

Correlation between dielectric and chemorheological properties during cure of epoxy-based composites

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A method for the complete thermal, rheological and dielectric characterization of an epoxy matrix for advanced composites is presented. The analysis of the dielectric response suggests that ionic resistivity data can be used to develop quantitative correlations with the materials properties during thermosets processing. Ionic resistivity and degree of reaction data are correlated during the cure of the studied epoxy matrix and good agreement between the model predictions and the experimental data is observed under isothermal and non-isothermal conditions. Moreover, degree of reaction data calculated from dielectric measurements are used in a chemorheological model for viscosity calculation, obtaining very good correlation between measured and predicted viscosity.

1. Introduction

A large amount of experimental and theoretical information about the basic phenomena that accompany epoxy-based composite processing, such as chemorheology and network formation, heat and mass transfer, formation and collapse of voids, generation and dissipation of residual stresses, interfacial adhesion, etc., has been produced in recent years [1–12]. As a consequence of this effort, more efficient processes and higher quality products can be obtained mainly in the field of high-performance composite materials, produced by autoclave lamination, for aerospace applications.

Nowadays, a further challenge is becoming more and more important in composite processing: cure monitoring and optimization. One answer to this challenge is the development and implementation of *in situ* sensors capable of providing information that can be correlated to the fundamental process variables, such as degree of reaction and viscosity, during cure. Research devoted to this objective has led to the development and implementation of dielectric sensors [13–15].

The dielectric behaviour of thermosets during cure was exhaustively analysed by Senturia and Sheppard [13]. However, intrinsic difficulties and unresolved issues relating to the generation and interpretation of

the data obtained from dielectric measurements are still not resolved [16].

The application of dielectric measurements to process control are characterized by three main features:

1. the ability of a dielectric sensor to give *in situ* and on-line measurements of some dielectric property during cure;
2. the development of fundamental or, at least, phenomenological models capable of correlating the dielectric measurements with the material properties changing during cure (e.g. degree of reaction and viscosity);
3. the implementation of such correlation in control and optimization algorithms.

Once these conditions are assessed, the optimization and control of the cure process could proceed according to the flow diagram shown in Fig. 1. Following this procedure, the *in situ* and on-line measurements of a dielectric property and temperature during cure are used to compute the degree of reaction and viscosity of the system. This information, integrated with the heat-transfer characteristics of the forming tool and the geometry of the part, can be used as input for a control and optimization module. This module, operating in a closed loop, optimizes the applied temperature and pressure and detects the end of the cure process. The flow diagram of Fig. 1 can be applied to

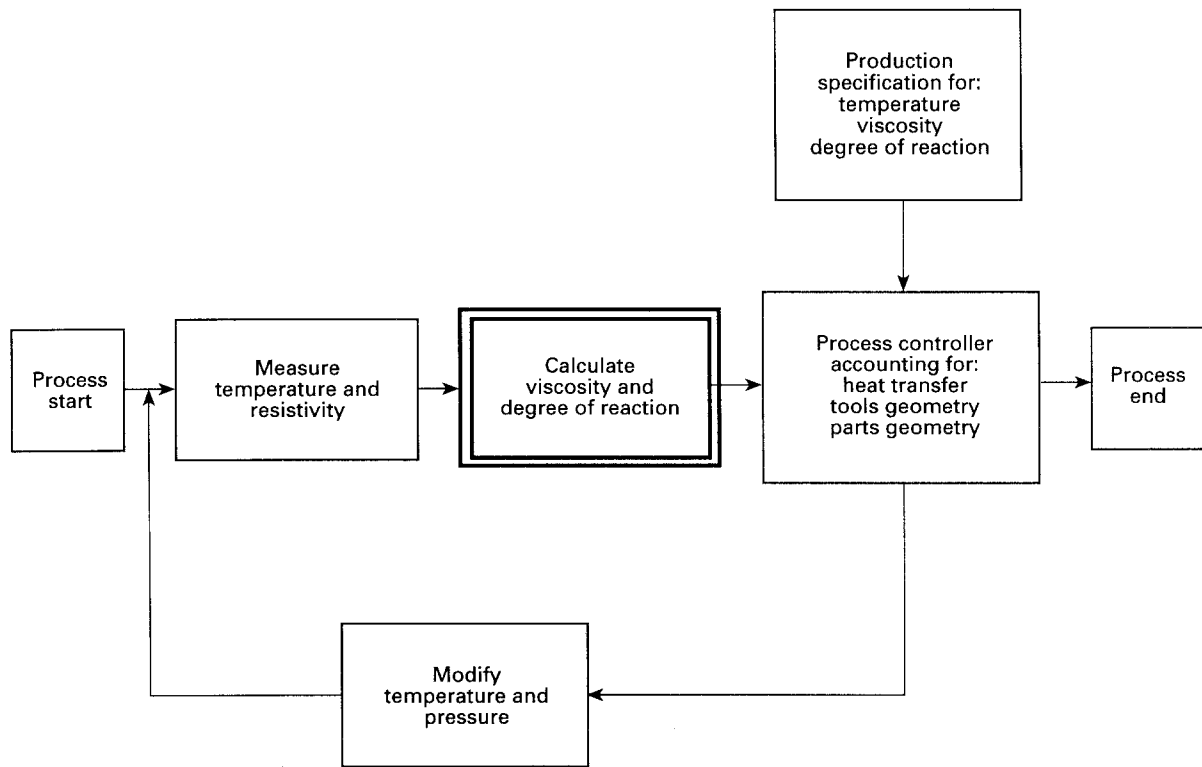


Figure 1 Flow diagram of control and optimization algorithm of the cure process.

