

# Dielectric Behavior at Microwave Frequencies of an Epoxy Resin During Crosslinking

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## SYNOPSIS

The dielectric behavior during the crosslinking process of a low molecular weight liquid diglycidyl ether of bisphenol-A (DGEBA) and ethylenediamine, as the curing agent, has been investigated at microwave frequencies (0.1–10 GHz) by means of the time domain reflectometry. It was found that both the real and the imaginary part of the dielectric constant, which regularly decreased as the cure reaction proceeded, were mainly affected by the disappearance of specific dipolar species, whose relaxation times did not change significantly. A simple model based on disappearance of dipoles agrees with the experimental data and explains the coincidence between kinetic data obtained by dielectrometry and calorimetry. The microwave dielectric constant can thus be used to directly measure in real time the conversion of the reaction. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

For many reasons it is important to know the physical properties and the actual chemical composition of thermosetting formulations in the course of their crosslink process. A number of technologies are in fact based on the possibility of having the polymer, in the early stages of its formation, freely flowing into molds or through fiber plies. Resin transfer molding, for instance, consists of injecting, at low pressure and possibly at room temperature, a liquid prepolymer (mostly unsaturated polyesters or epoxides) into a mold in which a reinforcing structure is sitting. Success consists of properly filling the mold, evacuating the air, and not modifying the geometry of the reinforcing structure. A similar situation is found in the vacuum bag formation of stacked prepregs. The resin, in many cases B-staged, has to liquify in order to permeate all strata, fill the interstices, and finally constitute the continuous component of the composite. Time allowed for this operation depends on the chemical reactivity of the specific prepolymer/hardener formulation in use. As the reaction proceeds, the average molecular weight

increases as does the viscosity, by far the most important physical parameter in thermosetting technology, that depends on the molecular weight of mixture components, temperature, and, in some cases, presence of inorganic fillers. Due to the complexity of real formulations (including continuous fibers) and the difficulty of reaching the reaction site (e.g., molds, vacuum bags) the viscosity cannot be directly measured. It is then customary to evaluate it indirectly by:

1. measuring physical quantities somehow to it related, for instance electrical conductivity;
2. computing it using chemorheological models, provided the actual chemical composition is known.

The second approach is particularly attractive because the knowledge of the chemical composition is the key factor to keep all aspects of the processing and subsequent quality control of manufactured items under control. Chemorheology does provide sophisticated models by which the viscosity of reacting media can be confidently evaluated.<sup>1–4</sup> Moreover, the long-term chemical stability of finished items depends on the final concentration of unreacted groups at the end of the cure stage. It is to

minimize the amount of such unreacted groups that often curing is followed by postcuring. This contrasts with the necessity to not push the crosslink density to the topological limit in order to prevent embrittlement of the polymer. Among the various techniques capable of yielding information on the chemical composition during crosslinking, those based on measuring the change of the electrical response throughout the network formation are very promising and to some extent already in use.<sup>5</sup>

In a previous work<sup>6</sup> we have shown that data of the conversion of a liquid diglycidyl ether of bisphenol-A (DGEBA)-type epoxy resin and ethylene diamine mixture, calorimetrically measured, totally coincided with the relative change of the loss factor measured at 2 GHz. This result still needs to be clearly understood because the events that modify the dielectric properties of the system are different from those that control the thermodynamics of the process. Calorimetry senses the heat generated from the disappearance and formation of chemical bonds; in the same conditions dielectrometry not only senses the modification of dipoles, originated by the appearance and disappearance of chemical bonds, but also the variation of the dipole mobility. Consequently the analysis of the dielectric behavior is definitely more complicated than that of the thermal behavior and, *a priori*, no coincidence should be expected between dielectric and calorimetric data.

However, the change with time of the microwave dielectric constant returns the same information as from calorimetry, provided a proper frequency is chosen.<sup>6</sup> In this paper we show that this result can be directly related to the dielectric behavior of the system and that, in the considered frequency range, a simple model based on dipole disappearance gives a rationale of the observed phenomena. Differences with the dielectric behavior of similar reacting systems at low frequencies are also considered.

