Dielectric Parameters to Monitor the Crosslink of Epoxy Resins

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ABSTRACT: Recent developments in dielectric monitoring of cure processes are considered. Direct current (dc) conductivity and dielectric data concerning the crosslinking of an epoxy resin are analyzed and compared with the results of late microwave experiments. The analysis of the dielectric behavior of the system carried out on a rather wide frequency interval (10^3–10^{10} Hz) has provided a deeper insight into the relationships between dielectric parameters (i.e., dc conductivity, permittivity, relaxation time and shape parameters, and the physical and chemical modifications of the systems). The results confirm the possibility to utilize dielectric quantities to obtain information on relevant parameters such as conversion, viscosity change, sol–gel transition, glass transition temperature, and dynamics of cooperative relaxation phenomena of the system. The required dielectric data can be gathered by simple methods that facilitate *in situ* applications. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 17–25, 1997

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INTRODUCTION

Goods manufacturers are nowadays dominated by the overwhelming demand for high quality. Quality, or at least reproducibility, can be assured only by monitoring and tracking all the intermediate steps from raw materials to final goods. In those productions that require using thermosetting polymers, such as, for instance, composite materials fabrication or assembling by adhesive consolidation, it would be of importance to be able to, by means of suitable techniques, gather information on the time evolution of the chemical processes that take the original fluid system to the final solid condition. For such a technique to be acceptable, a difficult condition to satisfy is the necessity to operate in real time and in the rather unclean industrial environment, which is often hostile to sophisticated equipment. Robustness in both hardware and software is an additional requirement that makes things more complicated. Several methods have been proposed and tested in laboratory conditions and many operate well; among the most promising, we include electric techniques, in use for almost sixty years, and spectroscopic IR techniques that take advantage of the use of optical fiber technology.[1,2]

Conductivity and low-frequency dielectric methods have already been in use in industrial environments, while high-frequency dielectric methods still remain in a developmental stage. A wider diffusion of dielectrometry was prevented by the lack of basic knowledge of the relationships

between molecular structure and macroscopic dielectric behavior. The inadequacy of reference data is an additional obstacle. The old theoretical approach is now about to be pushed aside by a more quantitative description of the dielectric phenomena.[3-6] New theoretical approaches are being developed to explain the relaxation behavior observed during polymer formation either by chain extension or by crosslinking.[7-9] Information on the actual viscosity and conversion[10-12,6] are already achievable with relative ease; and this, from an applicative point of view, is a first, important result. In addition, modern dielectrometry can yield a wealth of information on phenomena and parameters such on as intermolecular and intramolecular interactions, relaxation times of main and secondary relaxations, glass transition temperature, formation of charge complexes, phase separation, and charge hopping, and even on molecular and supramolecular structures.

This article analyzes the dielectric behavior of an epoxy resin during the crosslink process. The most relevant parameters characterizing the dielectric behavior will be examined, and their capability to provide real-time information on the advancement of the reaction, the viscosity change, the sol-gel transition, and glass transition temperature will be discussed.

MATERIALS AND EXPERIMENTAL METHODS

The epoxy prepolymer (EPON 828 EL by Shell Co.) was a low-molecular-weight liquid diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight of about 190. The curing agent was reagent grade ethylenediamine (EDA) by Carlo Erba, which was distilled under nitrogen and over potassium hydroxide shortly before using. Mixtures of two different compositions were used (EPON/EDA with molar ratios of 2 : 1 and 1 : 1 cured at 70 and 25°C, respectively).

The advancement of the reaction, as a function of time, was measured by calorimetry. Measurements were carried out using a Perkin-Elmer DCS-4 equipped with a 3600 data station and an Intracooler I apparatus.

