 yield ϵ' and ϵ'' whose values are invariant with respect to one's choice of either ω or τ as a variable. This means that a given shape of the complex plane plot can be obtained by varying either ω or τ. The latter occurs on increasing the chain length and/or number of cross-links in a thermoset. The observation of a skewed arc in Figure 3, therefore, clearly indicates a continuous increase in the relaxation time as the thermoset cures as a result of chemical reactions of the DGEBA with amines when both the chain length and the number density of cross-links increase.

We suggest that it is important to distinguish the parameter, γ, of eqs 2 and 3 from the Kohlrausch-Williams-Watts[23,24] parameter, β. Although our parameter γ in eq 2 has a phenomenological equivalence to the parameter β used in cases when the dielectric behaviors of chemically and physically stable substances are studied in the time or equivalently the frequency domain, the temperature variation of β has been shown to be the opposite to that of γ,[28] and in order to avoid confusion between β and γ, which is applicable to systems undergoing an irreversible chemical change with the passage of time, as is observed for the thermosets here, *we name γ, the curing parameter.* Although the introduction of the γ-parameter in addition to β may appear objectionable at first, this objection may be removed by a closer examination of the nature of processes in a thermoset and the above-mentioned differences.

(b) Relaxation Processes. Three relaxation processes, of which two occur at $T < T_g$, are widely recognized to occur in thermosets.[10,12,29-39] These are named γ-, β-, and α-processes in order of increasing temperature of their occurrence. When a thermoset is cured, the observation of its α-process in a dielectric measurement at kilohertz frequencies requires heating the sample to a temperature well above its T_g, where further curing and/or partial thermal degradation occur, both of which considerably alters its dielectric properties. Thus, only prior to a complete curing, where the T_g of the thermoset is relatively low, can the α-relaxation process be observed, although its peak position shifts to higher temperatures as further curing occurs during the measurement at temperatures above T_g, as is evident in Figure 4. This further curing progressively raises the thermoset's glass transition temperature[9,16] and the temperature of its α-relaxation. In such an experiment the temperature of the α-peak does not offer information on the molecular kinetics of a truly stable thermoset, but the height of the ϵ'' peak and the ϵ' values at temperatures above that of the α-relaxation peak do provide information on the magnitude of the decrease in ϵ_0 as the thermoset becomes further cured and its T_g increases. Figure 4 clearly shows that the value of ϵ_0 decreases on curing the thermoset for progressively longer periods of times. As is seen in Figure 4 and from the data listed in Table I, the decrease in $\Delta\epsilon$ $(=\epsilon_0 - \epsilon_\infty)$ occurs from a value of 12.9 for an initially ungelled and "uncured" sample to 5.1 for a sample kept for a total period of 180 min at 363 K and thermally cycled seven times between 77 and 363 K. This decrease, of course, includes the changes in the strengths of the γ- and β-relaxation processes that also occur during the same period.

The features of the sub-T_g or γ- and β-relaxations are also seen to change during the curing, but here their relaxation strengths are difficult to determine unambiguously. This is partly because their relaxation peaks have a large half-width and partly because the two peaks overlap, as is evident in Figure 4 and clearly seen in Figure 5.

When the relaxation peaks are broad, the temperature dependence of limited data on ϵ' and ϵ'' does not yield information on either the distribution of relaxation times and/or its change on aging when usual methods are used for the analysis. Therefore, we propose in the following first a new method for obtaining this information from the limited ϵ' and ϵ'' data and second the significance of the information obtained by this method.

An analysis that has been shown to be successful for the frequency and time dependence of the dielectric properties of most amorphous materials is in terms of an empirical Kohlrausch–Williams–Watts parameter,[23-27] β. As mentioned before, a value of $\beta < 1$, represents a stretched or nonexponential decay of polarization or electric field, according to the equation

$$\phi(t) = \exp[-(t/\tau)^{\beta}] \tag{7}$$

where τ is the relaxation time. Note that eq 7 and ones that follow here are deliberately distinguished from eqs 3–6 so as to avoid confusion between the relaxation time involved in the curing kinetics and the relaxation time for the generalized equations now developed. The complex permittivity therefore is given by