different processing technologies of thermoset-based materials. In particular, this approach has been applied to processes with long curing times, like autoclave lamination of high-performance composites [17]. In other processes, such as resin transfer moulding (RTM) and pultrusion, this approach can be applied following the processing behaviour of several parts during batch production.

Considering that the *in situ* monitoring of dielectric properties is currently available through the utilization of several commercial instruments equipped with special micro-dielectric sensors, and that control and optimization algorithms depend on the performance of advanced hardware modules, the use of dielectric properties to monitor material properties is mainly dependent on the availability of good correlations developed for different polymeric matrices. The aim of this study was the development of a relationship between a dielectric property (ionic resistivity) and the degree of reaction and viscosity during cure of an epoxy matrix for advanced composites. This correlation fulfils the second requirement for dielectric monitoring mentioned before and, being the core of the processing optimization scheme, constitutes the highlighted step indicated in Fig. 1.

2. Basis of dielectric behaviour

When a viscoelastic polymeric material containing permanent dipoles is placed in an alternating electric field the reorientation of dipoles upon the reversal of the electric field is not instantaneous. Consequently, when an alternating time-dependent voltage is applied to a parallel plate condenser, the corresponding time-

dependent current will lag behind the applied voltage by a phase angle δ . Applying the phenomenological theory of linear dielectric relaxation behaviour [18, 19], it can be shown that the complex dielectric constant is given by

$$\varepsilon^* = \varepsilon_u + (\varepsilon_r - \varepsilon_u)/(1 + i\omega\tau) \quad (1)$$

Equation 1 is the Debye equation for spherical dipoles [18]. In this equation, ε_u is the “unrelaxed” complex permittivity given only by the contribution of atomic and electronic polarization. The “relaxed” complex permittivity, ε_r , is obtained when the highest degree of dipole orientation is attained in the material at a given temperature and electric field. Parameters τ and ω are the relaxation time and angular frequency, respectively.

The real and imaginary components of ε^* can be obtained in the form

$$\varepsilon' = \varepsilon_u + (\varepsilon_r - \varepsilon_u)/(1 + \omega^2\tau^2) \quad (2)$$

$$\varepsilon'' = (\varepsilon_r - \varepsilon_u)\omega\tau/(1 + \omega^2\tau^2) \quad (3)$$

The dielectric constant or permittivity ε' , the dielectric loss, ε'' , and the dielectric $\tan \delta$, $\varepsilon''/\varepsilon'$, are the characteristic parameters that describe the polarization of a dielectric material by dipole orientation in an applied electric field.

However, the dielectric response of polymeric materials generally comprises two simultaneously occurring phenomena, dipole orientation and free-charge migration. This is particularly important in the studies of cure of thermoset polymers and their composites, where the initial resin viscosity is low and the migration of free ions gives rise to a significant ionic conductivity, σ , contribution in dielectric measurements.

In fact, at lower frequencies, ionic conductivity represents the main contribution to ϵ'' and Equation 3 must be modified

$$\epsilon'' = (\epsilon_r - \epsilon_u)(\omega\tau)/(1 + \omega^2\tau^2) + \sigma/\omega\epsilon_0 \quad (4)$$

where ϵ_0 is the permittivity of the free space, equal to $8.854 \times 10^{-12} \text{ Fm}^{-1}$.

Additional dielectric events should be also considered, such as electrode polarization [14] or Maxwell-Wagner polarization in heterogeneous systems [13], both of which can significantly affect the measured values of dielectric properties.

Moreover, the effects of dipole orientation are frequency dependent. In fact the application of an electric field causes a redistribution of charges within the dielectric, but only as long as those charges are mobile enough to respond within the time scale (frequency) of the field application. Then, in general, the lower the frequency the greater is the contribution of the ionic conductivity and vice versa, and, following Equation 4, the contribution of the dipole orientation to the dielectric loss response becomes negligible when

$$(\epsilon_r - \epsilon_u)(\omega\tau)/(1 + \omega^2\tau^2) \ll \sigma/\omega\epsilon_0 \quad (5)$$

At low frequencies, when this inequality holds, Equation 4 may be written as

$$\epsilon'' = \sigma/\omega\epsilon_0 \quad (6)$$

Therefore, in this situation, the ionic conductivity and the ionic resistivity, ρ , can be calculated from

$$\sigma = 1/\rho = \omega\epsilon_0\epsilon'' \quad (7)$$

3. Dielectric measurements for on-line cure monitoring

The major limitation of dielectric techniques for *in situ* monitoring of cure is the lack of both fundamental and phenomenological correlations between the dielectric signal and the processing parameters. Apart from the theoretical challenge, such information would be of considerable value to manufacturers of composites.

