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Relaxations in Thermosets. 24. Theory and Experiments on Nonisothermal Curing of Thermoset Polymers

M. G. Parthun and G. P. Johari*

Department of Materials Science and Engineering, McMaster University,
Hamilton, Ontario L8S 4L7, Canada

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ABSTRACT: A generalized formalism for the dielectric behavior of thermosets during their curing under isothermal and nonisothermal conditions has been developed. It is based on the theory that the relaxation time of a thermoset is related to the extent of chemical reaction. Changes in both the dc conductivity and dipolar orientation polarization have been considered as gelation and vitrification for a given heating rate occur. It is shown that the plots of the normalized complex permittivity measured for a fixed frequency during the curing on ramp heating are similar to those observed under isothermal conditions for which the curing parameter remains constant. The validity of the formalism has been tested by using data obtained for the curing of the diglycidyl ether of Bisphenol-A with ethylenediamine at two heating rates. The formalism is in satisfactory agreement with the measurement.

I. Introduction

The dielectric properties of a material strongly depend upon the frequency used for the measurement and its temperature. This dependence is readily studied when the chemical composition and the molecular bonding in the structure of a material remain unchanged during the course of measurements, as for example in amorphous thermoplastics, elastomers, and molecular and network glasses. However, if the chemical and molecular structures of a material irreversibly change as a result of chemical reactions during the course of measurement, as for example in the processing of thermoset polymers, the dielectric behavior becomes time dependent and its study becomes complicated. In our earlier papers of this series,[1-4] we developed a formalism for this behavior on the basis that the processes involved in the isothermal conversion of a liquid to a rigid solid, as in the processing of a thermoset polymer, can be treated in terms of a negative feedback between molecular diffusion and chemical reaction which ultimately causes the diffusion to become imperceptible, and the substance which was initially a liquid vitrifies. In the phenomenology of this chemically-controlled dipolar diffusion, the dc conductivity of the liquid approaches (but does not become zero) a singularity as the gel point is reached, and the relaxation time of the structure irreversibly increases with the reaction time according to a curve whose shape is sigmoidal and which qualitatively resembles the corresponding curve for the extent of chemical reaction plotted against time.[5] The changes in the dielectric,[1-5] Brillouin light scattering,[6] and ultrasonic properties[7-9] of the substance with time during this irreversible process are phenomenologically similar to those observed by varying the frequency in the isothermal measurements of a chemically and physically stable substance. This stems from the fact that, in the formalisms for relaxation functions, the terms ω, i.e., the frequency used for the measurement and τ, the relaxation time, appear as a product, $\omega\tau$, and the relaxation behavior of the substance becomes formally invariant of ω or τ.

From the point of view of processing of thermosets for structural and electronic applications, it is important to develop concepts that are useful for their curing in both the isothermal and nonisothermal, but controlled heating, conditions. Here we report a theoretical formalism for the general effects of a thermoset's curing on its dielectric properties. The formalism can be used for both curing under isothermal conditions and curing under controlled heating. The validity of the formalism is tested against the dielectric properties of an epoxide-based thermoset cured with a diamine.

II. Formalism for Dielectric Properties during Curing

As a thermoset cures on heating, its dielectric properties change with both temperature and time for two reasons: (i) the dc conductivity increases and the static permittivity and the relaxation time decrease as, for a fixed time, only the kinetic energy, kT, increases and (ii) spontaneous chemical reactions between its molecular components increase the size of the network structure formed as the cross-link density in it increases with time for a fixed temperature. Both aspects may be taken into account in a formalism in which the complete differential of the complex permittivity, ϵ^*, with respect to temperature and time is taken as

$$d\epsilon^*(\omega,T,t) = \left(\frac{\partial\epsilon^*(\omega,T,t)}{\partial T}\right)_t dT + \left(\frac{\partial\epsilon^*(\omega,T,t)}{\partial t}\right)_T dt \qquad (1)$$

where

$$\epsilon^*(\omega,T,t) = \epsilon'(\omega,T,t) - i\epsilon''(\omega,T,t) \qquad (2)$$

ω is the frequency used for the measurement, T is the temperature, and t is the time during the curing process.

The measured permittivity, ϵ', in ion-containing materials has contributions from both the space-charge and dipolar polarization such that

$$\epsilon'(\omega,T,t) = (Z_0 \sin(a\pi/2)\omega^{1-a})G_0^{\,2}(\omega,T,t) + \epsilon'_{\text{dip}}(\omega,T,t) \qquad (3)$$

and

$$\epsilon''(\omega,T,t) = \sigma_0(T,t)/\omega e_0 - (Z_0 \cos(a\pi/2)\omega^{-a}) \times G_0^{\,2}(\omega,T,t)/C_0 + \epsilon''_{\text{dip}}(\omega,T,t) \qquad (4)$$

where the first term on the right-hand side of eq 3 and the second term in eq 4 refer to a contribution from a "constant phase element" for an interfacial impedance which is in series with the bulk properties of a material. Here, Z_0 is the characteristic impedance of the electrode–insulator interface, G_0 is the measured conductivity, which is equal to the reciprocal of the resistivity, and C_0 is the geometric capacitance of the sample. Johnson and Cole,[10] McDonald,[11] and Tombari and Cole[12] have shown that a is equal

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to 0.5. ϵ'_{dip} and $\epsilon''_{\mathrm{dip}}$ are the contributions to ϵ' and ϵ'' from dipolar reorientation, σ_0 is the dc conductivity, and e_0 is the permittivity of free space (=8.8514 pF/m).

For most ionic liquids of relatively low conductivity, contributions from space-charge polarization are generally negligible, so that ϵ' and ϵ'' can be written as

$$\epsilon'(\omega,T,t) = \epsilon'_{\mathrm{dip}}(\omega,T,t)$$

$$\epsilon''(\omega,T,t) = \epsilon''_{\sigma}(T,t) + \epsilon''_{\mathrm{dip}}(\omega,T,t) \tag{5}$$

where $\epsilon''_{\sigma} = \sigma_0/\omega e_0$.