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty e^{-i\omega t}\left(-\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)\mathrm{d}t = \mathcal{L}\left(-\frac{\mathrm{d}\phi}{\mathrm{d}t}\right) \tag{8}$$

where $\mathcal{L}$ denotes a purely imaginary Laplace transform and all other quantities are as described previously. The Laplace transform has been numerically evaluated by Moynihan et al.[26] and Lindsey et al.,[27] and a quantity $N^*(\omega\tau)$ is accordingly defined by [26,27]

$$N^*(\omega\tau) = N' - iN'' = \mathcal{L}(-\,\mathrm{d}\phi/\mathrm{d}t) \tag{9}$$

where N' and N'' are the real and imaginary parts of the complex quantity N^*. They[26,27] have provided numerical values of N^* as a function of $\omega\tau$ for β values ranging from 0.30 to 1, and we have calculated $N^*(\omega\tau)$ for β values between 0 and 0.30 using the formalism given by Bendler et al.[40-42] (An appendix describing these calculations has been given elsewhere.[20])

Equations 8 and 9 represent the normalized values of ϵ^*, and therefore N' varies between 0 and 1 and N'' increases from 0 to a maximum value and then decreases to 0 as $\omega\tau$ increases. Furthermore, the value of β uniquely determines the value of $\omega\tau_m$ at which N'' reaches its peak value of N''_m, the half-width of the N'' peak, and N'_m, i.e., the value of N' when $N'' = N''_m$. Thus, if N'_m and N_m'' were known, the value of β could be determined by a procedure that we describe in the following.

By combining eqs 8 and 9 and separating the real and imaginary components of ϵ^* and N^*, we obtain

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)N' \tag{10}$$

and

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)N'' \tag{11}$$

Rewriting eqs 10 and 11 for conditions when $\omega\tau = \omega\tau_m$ or $N = N_m$ and $N'' = N''_m$, we obtain

$$\epsilon'_m - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)N'_m = \Delta\epsilon N'_m \tag{12}$$

and

$$\epsilon''_m = (\epsilon_0 - \epsilon_\infty)N''_m = \Delta\epsilon N''_m \tag{13}$$

where ϵ'_m and ϵ''_m are the values of ϵ' and ϵ'' when $\omega\tau = \omega\tau_m$ or at the position of the relaxation peak. By combining eqs 12 and 13, we obtain

$$\frac{\epsilon''_m}{\epsilon'_m - \epsilon_\infty} = \frac{N''_m}{N'_m} \tag{14}$$

and

$$\frac{\epsilon''_m}{\epsilon_0 - \epsilon'_m} = \frac{N''_m}{1 - N'_m} \tag{15}$$

Thus the magnitude of $\epsilon''_m/(\epsilon_0 - \epsilon'_m)$ becomes a measure of β from eqs 7–9 and 15, and an evaluation of ϵ''_m and ϵ'_m becomes sufficient for the calculation of the value of β for a relaxation process.

The values of both ϵ_0 and ϵ_∞ are known to be temperature-dependent for all materials, but for the sub-T_g relaxations this dependence is relatively small and can be neglected for our purposes here. We therefore assume that the values of both ϵ_0 and ϵ_∞ of the γ- and β-processes in the thermoset remain constant with changing temperature, so that the data from isochronal measurements shown in Figures 4 and 5 can be used to obtain the $\epsilon''_m/(\epsilon'_m - \epsilon_\infty)$ values for the sub-T_g relaxations. These values were calculated from the data listed in Table I and are plotted against the accumulated equivalent curing time (as defined in the next section) in Figure 6, where the values for the γ-relaxation process are seen to slowly decrease from a value of 0.18 to 0.16, which gives $\beta = 0.20$ decreasing to $\beta = 0.16$ from eq 10 and Table III in ref 20. The value for the β-relaxation process is initially 0.13 and increases to a constant value of 0.200, which gives, from Table III in ref 20, $\beta = 0.13$. The anomalous increase in the $\epsilon''_m/(\epsilon'_m - \epsilon_\infty)$ values at times early in the curing is an artifact due to large errors in the determination of the