It must be noted that the dielectric behaviour of a substance depends essentially on its structure and on the true electric field acting on it in the presence of an external macroscopic electric field. The available expressions for non-polar materials, when only electronic and/or atomic polarizations are observed, can well represent the dielectric properties for gas and liquid states. On the other hand, the development of expressions relating the molecular structure and the dielectric constant for simple polar substances in the liquid state, such as water, is a difficult matter as a consequence of the effect of the local electric field, usually different from the macroscopic one. The prediction of dielectric properties in the solid state is still more complex, not only as a consequence of the differences between the local and the macroscopic electric field but also because the dipoles are hindered in their motion. Reactive mixtures, such as epoxies and amines, presenting high molecular weights with many pendant polar groups, are much more complicated to

analyse. For these reasons, a fundamental relationship between the molecular structure and the dielectric behaviour of a polymeric reactive system cannot be found among the engineering approaches available in the literature, being closer to the advanced research on the solid-state physics than to the study of polymer processing. Furthermore, commercial systems of technological interest are normally complex formulations whose composition is usually unknown. Nevertheless, dielectric monitoring is, at the moment, the only technique that can perform *in situ* measurements related to the structural changes occurring during the polymerization of thermosets and, following the limitations mentioned, data obtained in such measurements have been correlated only qualitatively to fundamental processing parameters (viscosity and degree of reaction) [12, 15, 20]. Therefore, the development of phenomenological expressions accounting essentially for repetitiveness, accuracy and easy calibration procedures, is needed.

Following the technical discussion on dielectric behaviour, the experimentally measured parameters (ionic resistivity, ϵ' and ϵ'') that can be correlated with the materials properties (degree of reaction and viscosity), are briefly discussed below.

3.1. Ionic resistivity

The determination of ionic resistivity with the currently available sensor instruments is based upon the assumption that free migrating ions are initially present, although in small amounts, in the resin formulation. Free ions can be present as normal impurities, residues of precursor materials used in the synthesis of the polymer matrix or inorganic catalysers for the cross-linking reaction. Ionic resistivity depends on the ion charge, q , on the number of ions, n , and on a mobility factor, m , sensitive to the structural changes of the matrix

$$\rho \propto 1/qnm \quad (8)$$

The ionic resistivity changes during isothermal cure depend on the reduction of the ion mobility, m , related to the increase of the molecular weight of the resin and, after gelation, by the growth of a three-dimensional network that strongly limits the ion mobility. The type (Na^+ , Cl^- , H^+ , OH^-) and the concentration of free ions, as well as the effect that these two parameters exert on the dielectric measurements, have not been quantified. Considering the large variety of epoxy systems and their precursors, and the inevitable vicissitudes of the batch-to-batch characteristics and hygrothermal histories, it is clear that a fundamental correlation between the ionic resistivity and the above parameters would not be more useful than a calibration procedure for each batch. At present, however, such correlations either fundamental or phenomenological, are not available.

The condition mathematically expressed by Equation 5 occurs at a particular range of frequencies that is not known a priori, and should be identified for each chemical system. Thus, experiments must be performed at many frequencies until the right range is

identified (at which Equation 5 is satisfied). Two methods for the calculation of ionic conductivity of thermoset polymers during cure from dielectric measurements at conditions that satisfy Equation 5, have been described in detail by Day [20–22] and by Kranbuehl and co-workers [23–25].

The capacity of the dielectric analysis to develop a reproducible quantitative correlation between the measured ionic resistivity and the two major processing parameters, resin viscosity and degree of cure, is still not achievable and at the present time such correlations are at best, qualitative [11–20, 23, 25].

3.2. Dielectric constant and dielectric loss

Most of the research dealing with the dielectric constant and the dielectric loss has been devoted to the derivation of a fundamental expression for ϵ' (or ϵ'') which can then be used to describe the experimentally obtained results. Many difficulties arise from this approach because in polymeric systems the local internal electric field is not known. Its accurate determination is difficult, as the number of dipoles per unit volume is not fixed, and the response of different dipoles to the electric field varies as a function of the size of the segment to which the dipole is attached and the surroundings that hinder the dipole rotation to a different degree. Moreover, a direct correlation of ϵ' (or ϵ'') with viscosity and degree of reaction has never been attempted in the literature. The only exception is in a recent dielectric study of epoxy cure at microwave frequencies [26] where a reasonable agreement was reported between the degree of cure measured by differential scanning calorimetry and the normalized dielectric loss, $\epsilon''(t)/\epsilon''(0)$. The authors identified a frequency range in which the dielectric behaviour was dominated by the disappearance of epoxy groups, allowing for a direct correlation between the dielectric signal and the degree of cure. Although a fundamental model of dielectric behaviour was not utilized, the observed agreement suggests that further studies along these lines are promising. However no sensors are currently available for *in situ* monitoring of dielectric properties at microwave frequencies.