Evidently, ϵ' of a thermoset during its curing depends only upon the dipolar orientation polarization whereas ϵ'' depends upon both the ionic or dc conduction and dipolar orientation polarization. For analytical convenience here, the two processes are considered separately as follows:

(i) Orientation Polarization. In the absence of dc conductivity, the complex permittivity due to orientation polarization during the curing process of a thermoset is given by[2-4]

$$\epsilon^*(\omega,T,t) = \epsilon_\infty(T,t) + [\epsilon_0(T,t) - \epsilon_\infty(T,t)]\int_0^\infty \exp\left[-i\omega t'\left(-\frac{\partial\Phi(t')}{\partial t'}\right)\right] \mathrm{d}t' \tag{6}$$

where ϵ_0 and ϵ_∞ are the limiting low- and high-frequency permittivities, respectively, and t' refers to the time for the decay of polarization if the structure of the substance remained constant during the measurement time or that when the reaction occurred too slowly in comparison with the time for measurement. ω, T, and t refer to the angular frequency used for the measurement, the temperature of isothermal cure, and the time during the isothermal cure, respectively. The normalized complex permittivity N^* is defined as

$$N^* = \int_0^\infty \exp\left[-i\omega t'\left(\frac{\partial\Phi(t')}{\partial t'}\right)\right] \mathrm{d}t' = \mathcal{L}\left(-\frac{\partial\Phi}{\partial t'}\right) \tag{7}$$

where $\mathcal{L}$ represents the one-sided Laplace transform of the assumed stretched exponential relaxation function.[13,14]

$$\Phi = \exp(-[t/\tau]^{\gamma}) \tag{8}$$

and where γ is a parameter with values between zero and one. Thus

$$\epsilon^*(\omega,T,t) = \epsilon_\infty(T,t) + [\epsilon_0(T,t) - \epsilon_\infty(T,t)]N^*(\omega\tau(T,t)) \tag{9}$$

ϵ' and ϵ'' may now be written as

$$\epsilon'(\omega,T,t) = \epsilon_\infty(T,t) + \Delta\epsilon N'(\omega\tau(T,t)) \tag{10}$$

$$\epsilon''(\omega,T,t) = \Delta\epsilon N''(\omega\tau(T,t)) \tag{11}$$

where $\Delta\epsilon$ is the difference $[\epsilon_0(T,t) - \epsilon_\infty(T,t)]$ and N' and N'' are the real and imaginary components of the normalized complex permittivity, N^*.

During the curing of a thermoset at a constant heating rate, γ, ϵ_0, and ϵ_∞ change with temperature. For simplicity, we assume that the curing parameter, γ, remains constant during the curing and that the contribution from the orientation polarization, which is assumed to remain unchanged with the time of cure,[1-5] varies with the inverse of temperature according to the Curie equation, $\Delta\epsilon = A'/T$, where A' is a constant with time. ϵ' and ϵ'' may now be written as

$$\epsilon'(T,t) = \epsilon_\infty + \frac{A'}{T}N'(\omega\tau(T,t)) \tag{12}$$

$$\epsilon''(T,t) = \frac{A'}{T}N''(\omega\tau,(T,t)) \tag{13}$$

Accordingly, a normalized complex plane plot of N'' against N' or $(\epsilon''(T,t)T/A')$ against $[\epsilon'(T,t) - \epsilon_\infty]T/A'$ obtained from dielectric measurements during the ramp curing should be a skewed arc with its peak height and half-width determined by the values of the parameters A' and γ.

(ii) dc Conductivity. We now consider the change in the dc conductivity contribution to ϵ'' with increasing time and temperature during a thermoset's curing. The logarithmic variation of ϵ_σ'' with T and t is given by

$$\mathrm{d}\ln\epsilon''_{\sigma}(T,t) = (\partial\ln\epsilon''_{\sigma}/\partial T)_t\,\mathrm{d}T + (\partial\ln\epsilon''_{\sigma}/\partial t)_T\,\mathrm{d}t \tag{14}$$

where the first term on the right-hand side of eq 14 represents the fixed-time variation of ϵ''_{σ} with temperature and the second term the fixed-temperature variation of ϵ''_{σ} with time. Equation 6 may be written as

$$\mathrm{d}\ln\epsilon''_{\sigma}(T,t) = \frac{1}{\omega e_0}\left[\left(\frac{\partial\ln\sigma_0}{\partial T}\right)_t \mathrm{d}T + \left(\frac{\partial\ln\sigma_0}{\partial t}\right)_T \mathrm{d}t\right] \tag{15}$$

where σ_0 instead of ϵ''_{σ} is a variable on the right-hand side of eq 15. (The variation of σ_0 for a fixed time here means a condition when chemical and molecular structures of the thermoset are kept unchanged by preventing the curing process.)

In our earlier studies,[1-5] we have found that the dc conductivity of a thermoset during its curing decreases according to a power law

$$\sigma_0(T,t) = \sigma_0(T,t\rightarrow 0)\left[\frac{t_{\mathrm{gel}}(T) - t(T)}{t_{\mathrm{gel}}(T)}\right]^{x(T)} \tag{16}$$

where $\sigma_0(t\rightarrow 0)$ is the value of σ_0 at $t\rightarrow 0$ or the initial time, t_{gel} is the time taken to reach gelation point, and x is a critical exponent of the scaling equation used as a generalized property function by Stauffer et al.[15] and Djabourov.[16] The significance of x lies in recognizing that for a given time for gelation, its value determines the rate at which σ_0 decreases with time; the higher the value of x, the more rapid is the decrease of σ_0 with time. By differentiating the logarithmic form of eq 16 with respect to time, we obtain

$$\frac{\partial\ln\sigma_0(T,t)}{\partial t} = \frac{x(T)}{t - t_{\mathrm{gel}}(T)} \tag{17}$$