## EXPERIMENTAL

### Materials

The epoxy prepolymer (EPON 828 EL by Shell Co.) was a low molecular weight DGEBA with an epoxy equivalent weight of about 190. The curing agent was reagent grade ethylenediamine (EDA) by Carlo Erba. The amine was distilled under nitrogen and over potassium hydroxide shortly before using.

Stoichiometric mixtures were used as soon as complete mixing was obtained. Mixing and transfer into the dielectric cell took about 3 min.

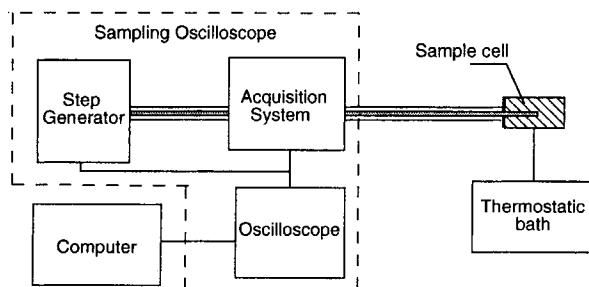
## Methods and Techniques

Dielectric measurements were carried out by using the time domain reflectometry technique in the infinite sample configuration.<sup>7</sup> A schematic of the experimental setup is in Figure 1. A sampling oscilloscope (Tektronix 11802) feeds a step voltage in the coaxial line; the pulse, reflected from the sample, is digitized, transmitted via IEEE488 to a computer (IBM PS/2-80) and then analyzed according to a method already described.<sup>7</sup> The apparatus operates in the frequency interval 0.1–20 GHz and, after recent improvements of data acquisition and processing procedure, a complete dielectric spectrum can be obtained in about 0.6 s. Temperature of the samples was kept stable at 70°C within 0.1°C by a thermostatic bath (Julabo FP50) and measured by a thermocouple thermometer (Flucke 2190A).

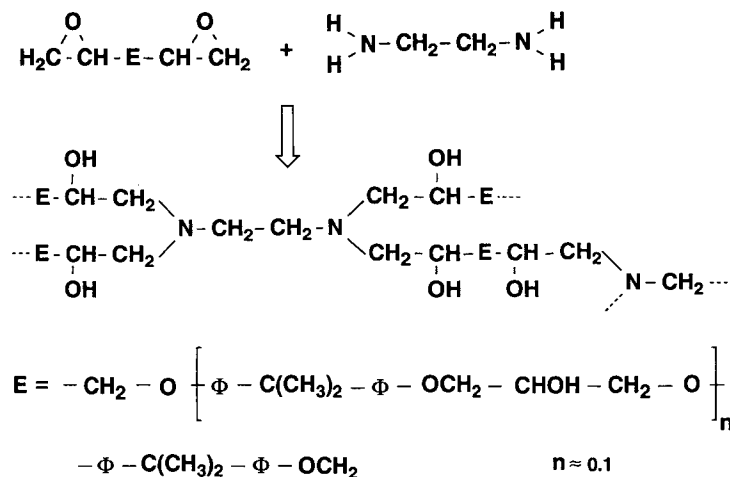
## RESULTS AND DISCUSSION

In order to gain an insight into the dielectric behavior of a reactive medium (such as a mixture of an epoxy resin and a diamine) it is first necessary to investigate the properties of pure components and of their mixture in the unreacted state. The resin and the amine we considered are relatively small molecules; in the liquid state their dipoles are consequently very mobile and the associated relaxations located at very high frequency.

The main contribution to the overall polarizability of the resin is given by the two terminal groups; due to the symmetry of the molecules (Fig. 2), only the components perpendicular to the longitudinal molecular axis contribute to the dielectric constant because parallel components cancel out. A Cole–Cole equation<sup>8</sup> was fit to the experimental data (Fig. 3). Fitting parameters were: relaxation time,  $\tau = 119$  ps; unrelaxed dielectric constant,  $\epsilon_0 = 9.2$ ; relaxed dielectric constant,  $\epsilon_\infty = 3.2$ ;  $(1 - \alpha) = 0.7$ , the value