4. Experimental procedure

4.1. Materials

The epoxy system analysed was a commercial grade resin (Hercules 8552) produced by Hercules, based on mixtures of *tetra-glicidyl diamino diphenyl methane* (TGDDM) epoxy resin, and *diamino diphenyl sulphone* (DDS) as hardener.

4.2. Apparatus and procedures

Dielectric analysis was performed under isothermal and non-isothermal conditions using a Micromet System II Dielectrometer. Data were collected between 10^{-1} and 10^5 Hz for each experiment.

The thermocalorimetric characterization was carried out in a differential scanning calorimeter (DSC) Mettler DSC 30, operating in the temperature range

between -50 and 350°C , in a nitrogen atmosphere and equipped with a liquid-nitrogen cooling system. The tests were performed both in isothermal and dynamic conditions on samples of 10–20 mg neat resin.

A Rheometrics dynamic visco-analyser operating at 1–10 Hz equipped with disposable parallel discs, was used for the rheological characterization.

5. Results and discussion

The ionic conductivity (or resistivity) can be considered as the more interesting dielectric parameter because it follows, at least qualitatively, the fundamental processing parameters (viscosity and degree of cure). The evaluation of ionic conductivity values from dielectric measurements was performed according to the inequality given by Equation 5. The procedure is shown in Fig. 2 for an isothermal cure experiment. By plotting Equation 7 for several frequencies, the effect of dipole relaxation can be easily recognized. Equation 7 should give the same values of conductivity at different frequencies when the dielectric response is dominated by ionic conductivity. However, if dipole relaxation effects give a significant contribution to the dielectric loss, an apparent frequency dependence of conductivity is obtained when Equation 7 is applied as shown in Fig. 2. In fact, the increase in the characteristic relaxation times of the resin during cure results in a change of frequency at which dipole relaxation significantly affects the dielectric loss. Therefore, ionic conductivity is correctly obtained when Equation 7 provides equal results at least for two different frequencies.

Following these considerations, as the typical relaxation time of the system at the beginning of the cure is very low, the conductivity should be obtained at low frequencies. But at low frequencies, in a low viscosity liquid, the ionic mobility may lead to polarization of the electrodes that leads to incorrect measurements [14]. Therefore, the correct measurement of ionic conductivity during the initial stages of cure, depends on the existence of a frequency range in which the dielectric loss is insensitive to both dipole relaxation and electrode polarization. For the studied resin, conductivity curves, obtained according to Equation 7 between 10 and 10^5 Hz reported in Fig. 2, are coincident

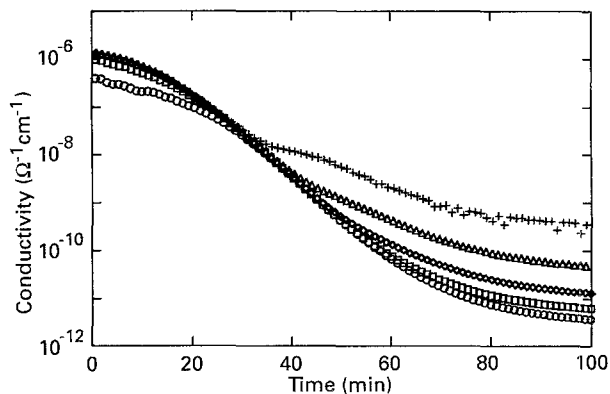


Figure 2 Ionic conductivity data obtained at 160°C applying Equation 7. (○) 1 Hz, (□) 10 Hz, (◇) 100 Hz, (△) 1000 Hz, (+) 10000 Hz.

in the first part of the curing process, indicating that no electrode polarization occurs in this frequency range and that the dipole relaxation contribution to dielectric loss is also negligible at the highest frequency used.

During polymerization, typical relaxation times increase with the molecular weight and dipole relaxation begins to contribute more and more to dielectric loss starting from the highest frequency. On the other hand, electrode polarization effects are inhibited by a reduction of the ion mobility as a consequence of the polymeric network growth. Therefore, as curing proceeds, ionic conductivity (or resistivity) can be obtained by appropriately selecting lower frequencies, as reported in Fig. 2.

5.1. Correlation between calorimetric and dielectric data

Isothermal and dynamic experiments conducted by DSC have been widely used for the indirect determination of the advancement of the cure in a thermosetting system assuming that the heat evolved during the polymerization reaction is proportional to the extent of reaction [27]. The advancement of the polymerization reaction is described in this case in terms of the degree of reaction, α , defined as

$$\alpha = 1/Q_T \int_0^t dQ/dt dt \quad (9)$$

where Q_T indicates the maximum amount of heat of reaction obtained during dynamic scans and dQ/dt is the heat flux measured from a baseline. The degree of reaction and resistivity obtained during isothermal cure show similar patterns as reported in Figs 3 and 4.

