Rheological Study of the Curing Kinetics of Epoxy–Phenol Novolac Resin

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ABSTRACT: The curing reaction of an epoxy–phenolic resin under different conditions was monitored using rheological measurements. The evolution of viscoelastic properties, such as storage modulus, G', and loss modulus, G'', was recorded. Several experiments were performed to confidently compare the rheological data obtained under varied curing conditions of temperature, catalyst concentration, and reactive ratios. The values of G' measured at the end of the reactions (at maximum conversion) were independent of the frequency and temperature of the tests in the range of high temperatures investigated. The overall curing process was described by a second-order phenomenological rheokinetic equation based on the model of Kamal. The effects of the epoxy-to-phenolic ratio as well as the curing temperature and the catalyst concentration were also investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4430–4439, 2006

Key words: epoxy–phenolic; rheokinetic; Kamal model

INTRODUCTION

Epoxy–phenolic resins (E–P) have been widely used as base materials for molding compounds for integrated circuit packaging.[1] The material employed in chip encapsulation is typically an E–P thermosetting polymer combined with numerous fillers and additives. These E–P resins show low viscosity, low water absorption, high adhesion, good flammability properties, and high toughness.[2,3] In this type of application, knowledge of the resin rheological behavior during flow and curing is of utmost importance to ensure adequate moldability of the packaging. These properties strongly depend on temperature, shear rate, and degree of curing.

The cure process of this type of reactive system usually involves the transformation of low molecular weight monomers from the liquid to the solid state. The transformation occurs by the formation of a polymer network, through the chemical reaction of the reactive groups of the system.[4] Thus, two stages can be distinguished in the curing process, limited by the gel point. The initial part of the process is dominated by the viscous behavior of the oligomeric growing species. Thus, the loss modulus of the material, G'', is larger than the storage modulus, G', which represents the elastic part of the response and is negligible at this stage. Actually, G' tends to zero at low enough frequencies of the dynamic test. As the size of the species grow due to the copolymerization reaction, G'' increases, but G' grows faster, so that at some point close to the gel point G' becomes larger than G''. Both moduli level off as the reaction comes to completion.

The sol–gel transition is a critical phenomena that must be known before one can address the material processing analysis. The identification of the gel conversion and the gel time helps to obtain desirable products under appropriate processing conditions and methods. The gel point is associated with the appearance of an equilibrium modulus or solidlike viscoelastic behavior. Beyond the gel point, the material is unable to flow and thus, the processability of the material is greatly reduced. Consequently, mold filling and other simple shaping methods are impossible beyond the gel point.[5]

The gel point has been measured by identifying the time at which an insoluble gel appears. This is usually done by visual inspection, solubility methods, or introducing a wire (or any other thin solid)

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into the reacting sample and measuring the time at which the wire cannot be moved or at which its movement results in the movement of the whole sample as a solid plug. This last method is quite simple, but mostly indicated for stepwise polymerizations in which there is a fast change from liquid to solid at relatively high conversions.

Rheology is also frequently used because it is sensitive to determine the point of gelation. Maybe the most popular way to study the gelation has been developed by Tung and Dynes.[6] They defined the gelation as the crossover between the storage modulus (G') and the loss modulus (G''). The use of this method although not strictly correct, due to the dependence of the rheological properties with the frequency, is very simple to apply and gives the correct trends when comparing the effects of varying reaction parameters in a given system. Winter and Chambon[7,8] studied the gelation of different systems and concluded that at the gel point the storage modulus and the loss modulus conform to the same scaling law with frequencies and consequently tan δ is frequency independent.[9,10]

Traditionally, a chemical approach has been adopted in studies of the crosslinking process of reactive resins.[11,12] The conversion of reactive groups has been followed using methods such as calorimetry and infrared spectroscopy.[13–17] Although these analyses are quite useful for studying the curing reaction (kinetics and mechanisms), they usually do not offer direct insight into the changes that occur in bulk properties of the curing systems. Other approaches consist of monitoring physical behavior, such as changes in viscosity, density, refractive index, etc.[18] These are a direct consequence of the changes explained before and analogously, the formation of a polymer network structure can be investigated using rheological measurements of parameters such as storage modulus, G', and loss modulus, G''.