**Figure 1** Block diagram of the time domain reflectometry (TDR) apparatus.



**Figure 2** Schematic of the crosslinking reaction of the EPON 828 with EDA as the curing agent.

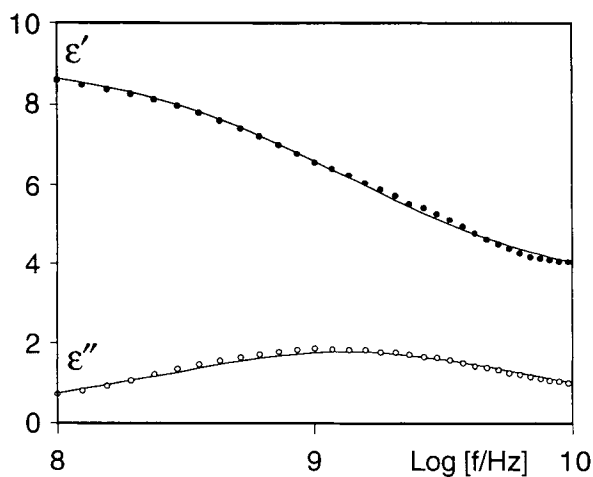
of the exponent  $(1 - \alpha)$  is indicative of a relatively broad distribution of relaxation times. The loss factor  $\epsilon''$  is maximum at about 1.3 GHz.

As for the epoxy prepolymer, the contribution to the dipolar momentum of the amine is given by components perpendicular to the C—C bond (Fig. 2); in the explored frequency range only the beginning of the relaxation can be observed (Fig. 4). A best fitting, based on the Debye–Pellat equations,<sup>9</sup> yields values of the dielectric parameters ( $\epsilon_0 = 10.7$ ,  $\epsilon_\infty = 2.2$ ,  $\tau = 3.3$  ps) that indicate that the maximum of the loss factor occurs at about 50 GHz.

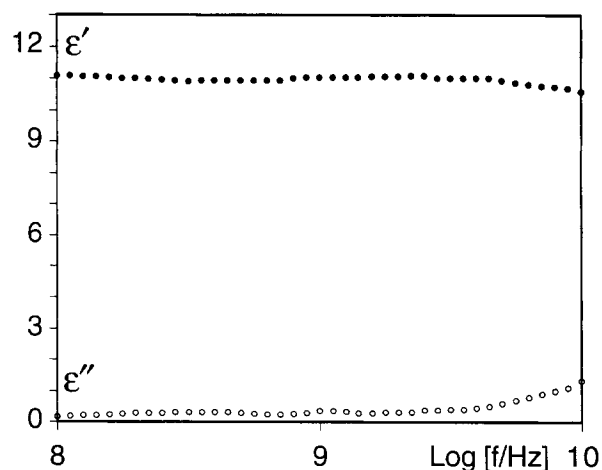
The overall dielectric relaxation spectrum of the stoichiometric EPON/EDA mixture slightly differs

from that of the neat resin (Fig. 5). In fact, the presence of the cure agent brings about a decrease of viscosity and adds new dipolar species to the mixture.

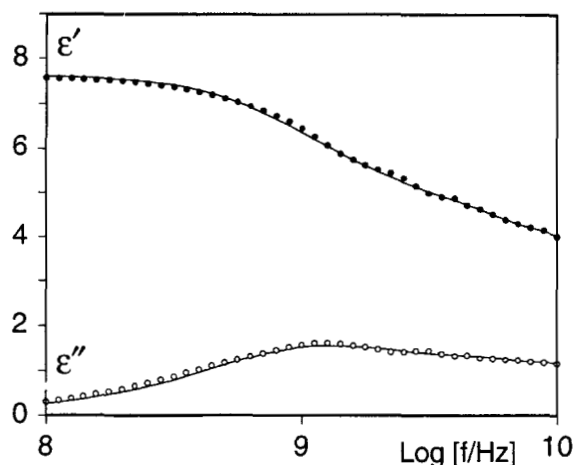
After mixing, a chemical reaction between the resin and amine starts and eventually a crosslinked structure develops, as schematically illustrated in Fig. 2. From a chemical point of view the reaction goes through a number of steps in which secondary and tertiary amines form. To interpret the evolution of the dielectric parameters during the reaction, one should know the dielectric behavior of all intermediate products; this would introduce a terrible complication in the development of a dielectric model without giving any chance to distinguish, in the ex-



**Figure 3**  $\epsilon'$  and  $\epsilon''$  versus log of frequency for the neat resin at 70°C. Continuous line is the best fitting Cole–Cole equation.