The heat of reaction developed during an isothermal test, Q_{it} , is usually lower than Q_T indicating that the polymerization process cannot be completed under these conditions. Then, the final degree of reaction achieved during isothermal tests can be calculated as $\alpha_m = Q_{it}/Q_T$ [27]. In fact, the structural changes produced by the polymerization reactions are associated with an increase of the glass transition temperature, T_g , of the reactive polymer. When the

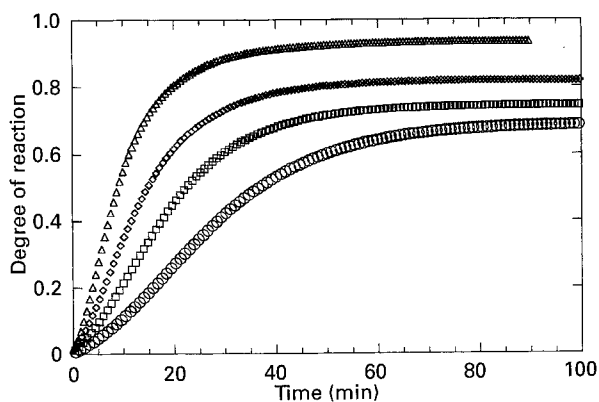


Figure 3 Isothermal degree of reaction data obtained from calorimetric analysis. (○) 160°C, (□) 170°C, (◇) 180°C, (△) 190°C.

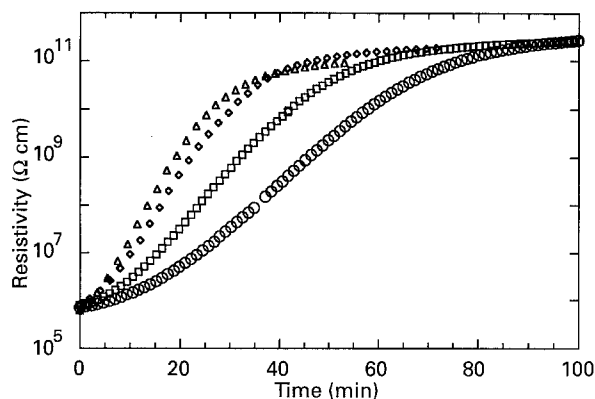


Figure 4 Isothermal resistivity data obtained from dielectric analysis. For key, see Fig. 3.

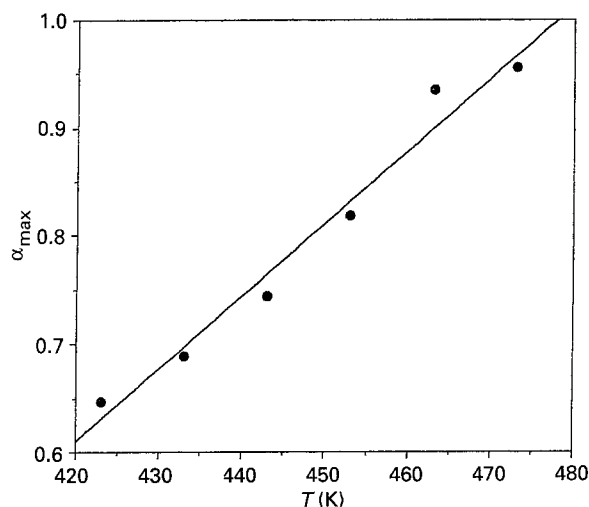


Figure 5 Maximum degree of reaction obtained in isothermal DSC data.

increasing T_g approaches the isothermal cure temperature the molecular mobility is strongly reduced and the reaction becomes diffusion controlled and eventually stops. The behaviour of α_m as a function of the isothermal test temperature is reported in Fig. 5 where a linear dependence between α_m and T is observed

$$\alpha_m = a + bT \quad (10)$$

This behaviour recalls the dependence between the glass transition temperature and the degree of reaction for a reactive polymer. In fact, it is possible to assume that the value of T_g reached by the polymeric matrix during the isothermal test is of the order of the value of the test temperature. The values of the parameters a and b , computed from the straight line in Fig. 5, are given in Table I.

The ionic resistivity of the resin depends on the mobility of ions, related to the network development which is a function of the advancement of the polymerization reaction, the most interesting variable for cure monitoring from the technological point of view. As shown by Day [20], a simple linear transformation of the logarithm of resistivity data is not able to fit the degree of reaction obtained from calorimetric measurements. Therefore, the changes in resistivity