Dielectric measurements in the 10^3 to 10^7 frequency interval were made by means of an impedance analyzer (HP4194A) controlled via IEEE488 by a personal computer. The sample cell consisted of a simple cylindrical capacitor whose tempera-
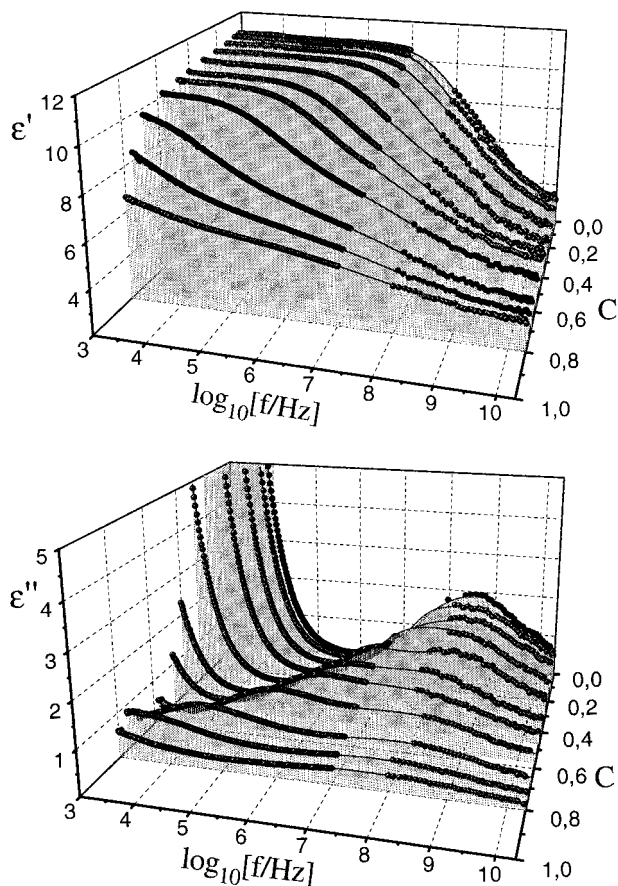
Figure 1 Three-dimensional plot of ε' and ε'' versus conversion C and $\log_{10}$ of frequency for the DGEBA/EDA 1 : 1 mixture cured at 25°C. The black spheres are from experimental data; contour lines of the shaded areas are from fit equations.

ture was controlled within 0.1°C by means of a thermostatic bath.

In the $10^8 - 2 \cdot 10^{10}$ frequency interval, the measurements were performed by using the time domain reflectometry technique in the infinite sample configuration. The apparatus and experimental measurement procedure were described in Fioretto et al.,[13] Casalini et al.,[14] and Cole et al.[15]

RESULTS AND DISCUSSION

For seek of clarity, we will divide this section according to the different information yielded by the dielectric data collected at different times of reaction in a wide frequency interval (Fig. 1).

Monitoring of Conversion

This has been, since the beginning of dielectrometry applications, the main objective, and a wealth of papers has been written on this topic. Here, we limit the discussion only to those results of general validity, which are supported by a satisfactory explanation of the underlying phenomena. Three different approaches have been tried for monitoring purposes based on the completely relaxed dielectric constant ε_0, the apparent conductivity σ, and the change of both the real ε' and imaginary ε'' part of the permittivity at a fixed microwave frequency. If the dielectric constant is measured at sufficiently low frequency, it can be taken as equivalent to the completely relaxed dielectric constant; the Senturia's dipole disappearance model can then be applied.[4,16-18]

In fact, according to the static dielectric theory, ε_0 can be related to the mean square dipole moment $\langle \mu_i^2 \rangle$ of the ith dipolar species by the Onsager–Kirchwood–Frölich equation,[19] as follows:

$$f(\varepsilon_0) = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} = \frac{4\pi}{9kT}\sum N_i \langle \mu_i^2 \rangle \quad (1)$$

where ε_∞ is the unrelaxed permittivity; N_i is the volume concentration of the ith dipolar species; and k and T are the Boltzmann constant and the absolute temperature, respectively. Equation (1) shows that, for a system of different species of noninteracting dipoles, the quantity $f(\varepsilon_0)$ is linearly related to dipole concentrations N_i, provided the system is kept at constant temperature and the mean square dipole moment of each species does not change.