The main variable for studying the rheological evolution during the curing of thermoset polymers is the storage modulus, G', which is proportional to the crosslinking density of the network being formed by chemical bonds.[19,20] This technique permits to analyze the effects of catalyst concentration, temperature, and stochiometry of the reaction on the cure process. Another relevant parameter is the value of the storage modulus at the end of the curing reaction, G'_∞. This value is proportional to the maximum crosslinking density of the network reached under given curing conditions.

In this article, the formation of the polymer network structure of an epoxy-phenolic matrix is evaluated using rheological parameters. Complementary experiments are performed to validate the methodology used. Thus, gel times are determined by the wire technique, and rheological measurements and the results are compared. The rheological properties are determined during isothermal curing using parallel plate geometry, while the cure kinetics are derived from the data. The effect of varying the epoxy-to-phenolic ratio, the curing temperature, and the catalyst concentration on the kinetics of the curing reaction is investigated. The autocatalytic model developed by Kamal is used to analyze the kinetics of modulus development.

EXPERIMENTAL

Materials and sample preparation

Epoxy–phenolic (E–P) networks were synthesized by reacting a novolac type phenolic resin (Georgia Pacific, US, laboratory grade reagent) and an epoxy resin, diglycidyl ether of bisphenol A (Epon 828, equivalent weight 187 g/equiv.) using triphenylphosphine as catalyst (Fluka A.G., US, analytical reagent). The amount of catalyst added is reported based on the weight of epoxy. All materials were used as received.

The average number molecular weight, (M_n), of the novolac was calculated from the number of phenolic units (n) in the novolac resin, which was determined from the ratio of methylene, [CH_2], to aromatic, [AR], protons of the H NMR spectrum, as shown in the following equation[21]:

$$\frac{[CH_2]}{[AR]} = \frac{2n-2}{3n+2} \tag{1}$$

The calculated results are $M_n \sim 1198$ g/mol and $n = 11.4$ phenolic groups per molecule, respectively. The value of the molecular weight was confirmed by mass spectroscopy, which yielded a value of 1049 g/mol. This last value was used in this work.

The curing E–P reaction proceeds via nucleophilic addition of the phenolic hydroxyl onto the epoxy group.[22] Figure 1 shows a schematic of the synthesis of E–P from the reaction of the epoxy and the novolac.

Considering the chemical structure of the monomers, the crosslinking density of the resultant networks should decrease as the phenolic resin is added in increasing excess with respect to the epoxy groups. At the same time, there is an increase in intramolecular forces due to an increase in hydrogen bonding formation from the large amount of unreacted phenol.[22,23]

Table I gives the details of the weight percentage and equivalent weight ratios of epoxy-to-novolac used. Also given in Table I are the identification codes assigned to the materials synthesized.

Methods and techniques

Rheological measurements

The change in rheological properties during the curing reaction was monitored under isothermal condi-