**Figure 4**  $\epsilon'$  and  $\epsilon''$  versus log of frequency for pure EDA at 70°C.



**Figure 5** Dielectric relaxation spectrum of the stoichiometric EPON/EDA mixture, at 70°C, soon after mixing.

perimental data, the contribution of the various amines because the associated relaxation spectra substantially overlap (the nature of the dipoles and their dynamics are substantially similar). The dielectric description we propose to interpret high frequency dielectric data is based on the simple assumption that the real chemical process develops according to the scheme in Figure 2, that is, at each time, the reactive mixture is composed of the epoxy prepolymer, the unreacted amine, and a product that carries unreacted epoxy rings, tertiary amine groups, and hydroxyl groups. As the reaction proceeds some dipoles disappear (epoxy dipoles), others modify (amine dipoles), and still others appear (hydroxyl dipoles). The dielectric constant reflects all these changes in that it depends on the total number of dipoles per unit volume and on their dynamics; the mobility of dipoles varies because they are incorporated into growing molecules and because the viscosity of the medium increases as the reaction goes on. Additionally, the dielectric constants change as a consequence of the variation of the specific volume associated with the change of the packing efficiency during the reaction (the volume contracts during a polymerization).

Before analyzing the specific dielectric properties of our EPON/EDA system, it is useful to consider some basic concepts that can clarify some peculiarities of the behavior of polymerizing media.

According to the linear response theory (LRT) the complex dielectric constant  $\epsilon$  of a system can be described by the following equation.<sup>10</sup>

$$\epsilon - \epsilon_{\infty} = (\epsilon_0 - \epsilon_{\infty}) \int_0^{\infty} e^{-i\omega t} \left( -\frac{dH}{dt} \right) dt \quad (1)$$

where  $\epsilon_0$  and  $\epsilon_{\infty}$  are the permittivities at the low and high frequency limits, respectively.  $H$  is the response function of the system to a step electric field and describes the dynamics of the system by means of the relaxation time  $\tau$ .

At low frequencies, the main contribution to the change of permittivity during a polymerization process comes from the variation of the macroscopic viscosity that affects the relaxation time of dipoles associated with relatively massy molecular groups. The change of viscosity mainly modifies the integral term (Laplace transform) in eq. (1), whereas the dielectric strength ( $\epsilon_0 - \epsilon_{\infty}$ ) remains substantially stable.<sup>11</sup>

At very high frequencies, that is microwaves, massy groups are substantially at rest and only highly mobile groups can react to the external field. Because such groups experience a macromolecular environment, that is they mainly interact with much bigger molecules, their response to the macroscopic viscosity is very weak.<sup>12</sup> Therefore, in the microwave region, the polarizability is related to dipoles associated with small molecular groups whose mobility is only slightly affected by the large increase of bulk viscosity that characterizes the polymerization of liquid monomers. In these conditions, the change of permittivity can be mainly ascribed to the variation of the dielectric strength,  $\epsilon_0 - \epsilon_{\infty}$ , caused by the disappearance of specific dipoles located on molecular groups undergoing chemical modification. In general, a chemical reaction can influence the polarizability of polymerizing systems because: (1) dipolar groups disappear or modify (e.g., from primary to secondary amine groups), (2) dipoles are incorporated in a rigid molecular structure without any appreciable change of charge distribution. In the last case, dipoles remain substantially unchanged but their orientational properties, in static and dynamic fields, become very different. The reduction of mobility consequently causes a decrease of the high frequency complex dielectric permittivity, very similar to that observed in the case of a real disappearance of dipoles.

To better clarify this concept, we assume that the polymerizing mixture behaves as a system having two dielectric relaxation processes, widely apart, and that the net effect of the reaction consists of moving dipolar groups from the process at high frequency to that at low frequency, with no other modification. The dielectric constant, at the low frequency limit, remains constant, whereas at intermediate frequencies the dielectric constant changes according to the rate of dipole transfer, even if the total number of dipoles may not change.