For a system in which molecular groups possessing dipolar charge distribution are modified by a chemical reaction, a change of the quantity in the right side of eq. (1) is likely to occur. As a consequence, the change of $f(\varepsilon_0)$ can, in principle, be used to monitor the advancement of the reaction.

In the particular case of an isothermal process in which the mean square dipole moments of the involved molecular groups remain constant, and only the dipole population modifies; the change of $f(\varepsilon_0)$ is linearly dependent on N_i and, therefore, on the conversion. This condition is verified for epoxy systems,[4,18-20] for which a further simplification can be proposed. It is easy to verify that

$$\frac{df(\varepsilon_0)}{d\varepsilon_0} = (\varepsilon_\infty + 2)^{-2} \cdot \left[2 + \frac{\varepsilon_\infty^2}{\varepsilon_0^2} \right] \quad (2)$$
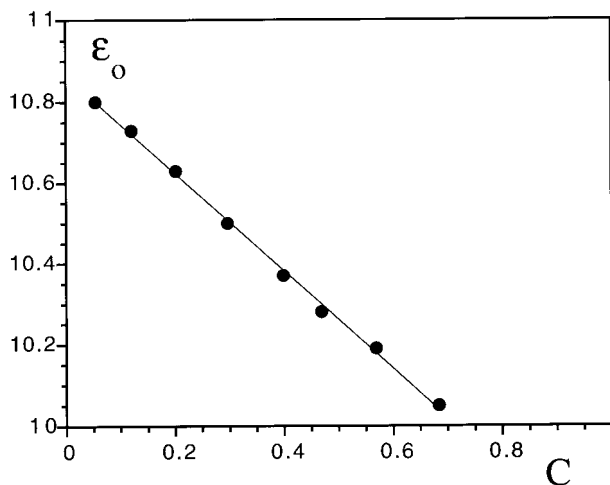

Figure 2 The static dielectric constant ε_0 versus conversion C of DGEBA/EDA 1 : 1 mixture cured at 25°C. The solid line is the linear fit equation [$\varepsilon_0(C = 0)$ = 10.87; $\varepsilon_0(C = 1)$ = 9.66].

Taking the usual values of ε_0 and ε_∞ that characterize epoxy systems, it is readily seen that the left-hand derivative in eq. (1) varies by no more than 2% from the start to the end of reaction when amines are used as the hardeners; as a consequence, $f(\varepsilon_0)$ and ε_0 are linearly related, and the corresponding quantities obtained by normalizing with respect to the values at zero conversion (C = 0) and full conversion ($C = 1$) are identical. In Figure 2 is shown the linear variation of ε_0 versus conversion C, as measured by calorimetry, of a DGEBA epoxy resin in the presence of ethylene diamine at 25°C (the solid line represents the linear fit to experimental data). In these conditions, the normalized quantity E_0, related to ε_0, is defined with respect to the time of reaction t by the following equation:

$$E_0 = \frac{\varepsilon_0(t) - \varepsilon_0(C = 0)}{\varepsilon_0(C = 1) - \varepsilon_0(C = 0)} \quad (3)$$

and can represent the conversion.

To calculate E_0, one needs the limit values of ε_0 at $C = 0$ and $C = 1$. The former, that at the start of the reaction, is readily accessed; while the latter, that at full conversion, cannot be directly measured because full conversion is never achieved in crosslinked systems. We can estimate, however, ε_0 ($C = 1$) by the linear fit in Figure 2. Figure 3 shows that E_0 closely parallels the calorimetric conversion. E_0 can thus be given the
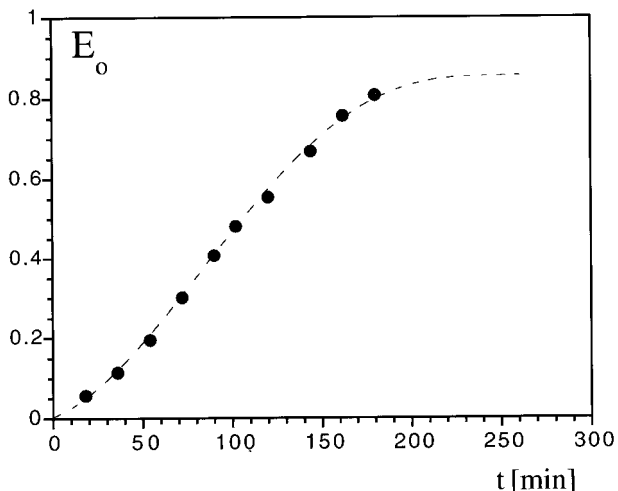
Figure 3 Dielectric conversion E_0 (full dots) and calorimetric conversion (dashed line) versus reaction time t for the isothermal cure at 25°C of DGEBA/EDA 1 : 1 mixture.