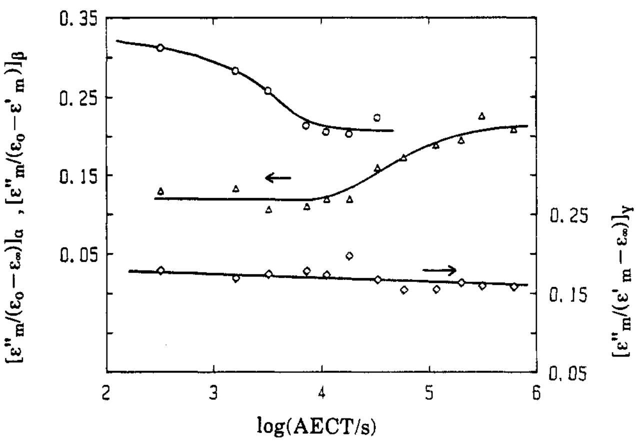

Figure 6. Values of $\epsilon''_m/(\epsilon'_m - \epsilon_\infty)$ for the γ-relaxation, $\epsilon''_m/(\epsilon_0 - \epsilon'_m)$ for the β-relaxation, and $\epsilon''_m/(\epsilon_0 - \epsilon_\infty)$ for the α-relaxation processes plotted against time for the curing and postcuring of the DGEBA-(0.3 DDM–0.7 DDS) thermoset. See text for details.

relatively small height of the β-relaxation peak which carries with it a partial contribution from the γ-relaxation process, particularly when in this thermoset $T_{m,\beta}$ is close to $T_{m,\gamma}$, as is seen in Table I and Figures 4 and 5.

As mentioned earlier here, both ϵ''_m and $\Delta\epsilon$ for the α-relaxation process of the thermoset could be measured, and the plot of $\epsilon''_m/(\epsilon_0 - \epsilon_\infty)$ against the accumulated equivalent curing time obtained from these data is shown in Figure 6. This ratio decreases with the accumulated equivalent curing time from 0.31 to a constant value of 0.21, which in turn correspond to $\beta = 0.60$ and 0.40, respectively, according to the calculated values listed in ref 20. The decrease in the value of β for the α-relaxation process that is observed when further curing of the DGEBA–(0.3 DDM–0.7 DDS) occurs seems to be associated with the increase in the number of cross-links in the network-forming polymers. Since the ratio $\epsilon''_m/(\epsilon_0 - \epsilon_\infty)$ for the α-process which is plotted against time in Figure 6 reaches a limiting value, the value of β also reaches a limiting value of 0.4 at $t > 10$ ks. In our isothermal curing experiment at 377 K in Figures 1–3, the limiting value of β would be reached in a relatively short time (or less than 10 ks). Since our calculations of ϵ^* in Figures 1–3 are in the time range of 20–80 ks of the isothermal cure, the value of γ used in our calculations seems intriguingly similar to the limiting value of β and this underscores the correctness of our first approximation that β remains constant with the curing time at later stages of the cure and serves as a witness for the self-consistency of the procedures we have used here.

(c) Accumulated Equivalent Curing Time. We now begin our discussion of the changes in the strengths of the various relaxation processes by introducing the concept of accumulated equivalent curing time as follows: Since a thermoset undergoes curing or cross-linking reactions at all temperatures, howsoever insignificant in their effects, it is important, both theoretically and technically, to consider the extents of (i) the curing that occurs during the period it takes for the thermoset to reach a certain value of T_{cure}, (ii) the curing during the period it is kept at T_{cure}, and (iii) the curing during the period of its cooling from T_{cure} to a much lower temperature. In our studies, the last factor has been minimized by quenching the thermoset sample to 77 K, but both the first and second factors are significant, as may be seen from the following considerations:

The kinetic theories of the polyaddition reactions of epoxide thermosets have been successfully discussed in terms of two kinetic constants, which have been found by various workers[7,8,43,44] to depend upon the temperature of the curing reaction and to obey an Arrhenius rate equation. Therefore, Δt, the time required for the curing reaction to reach a predefined extent or state of chemical and physical structures of the thermoset, varies with the temperature at which the thermoset is kept according to the equation[7,8,43,44]

$$\Delta t(T) = \Delta t_0 \exp(E/RT) \tag{16}$$

where Δt_0 is the limiting value of Δt as $T \rightarrow \infty$, E is the activation energy, and R is the gas constant. Since the dielectric properties of a thermoset change during its curing, one may characterize a given physical state or chemical structure by its ϵ_0, ϵ_∞, the relaxation time, and the distribution of relaxation times. Since ϵ'' has a unique value at ϵ''_m, which is determined by all the four quantities according to eq 13, the value of ϵ''_m can be used, as an approximation, to represent the chemical and physical states of a thermoset or alternatively the extent of chemical reactions it has undergone. In an earlier paper, we have shown[28] that

$$\Delta t(T) = t(\epsilon''_m) = t_0 \exp(E/RT) \tag{17}$$

where E was found to be 45 kJ/mol for the DGEBA-based thermoset cured with either DDM or DDS. From calorimetric studies, Barton[45,46] has reported that the values of E are 43 and 53 kJ/mol, respectively, for the chemical reaction kinetics of DGEBA-based thermosets. The value of the activation energy term is found to be identical for both DGEBA–DDM and DGEBA–DDS thermoset cures. Thus, though the curing kinetics of the DGEBA–(0.3 DDM–0.7 DDS) involves four kinetic constants, this value of 45 kJ/mol is applicable, and this allows us to use eq 17 for further development of the formalism here.

As is well-known, the curing reactions occur at all temperatures, albeit at different rates. Therefore, $\Delta t(T_{cure})$, i.e., the time for achieving a certain extent of cure at T_{cure}, is related to the time $\Delta t(T'_{cure})$ for achieving the same extent of cure at T'_{cure}, by the equation

$$\Delta t(T_{cure}) = \Delta t(T'_{cure}) \exp[(E/R)(1/T_{cure} - 1/T'_{cure})] \tag{18}$$

If the thermoset is cured in steps by keeping at various temperatures T_i for periods of Δt_i, eq 18 becomes

$$\Delta t(T_{cure}) = \sum_i \Delta t_i \exp[(E/R)(1/T_{cure} - 1/T_i)] \tag{19}$$

So, eq 19 can be used to determine the equivalent time for an identical extent of the cure at different temperatures for the isothermal curing procedures.

When the temperature is increased at a constant rate, q ($=\partial T/\partial t$), the temperature of the sample at any given time, t, within the interval from t_0 (at T_0) to t_{cure} (at T_{cure}) is given by

$$T_{cure} - T_0 = q(t_{cure} - t_0) \tag{20}$$

By converting the summation of eq 19 into an integral and combining it with eq 20, we obtain

$$\Delta t(T_{cure}) = \int_{t_\infty}^{t_{cure}} \mathrm{d}t(T) \exp[(E/R)(1/T_{cure} - 1/T)] \tag{21}$$

Equation 21 may be written as

$$\Delta t(T_{cure}) = \frac{\int_{T_0}^{T_{cure}} \exp(-E/RT)\, \mathrm{d}T}{q \exp(-E/RT_{cure})} \tag{22}$$

The integral in eq 22 does not have an analytical solution. Nevertheless, it can be numerically evaluated. For

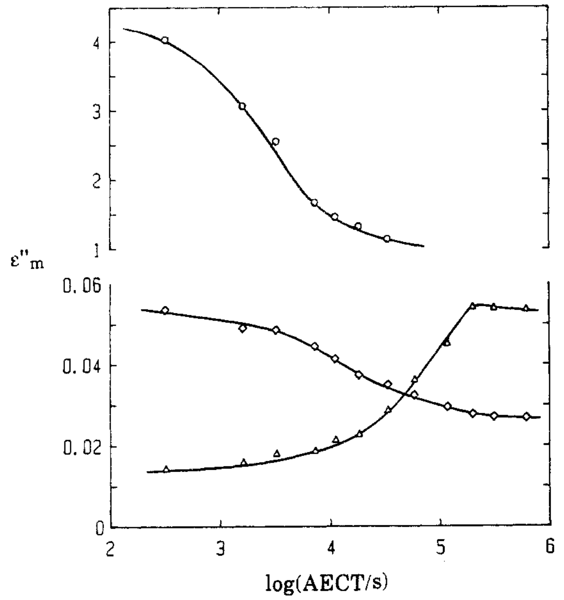

Figure 7. ϵ''_m, the height of ϵ'' peak for the γ-, β-, and α-relaxation processes plotted against the accumulated equivalent curing time.