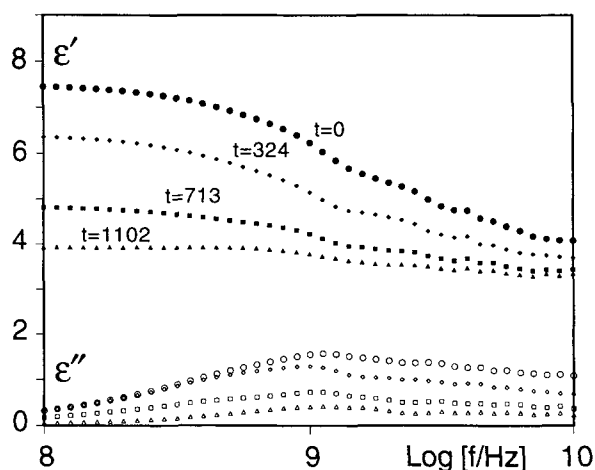
The increase of the bulk viscosity, dramatic on approaching gelation, modifies the location of both relaxation processes on the frequency scale, though to a different extent. The low frequency process, originated by bulky and idling groups of the growing macromolecules, is not only very sensitive to viscosity but its evolution with time parallels that of viscosity. It is even possible to take advantage of this effect to measure the viscosity of the mixture<sup>13-16</sup> (and indirectly the chemical composition). The high frequency process is, on the contrary, substantially independent of bulk viscosity.

The relaxation times of relatively small molecular groups range, at room temperature, from a few picoseconds to some hundredths of picoseconds; we can therefore apply dielectrometry at microwave frequencies (1–100 GHz) to polymerizing systems because these frequencies fall about in the middle of the two relaxation regions.

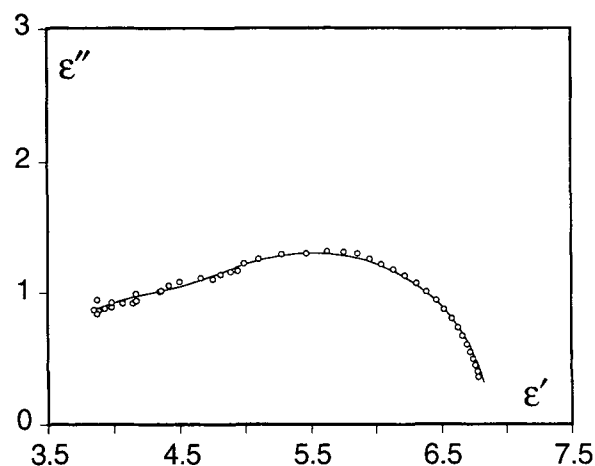
The characteristics of the dielectric behavior, at microwave frequencies, of polymerizing systems can be itemized as:

1. dielectric relaxations of small molecular groups become observable;
2. the dynamics of small dipolar groups is slightly affected by the bulk viscosity;
3. the variation of concentration of specific dipoles can be better evidenced;
4. an apparent disappearance of dipoles can occur in the experimental window.

The last two features need to be considered when dielectric parameters are used to describe the chem-



**Figure 6** Dielectric relaxation spectrum of the stoichiometric EPON/EDA mixture, at 70°C, at specified reaction times (in seconds).



**Figure 7** Cole-Cole plot for the EPON/EDA reacting mixture (conversion = 0.2). Continuous line is the best fit obtained by combination of a Cole-Cole and a Debye equation.

ical evolution of the system; this is well illustrated in the case here considered.

Figure 6 shows dielectric data relative to the stoichiometric mixture of EPON/EDA at different reaction times. The relaxation strength regularly decreases whereas the relaxation times are barely affected. The change of relaxation times is negligible in comparison with the enormous variation of viscosity that has been shown to be the primary source of the large increase of the relaxation times associated with the low frequency dispersion.<sup>11,13,14</sup> Equation (2) can be used to fit experimental data as shown in Figure 7 for a conversion of 0.2:

$$\epsilon - \epsilon_{\infty} = \frac{\epsilon_0 - \epsilon_1}{1 + (i\omega\tau_c)^{1-\alpha}} + \frac{\epsilon_1 - \epsilon_{\infty}}{1 + i\omega\tau_D} \quad (2)$$