meaning of dielectric conversion. It is to be noted that ε_0 changes by only about 10%; consequently, for the accuracy of E_0 to be within 10^{-2}, ε_0 has to be measured with a relative error of 10^{-3}. Such accuracy was obtained, in our case, by a proper numerical treatment of the dielectric data measured as a function of frequency.[4] As a rule, ε_0 can be determined by a statistical averaging of an adequate number of data points taken at a fixed low frequency. Direct current measurements are not convenient because noise and electrode polarization effects mask the polarization of the sample that usually constitutes the dielectric of a capacitor; for these reasons, it is advisable to use alternating current (ac) frequency measurements at a frequency sufficiently low so as to minimize contributions to the dielectric constant originated by relaxation phenomena. In any case, $\varepsilon_0(C = 1)$ has to be known in advance if real-time monitoring is required. Additionally, real-time capabilities are preserved only if measurements are made at sufficiently high rate compared to the rate at which chemical changes take place in the system.

The conversion in crosslinking epoxy resins has also been accurately monitored by measuring the variation of the conductivity caused by the progressive decrease in diffusive mobility of impurity ions.[6,21] The dc conductivity is a quantity of limited utility since it tends to level off at gelation and it becomes less sensitive to further chemical changes that occur beyond gelation. However, if conductivity is measured at a proper low fre-

quency, some dielectric contribution may be picked up, and the resulting apparent conductivity is better suited for monitoring the final part of the reaction. Additionally, spurious effects due to electrode polarization become minimal.[6]

A modified version of the disappearance model can be applied to substantiate the monitoring capabilities of the real and imaginary parts, ε' and ε'', of the dielectric permittivity, $\varepsilon = \varepsilon' - i\varepsilon''$, at microwave frequencies.[3,4] The first successful application of microwave dielectrometry was found in the monitoring of the fast photoinitiated radical chain polymerization of butyl acrylate.[22,23] A polymerization reaction converts small molecules into bigger ones. Often, dipolar groups are associated to the monomers. Such dipoles are strongly affected by both the changes at the molecular level brought about by the chemical reaction and by the physical modification of their environment that is becoming macromolecular in nature. If dielectric measurements are carried out at very high frequency, it is possible to isolate the contribution of small dipolar groups. As a first approximation, very high frequency dielectrometry is capable of sensing the disappearance of monomer molecules as they are incorporated, modified or not, in the growing macromolecular structure.

A number of articles,[4,5,24–26] mostly concerned with the setting of epoxies, detail the monitoring applications of dielectrometry and underline the advantages of this technique. We recall the facts that measurements are not affected by stray effects, such as electrode polarization, and that dc conductivity and the kinetics of the process can be followed in real time simply by tracking the value of ε' or ε''.