Now the temperature dependence of σ_0 for chemically and physically stable materials is given by the Arrhenius equation

$$\sigma_0(T) = \sigma_\infty \exp(-[E_\sigma/RT]) \tag{18}$$

where σ_∞ is the dc conductivity at $T \rightarrow \infty$, E_σ is the activation energy, and R is the gas constant. By differentiating the logarithmic form of eq 18 with respect to temperature, we obtain

$$\partial\ln\sigma_0(T)/\partial T = E_\sigma/RT^2 \tag{19}$$

and substituting eqs 17 and 19 into eq 14

$$\mathrm{d}\ln\epsilon''(T,t) = \frac{1}{\omega e_0}\left[\frac{x(T)}{t - t_{\mathrm{gel}}(T)}\,\mathrm{d}t + \left(\frac{E_\sigma}{RT^2}\right)\mathrm{d}T\right] \tag{20}$$

During the curing of a thermoset by heating at a constant rate, $q = \mathrm{d}T/\mathrm{d}t$, measurements are usually made as a function of temperature rather than time. Therefore, the formalism needs to be developed in terms of the temperature derivative alone. Replacing $\mathrm{d}t$ by $\mathrm{d}T/q$ in eq 20

$$\mathrm{d}\ln\epsilon''(T,t) = \frac{1}{\omega e_0}\left[\frac{x(T)}{q}\left(\frac{\mathrm{d}T}{t - t_{\mathrm{gel}}(T)}\right) + \left(\frac{E_\sigma}{RT^2}\right)\mathrm{d}T\right] \tag{21}$$

For ramp heating from an initial time $t_i = 0$ and temperature T_i to a final time t and temperature T, respectively

$$t = \int_0^t \mathrm{d}T = \int_{T_i}^{T} \mathrm{d}T/q = (T - T_i)/q \tag{22}$$

and replacing the term t in the denominator of the first term on the right-hand side of eq 21

$$\mathrm{d}\ln \epsilon''(T,t) = \frac{1}{\omega e_0}\left[\frac{x(T)}{q}\left(\frac{\mathrm{d}T}{q^{-1}(T - T_i) - t_{\mathrm{gel}}(T)}\right) + \frac{E_\sigma}{RT^2}\mathrm{d}T\right] \tag{23}$$

From the measurements made by Mangion and Johari[1,2] and Parthun and Johari,[3,5] x for the curing of a thermoset increases linearly with temperature in a relatively narrow range, or $x = \kappa T$, where κ is a constant for a thermoset. This implies that as $T \rightarrow 0$ K, $x \rightarrow 0$, or that no gelation occurs, and according to eq 16, $\sigma_0(T)$ approaches zero. Substituting for $x = \kappa T$ into eq 23 gives

$$\mathrm{d}\ln \epsilon''_\sigma(T,t) = \frac{1}{\omega e_0}\left[\frac{\kappa}{q}\left(\frac{T\,\mathrm{d}T}{q^{-1}(T - T_i) - t_{\mathrm{gel}}(T)}\right) + \frac{E_\sigma}{RT^2}\mathrm{d}T\right] \tag{24}$$

We now consider the temperature dependence of the time for gelation, t_{gel}, during the curing of a thermoset. It has been found from our earlier work[3,5] that t_{gel} decreases with increasing temperature according to the equation

$$t_{\mathrm{gel}} = A\exp(B/T) \tag{25}$$

where A and B are empirical constants characteristic of a thermoset. By substituting eq 23 into eq 24, we obtain

$$\mathrm{d}\ln \epsilon''_\sigma(T) = \frac{1}{\omega e_0}\left[\left(\frac{\kappa}{(T - T_i) - qA\exp(B/T)}\right)T\,\mathrm{d}T + \frac{E_\sigma}{RT^2}\mathrm{d}T\right] \tag{26}$$

For heating at a linear rate from T_i to T, as in ramp curing, it is necessary to integrate eq 26 from T_i to T, so that

$$\int_{T_i}^{T}\mathrm{d}\ln \epsilon''_\sigma(T) = \frac{1}{\omega e_0}\left[\int_{T_i}^{T}\left[\frac{\kappa}{(T - T_i) - qA\exp(B/T)}T\,\mathrm{d}T\right] + \int_{T_i}^{T}\left(\frac{E_\sigma}{RT^2}\mathrm{d}T\right)\right] \tag{27}$$

The first integral on the right-hand side of eq 27 could not be analytically solved but can be evaluated by using an expression in Taylor series from an initial temperature T_i, which gives sufficiently accurate values from an expansion only up to the fourth power. This gives the numerical value for the first integral on the right-hand side of eq 27. This numerical value is referred to as Taylor (T) for convenience. Solving for the remaining integral terms in eq 27 gives

$$\ln \epsilon''_\sigma(T) - \ln \epsilon''_\sigma(T_i) = \frac{1}{\omega e_0}\left[\mathrm{Taylor}\ (T) + \frac{E_\sigma}{R}\left(\frac{1}{T_i} - \frac{1}{T}\right)\right] \tag{28}$$

or

$$\ln \epsilon''_\sigma(T) = \frac{1}{\omega e_0}\left[\ln \sigma_0(T_i) + \mathrm{Taylor}\ (T) + \frac{E_\sigma}{R}\left(\frac{1}{T_i} - \frac{1}{T}\right)\right] \tag{29}$$

where $\sigma_0(T_i)$ is the conductivity at the temperature T_i or at time $t_i = 0$. The increase in $\sigma_0(T_i)$ with increasing temperature is given by the Arrhenius equation or eq 18. By substituting eq 18 into eq 29, we obtain

$$\ln \epsilon''_\sigma(T) = \frac{1}{\omega e_0}\left[\left(\ln \sigma_\infty - \frac{E_\sigma}{RT_i}\right) + \mathrm{Taylor}\ (T) + \frac{E_\sigma}{R}\left(\frac{1}{T_i} - \frac{1}{T}\right)\right] \tag{30}$$

or

$$\ln \epsilon''_\sigma(T) = \frac{1}{\omega e_0}\left[\ln \sigma_\infty + \mathrm{Taylor}\ (T) - \frac{E_\sigma}{RT}\right] \tag{31}$$

or

$$\epsilon''_\sigma(T) = \exp\left[\frac{1}{\omega e_0}\left(\ln \sigma_\infty + \mathrm{Taylor}\ (T) - \frac{E_\sigma}{RT}\right)\right] \tag{32}$$