TABLE I Parameters of Equations 10–13

$a = -2.211$	$b = 0.006715\text{K}^{-1}$		
$p = 1.75$	$C_1 = 25.1$	$C_2 = 37.4\text{K}$	$\rho_{go} = 7 \times 10^{14}\ \Omega\text{cm}$
$\ln(k) = 1.372\ \Omega\text{cm}$	$E/R = 11076\ \text{K}^{-1}$ for $T < T_{g\infty}$		
$\ln(k) = -31.43\ \Omega\text{cm}$	$E/R = 26959\ \text{K}^{-1}$ for $T > T_{g\infty}$		
$T_{go} = 267\ \text{K}$	$T_g = 500\ \text{K}$		

must be modelled either (i) based on the knowledge of the number and type of ions present in the resin (with the technological limits above underlined); or (ii) use an empirical relationship between resistivity, ρ , and degree of reaction, α , taking into account the effects of temperature. After an accurate analysis of the general behaviour of both phenomena, the following simple expression is proposed for the isothermal cure

$$\alpha = \alpha_m \frac{\log \rho - \log \rho_0}{\log \rho_{\max} - \log \rho_0} \left(\frac{\log \rho_{\max}}{\log \rho} \right)^p \quad (11)$$

where ρ_0 is the ionic resistivity of the unreacted resin, ρ_{\max} is the maximum value reached at the end of an isothermal cure and p is an empirical parameter. In Fig. 6, the degree of reaction versus time curves obtained from calorimetric analysis show good correlation with resistivity data processed using Equation 11, at four different temperatures. An average value of $p = 1.75 \pm 0.05$, independent of temperature, was obtained by regression analysis for the temperature range analysed. The better correlation observed at lower degree of reaction may be attributed to the intrinsic inaccuracy occurring on integration of low DSC heat-flux signals in the last part of the reaction. It should be noted that α_m must be included in Equation 11 in order to take into account the incomplete polymerization reaction characteristic of the isothermal experiments.

In order to extend the proposed model to the calculation of the degree of reaction in non-isothermal conditions the temperature dependence of Equation 11 parameters must be included. The ionic resistivity of the unreacted resin, ρ_0 , can be modelled with the classic William, Landel and Ferry (WLF) equation [19], originally developed to describe the temperature dependence of polymer viscosity applying concepts of mobility associated with the free volume [28–30]

$$\rho = \rho_{go} \exp \frac{C_1(T - T_{go})}{C_2 + T - T_{go}} \quad (12)$$

where C_1 and C_2 are constants, and ρ_{go} is the pre-exponential constant representing the resistivity of the unreacted resin at the glass transition temperature, T_{go} . Fig. 7 shows a good correspondence between a WLF expression and the experimental data obtained at different heating rates. The parameters of Equation 12 were obtained by non-linear regression and are listed in Table I.

A more complex situation for ρ_{\max} must be considered. Because, in isothermal calorimetric experiments, the polymerization reaction can stop before completion as a consequence of vitrification [9–12], the resistivity measured at the completion of an isothermal polymerization process will be a function of

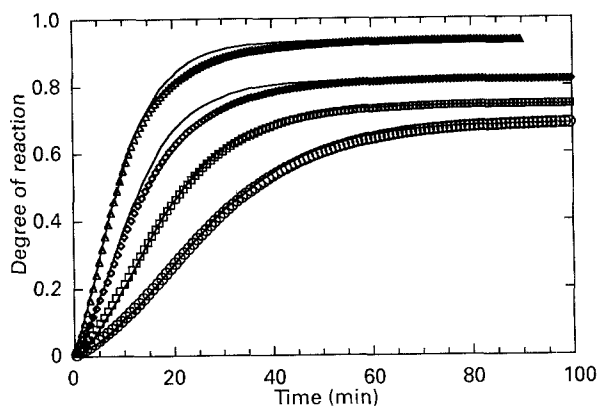


Figure 6 Comparison between experimental degree of reaction data and (—) model predictions in isothermal conditions. For key, see Fig. 3.

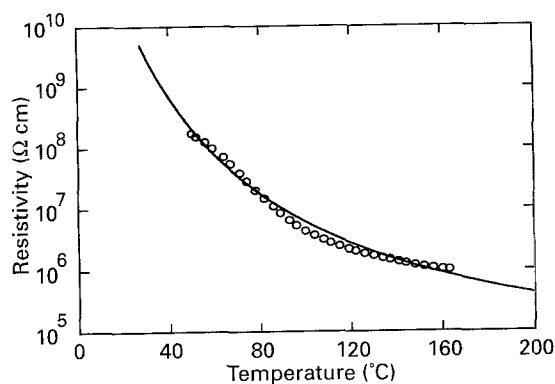


Figure 7 Temperature dependence of the resistivity of the unreacted system: (○) experimental data, (—) model predictions.

the final degree of reaction, α_m , reached by the system and of the cure temperature. On the other hand, in calorimetric experiments performed at constant heating rates, the sample temperature is always higher than the actual glass transition and termination does not occur for vitrification but for ordinary chemical processes allowing the development of the maximum glass transition temperature, $T_{g\max}$, of the system. For this reason, the sample temperature at the end of the cure is higher than $T_{g\max}$ and, therefore, the resistivity, ρ_{\max} , is measured for a rubbery polymer. In fact, the values of ρ_{\max} obtained under isothermal conditions, corresponding to lower mobility conditions, are one order of magnitude lower than those obtained at temperatures lower than $T_{g\max}$. This behaviour is shown in Fig. 8 where the resistivity of glassy samples, obtained at the end of isothermal curing experiments, and of rubbery samples measured at temperatures higher than $T_{g\max}$, are represented. A drop in the resistivity