The present system was also cured at 70°C, and ε' and ε'' were measured at the frequency of 2.5 GHz. The variation was about 40% for ε' and more than 95% for ε'' (Fig. 4), therefore much larger than the variation of ε_0 previously considered. The dielectric conversion $D(t)$ is defined as

$$D(t) = \frac{\varepsilon(t) - \varepsilon(C = 0)}{\varepsilon(C = 1) - \varepsilon(C = 0)} \qquad (4)$$

where ε can be the real or imaginary part of the dielectric constant, t indicates the time elapsed from the beginning of the process and $\varepsilon(C = 0)$ and $\varepsilon(C = 1)$ are the values of ε at the beginning and at the end of the reaction. The latter value
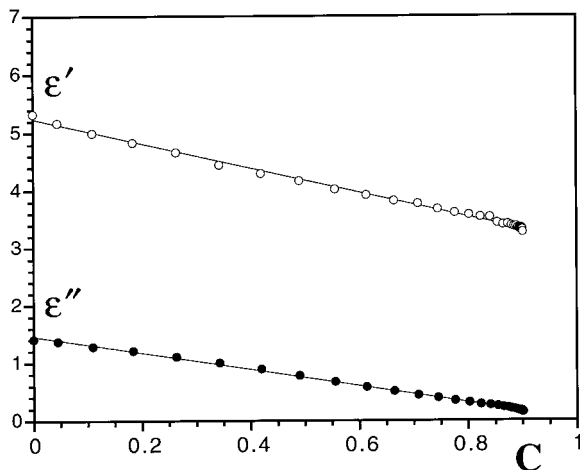
Figure 4 ε' and ε'' at 2.5 GHz versus conversion C of DGEBA/EDA 2 : 1 mixture cured at 70°C. The solid lines are the linear fit equations.

Figure 5 Dielectric conversion D calculated from both ε' (open dots) and ε'' (full dots) data and calorimetric conversion (dashed line) versus reaction time t for the isothermal cure at 70°C of DGEBA/EDA 2 : 1 mixture.

cannot be directly measured because the system never reaches a complete conversion; it must be determined by the same data fit in Figure 4 (solid line).
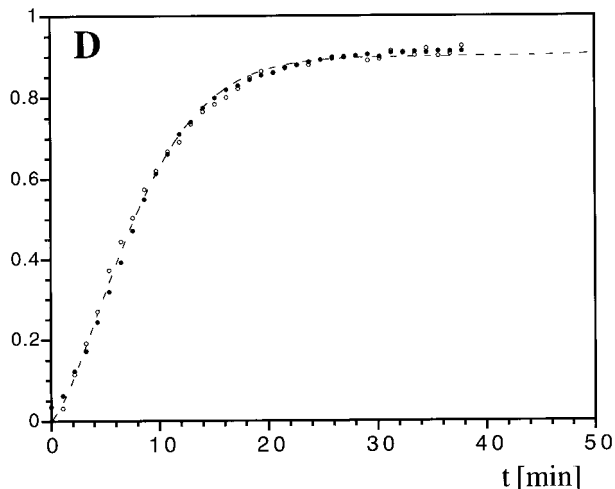
If at full conversion it is assumed that $\varepsilon'' \sim 0$, that is, relaxations are no more active at the actual frequency, we have

$$D(t) = 1 - \varepsilon''(t)/\varepsilon''(C = 0) \qquad (5)$$

and only raw experimental data are needed to calculate $D(t)$. For the present system, the linear fit shown in Figure 4 yields $\varepsilon''(C = 1) = 0, 02$ so that the ratio in eq. (5) is suitable to measure the conversion,[12] which, at this frequency, can be made with greater accuracy due to the larger variation of ε' and ε''.

In Figure 5, $D(t)$, obtained from both ε' and ε'', is compared with the calorimetric conversion $C(t)$; the agreement between calorimetry and dielectrometry is excellent. The match is expected to even be better if one uses data obtained by a single frequency technique than those of the time domain reflectometry. Accurate experimental data allow simple and real-time calculation of the rate of reaction.[27,28]

