Comments on "Relaxations in Thermosets. 23. Dielectric Studies of Curing Kinetics of an Epoxide with Diamines of Varying Chain Lengths"†

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Parthun and Johari[1] recently carried out a detailed dielectric study of the curing kinetics of diglycidyl ether of Bisphenol A (DGEBA) based thermosets. The observed dielectric response during thermoset cure has become quite well-defined in the literature over the last 5 to 10 years. The extensive analysis by Parthun and Johari as applied to these thermosets thus appears unnecessary and, in some instances, incorrect. A brief review of what is commonly understood about the dielectric response during thermoset cure and its applicability to the work of Parthun and Johari is presented here.

Extensive literature is available on the dielectric monitoring of the cure of thermosetting materials (with particular emphasis on epoxy resins). An excellent review by Senturia and Sheppard[2] (118 references) summarizes the typically observed dielectric phenomena during cure and its molecular origins. The measured dielectric loss factor, ϵ'', is generally represented[2-7] by the sum of two terms:

$$\epsilon'' = \epsilon''_{\mathrm{d}} + \sigma/(\epsilon_0\omega)$$

a dipole contribution term, ϵ''_{d}, and a conductivity contribution term where σ is the dc conductivity, ϵ_0 is the permittivity of free space, and ω is the angular frequency. It is generally known and accepted that the dielectric response in the early part of cure is dominated by ionic conductivity effects. The dipolar contribution to the measured loss factor is considered negligible, and the following expression is considered accurate in this region:

$$\epsilon'' = \sigma/(\epsilon_0\omega)$$

Again, this is generally known and accepted. This conductivity is attributed to the ionic impurities inherently present from the resin synthesis process.

It is also generally accepted that the onset of molecular gelation has *no* corresponding event in the dielectric response. Since either ionic conductivity or dipole orientation is being monitored, only motions at a much smaller scale than those being affected by macroscopic gelation are being monitored. One would not expect gelation to be observed through dielectric techniques. Senturia and Sheppard present a very well-referenced discussion of this.

The dielectric response observed by Parthun and Johari in their Figures 1 and 2 is a very typical response for an isothermal cure of an epoxy resin system cured at a temperature below its ultimate glass transition temperature. This response has been attributed by others[2,4-6] to an initial ionic conductivity dominated region followed by a dipole orientation dominated region as the conductivity continually decreases during cure. The peak in the dielectric loss factor has been attributed by others[2,4,5] to vitrification. This peak simply represents the time the glass transition temperature of the curing mixture reaches the cure temperature at the measurement frequency. Again, Sheppard and Senturia present a very well-referenced discussion of the dielectric phenomena observed by Parthun and Johari in their Figures 1 and 2.

A number of specific points regarding the work by Parthun and Johari require comment. They first convert the complex permittivity to a complex "electrical modulus". This may be mathematically interesting, but it remains the same data (analogous to converting complex mechanical compliance to a complex modulus). There appears to be no benefit to this conversion, and it only serves to put the data in a form not commonly used in the discussion of dielectric properties of polymeric materials. As stated above, the region where conductivity is dominant is the region where the measured ϵ'' is inversely proportional to ω. Conductivity is easily determined from a plot of measured ϵ'' vs ω at any point in time during the cure. The instrumentation being utilized by Parthun and Johari is fully capable of such measurements.

Second, Parthun and Johari define two parameters, t_{gel} and t_0, which represent the time to form a gel and the time when the dc conductivity "formally" goes to zero, respectively. The t_{gel} parameter is derived from a power law expression and the t_0 parameter is derived from an exponential expression. Both are based on the point in time when conductivity reaches a value of zero. As stated above, there is *no* dielectric event associated with the process of gelation. There is no reason why the diffusion of ions would stop at the onset of macroscopic gelation. Although the conductivity is continually decreasing during cure, no material has zero conductivity. The above parameters are thus strictly empirical. Also, even though they are both based on the conductivity approaching zero, different values are obtained for t_{gel} and t_0 for the same cure. Use of these parameters to physically interpret cross-linking systems is meaningless. Parthun and Johari have also shown an obvious frequency dependence of these parameters, thus showing neither represent the point of gelation. They dismiss this obvious frequency dependence by attributing a significant and unlikely error to their time measurement.

Third, Parthun and Johari use the value of ϵ' as time approaches zero, $\epsilon'(t \rightarrow 0)$, in their derivations. The value of ϵ' is a function of cure. At any point of time into cure, ϵ' is a unique function of frequency for the assembly of molecules present at that time. To use a value for $\epsilon'(t \rightarrow 0)$ for a partially cured material is meaningless since it represents the dielectric properties of a different collection of molecules. Derivations based on the use of this limit are not necessarily valid.

Fourth, there is no apparent reason for the definition of the "new" parameter, γ. Parthun and Johari have assumed no physical and chemical changes taking place in the timeframe of measurement and are thus restating the Kohlrausch-Williams-Watts parameter, β. The values reported for γ appear to represent some average value of β. Also, the evaluation of a value for γ may be inherently flawed since it is dependent on a derivation based on the value of $\epsilon'(t \rightarrow 0)$.

Fifth, a number of errors and/or omissions exist in the text of Parthun and Johari.

(a) Values for the times to the peaks in M'' referred to in the text are not in Table I.

(b) The second paragraph on p 3255 has $\epsilon'(t \rightarrow \infty)$ and should be $\epsilon'(t \rightarrow 0)$ (although use of this limit is questionable as stated previously).

(c) There is an inconsistency between the text and Figures 7, 8, and 10 as to the cure temperatures represented.

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† *Macromolecules* 1992, *25*, 3254.

(d) In the discussion of values of γ on p 3263, reference to Figure 15 should be to Figure 14.

(e) The authors suggest that their DGEBA/diaminodiphenyl sulfone data in Figure 15 and the work of Enns and Gillham[8] are qualitatively similar. This is incorrect. Enns and Gillham show a straight line for a plot of the logarithm of "gel" time vs the inverse of the absolute cure temperature while the authors show a curved plot.

(f) Figure 17 is incorrect. The plot of dielectric loss factor vs cure time at various frequencies shows the lowest frequency curve to have the earliest dipole relaxation peak. This is the exact opposite frequency dependence that one should obtain.

In summary, Parthun and Johari[1] have carried out a number of questionable derivations and analyses, virtually ignoring the extensive literature available on the dielectric monitoring of thermoset cure. Instead, they reference their own series of papers, essentially all of which were published after the work referenced in these comments. This preceding work shows that Parthun and Johari have presented very little new information and have interpreted some of the dielectric phenomena incorrectly, as addressed in these comments. In addition, they lack supporting experimental evidence for the processes they claim to measure. Their entire analysis is based on dielectric techniques with no measurement of, or reference to, the chemical and/or physical changes taking place in the specific resin systems they investigated. Finally, beyond these fundamental points, the paper was carelessly assembled, as indicated by the number of errors and/or omissions in the text.

References and Notes

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