According to eq 32, the change in the ϵ'' from dc conductivity alone during the curing of a thermoset is caused by two temperature-dependent variables, namely, (i) an extrinsic variable, which is through the numerical values of Taylor (T) and which implies an approach to gelation, and (ii) an intrinsic variable, which is through the activation energy term and which implies an inverse exponential dependence of σ_0 with temperature.

(iii) General Equation for Dielectric Properties during the Curing Process. We now obtain a general expression for the change in ϵ' and ϵ'' during the curing of a thermoset by combining the dipolar relaxation and dc conduction processes as

$$\epsilon'(\omega,T) = \epsilon_\infty(T) + \frac{A'}{T}N'(\omega\tau(T)) \tag{33}$$

and

$$\epsilon''(\omega,T) = \frac{A'}{T}N''(\omega\tau(T)) + \exp\left[\frac{1}{\omega e_0}\left(\ln \sigma_\infty + \mathrm{Taylor}\ (T) - \frac{E_\sigma}{RT}\right)\right] \tag{34}$$

In eq 34, the first term represents the contributions from the dipolar reorientation and the second those from dc conduction.

Prior to using the generalized eqs 33 and 34 for analyzing the results of ramp curing of thermosets, we examine the qualitative nature of these equations as follows: For a fixed-frequency measurement, the change in ϵ'' is first dominated by the exponential, or second, term in eq 34. The importance of the linear, or first, term increases with increasing temperature but only before ϵ'' reaches a maximum value.

To calculate ϵ' and ϵ'' from eqs 33 and 34, knowledge of the relaxation time at different extents of cure at each temperature is required. For this purpose, we examine the shape of the plots of the extent of cure, α_{cure}, against time of cure of a thermoset at a fixed temperature. These plots, illustrated in Figure 1, have a sigmoidal shape similar to that of the plots of log τ against log (time) generally observed for thermosets during their curing. As a first approximation, we consider that τ is related to α_{cure} by an equation

$$\tau(T,t) = \tau(T,0)\exp[S\alpha^n_{\mathrm{cure}}(T,t)] \tag{35}$$

where $S = \ln(\tau(T,0)/\tau(T,\infty))$ and $\tau(T,0)$ and $\tau(T,\infty)$ are constants. They normalize the plot of $\ln[\tau(T,t)]$ so that its value varies between zero and one and n alters the shape of the plot so that a plot of $\ln \tau(T,t_{\mathrm{gel}})$ against t can be made to correspond with the plot of $\alpha_{\mathrm{cure}}(T,t_{\mathrm{gel}})$ against t. (When $n = 1$, α_{cure} is directly proportional to $\ln \tau$.) Within this approximation, τ can be calculated from the

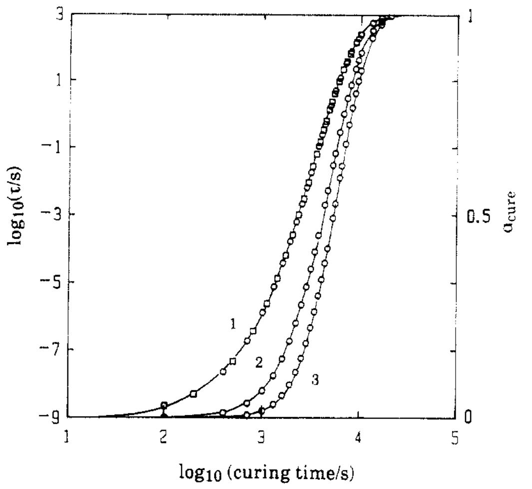

Figure 1. Calculated values of the extent of cure (denoted by □) and of the relaxation time (denoted by ○ in curves 1, 2, and 3) plotted against the logarithm of curing time at a fixed temperature. Curves 1, 2, and 3 correspond to the values of $n = 1$, 2, and 3 in eq 35. $\tau(t{=}0) = 1$ ns, $\tau(t{\rightarrow}\infty) = 1$ ks; $T = 300$ K; the preexponential factor and the activation energy for the curing reactions are 1.5×10^5 s^{-1} and 50 kJ/mol.

$a_{\rm cure}$ values obtained from the calorimetric data of curing kinetics. Barton[17] has shown that the change in $a_{\rm cure}$ during the ramp curing at a rate q is given by an empirical equation

$$\int_0^{a_{\rm cure}} \frac{{\rm d}a_{\rm cure}}{{\rm f}(a_{\rm cure})} = \frac{C}{q}\int_{T_{\rm i}}^{T} \exp(-(E/RT)\,{\rm d}T) \qquad (36)$$

where C is a constant, $T_{\rm i}$ is the initial temperature, E is the average activation energy for chemical reactions, and ${\rm f}(a_{\rm cure})$ is a function of $a_{\rm cure}$. For ${\rm f}(a_{\rm cure}) = 1 - a_{\rm cure}$, eq 36 may be integrated to give

$${\rm f}(a_{\rm cure}) = -\ln(1-a) = \left(\frac{CE}{qR}\right){\rm p}\left(\frac{E}{RT}\right) \qquad (37)$$

or

$$a_{\rm cure} = 1 - \exp\left[-\left(\frac{CE}{qR}\right){\rm p}\left(\frac{E}{RT}\right)\right] \qquad (38)$$

where ${\rm p}(E/RT)$ is an integral given by

$${\rm p}(y) = -\int_{y_{\rm i}}^{y}\left(\frac{e^{-y}}{y_2}\right){\rm d}y \qquad (39)$$

For $y \geq 15$, the approximate value of the integral of eq 39 may be determined by a series expansion.