Although the actual accuracy of the D data in Figure 5 may not be sufficient to enable direct calculation of the rate of reaction, the use of a proper fit equation eases the situation. In Figure 6, the equation fitted to experimental ε'' data is

plotted along with its time derivative. A maximum appears at conversion of about 0.3 as a result of counterbalancing between the autocatalitic effect and the consumption of reactive groups. The kinetic behavior of thermosetting systems can be roughly thought to fall under two different regimes. In the first part of the reaction, when the viscosity of the medium is low, the rate of reaction obeys conventional kinetic equations (chemical
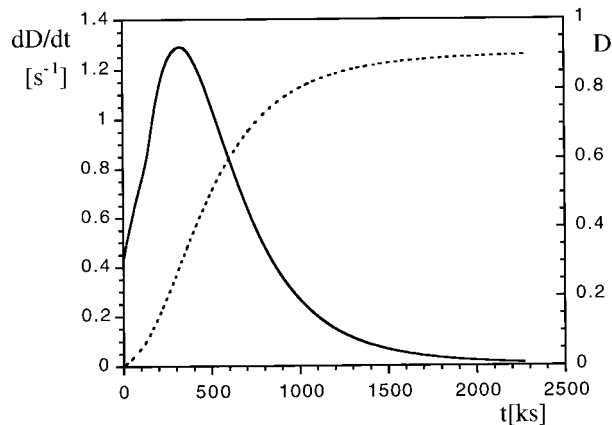
Figure 6 Conversion D obtained by a general fit of the ε'' data of Figure 5 (dotted line) and the corresponding rate of reaction (solid line) plotted versus time of reaction t.
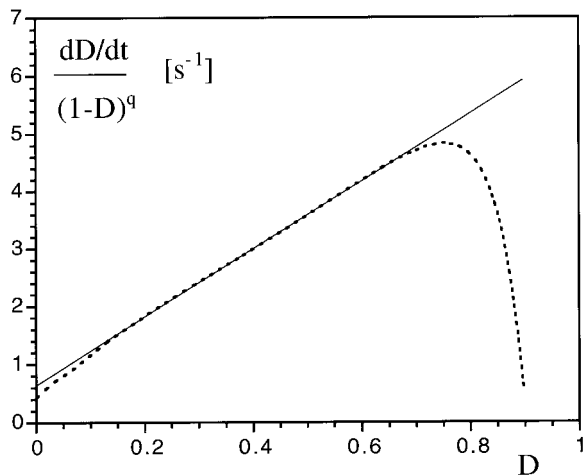
Figure 7 The reduced rate of reaction versus conversion D ($p = 1$; $q = 1.75$).

stage). When the viscosity becomes sufficiently high, the rate at which reactive molecules meet is controlled by mobility (diffusion stage) more than by the concentration of reactive molecules. In general, a kinetic equation of the type[12]

$$\frac{dD}{dt} = (k_1 + k_2 D^p)(1 - D)^q \qquad (6)$$

is obeyed when the system is in the chemical stage. Then a plot of $(dD/dt)(1 - D)^q$ (reduced rate) versus D^p should yield a straight line. In Figure 7, it is shown that linearity is found for conversion up to about 0.7. Above this value, the system enters the diffusion stage, the rate of reaction decreases, and gelation or vitrification phenomena occur.

Monitoring of Viscosity

Though epoxy systems are good insulators, a certain level of conductivity (of the order of 10^{-8} S/cm) is customarily observed as the consequence of the presence of ionic impurities. Conductivity measurements have been employed extensively to monitor the viscosity η of the prepolymer during setting. The resistivity (σ^{-1}) was demonstrated to be proportional to viscosity at least up to the diffusion controlled regime[10,29–31] and to become nearly stable afterward. The determination of small conductivities under dc electric fields is largely influenced by electrode effects; low-fre-

quency ac measurements are therefore preferred.[24] However, under ac fields, current can be produced either by free ions or by bound charges; to distinguish these contributions, the conductivity has to be measured at different frequencies. The conductivity due to free charges is stable as the frequency increases, but it does not when bound charges come into play; this allows choosing the correct frequency at which measurements have to be made.