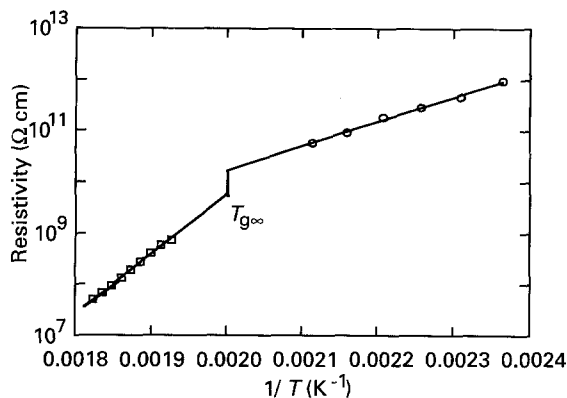


Figure 8 Temperature dependence of resistivity at the end of the cure (experimental data and model predictions). Resistivity of (○) glassy polymer, and (□) rubbery polymer.

values is observed, corresponding to the maximum glass transition temperature, and the linear behaviour of the logarithm of the resistivity as a function of $1/T$ indicates that the temperature dependence of ρ_{\max} , for the glassy and rubbery polymer, may be well represented by an Arrhenius equation

$$\rho_{\max} = K \exp(E/RT) \quad (13)$$

The parameters for Equation 13 are given in Table I for both temperature ranges. The comparison between calorimetric results and the predictions of the complete model (Equations 10–13) obtained at 3°C min^{-1} and in a simulation of a typical autoclave cycle, are shown in Figs 9 and 10. The same average value of the parameter p obtained from isothermal analysis ($p = 1.75$) was used for non-isothermal conditions. Although a generally good correlation between experimental data and model predictions was obtained, some discrepancies can be observed. In Fig. 9, a deviation of model predictions at higher degree of reaction values can be attributed to the normal inaccuracy in the detection of the reaction end related to both experimental methods. Moreover, in the autoclave cycle simulation (Fig. 10), the sudden drop in the dielectric loss attributed to vitrification, is reflected in the model results in an anomalous behaviour in the last part of the cure. The proposed model is able to provide satisfactory predictions of degree of reaction values in isothermal and non-isothermal conditions allowing the quantitative determination of the advancement of the cure process.

5.2. Correlation between rheological and dielectric data

There are two different phenomena which govern the viscosity of a thermoset. One phenomenon is the growing size of the molecules during curing which increases the viscosity of the resin. The other is the effect of temperature on the molecular mobility. For thermosets with complicated reaction mechanisms or where the composition and functionalities of the molecules in the resin mixture are unknown, an empirical approach is necessary. In order to describe the viscosity of the commercial epoxy system studied in this

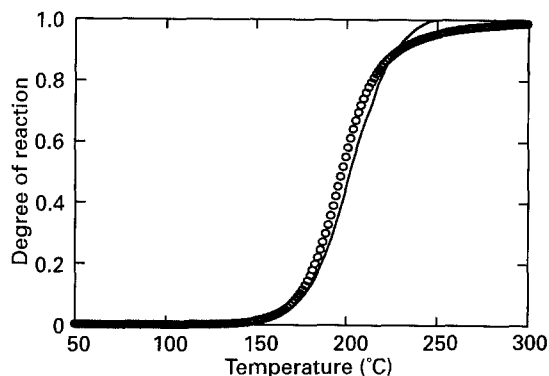


Figure 9 (●) Experimental degree of reaction data and (—) model predictions obtained at constant heating rate (3°C min^{-1}).

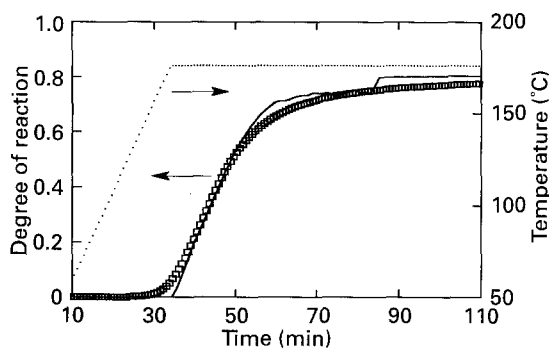


Figure 10 Comparison between (○) experimental degree of reaction data and (—) model predictions in a typical autoclave cycle simulation. Heating rate = 5°C min^{-1} .

work, Opalicki and Kenny [31] adopted the following model

$$\eta = \eta_{\text{go}} \exp \frac{C_{1\eta} [T - T_g(\alpha)]}{C_{2\eta} + T - T_g(\alpha)} [\alpha_g / (\alpha_g - \alpha)]^n \quad (14)$$

where η is the viscosity, α_g is the extent of reaction at the gel point and $C_{1\eta}$, $C_{2\eta}$ and n are constants to be determined by regression analysis of the experimental data. The dependence of T_g from the degree of reaction is well represented by a linear relationship

$$T_g = q + \alpha x \quad (15)$$

The parameters of the rheological model given by Equations 14 and 15, as reported by Opalicki and Kenny [31] are summarized in Table II.

