Authors' Response to Comments on "Relaxation in Thermosets. 23. Dielectric Studies of Curing Kinetics of an Epoxide with Diamines of Varying Chain Lengths"

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In response to the preceding comments by Zukas,[1] we restate that Parthun and Johari's[2] study focuses on the dynamics of a macromolecule's irreversible growth, as in the curing of thermosets and other living polymerization processes. While we fully accept the point that we have been negligent in correcting the page proofs and regret the resulting inconvenience to the author,[1] we emphasize that the points raised require no alteration of our conclusions. It is regrettable that the author[1] did not approach us on this matter. Part 4 of this series (*J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1621), which first provided the formalism, could also have been consulted by the author.[1]

Although readers would be able to determine the realm and relative merits of the preceding comments[1] and would find that all have been anticipated in our earlier papers of this series, it seems necessary here to provide a rebuttal to the points raised, as follows:

(1) References to the previous work on the subject have indeed been given in the earlier papers of this series[3] and therefore have not been repeated in ref 2. An an example, one of us has stated[4] the following:

"An excellent review of the studies up to 1986 has been given by Senturia and Sheppard (1986). For the readers convenience, they have included, in this review, the details of measurement methods and a comprehensive bibliography with 118 references on the dielectric studies of various pure epoxies and their composites." The paragraph that follows[4] provides more references to the literature since 1986 than included in the preceding comments.[1] Perhaps we should also be explicit in saying that the basic equation for ϵ'' ($=\epsilon''_{\text{dipole}} + \sigma_{\text{dc}}/\omega e_0$), reviewed in refs 1 and 3, was *the starting point* of the formalism given in our papers.

(2) The interpretation of ϵ'' in terms of dc conductivity (i.e., charge transport) and polarization (dipolar reorientation) is unquestionable. However, the mechanisms for charge transport and dipolar orientations are often interpreted differently and therefore are occasionally debated. We restate[3–7] that the dielectric response during the isothermal curing of a thermoset is determined by at least seven effects, as follows:

(i) A general decrease in the dc conductivity as (a) the diffusion coefficient and population of impurity ions in the liquid decreases—the latter as a result of a decrease in ϵ_0 (see ref 8); (b) the population of zwitterions formed during the reactions[9,10] and their diffusion rate decrease; and (c) any proton transport along the H-bonded network, when present in the liquid, is disrupted prior to the full chemical conversion. These also alter the interfacial polarization and thus affect both ϵ' and ϵ''.

(ii) An increase in the molecular diffusion or relaxation time as a result of which the dielectric permittivity, ϵ', as measured for a fixed frequency, monotonically decreases toward a value corresponding to the infrared region.

(iii) A change in the number of dipoles per unit volume, and therefore in $\Delta\epsilon$, the contribution to the permittivity from orientation polarization, as a result of both the chemical reactions that alter the dipole moment and the volume contraction that raises the number density of the dipoles.

(iv) The splitting of a unimodal relaxation function into a bimodal relaxation function.[7]

(v) A change in the dielectric relaxation function, or distribution parameter, as the chemical structure of the liquid changes and its viscosity and density increase.[7]

(vi) A change in $\Delta\epsilon_{\text{IR}}$, the contribution to the permittivity from infrared polarization, as the vibrational frequencies of the various modes in the structure change on both chemical reaction and spontaneous densification.

(vii) A change in the optical refractive index or optical polarization as the macromolecule forms and the reacting mixture densifies.

The dc conductivity should be attributed to at least three processes, namely, (a) the migration of impurity ions both in the epoxy resin *and the curing agent*, (b) formation of zwitterions[9] when the amine is devoid of protons (i.e., when curing with a tertiary amine),[10] and (c) proton transfer along the H-bonded network of the amines. In view of these, it is difficult for us to accept the assertion that "this conductivity is attributed to ionic impurities inherently present from the resin synthesis process".[1]

(3) While we agree that "gelation has *no* corresponding event in the dielectric response" (see also ref 4, p 191), we point out to the author[1] that gelation is rarely observed as an event or a discontinuity in a measurable property. Properties change usually according to an equation in which their value approaches, but does not attain, the ultimate values of infinity or zero corresponding to the critical point. This effect is seen for example in the Newtonian viscosity[11] and dc conductivity in the percolation theory.[12] In reality, this approach toward the critical point either cannot be followed or is interrupted by other effects. The relative merits of the fit for gelation and Vogel–Fulcher–Tamman like equations (both did appear in several earlier papers[3–6,10]) was determined by our data—which are not in dispute—that show t_{gel} to be invariant of the ac frequency and t_0 to be variant.[5]

It is worth noting that we had systematically studied the curing kinetics of the thermosetting mixtures by DSC methods at temperatures of our dielectric studies and had calculated the extent of reaction, α (see ref 13). At t_{gel}, calculated from eq 11 in refs 2 and 5, $\alpha_{\text{crit}} = 0.56$–$0.70$. According to Flory's theory[14] for the gel formation in such cases (i.e., a mixture of 2 mol of difunctional and 1 mol of tetrafunctional molecules) $\alpha = 0.60$. Stockmayer's[15] calculations show this value to be uncertain by as much as 5%, and the effect of steric hindrance introduces further uncertainty in this value. There is also an uncertainty in our determination of t_{gel} from dielectric measurements and in estimating α from DSC; the latter, we point out, is caused by the enthalpy released on structural relaxation of the network as its $T_g \rightarrow T_{\text{cure}}$, and which contributes to the exotherm (the details are given in *Disorder Effects in Relaxation Processes*; Richert, R., Blumen, A., Eds.; Springer-Verlag: Berlin, FRG, in press). Within these experimental uncertainties, the experimental and theoretical values of α at t_{gel} are not in serious disagreement (detailed arguments are given in ref 13). Further comparison of the t_{gel} against values estimated from dynamic mechanical and viscosity measurements for other thermosets is already given in part 4 in this series of papers.