The percolation approach at gelation describes the conductivity behavior during crosslinking by the following equation[7]:

$$\sigma = \sigma_0 \left[\frac{(C_{gel} - C)}{C_{gel}} \right]^x \qquad (7)$$

This equation shows that conductivity decreases as the conversion approaches the gelation value, C_{gel}; the exponent x has a universal value (~ 3.3). The conductivity of the epoxy system is plotted in Figure 8 as a function of conversion; the solid line is eq. (7), and the gel point is taken at $C_{gel} = 0.69$. A discussion on the reliability of the determination of the gel point by this method is in Casalini et al.[7] By means of measurements of conductivity, it is then possible, with acceptable accuracy, to obtain the viscosity profile in the first part of the reaction.[10,30] This result should be compared with
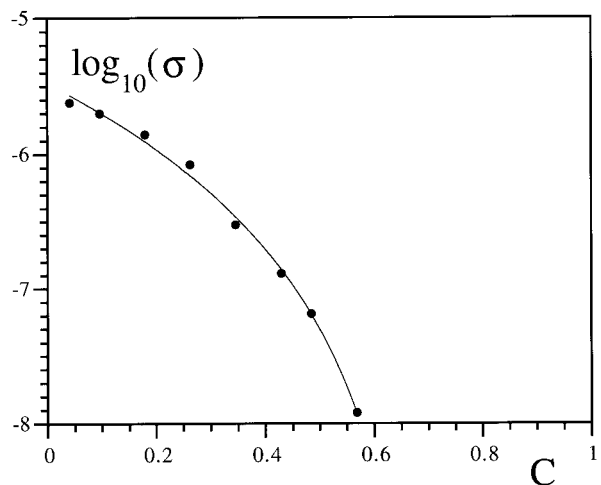
Figure 8 Log of conductivity σ [S/m] versus calorimetric conversion C for the isothermal cure at 25°C of DGEBA/EDA 1 : 1 mixture. The solid line represents eq. (7).
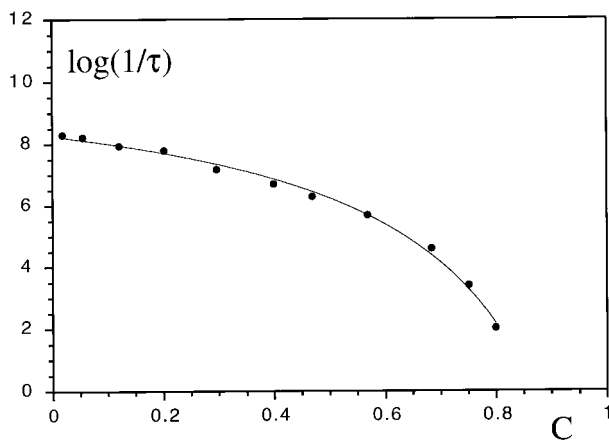
Figure 9 Log of relaxation time, in seconds, versus conversion C for the isothermal cure at 25°C of DGEBA/ EDA 1 : 1 mixture. The solid line represents eq. (8).

the viscosity profile given by chemorheological models.[32,33]

A different approach for monitoring the rheological behavior is based on the variation of some dynamic parameters of the low-frequency dielectric relaxations. The most useful parameter is the main relaxation time τ, related to the reorientational mobility of the whole molecule. In fact, in a system that polymerizes, the main relaxation time increases by several orders of magnitude; the rate of variation of τ increases dramatically as the glass transition is approached (Fig. 9), but it does not show appreciable variation at gelation. This behavior has been very recently recognized to conform with a Vogel−Fulcher (VF) type equation if the independent variable is conversion.[34] The fit line in Figure 9 is the following equation:

$$\log_{10}\left(\frac{\tau_0}{\tau}\right) = \frac{F}{C - C_0} \qquad (8)$$

where τ_0, F, and C_0 are fit parameters. Since $C < C_0$, we have $\tau > \tau_0$; τ_0 is simply a reference value for the time scale of the system: at $C = 0$, the actual relaxation time is higher than τ_0 by (F/C_0) orders of magnitude.