The availability of an *in situ* measurement technique of a structure sensitive parameter such as ionic resistivity and its correlation with the degree of reaction allows the calculation of viscosity on-line during cure. In order to reach this objective, degree of reaction values obtained by applying the complete model (Equations 10–13) can be used in the chemorheological model (Equations 14 and 15) for viscosity calculation. The comparison between experimental data and model results is very satisfactory for isothermal (Fig. 11) and non-isothermal conditions (Figs 12 and 13) leading to reliable quantitative predictions of viscosity during cure.

The correlation between resistivity and degree of reaction can be considered a powerful tool for the

TABLE II Parameters of the chemorheological model (Equations 14 and 15)

$C_{1\eta} = 32.7$	$C_{2\eta} = 37.4 \text{ K}$	$\eta_{g0} = 10^{12} \text{ Pa s}$	
$n = 1.91$	$\alpha_g = 0.271$	$q = 267 \text{ K}$	$s = 232 \text{ K}$

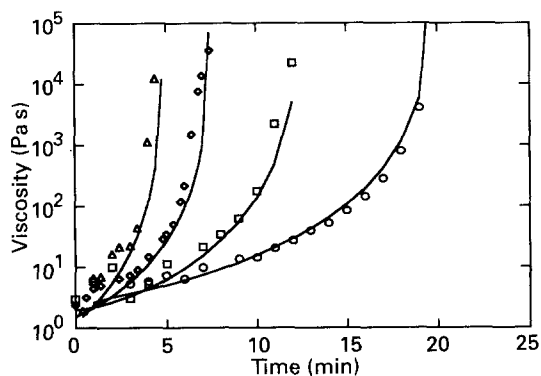


Figure 11 Comparison between experimental viscosity data and (—) model predictions in isothermal conditions. For key, see Fig. 3.

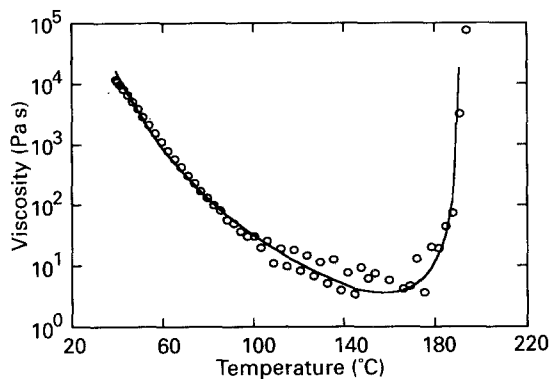


Figure 12 (○) Experimental viscosity data and (—) model predictions obtained at constant heating rate (3 °C min^{-1}). The degree of reaction used in the chemorheological model was calculated from resistivity measurements.

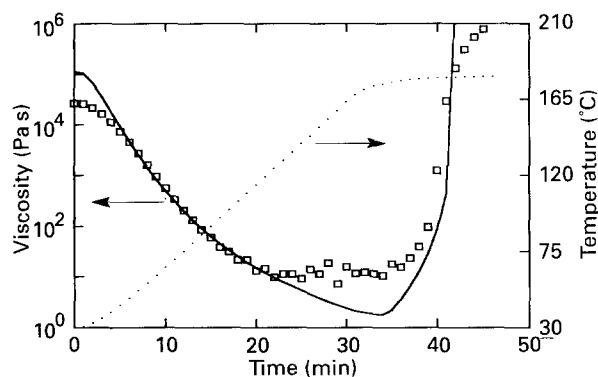


Figure 13 Comparison between (○) experimental viscosity data and (—) model predictions in a typical autoclave cycle simulation. The degree of reaction used in the chemorheological model was calculated from resistivity measurements.

determination of the end of the cure and for the monitoring of the viscosity evolution up to the gel point. Optimization criteria, accounting for the degree of reaction and viscosity data obtained on-line from dielectric sensors, must determine the temperature and pressure profiles capable of realizing optimum conditions for all the laminates under cure.

6. Conclusion

The thermal, rheological and dielectric characterization of an epoxy matrix for advanced composites has been performed. The experimental results have been processed to develop a relationship between the ionic resistivity and the degree of reaction during the cure process of an epoxy matrix for advanced composites. A good agreement between the proposed model and the experimental data has been observed in isothermal conditions. Moreover, accounting for an appropriate temperature dependence of the initial and final values of the resistivity, non-isothermal degree of reaction data have been well represented by the proposed model. Finally, degree of reaction data calculated from dielectric measurements have been used in a chemorheological model for viscosity calculation, obtaining very good correlation between measured and predicted values in isothermal and non-isothermal conditions. The developed correlation may be considered as a significant contribution to the development of process control algorithms.

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