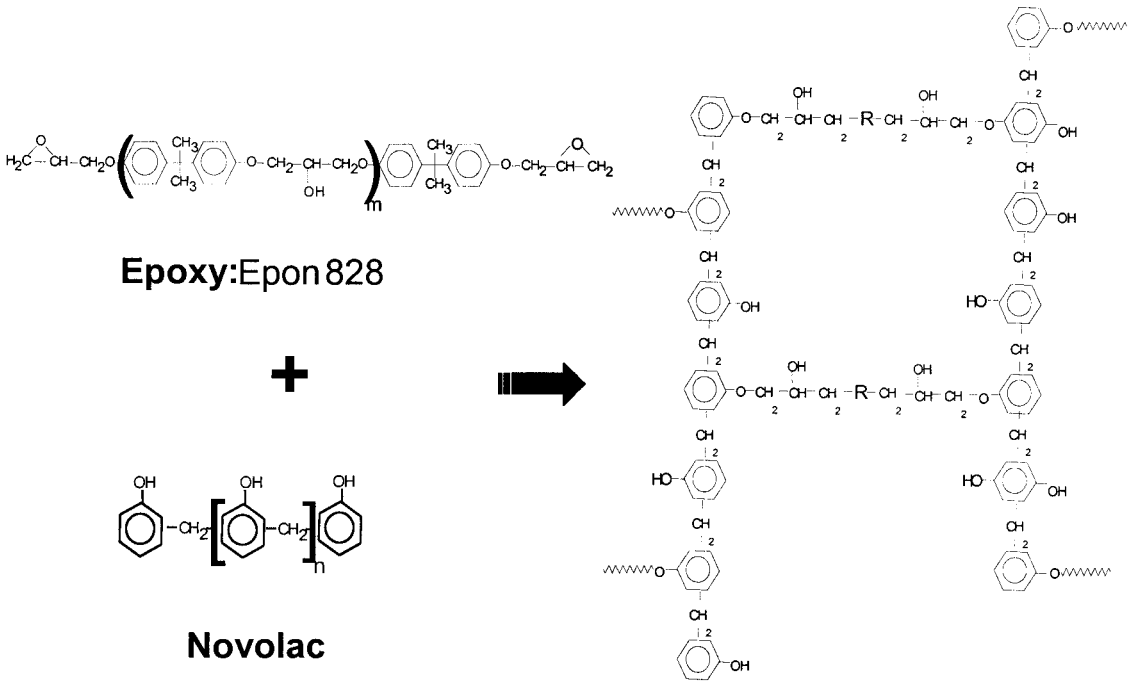

Figure 1 Schematic of the E–P synthesis reaction.

tions using a Rheometrics ARES rheometer (equipped with a 200 g cm transducer). The polymer sample was heated using a forced convection heating oven with temperature stability to ± 0.2°C. All experiments were performed under a continuous purge of dry nitrogen to prevent oxidative and hydrolytic degradation. A parallel plate geometry (diameter = 25 mm, gap = 1 mm) was used in studying the time dependence of the storage and loss modulus. The sample was placed between the preheated plates and the run was begun immediately to reduce any missing information at the beginning of the reaction. Oscillatory dynamic data were collected as a function of time (t). The linear viscoelastic response characterized the entire range of strain amplitudes used in this work (5–0.01%).

Thermal measurements

The glass transition temperatures (T_g) and the storage (G') and loss (G'') modulus of the cured resins were determined by dynamic mechanical analysis. Dual cantilever beam samples (3 mm × 5.5 mm × 60 mm) were clamped in the frame and scanned from 25 to 300°C at a rate of 10°C/min, using a load frequency of 1 Hz. T_g was determined from the peak in the G'' spectrum.

Gelation time

Gelation time was measured by curing samples in an oil bath at different temperatures. A set of glass thin tubes containing the reactive sample was immersed in an oil bath kept at constant temperature. Gelation times were measured by gently pulling a thin wire, immersed in the sample, taking the gel time as the time at which the whole tube was lifted by pulling the wire. The gel points were further confirmed by solubilizing (or partially solubilizing) the reacted samples at specified times in acetone at room temperature.

Gel times were also measured as the time for the crossover of G' and G'' in the rheological measurements (already described). The Winter method was also used in a stoichiometric sample.

The sol and gel fractions of completely cured samples prepared in nonstoichiometric ratios were determined by placing the samples in acetone for a specified time. The samples were taken from the solvent at given times, then the solvent was evaporated and the residual weight was registered. The extraction of soluble material was continued in renewed solvent until achieving constant weight of the extracted sample.

RESULTS AND DISCUSSION

Cured samples

Figure 1 shows a schematic of the crosslinking reaction, where the epoxy resin is acting as the cross-

TABLE I
E–P Formulation

Formulation epoxy (E)–phenolic(P)	E–P (wt %/wt %)	E–P equiv/equiv
E–P(67/33)	67/33	1/1
E–P(50/50)	50/50	1/2
E–P(35/65)	35/65	1/4

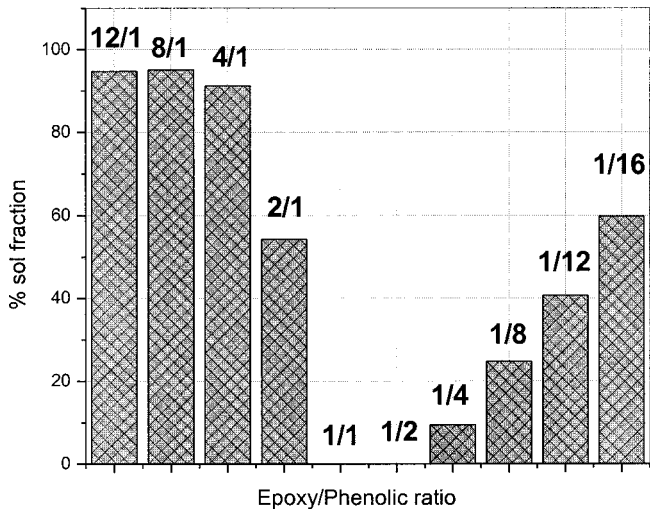

Figure 2 Sol and gel fractions for the epoxy–phenolic networks.

linker of the novolac longer chains. The equivalent weights of the reactive substances can be calculated, as described previously. Furthermore, if only the reaction shown in Figure 1 occurs, one expects maximum mechanical properties (a perfect network) and the lowest soluble fraction (actually zero) at $r = 1$, where r is the molar ratio of epoxy-to-hydroxyl phenolic groups available for reaction. Also, one can calculate the critical value of ''r'' at which gelation cannot occur because the epoxy (or the novolac) is present in sufficient excess.