This equation is a superposition of two separate Cole-Cole and Debye relaxation processes of strength  $(\epsilon_0 - \epsilon_1)$  and  $(\epsilon_1 - \epsilon_{\infty})$ , respectively. Asymmetric functions, as Cole-Davidson or Havriliak-Negami,<sup>10</sup> are not satisfactory in this case. A preliminary analysis of experimental data at different conversions indicates that the nature of the relaxation processes remains basically unchanged as the reaction proceeds, at least up to conversions of about 0.7. For conversions higher than 0.7 data can no longer be interpreted by superposition of simple relaxation equations; the dielectric constant however can still be used to measure the conversion up to completion of the reaction.<sup>6,17</sup> Although the numerical analysis of experimental data is not yet complete, this pattern of behavior is consistent with the

simple model based on the disappearance, both real and apparent, of some dipolar species and on our assumption that the relaxation times are only slightly affected by viscosity.

By comparing the behavior of pure components (Figs. 3,4) and of their mixture (Fig. 5) it becomes clear that the main dielectric relaxation in the considered frequency interval is that of the resin. We can attribute the variation with time of the loss factor to the change of concentration of dipoles associated with the epoxy molecule because contributions of other dipoles, either initially present or formed in the course of the reaction, fall outside of the experimental window. In order to validate the model, a side experiment has been carried out to measure, by calorimetry, the actual concentration of epoxy groups during the reaction<sup>6</sup>: the coincidence of calorimetric conversion data and the variation of the loss factor  $\epsilon''$ , at a proper frequency, supports the above conclusion.

This way of reasoning cannot be extended to  $\epsilon'$  because dipoles, whose relaxations are located at very high frequencies, contribute to this quantity. Strictly speaking,  $\epsilon'$  senses the disappearance of epoxy rings, the generation of hydroxyl groups, and of secondary and eventually tertiary amines. Schematically we can separate the effects on  $\epsilon'$  as follows:

1. the decrease of epoxy groups, whose relaxation is just within the experimental window, produces a decrease of  $\epsilon'$ ;
2. the formation of hydroxyl groups introduces a new relaxation mechanism, whose maximum is located at very high frequencies, outside our experimental window; this gives a positive contribution to  $\epsilon'$ ;
3. the modification of the chemical nature of the amine produces a large shift of the relaxation maximum of the amine dipole from high to low frequencies, thus reducing the contribution to  $\epsilon'$  (apparent disappearance).

Summation of all such effects produces, in this case, a decrease of  $\epsilon'$  that can still be simply related to chemical conversion, as will be shown later.

This picture undoubtedly oversimplifies the behavior of our system. For instance, during the reaction a number of epoxy groups are incorporated into molecules of growing complexity; this should cause an increase of the associated relaxation time (blocking effect) and even modify the relaxation mechanism. At microwave frequencies the change of the relaxation time seems not to be very large and the presence in the experimental window of

contributions from both free and blocked epoxy groups should produce a broadening of the  $\epsilon''$  dispersion curve.

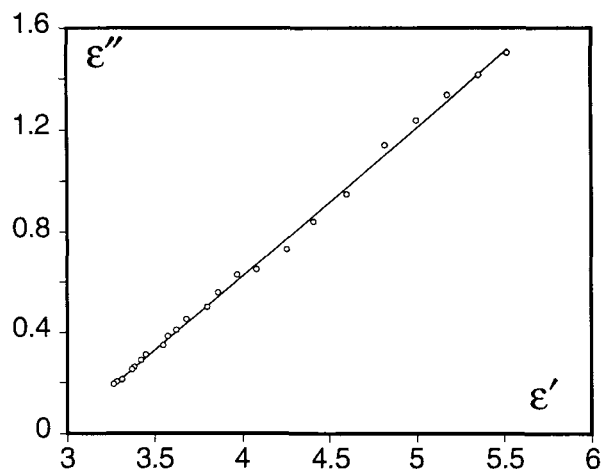
Experiments performed at low frequencies (under 50 MHz, where relaxations of large molecules are located), showed a large modification of the relaxation time distribution. Huraux et al.<sup>13,14</sup> reported Cole-Cole diagrams, at different times of reaction, of a DGEBA resin, cured with an aliphatic diamine. Data show a very large increase of the average relaxation time, paralleled by a marked widening of the relaxation time distribution, associated with an increase of molecular complexity.