Substituting for $a_{\rm cure}$ from eq 38 into eq 35 gives

$$\ln\tau(T) = \ln\tau(T,0) + S\left(1 - \exp\left[-\left(\frac{CE}{qR}\right){\rm p}\left(\frac{E}{RT}\right)\right]\right)^n \qquad (40)$$

The relaxation time may thus be calculated from the knowledge of average activation energy E for the chemical reactions, constant C, n, and $\tau(T,0)$ and $\tau(T,\infty)$, which in turn may be used to calculate ϵ' and ϵ'' at different temperatures from eqs 33 and 34, respectively. For $E = 50$ kJ mol^{-1}, $C = 5 \times 10^9$ s^{-1}, $n = 1$, $q = 1$ K min^{-1}, $\tau(T,0) = 10^{-9}$ s, and $\tau(T,\infty) = 10^3$ s, the experimental $a_{\rm cure}$ and ln (τ) curves superpose, and for $A' = 1050$ K^{-1}, $\omega = 6.28$ krad, $E_\sigma = 30$ kJ mol^{-1}, $\kappa = 0.0087$ K^{-1}, $A = 9.2$ μs, $B = 6232$ K^{-1}, and $\sigma_\infty = 18.66$ kS m^{-1}, we calculate the $\epsilon''_{\rm dip}$ and ϵ''_σ as a function of temperature. Their plots against temperature are shown in Figure 2, which includes the combined plot of $\epsilon'' = (\epsilon''_{\rm dip} + \epsilon''_\sigma)$. The combined plot shows that as the temperature is increased, ϵ'' initially decreases, reaches a mininum which is followed by a peak, and thereafter decreases to a nearly constant value. The peak in ϵ'' is broad due to our simplifying assumption for $n = 1$. For higher values of n, which are needed to convert $a_{\rm cure}$ into ln (τ) such that at the $a_{\rm cure}$ ($t_{\rm gel}$), the $\tau(t_{\rm gel})$ corresponds to the measured dielectric relaxation time, the peak would become narrow.

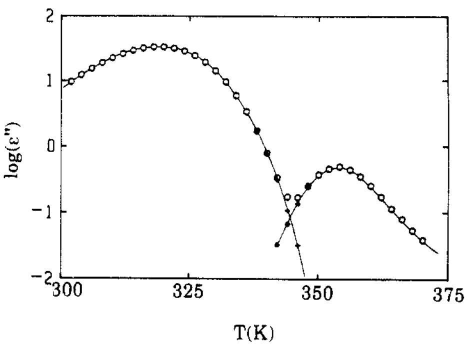

Figure 2. Calculated contribution to ϵ'' from both dc conductivity and orientation polarization plotted against the temperature during ramp curing. Also shown is the sum of the two contributions. The parameters used for the calculations are given in the text.

For the sake of consistency, we now examine whether eqs 33 and 34 provide a physically plausible description of the ϵ' and ϵ'' data in the limits of $q \rightarrow 0$ and $q \rightarrow \infty$. As $q \rightarrow 0$, the dielectric behavior of a thermoset during ramp curing is formally the same as for isothermal curing and therefore the plots of ln (τ) against T would be sigmoidal as observed in several of our studies on isothermal curing reported earlier.[1-5] In contrast, as $q \rightarrow \infty$, the total time for the cure approaches zero and the chemical and physical structure of the thermoset remains unchanged. A plot of its relaxation time against temperature would therefore be identical to that of a chemically and physically stable liquid mixture, namely that τ would exponentially decrease with increase in temperature according to

$$\tau = \tau_0 \exp(E_{\rm a}/RT) \qquad (41)$$

where τ_0 is the relaxation time as $T \rightarrow \infty$ and $E_{\rm a}$ is the activation energy for relaxation. Thus, as the heating rate is increased from $q \rightarrow 0$ to $q \rightarrow \infty$, the shape of the plots of log τ against T would continuously change from a nearly vertical line, in which τ increases with temperature, to broader shapes leading to the ultimate shape in which the relaxation time exponentially *decreases* with increase in temperature. The first condition follows from eq 40 by replacing q with a vanishingly small value such that the $\exp[-(CE/qR)]$ approaches unity and the second condition by replacing q with infinity so that the second term on the right-hand side of eq 40 becomes negative and τ decreases with increase in the temperature.

To obtain the change in ϵ' and ϵ'' on ramp curing in the limits of $q \rightarrow 0$ and $q \rightarrow \infty$, we first consider the Laplace transform of the relaxation function integral in eqs 12 and 13, which is written as a product of the temperature-dependent orientation polarization $\Delta\epsilon = A'/T$ and $N'(\omega\tau)$ or $N''(\omega\tau)$. When $q \rightarrow 0$, $\Delta\epsilon$ remains constant, as assumed here, and N' and N'' change only because τ increases. This is the condition for isothermal curing for which $\epsilon^*(\omega,t)$ is written as

$$\epsilon^*(\omega,t) = \epsilon_\infty(t) + [\epsilon_0(t) - \epsilon_\infty(t)]\int_0^\infty e^{-i\omega t'}\left(-\frac{\partial\Phi(t')}{\partial t'}\right){\rm d}t' \qquad (42)$$

where all the terms are as defined earlier, and

$$\int_0^\infty e^{-i\omega t'}\left(-\frac{\partial\Phi(t')}{\partial t'}\right){\rm d}t = N^*(\omega,\tau(t)) = N'(\omega,\tau(t)) - iN''(\omega,\tau(t)) \qquad (43)$$

and

$$\epsilon'(\omega,t) = \epsilon_\infty(t) + [\epsilon_0(t) - \epsilon_\infty(t)]N'(\omega,\tau(t)) \qquad (44)$$

$$\epsilon''(\omega,t) = [\epsilon_0(t) - \epsilon_\infty(t)]N''(\omega,\tau(t)) \qquad (45)$$

and the plots of ϵ' and ϵ'' against the curing time are identical to those for the isothermal curing.