We suggest that experiments for determining gelation time using other chemical and physical methods will

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further resolve this issue and are obviously necessary before accepting any views on the still, as yet pending,[16] subject.

(4) It is difficult for us to accept the assertion that the peak that appears in the dielectric loss factor during kinetic measurements be attributed to vitrification and that "this peak simply represents the time the glass transition temperature of the curing mixture reaches the cure temperature at the measurement frequency".[1] In our experience, the vitrification time and the glass transition temperature do not vary with the measurement frequency. (A thermosetting mixture is quite fluid at a curing time when the loss peak appears at a measuring frequency of 100 MHz.[7,17]) We would like to restate that *the* ϵ'' *peak is due to the* α*-relaxation process and is not due to vitrification*. Perhaps their[1] definition of glass transition and vitrification differs from the widely accepted definition.

(5) The modulus formalism has been used in the discussion of a polymer's dielectric properties for some time (see refs 18–20). It has appeared as $1/\epsilon^*$ in ref 21 and has since proven to be invaluable in resolving the dielectric polarization from dc conduction, or vice versa, when no ϵ'' peak is observable.[18-20]

We would also like to point out that the region where conductivity is dominant is *not* always the region where ϵ'' is inversely proportional to ω. When interfacial polarization is present, ϵ'' at the low-frequency end of the frequency spectrum varies with $\omega^{1/2}$.[22-24]

In our experience, the dc conductivity of a thermosetting mixture during its curing *cannot* be measured by the procedure mentioned in ref 1, simply because such measurements require data over a frequency range low enough that the ac conductivity remains constant with changing frequency, and, as the time required for measurements at such low frequencies becomes longer, the extent of chemical and physical changes within the thermoset becomes undesirably significant during the measurement period. Thus, according to the accepted definition that $\sigma \rightarrow \sigma_0$ as $\omega \rightarrow 0$, σ_0 for a time-variant system cannot be measured by the method suggested in ref 1. The formalism in terms of M^* becomes necessary.

(6) Strictly speaking, all seven effects given in (2) here should be included in a rigorous mathematical treatment of the dynamics of irreversible growth of a macromolecule or curing of a thermoset mixture. But our current knowledge of the subject allows us to include only (i) and (ii), and, thus, approximations are to be made for others or else arguments that their contributions are insignificant relative to those of (i) and (ii) be given. ϵ_0 is found to decrease by at most 20% during the curing of a thermoset.[7] In comparison with the concurrent 11 orders of magnitude or more increase in τ, the decrease in ϵ'' due to change in ϵ_0 is negligible and does not affect the analysis done in our paper, within the quoted terms. Any demonstrable, rigorous formalism should contain all of the seven, or more, effects. It can, of course, be easily written in a manner similar to eqs 6.2 and 6.3 in ref 4, but without our ability to determine the changes in the various coefficients, it cannot be used.

(7) Both parameters β and γ are empirical but differ in their significance. β has a meaning in terms of the decay function Φ that takes it back to the frequency domain. γ does not have this meaning. Therefore, it should not appear to represent some average value of β. The two also are seen to have converse temperature dependence: β increases but γ decreases with increasing temperature,[3-6] and studies have shown that the magnitude of the two differs considerably.[7] Nevertheless, γ does have a technical importance in that its value determines the maximum ϵ'' a curing thermoset will reach and the slowness with which it will approach vitrification.

(8) We regret that typesetting errors appeared in the printed version of our paper. We submitted for publication an erratum, but ref 1 reached the Journal first. These are as follows. (a) Line 15, column 1, p 3255: $\epsilon'(t \rightarrow \infty)$ should read $\epsilon'(t \rightarrow 0)$. (b) Last line in column 1, p 3256: delete sentence from "where second peak". (c) Equation 14a: $\epsilon(t)$ should read $\epsilon_0(t)$. Equation 15: the negative sign should be outside the brackets. (d) Line 5, column 2, p 3260: 313.5 and 305.2 K should read 324 and 304.2 K. (e) Caption to Figure 8: 324 K should read 304.2 K. (f) Line 3 from bottom, column 1, p 3261: 323 K should read 324 K. (g) Line 1, second column, p 3261 and Figures 12 and 13: 305 K should read 304.2 K. (h) Caption to Figure 10: 350 K should read 304.2 K. (i) Last line in column 2, p 3263: Figure 15 should read Figure 14. (j) Caption to Figure 15: numbers (5) and (6) should be reversed. (k) Caption to Figure 17: numbers (1) through (5) should be reversed. (l) Acknowledgment: McMaster should read Master. These do not alter our conclusions.

References and Notes

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