Following the Flory–Stockmayer ideal modeling of a network[20] or the Macosko–Miller[24,25] approach, these critical values of r can be calculated from

$$r_{\text{crit}} = 1/[(f-1)(g-1)] \quad (2)$$

where f and g are the functionalities of the epoxy resin and the novolac, respectively. In this case, $f = 2$ and $g = 11.4$.

Using eq. (2) and considering the case in which the epoxy is the reactive added in excess to the stoichiometry and thus the novolac is expected to reach complete conversion at the end of the reaction, the value of the critical ratio at which the mixture barely gels can be calculated, $r_{\text{crit}} = 10.4$ (excess epoxy). Larger excess would lead to a completely soluble material. The other critical value, which corresponds to the case in which there is an excess of novolac, is equal to 1/10.4 or 0.096.

Investigation of samples cured in large excess of epoxy or novolac groups was undertaken by immersing samples (divided in small pieces) at room temperature in acetone for a month. Figure 2 summarizes the results. Samples prepared near the stoichiometric ratio ($r = 1$) did not present any soluble material (no sol fraction), while the sol fraction grew as reactives were added in excess. When excess epoxy groups were present in the $r = 8/1$ to 12/1 ratio, the fraction of soluble material was nearly 100%, yielding agreement with model predictions. Some errors are expected in room-temperature extractions, particularly because of the large stoichiometric imbalances required. However, when working with excess phenolic groups, it is clear that even at $r = 1/16$ the sol fraction is far from 100%, contrary to model predictions. Futhermore, preparation of samples with larger stoichiometric imbalance was difficult because of the increasing errors in the weights of the reactive added in defect and the catalyst. These results indicate that other reactions may occur at the same temperature. Further reaction of the secondary OH formed when the epoxy groups open, may react with the excess of phenolic groups. This ether formation would shift the critical ratio to larger imbalances. Alternatively, some linkages may not be statistically distributed, causing sterically induced gelation between adjacent chains. Such gelation could be induced by local inhomogeneities on the r value due to the complexities of mixing largely imbalanced samples.

Dynamic oscillatory tests

The reaction between the stoichiometric-balanced epoxy and novolac mixture was investigated by rheological measurements of G' and G'' versus time, as exemplified in Figure 3. At the beginning of the reaction, the moduli increase slowly, and the loss modulus G'' is greater than the storage modulus G'. These two curves intersect and crossover near the gel point. This intersection provides one criterion for calculating the time

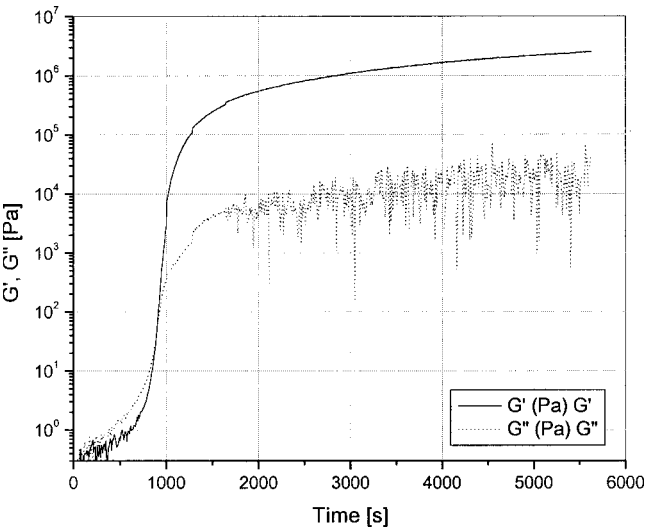

Figure 3 G' and G'' versus time of the E–P reaction. Sample: E–P (67/33), 0.1 wt % TPP, ($r = 1.00$) at 150°C.