example, our calculation based on eqs 18–22 shows that heating a thermoset from 77 to 363 K, at a rate of 1 K/min, as in this study, is equivalent, in terms of the extent of cure, to a period of 21 min of isothermal cure at 363 K. Alternatively, cooling a sample at 0.5 K/min from 363 to 300 K is equivalent to a period of 42 min of isothermal curing at 363 K. A comparison of these values against the isothermal curing times given in the first column of Table I underscores the importance of the concept of accumulated equivalent curing time, which we abbreviate to AECT. We suggest that this quantity is an important parameter for the control of the thermoset curing process.

The values of AECT for the different stages of curing and postcuring of the DGEBA–(0.3 DDM–0.7 DDS) thermoset were calculated from the knowledge of our experimental procedure. The calculated values of AECT are listed in Table I, along with the thermal history of the sample. It is important to note that, after the curing has reached near completion, i.e., when the thermoset has become a glass with viscosity greater than 10^{13} P, eq 2 is not valid for further cross-linking in the thermoset. Therefore, any further cure that occurs as a result of localized chemical reactions and spontaneous densification on physical aging of its amorphous state would alter the properties of a thermoset in a manner different from that during the early stages of curing, where chemical reactions are controlled by long-range diffusion and where densification is a result of the chemical reactions mainly between the epoxide and the cross-linking agents.

(d) Effect of Cure and Postcure on Relaxations. With increase in the AECT, the heights of both the γ- and α-relaxations monotonically decrease, but that of the β-relaxation at first increases, reaches a maximum value of ϵ''_m of 0.054 after an AECT of 199 ks, and then decreases, as is seen in Table I and Figure 7. The temperature of all relaxation peaks is also seen to generally increase, but the smallest increase by 2K is for the γ-, and the largest increase by 71 K is for the α-relaxation process after an AECT of 33 ks. As seen in Table I, in the ungelled state of the thermoset, the value of ϵ''_m for the γ-process is nearly 3.8 times the value for the β-process, but after an AECT of 613 ks, the ϵ''_m for the γ-process is about half of that for the β-process. These observations are seen in the data in Table I and more obviously in the plots of Figure 5, where the β-relaxation process appears to grow at the expense of the γ-relaxation process. The decrease in ϵ''_m for the α-relaxation process is of course associated with a decrease in the dipole moment per unit monomer, as is known for polymeric materials in general.[47]

The lowest temperature or γ-peak has not been dielectrically characterized before, but a mechanically analogous peak has been attributed to the localized motions of polymeric sequences consisting of at least four carbon atoms by Ochi et al.[29–32] The height of the γ-peak or the value of ϵ''_m decreases from 0.0537 in the ungelled mixture to half of the value (0.0268) after an AECT of 613 ks, but its position remains virtually unchanged at 147 ± 3 K. Hence it seems that the γ-peak is partly due to local motions of those dipoles that remain as the unreacted components during the curing of the thermosets. The dipoles may be the unreacting parts of the DGEBA polymer chain including the unreacted epoxy groups and/or free aminodiphenyl or primary amine groups, in accordance with the previous attribution of the mechanically observed γ-process by Ochi et al.[29–32] to the local motion of polymer segments consisting of at least four carbon atoms.