Within the conceptual frame of LRT, two different response functions should be considered in this context: one to take into account the dynamics of dipoles at a given chemical composition of the system, the other to account for the change, with time, of its chemical nature. Mangion et al.<sup>11,18</sup> have recently shown that the time dependence of the dielectric constants of a DGEBA/aromatic amine system during isothermal cure, measured at 1 kHz, is well described by a stretched exponential function (Kohlrausch-Williams-Watts), thus demonstrating the great influence of the change of relaxation times, induced by viscosity, on the dielectric behavior. This was graphically evidenced by means of Argand diagrams ( $\epsilon''$  versus  $\epsilon'$ , taken at different cure times).

Argand diagrams obtained by plotting  $\epsilon''$  versus  $\epsilon'$ , measured at a fixed frequency and different times of cure, are not equivalent to similar diagrams obtained by plotting the same quantities measured at different frequencies (Cole-Cole plots). Seferis et al.,<sup>15,16</sup> for instance, found that dielectric data, as a function of frequency, for a crosslinking epoxy resin, were well described by a Cole-Cole equation; on the contrary, for the same system, data obtained at constant frequency, as a function of cure time, were well described by a Kohlrausch-Williams-Watts function.

Our data (Figs. 7, 8) indicate that at microwave frequencies ( $\epsilon''$ ,  $\epsilon'$ ) diagrams are very different, depending on whether data are considered as a function of frequency or cure time, because the disappearance of dipoles dominates over the variation of relaxation times. This conclusion is supported also by data obtained, at about 10 GHz, for the photoinitiated polymerization of *n*-butyl acrylate, for which it was proven that only disappearance (apparent) of dipoles takes place<sup>19-21</sup>; the relative ( $\epsilon''$ ,  $\epsilon'$ ) diagram was in fact very similar to that in Figure 8.

In a previous work we showed<sup>6</sup> that the normalized quantity  $[\epsilon''(t_c = 0) - \epsilon''(t_c)] / [\epsilon''(t_c = 0) - \epsilon''(t_c = \infty)]$ , measured at 2 GHz for different cure times,



**Figure 8** Argand diagram for  $\epsilon'$ ,  $\epsilon''$ , at 2 GHz and at different cure times, for the stoichiometric EPON/EDA mixture, at 70°C. Line is the least square best fit.

$t_c$ , for the same system examined in this paper and assuming that the  $\epsilon''$  for the completely reacted system,  $\epsilon''(t_c = \infty)$ , was nil, coincided with the calorimetrically determined conversion. We were however unable to use  $\epsilon'(t_c)$  data to define a similar normalized variable because, due to experimental difficulties,  $\epsilon'$  of the completely reacted system,  $\epsilon'(t_c = \infty)$ , could not be determined. Data in Figure 8 indicate that a linear relationship exists between the two quantities:

$$\epsilon' - 3 = 1.8\epsilon'' \quad (3)$$

By combining the condition  $\epsilon''(t_c = \infty) = 0$  and eq. (3) we can now estimate that  $\epsilon'(t_c = \infty) \sim 3$  and consequently utilize also  $\epsilon'$  data to analyze the conversion of that reaction.

Microwave dielectrometry appears to be very suitable to measure the conversion of a polymerization reaction. This was first evidenced for the polymerization process of *n*-butyl acrylate<sup>19-21</sup> and then for the crosslinking reaction of an epoxy resin<sup>6</sup>; recently other authors<sup>22,23</sup> have tried to monitor the microwave dielectric properties of epoxy systems at fixed frequency. Data generated by this approach cannot be adequately used to understand the complex dielectric behavior of chemically reacting systems.