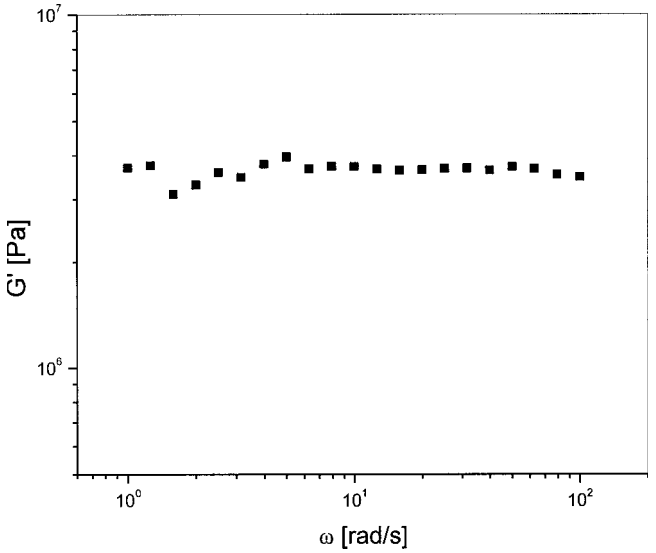

Figure 4 G' versus frequency. Sample: E–P (67/33), 0.1 wt % TPP, ($r = 1.00$) at 150°C.

for the appearance of a gel fraction. However, this condition is not always coincident with the true gel point, as explained by Winter's criterion.[7–10,26–29] This point is discussed in more detail in a following section.

Moduli of the samples at the end of the reaction

Samples were cured directly between the parallel plates in the rheometer to follow the development of the modulus in the piece. The tests were terminated when the G' curve reached a constant value, and the maximum G' was obtained under those reaction conditions. To characterize the networks, tests were performed to ensure that the ultimate G' values were independent of test frequency. Figures 3 and 4 show an example of the results of this part of the study. First G' and G'' were measured as a function of the time of reaction while curing (Fig. 3). Low strains were used to minimize changes in the network structure due to the sinusoidal shearing. During a second step, a frequency sweep of the sample was performed to ensure that the ultimate G' value was independent of test frequency (Fig. 4). As shown in Figure 4, G' was not a function of ω at the end of curing, and this was the case for all samples studied. Thus, the values of G' reached at different temperatures, catalyst concentrations, or reactive ratios can be compared with confidence.

Finally, in a third step, the sample was cooled while being subject to sinusoidal oscillations. The test was performed to confirm that the G' value at the end of reaction was independent of the temperature. T_g of the sample was lower than the curing temperature utilized. Thus, it could be concluded that G' was essentially dependent on the structure of the network and not on temperature, strain, or test frequency.

In Table II, the recorded G'_∞ rubber values determined from rheometric data are summarized as a function of the stoichiometric ratio, catalyst content, and curing temperature. As expected, when the ratio of the reactive functional groups is close to one, the modulus of the sample is a maximum. As more phenolic resin is added, the epoxy precursor is insufficient to completely crosslink the novolac chains, and a less perfect network results, yielding a lower modulus at complete conversion of the limiting reactant.

If the glassy modulus (in this case, the room temperature modulus) is analyzed instead of the rubbery value, a different trend is observed (see Table III). The glassy modulus depends not only on the crosslinking density of the network, as it occurs with the rubber modulus, but also on the cohesive energy of the material. The novolac chains can interact with each other not only through the chemical bonds formed through the reaction with the epoxy groups, but also through physical hydrogen bonding. As the novolac concentration is increased in the reactive mixture, these two interactions show opposite trends. The physical interactions increase, while the effect of chemical crosslinking diminishes. Thus, the modulus of the system increases as the ratio changes from 1 to 0.5, but drops as more phenolic is added, $r = 0.25$. A similar phenomenon can be observed in the behavior of the glass transition temperature. However, because this parameter is most sensitive to the structure of the copolymer, the lowest T_g appears for the most defective material, $r = 0.25$.