The mechanically observed β-relaxation process in the amine-cured thermosets has been attributed by Ochi et al.[29–32] to the motions of hydroxyl ether groups and other (unspecified) parts of the network, while Keenan et al.[34] have attributed the same relaxations to a crankshaft rotational motion of the glycidyl portion of the epoxide group within the thermoset's network. As seen in Figures 4, 5, and 7, curing increases its ϵ''_m value by a factor of 4 for the DGEBA–(0.3 DDM–0.7 DDS) thermoset. Thus, the β-relaxation appears to be assignable to the local motion of the dipolar groups that are created during the cross-linking reactions. These are the hydroxyl ether groups and the secondary or tertiary amines, which are in accord with the suggestions made by both Keenan et al.[34] and Ochi et al.[29–32]

The decrease in the strength of the γ and the increase in that of the β-relaxation seen in Table I and Figure 7 is, of course, a reflection of further curing in the two thermosets which dominates the change in their measured ϵ''_m. Physical aging or structural relaxation decreases ϵ''_m, and, near the peak of the plot in Figure 7, the two effects annul each other. For a longer time of curing, the physical aging effect dominates, and the decrease in the strength of γ- and β-relaxations (Figures 4–6) in the thermoset at long curing times becomes qualitatively similar to the aging effects observed in thermoplastics.[16]

There is of course some merit in considering these effects in general physical terms without assigning a particular mode of motion for each process. The probability of efficient packing in a thermoset is expected to progressively diminish as the reaction becomes diffusion-controlled and as the "internal viscosity of the gel" increases, thereby allowing regions with greater variance of packing density or defect sites that contain particular dipolar groups. It follows therefore that the observed increase in the strength of the β-peak may also be partly associated with an increase in chain length during curing, an aspect of the study that has important implications for our concepts of the structure of a polymer.

We had earlier shown that the number of molecules contributing to the β-relaxation varies with both the nature of molecular packing in a glass as well as the nature of disorder in its rigid matrix. As reviewed elsewhere,[48] it is highest for amorphous polymers and rigid molecular glasses, lower for glassy liquid crystals, and lowest for the glasslike state of orientationally disordered crystals. Furthermore, the strength of the sub-T_g relaxation in at least one polymer,[47] namely poly(propylene oxide) increases with the increase in its chain length or molecular weight. Our results here, showing that the β-relaxation peak becomes increasingly more prominent as the number of cross-links and the chain length increases, are further confirmation of our earlier finding for a linear chain polymer.[47]

Conclusions

A detailed dielectric study during the curing of DGEBA with mixed aromatic amines from its sol to gel to glass transformation shows time-dependent changes that can be understood in terms of the dc conductivity, contribution to orientation polarization, and their respective temperature variations. The complex plane plot of the permittivity has the shape of an arc, which is skewed at both the limiting short- and long-time intercepts for the dipolar processes. This shape can be fitted to a stretched exponential functional form $\phi(t) = \exp(t/\tau)^{\gamma}$, with $\gamma = 0.4$. The evolution of dielectric features during the curing of thermosets is phenomenologically similar to the evolution of dielectric features with increasing frequency of measurements in physically and chemically stable dipolar liquids and solids. γ is regarded as a useful parameter in the curing kinetics of thermosets.

It is shown that accumulated equivalent curing time for the curing of a thermoset is a more useful concept than the isothermal curing time itself. Theoretical justification based on the chemical kinetics of thermosets confirms the usefulness of this concept.

A method for the analysis of the distribution of relaxation times using limited data on the ϵ' and ϵ'' of the sub-T_g relaxation is developed. The analysis by this method shows that the distribution parameter for the γ-relaxation process in the thermoset slightly decreases but that for the α-relaxation process rapidly decreases and reaches a limiting value with curing and aging time.

The cross-linking of the epoxide molecules by DDM and DDS increases the strength of its β-relaxation, despite the fact that the density increases on curing. This increase in strength is consistent with the mechanism of β-relaxation process, which involves motions of the –OH groups that are formed during the cure and require a relatively small volume for their rotation. The strength of γ-relaxation process monotonically decreases on aging.

The sub-T_g relaxations become progressively more separated from the α-relaxation as the network is formed. This behavior is similar to that observed when the molecular weight of a thermoplastic is increased.

Aging of the thermoset affects its dielectric behavior for five different reasons, the predominant amongst which is the chemical reactions at the early cure period. This causes the strength of β-relaxation to increase and change its rate. At long curing times, structural relaxation becomes predominant and consequently the strength of β-relaxation decreases, as is observed for thermoplastics.

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