According to Debye−Maxwell equation,

$$\tau = \frac{4\pi a^3}{kT}\,\eta \qquad (9)$$

where the molecule is considered a sphere of radius a, the relaxation time τ is proportional to

the bulk viscosity η, as it has been verified in a number of experiments. Equation (9) is verified also for polymerizing systems before the gelation. Accordingly, the relaxation time can be used to monitor the viscosity, and suitable viscosity−relaxation time models can be applied.[10,25,35]

Determining T_g

The plot in Figure 9 also permits evaluating the actual value of the glass transition temperature of the system. This can be made on the ground of a dielectric definition, commonly accepted, of the glass transition temperature as the one at which the relaxation time is 10^2 s. It is of interest to point out that by this approach, it is possible to calculate, or at least evaluate, the T_g of a system during reactions, even those that are not isothermal. We consider this procedure to give more reliable results than calorimetry, which requires heating the sample so that the system continues to evolve before a more or less evident change in specific heat is detected by the calorimeter. By carrying out isothermal cure reactions at different temperatures, it is possible to establish correlations between T_g and conversion. Alternatively, by determining the more usual VF behavior of the relaxation time by changing the temperature of the system at different conversions, the dielectric glass transition temperature as a function of conversion can be again tabulated. The two procedures are equivalent in principle, but the experiment based on temperature variation might be affected by spurious effects, such as phase separation phenomena, as well as conversion stability under temperature span.

Monitoring of Dynamical Properties by the Shape Parameters

The two shape parameters α and β, characterizing the Havriliak−Negami relaxation function[19] commonly used to describe complex systems such as polymers, are also useful to investigate the structural changes that occur in reacting systems. The interest in these parameters for this application is very recent,[3,7] and, as of yet, only few remarks can be made. In Figure 10, both α and β are plotted vs. conversion for our system; the linear increase of α, also observed in other similar systems,[8] indicates an increase of intermolecular interactions as macromolecules grow. The parameter β remains substantially constant except for a
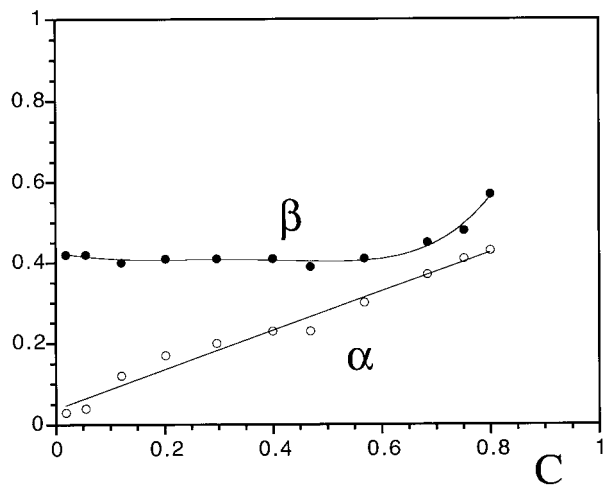
Figure 10 Shape parameters, α and β, of the main relaxation versus conversion C for the isothermal cure at 25°C of DGEBA/EDA 1 : 1 mixture. The solid lines are a guide for the eyes.

limited increase at the end of the reaction; at this time, an acceptable explanation cannot be given, though we only note that the effect is observed just after gelation (Fig. 10).

CONCLUSIONS

Tracking the change of electric properties in systems undergoing chemical modifications is a powerful method for obtaining information of the kinetic and rheological behavior of the system.

We have shown that this occurs in the case of amine–epoxy crosslinking systems, where a linear dependence between the static dielectric constant ε_0 and conversion is observed, though the overall variation of ε_0 is rather small. The same pattern of behavior was observed for the permittivity measured at microwave frequency with the advantage of a much greater sensitivity. For a more comprehensive analysis, a wideband technique should be preferred, but for practical application, a single frequency technique is advisable not only for accuracy and rate but also for simplicity and cost.[36] The dc electric conductivity and relaxation time can be related to the viscosity changes of the system. The main relaxation time that obeys a Vogel–Fulcher type equation having the conversion as independent variable allows evaluation of the glass transition temperature of the system. Experimental evidence is being collected that suggests that the shape parameters

of the main relaxation reflect the change of the relaxation mechanism of the system during the chemical process.

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