Curing process

Gel times

Gelation times were determined from rheological measurements and using the tube technique previously described. In the rheological determinations

TABLE II
Rubbery Modulus (G'_∞) as a Function of the Stoichiometric Ratio, the Catalyst Content, and the Isothermal Temperature

E–P formulation	Temperature (°C)	G'_∞ rubber (MPa) rheometer
E–P(67/33), 0.1 wt % TPP ($r = 1.00$)	150	2.47
	160	2.41
	170	2.31
E–P(67/33), 0.3 wt % TPP ($r = 1.00$)	150	3.00
	160	2.13
	170	2.17
E–P(50/50), 0.1 wt % TPP ($r = 0.50$)	150	1.75
	160	1.50
	170	1.46
E–P(35/65), 0.1 wt % TPP ($r = 0.25$)	150	0.79

TABLE III
Glass Modulus (G'_{glass}) and Glass-Transition Temperarure (T_g) as a Function of the Stoichiometric Ratio

E–P formulation	G'_{glass} (GPa) at 25°C	T_g (°C)
E–P(67/33), 0.1 wt % TPP, ($r = 1.00$)	3.92	125
E–P(50/50), 0.1 wt % TPP, ($r = 0.50$)	4.11	133
E–P(35/65), 0.1 wt % TPP, ($r = 0.25$)	3.99	110

and as a first approximation to the problem, the gel time was taken as the time at which the G' and G'' curves intersected or crossed (described in the previous section).

The values obtained from both techniques are illustrated in Figure 5. The techniques yield good agreement in spite of some inherent difficulty in the rheological measurements in determining the exact gel time. These difficulties arose because sample loading is not immediate. Specifically, there is a short transient stage during which the sample reaches the test temperature and the measurements begin. Consequently, the times registered by this method are shorter than those registered with the tubes immersed in oil. Measuring the time from the moment of loading the sample could be another possibility, in that case the absolute values of the gel times would be longer than those plotted in the Figure 5 but the general trend would be the same.

Figure 5 also shows that for a given amount of catalyst, the gel time increases as the temperature of the reaction decreases, or as the functionality ratio departs from unity. Both effects were expected. In particular, because the reaction occurring under stoichiometric imbalance requires a higher conversion of the defective reactant to form a gel, a longer gel time is measured.

An assessment of alternative methods for determining gel time reveals advantages and drawbacks. As described above, the crossover of G' and G'' is the point at which the viscous and elastic contributions are equal at the frequency of the test. While this is a simple technique for determining gel time, it does not always correspond to the true gel point. Winter and Chambon[7] studied gelation of different physical and chemical networks and found that gelation generally occurs at the crossover when the networks are chemically linked and are ideally formed at $r = 1$. A more general approach would be to determine the gel point by locating the point at which the plots of log G' and log G'' versus log frequency are linear and parallel at all frequencies, though not necessarily coincident. Of course, to experimentally assess this condition would require to freeze the reaction at different times and to perform a frequency sweep of the sample. Alternatively, the same curing reaction could be carried out from time zero up to constant final G' at different constant frequencies, then performing a time sweep. The final G' value in all the runs should be equal, since it was already shown that this value is not a function of the test frequency. The linear parallelism of G' and G'' in a frequency sweep (log-log scales) at the gel point indicates that tan δ is a constant and frequency independent. In other words, time sweep curves performed at different frequencies would show that there is a time at which all tan δ curves crossover (tan δ value independent of frequency) indicating the true gel point of the sample. Besides, at the gel point, viscosity is infinite and equilibrium modulus ($G'_{\omega\to 0}$) tends to zero. Further increase of the modulus occurs as a consequence of advance of reaction. Of course, infinite viscosity cannot be measured and zero frequency tests cannot be performed, but the trends are clearly observable. In this study, at the gel point, G' should be negligible at the lowest frequencies of the test.

The results of performing such a test are shown in Figure 6. All curves converge to a single G' value at long reaction times, and all tan δ curves crossover at a single point at the gel point. The gel time determined from this test is of the same order of magnitude as that measured with the tube technique. The latter technique yields a value of $\sim$ 14 min, while the former technique predicts a value of 13 min for the same sample. The results in the plot are consistent with an equilibrium modulus approaching a zero value at $\omega\to 0$. However, the determination of the gel time by this method is relatively cumbersome and mostly time consuming. Thus, because of the simplicity of the tube and moduli crossover techniques described before, and because the goal of this study was to establish the trend of gel time with cure temperature and with