However, as $q \rightarrow \infty$, the situation becomes complicated but can be resolved by using L'Hospital's rule in the equation

$$T = qt - T_i \qquad (46)$$

where T_i is the temperature at $t = 0$ and when $q \rightarrow \infty$, $T \rightarrow \infty$. Since for $T \rightarrow \infty$, both the first and second terms in eq 28 become zero, $\epsilon'' \rightarrow 0$. This continuous change in the shape of the plot of log ϵ'' against temperature is shown in Figure 3, where ϵ'' was calculated for q in the range 10^{-4}–10^4 K/min, $A = 90\ \mu$s, $B = 6232$ K^{-1}, $\kappa = 0.01$ K^{-1}, and $E_\sigma = 30$ kJ mol^{-1}. It is evident that as q is increased, the shape of the plot gradually approaches that given by the relation

$$\epsilon'' = \frac{1}{\omega e_0} \exp\left[-\left(\frac{E_a}{RT}\right)\right] \qquad (47)$$

Thus the formalism for the dielectric behavior of a thermoset during its nonisothermal curing provides a satisfactory description of the changes in ϵ' and ϵ'' with change in the heating rate.

III. Experimental Test of the Formalism for Ramp Curing

To test the validity of the preceding formalism, ϵ' and ϵ'' of a thermoset polymer based on the resin diglycidyl ether of Bisphenol-A (DGEBA) cured with ethylenediamine (EDA) were measured for a fixed frequency of 1 kHz during its curing on heating at a constant rate of 0.5 and 1.0 K/min over the temperature range 300–375 K. The equipment and procedure for these measurements are described in the preceding paper. The glass transition temperature for the thermoset in its cured state is about 360 ± 10 K, as Horie et al.[18] reported, and since no significant curing occurs above this temperature, the upper limit of the temperature–time cure ramp was justifiably kept at 375 K. The change in the dielectric properties as measured at 1-kHz frequency for the two heating rates is shown in the plots of ϵ', ϵ'', and tan δ ($=\epsilon''/\epsilon'$) against temperature in Figure 4.

Typically, ϵ' initially decreases rapidly, with a gradual slowing of the rate as the temperature increases. This slowing is interrupted by a rapid step decrease toward a value whose magnitude and position depend on both the heating rate and the nature of the curing agent. On further heating at a constant rate toward the upper limiting temperature, ϵ' slowly and continuously increases. The ϵ'' of the thermoset initially increases with increasing temperature toward a broad, shallow maximum, following which it decreases increasingly rapidly toward a local minimum. From this minimum, ϵ'' rises to a sharp peak which is followed by a decrease toward a plateau value. On continued heating, ϵ'' begins to increase gradually. tan δ behaves in a qualitatively similar manner during the curing, but with different quantitative values of the peak height and peak position.

The magnitude of the step decrease in ϵ' for each thermoset is seen in Figure 4 to be greater for $q = 0.5$ K/min than for $q = 1.0$ K/min. The amount of decrease is 3.45 for $q = 0.5$ K/min and 2.91 for $q = 1.0$ K/min. The magnitude of ϵ' after the step decrease also depends on the heating rate q. It is 4.45 for $q = 0.5$ K/min and 4.58 for $q = 1.0$ K/min.

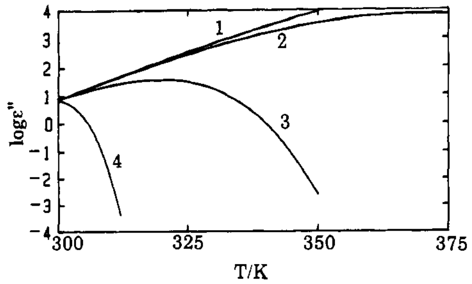

Figure 3. Calculated values of ϵ'' for a thermoset during its ramp curing at different rates plotted against the temperature. Curves labeled 1, 2, 3, and 4 refer to the heating rate, $q = 10^{-4}$, 10^{-2}, 10^0, and 10^2 K/min, respectively.

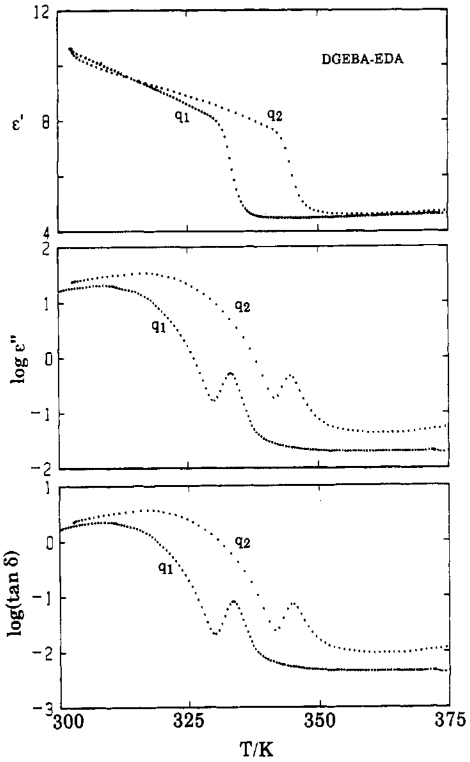

Figure 4. Dielectric permittivity, loss, and loss tangent of the DGEBA–EDA thermoset measured for a fixed frequency of 1 kHz plotted against temperature during its curing on heating at rates indicated on the plots. $q_1 = 0.5$ K/min; $q_2 = 1.0$ K/min.