## CONCLUSIONS

The results so far obtained applying microwave dielectrometry to crosslinking (e.g., epoxy resins) and

not crosslinking (e.g., *n*-butyl acrylate) systems show this technique possesses an analytical character. A simple model based on dipole disappearance suffices, to a first approximation, to interpret experimental data. This very crude model could be refined if more accurate dielectric data were available and deconvolution analysis of the complex relaxation processes were improved. For this purpose, it is important to enhance the wide frequency measurement techniques in order to fulfill the severe requirements imposed by the time evolution of the systems under consideration. It is in any case necessary to gather data both in the frequency and the (reaction) time domains because a number of different dipoles contributes to the overall polarizability and no satisfactory theories are available to link dipole dynamics to macroscopic properties. It is for these reasons that attempts to interpret the evolution of dielectric properties during crosslinking reactions, at fixed frequency, are not fully satisfactory.

Basically, the difference between low and high frequency dielectrometry is that the former is dominated by the effect of the viscosity on dipole mobility. High and low frequency dielectrometry complement each other and are both necessary to fully understand the behavior of chemical changing systems. However, keeping track of the effect of viscosity on the distribution of relaxation times cannot give information in real time because data concerning the complete process are the first to be collected. At high frequency the diminished importance of viscosity effects greatly simplifies the interpretation of dielectric data and, more importantly, permits using them to monitor chemical processes.

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## REFERENCES

1. K. M. Hollands and I. L. Kalnin, *Epoxy Resins*, Adv. Chem. Series 92, American Chemical Society, Washington, D.C., 1970.
2. M. B. Roller, *Polym. Eng. Sci.*, **15**, 406 (1975).
3. J. Halpin, A. Apicella, and L. Nicolais, *Polymer Processing and Properties*, G. Astarita and L. Nicolais, Eds., Plenum Press, New York, 1984.
4. G. Schmitt, J. Wiley, and J. Gotro, *Polym. Eng. Sci.*, **29**, 329 (1989).
5. S. D. Senturia, *Adv. Polym. Sci.*, **80**, 1 (1986).

6. S. Carrozzino, G. Levita, P. A. Rolla, and E. Tombari, *Polym. Eng. Sci.*, **30**, 366 (1990).
7. R. H. Cole, S. Mashimo, and P. Winsor, IV, *J. Phys. Chem.*, **84**, 786 (1980).
8. C. J. F. Böttcher, *Theory of Dielectric Polarization*, Vol. II, Elsevier, Amsterdam, 1973, p. 62.
9. C. J. F. Böttcher, *Theory of Dielectric Polarization*, Vol. II, Elsevier, Amsterdam, 1973, p. 39.
10. C. J. F. Böttcher, *Theory of Dielectric Polarization*, Vol. II, Chap. 9, Elsevier, Amsterdam, 1973.
11. M. B. M. Mangion and G. P. Johari, *J. Polym. Sci. B, Polym. Phys.*, **29**, 1127 (1991).
12. M. Davies, in *Dielectric Properties and Molecular Behaviour*, T. M. Sudgen, Ed., Van Nostrand, London, 1969, p. 312.
13. C. Huraux and A. Soualmia, *C. R. Acad. Sci.*, **B-277**, 497 (1973).
14. A. Soualmia, C. Huraux, and B. Despax, *Makromol. Chem.*, **183**, 1803 (1982).
15. J. W. Lane and J. C. Seferis, *Polym. Eng. Sci.*, **26**, 346 (1986).
16. J. W. Lane, J. C. Seferis, and M. A. Bachmann, *J. Appl. Polym. Sci.*, **31**, 1155 (1986).
17. C. Carlini, G. Levita, and P. A. Rolla, *Proc. Am. Chem. Soc.*, **66**, 472 (1992).
18. M. B. M. Mangion and G. P. Johari, *Polymer*, **32**, 2747 (1991).
19. C. Carlini, M. Martinelli, P. A. Rolla, and E. Tombari, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 5 (1985).
20. M. Martinelli, P. A. Rolla, and E. Tombari, *IEEE Trans. Instrum. Meas.*, **IM-34**, 417 (1985).
21. C. Carlini, M. Martinelli, P. A. Rolla, and E. Tombari, *J. Polym. Sci. B, Polym. Phys.*, **25**, 1253 (1987).
22. E. Marand, K. R. Baker, and J. D. Graybeal, *Macromolecules*, **25**, 2243 (1992).
23. J. Jow, M. C. Hawley, M. Finzel, J. Asmussen, H. H. Lin, and B. Manring, *Microwave Theory Tech.*, **MTT-35**, 1435 (1987).

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