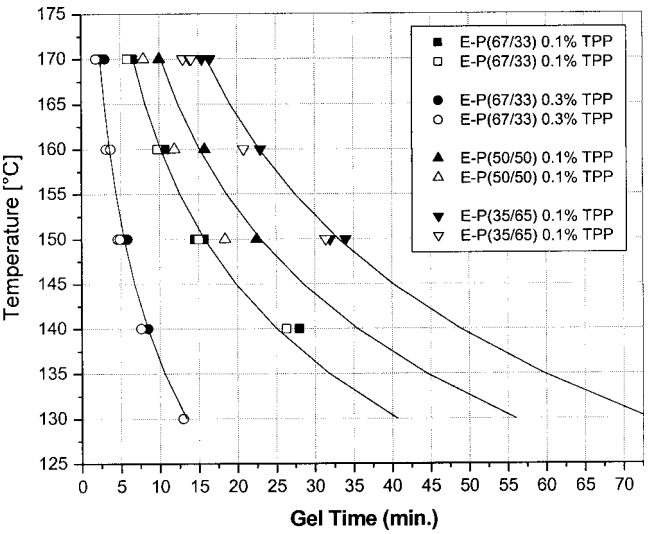

Figure 5 Gel time determined from rheological measurements (open symbols) and from samples cured in an oil bath (closed symbols) at constant temperature.

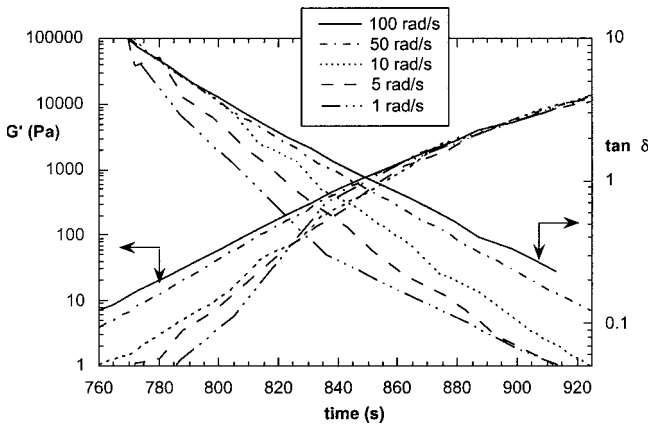

Figure 6 Time sweep curves performed at different frequencies. Sample: E–P (67/33), 0.1 wt % TPP, ($r = 1.00$) at 150°C.

functionality ratios, only the results obtained with those methods are reported in Figure 5.

Results reported in Table II show that G'_∞ is essentially constant with the test temperature, as discussed previously. Small differences can be explained by the fact that different mixtures have to be prepared for each run. Thus, there is an inevitable experimental error that arises from small differences in formulations. Another interesting observation is that the final modulus is independent of catalyst concentration. This indicates that varying the catalyst percentage produces changes in the rate of reaction, but not in the structure of the network being formed. This will reduce the complexity of the rheokinetic modeling discussed below.

Reaction kinetics

A simple calculation of the activation energy of the crosslinking reaction can be performed from the gel time data obtained at different temperatures. A general expression for the kinetics rate is:

$$\frac{dx}{dt} = k(T)f(x) \tag{3}$$

where x is the global conversion, k the kinetics constant, and $f(x)$ is a general form of the function of the reaction rate with conversion.

The kinetic constant can be expressed through an Arrhenius type equation to represent the functionality of k with temperature:

$$k = A\ \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where A is a pre-exponential constant, E_a the apparent activation energy, R is the gas constant, and T is the absolute temperature.

If the network structure is only dependent on the advance of reaction, eq. (3) can be written as:

$$\frac{dx}{f(x)} = k\ dt \tag{5}$$

and further integrating the expression from initial time to t_{gel}

$$\int_0^{x_{\text{gel}}} \frac{dx}{f(x)} = cte = \ k\ t_{\text{gel}} = A\ \exp\left(-\frac{E_a}{RT}\right) t_{\text{gel}} \tag{6}$$

where x_{gel} is the global conversion at gel time.

Consequently, the gel time is related to the cure temperature according to:

$$\text{In}\ t_{\text{gel}} = cte + \frac{E_a}{RT} \tag{7}$$

From the linear fitting of this equation the value of the activation energy of reaction was calculated. The results are reported in Table IV and show that E_a is independent on catalyst concentration and stoichiometric ratio. A smaller value is calculated if the phenolic resin is present in excess. The curves calculated from eq. (7) are included in Figure 5 together with the experimental results, showing a very good agreement. Further discussion on energy activation values will be pursued in the following section.