The relative heights of the peaks in ϵ'' in Figure 4 also depend on both the heating rate and the curing agent used. The height of the second peak in ϵ'' is 0.51 for $q = 0.5$ K/min and 0.45 for $q = 1.0$ K/min. The value of ϵ'' following the second peak increases as the heating rate of the thermosetting mixture is increased. It is 0.019 for $q = 0.5$ K/min and 0.042 for $q = 1.0$ K/min.

In our earlier studies,[1-5] a method was outlined for determining the time during the isothermal cure up to which the measured dielectric loss is dominated by the dc conductivity. This is done by constructing the complex plane plots of M'' against M', whose shapes indicate a Maxwellian conductivity relaxation. The plot of M'' against M' for both heating rates, 0.5 and 1.0 K/min, had during the initial stage of the curing the shape of a semicircular arc. Deviations from this shape appeared at the later stages of cure, so that M'' reached a minimum value rather than zero. Following the semicircle, a skewed arc appeared. In our earlier studies[1-5] we have shown that, for times of cure less than the time to reach the minimum in M'', ϵ'' is dominated by the dc conductivity during the initial stages of cure. At times after the minimum in M″, the dc conductivity is effectively zero or negligible so that the skewed arc, which thereafter appears, results from the contribution to ε″ or M″ from the dipolar reorientation. Since the plots of M″ against M′ for thermosets being cured by ramp heating had shapes similar to the plots for a thermoset cured isothermally, the change in the dc conductivity is taken as the main reason for changes in the ε″ and M″ in the early stages of ramp curing and changes in the dipolar relaxation time for those in the later stages.

In eq 34 for the ramp-curing formalism, ε″ is defined in terms of contributions from both dc conductivity and dipolar relaxation. Because the two processes give different shapes to the plots of M″ against M′, it seems reasonable to analyze the dielectric data separately, with the behavior in the initial stages of the cure being largely determined by the dc conductivity according to eq 32 and that in the later stages by a dipolar reorientation process according to eqs 33 and 34 as follows:

The change in the dc conductivity during ramp curing can be written from eq 31 as

$$\ln \sigma_0(T) = \ln \sigma_\infty(T_i) + \text{Taylor }(T) - \left(\frac{E_\sigma}{RT}\right) \qquad (48)$$

where all parameters are as defined earlier. There are two unknown variables in eq 48, one E_σ, the activation energy for the dc conductivity, and second κ, which is a constant in the linear relation between the power law exponent and temperature, $x = \kappa T$. An algorithm was written to calculate σ through a reiterative procedure from eq 48 using two parameters κ and E_σ such that the mean square difference between the experimental and calculated values was a mininum. The calculated and experimental σ values are plotted against temperature in Figure 5 for the ramp curing at 0.5 and 1.0 K/min for the thermoset, and the values of E_σ and κ are listed in Table I. In all cases, the experimental and calculated values are seen to be in good agreement, and the curves for the two sets of data agree within the experimental errors.

As seen in Table I, E_σ remains constant with increase in the heating rate but κ increases. This increase in κ seems consistent with the observation that for isothermal curing, i.e., when $q = 0$, κ is finite and the gelation point is reached within a measurable period. But, when $q \rightarrow \infty$ and gelation does not occur because no time is available for chemical reactions to begin and network formation does not occur.

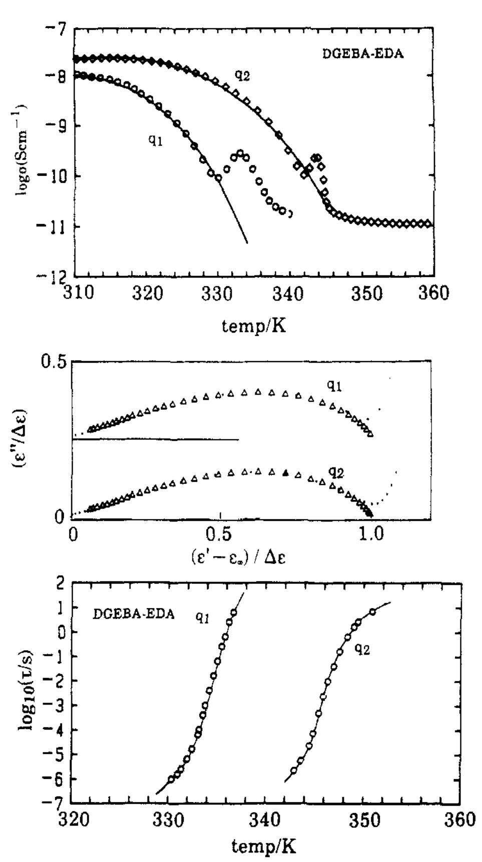

Figure 5. Calculated dc conductivity and normalized permittivity and loss compared against the measured value and the calculated relaxation time for the DGEBA–EDA thermoset plotted against the temperature during their curing at two heating rates. $q_1 = 0.5$ K/min; $q_2 = 1.0$ K/min. The smooth line for conductivity and triangles for the normalized ε′ and ε″ are the calculated values.

Table I
Parameters Used To Calculate the Dielectric Properties during the Nonisothermal Curing of the DGEBA–EDA Thermosets Heated at Two Rates[a]

q (K/min)	ϵ_∞	γ	E_σ (kJ/mol)	κ (K^{-1})	A' (K^{-1})
0.5	4.55	0.26	39.5	0.0087	1150
1.0	4.55	0.25	39.5	0.0102	1010

[a] The mean square error between the calculated and experimental data using these parameters is less than 0.037, which is calculated for ln σ. The idividual errors of calculated data points may be seen in Figure 5. The uncertainty in γ may be as high as 0.02 and in ϵ_∞, 0.05.

We now consider the changes in the dielectric behavior as a result of changes in its relaxation time. At temperatures greater than where the minimum in the plots of ε″ against temperature in Figure 4 appears, the data need to be analyzed according to eqs 12 and 13 for the dipolar relaxation process. The skewed arc in the plots of ε″ against ε′ has been previously analyzed according to the formalism developed for the isothermal curing kinetics.[1-5] Similarly, for the ramp-curing kinetics we consider the normalized complex plane plots of $[\epsilon''/\Delta\epsilon]$ against $[(\epsilon' - \epsilon_\infty)/\Delta\epsilon]$, where $\Delta\epsilon = A'/T$. For fixed-frequency measurements at 1 kHz during the ramp curing at 0.5 and 1.0 K/min, these plots are shown also in Figure 5. To calculate the data from the formalism, it was necessary to determine the values of the parameters A', ϵ_∞, and γ. This was done by using an algorithm which normalized the experimental data by using A' ($=\Delta\epsilon T$) and ϵ_∞ so that the intercepts of the plots on the $[(\epsilon' - \epsilon_\infty)/\Delta\epsilon]$ axis were 0 and 1. The parameter γ was then adjusted by a reiterative procedure such that the difference between the calculated and experimental data was minimum. The calculated and experimental values are shown also in Figure 5. For all sets of data, the agreement between the theory and the experiment is seen as satisfactory, with deviations occurring only at long times of cure when $\epsilon''(t \rightarrow \infty)$ does not reach zero.

The values of the parameters A', E_σ, κ, ϵ_∞, and γ used for the calculations are also listed in Table I for both heating rates used for curing the three thermosets. A' is expected to remain unchanged with change in the heating rate, but here it decreases by as much as 10%. This decrease is clearly due to our assumption that $[\epsilon'(t \rightarrow 0) - (\epsilon'(t \rightarrow \infty)]$ is independent of the curing time and through it of the curing temperature. As expected, ϵ_∞ remains independent of the heating rate. κ increases and γ decreases with increase in the heating rate. A discussion of the change in the γ parameter with increase in the size of the curing agent has already been given in the preceding paper.[5]

Physical properties of thermosets change as the relaxation time of its structure continuously increases during its curing at a certain heating rate. In the limit $q \rightarrow 0$, the increase in the relaxation time corresponds to that observed during isothermal curing. But in the limit $q \rightarrow \infty$, curing does not occur and the relaxation time is therefore expected to decrease with increase in the temperature according to eq 41, as for chemically and physically stable liquids in general. Thus as q is increased there is a gradual transition in the shape of the plots of log τ against temperature from a positive slope toward a negative slope.

As in our earlier work,[1-5] τ can be determined from the complex plane plots of $\epsilon^*(\omega,T)$ in Figure 5 or from the plots of $\epsilon'(\omega,T)$ against the temperature in Figure 4. This was done according to the procedure outlined in earlier papers,[1-5] and the plots of log τ against temperature are shown also in Figure 5 for the thermosets measured on heating at two different rates. Here the plots are sigmoidal with a point of inflection and resemble the plot of the extent of chemical reaction or the degree of cure of the thermoset plotted against the temperature. The slope at the point of inflection, i.e., $(\partial \log \tau/\partial T)_g$, decreases with increase in the heating rate, which implies a decrease in the maximum rate of cross-linking with increase in the heating rate used for curing.

Figure 5 also shows the expected change in the shape of the curves with increase in the heating rate. The inversion in the slope of the plot which is expected to occur for a much higher heating rate could not be observed here because, during the period required for one dielectric measurement when the heating rate is high enough to observe this inversion, the change in the temperature of the sample is too rapid to ascertain it.

IV. Conclusions

Dielectric studies of thermosets during their nonisothermal curing show changes in the properties which can be described in terms of a generalized formalism developed here. Calorimetric and dielectric data obtained from isothermal curing can be used to obtain the changes in the dielectric properties of a thermoset during its ramp curing. The formalism is useful for determining the curing kinetics of a thermoset polymer.

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References and Notes

(1) Mangion, M. B. M.; Johari, G. P. *Macromolecules* **1990**, *23*, 3687.
(2) Mangion, M. B. M.; Johari, G. P. *J. Polym. Sci., B: Polym. Phys.* **1991**, *29*, 437, 1117, 1127.
(3) Parthun, M. G.; Johari, G. P. *J. Polym. Sci., B: Polym. Phys*, in press.
(4) Johari, G. P.; Mangion, M. B. M. *J. Noncryst. Solids* **1991**, *131*, 921.
(5) Parthun, M. G.; Johari, G. P. *Macromolecules*, in press.
(6) Mangion, M. B. M.; Vanderwal, J.; Walton, D.; Johari, G. P. *J. Polym. Sci., B: Polym. Phys.* **1991**, *29*, 723.
(7) Alig, I.; Hausler, K. G.; Tanzer, W.; Unger, S. *Acta Polym.* **1988**, *39*, 269.
(8) Alig, I.; Hausler, K. G.; Nancke, K.; Tanzer, W.; Wartewig, S. *Acta Polym.* **1989**, *40*, 508.
(9) Alig, I.; Johari, G. P. *J. Polym. Sci., B: Polym. Phys.*, in press.
(10) Johnson, J. F.; Cole, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 4536.
(11) McDonald, J. R. *Impedance Spectroscopy*; Wiley: New York, 1987; p 23.
(12) Cole, R. H.; Tombari, E. *J. Noncryst. Solids* **1991**, *131*, 969.
(13) Kohlrausch, R. *Pogg. Ann. Phys. Chem.* **1854**, *91*, 179.
(14) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.
(15) Stauffer, D.; Coninglio, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 105.
(16) Djabourov, M. *Contemp. Phys.* **1988**, *29*, 273.
(17) Barton, J. M. *Adv. Polym. Sci.* **1985**, *72*, 111.
(18) Horie, K.; Hiura, H.; Sawada, M.; Mita, I.; Kambe, H. *J. Polym. Sci., Part A* **1970**, *8*, 1357.

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