Rheokinetics model

The curing kinetics of epoxy resins with novolac and other crosslinking agents are often modeled using Kamal's kinetic expression for the reaction rate, as follows[30–32]

$$\frac{dx}{dt} = (k_1 + k_2 x^m)(1 - x)^n \tag{8}$$

This type of equation has been successful in describing systems where there is a maximum in the isothermal reaction rate. This is a characteristic of autocatalytic processes, such as the cure of an epoxy resin with novolac.[33] If the noncatalyzed path of the reaction is negligible with respect to the autocata-

TABLE IV
Activation Energy from Get Time

System	TPP (wt %)	E_a (kJ/mol)
E–P(67/33)	0.1	67.0
E–P(67/33)	0.3	63.6
E–P(50/50)	0.1	63.2
E–P(35/65)	0.1	56.4

lyzed path, then the above expression can be simplified to

$$\frac{dx}{dt} = kx^m(1-x)^n \tag{9}$$

where the constant k_1 has been taken equal to zero.[8]

Another simplification of the kinetic expression applied to epoxy–phenolic reactions is the assumption that the sum of the exponents in eq. (4) converge to 3.[28] Using this simplification, eq. (9) can be written as:

$$\frac{dx}{dt} = kx^m(1-x)^{3-m} \tag{10}$$

These models are flexible enough to give good fitting curves for the autocatalytic regime of the reaction. The kinetic constants were expressed using an Arrhenius type of equation [eq. (4)].

This model has been utilized to study the curing kinetics of different thermoset systems using differential scanning calorimetry (DSC).[14,15,32,34–38] The rheokinetics method is a physicochemical method similar to calorimetry,[19] where the chemical and viscosity changes due to reaction are combined. In the present work, an approach similar to the one used to model calorimetric data has been applied to the epoxy–phenolic curing rheokinetics data, using eqs. (9) and (10).

$$\frac{d\beta}{dt} = k'\beta^m(1-\beta)^n \tag{11}$$

$$\frac{d\beta}{dt} = k'\beta^m(1-\beta)^{3-m} \tag{12}$$

where β is the rheological conversion defined as a function of storage modulus $G'_{(t)}$ in

$$\beta = \frac{\log(G'_{(t)}) - \log(G'_0)}{\log(G'_\infty) - \log(G'_0)} \tag{13}$$

where g'_0 is the value of storage modulus at zero time, and G'_∞ is the storage modulus for maximum degree of crosslinking. k' is the rheokinetics constant.

Although this is a phenomenological model, it offers an easy way to determine the effect of catalyst concentration and stoichiometric formulation on the rheokinetics parameters. The model can only be used if the curing temperature is greater than the glass transition temperature for maximum crosslinking degree ($T_{g\infty}$). This assumption has been validated and discussed previously in this article. For lower curing temperatures, the diffusion control on the rate of chemical reaction must be considered.[34–38] In this analysis, only curing temperatures greater than $T_{g\infty}$ were considered.

A nonlinear regression analysis based on Marquardt's method was used to determine the best fitting parameters to eqs. (11) and (12).[39]

The simplified model requires the use of a ''seed'' to be numerically solved (an initial rheological conversion). In this case, the initial rheological conversion (seed at time = 0) was taken as 10^{-9}. Smaller values of initial rheological conversion did not produce any change in the fitting parameters obtained from the nonlinear regression analysis, or in the predictions obtained by integration of the expression of reaction rate in the model.

Table V shows the calculated values obtained from this method for the different E–P systems during isothermal experiments. The values of the fitting parameter obtained for eqs. (7) or (8) indicated that the assumption of $m + n = 3$ was reasonable. Consequently, the simplified model [eq. (8)] was adopted in further calculations. The use of this model is useful for the prediction of the elastic properties development, because it provides a tool for predicting the time to reach a particular modulus, sufficient to allow for piece demolding.

The effect of catalyst concentration on the rheokinetics parameters can be evaluated by comparing the system E/P = 1 with different percentages of TPP. The k' values at 150°C (Table V) increase between three and six times when the TPP percentage increases from 0.1 to 0.3 wt %. Comparison of activation energy values for the two TPP concentrations considered indicates that this value is not much affected by changes in catalyst concentration. However, the reported k values show that the variations in the kinetic constant are related to important variations in the pre-exponential factors, A. Similar results reported elsewhere for similar systems using a calorimetric method,[2,33] indicated that the velocity of the reaction increases with catalyst content in the same way, while the reaction mechanism is not modified. Consequently, no changes were registered in the activation energies.

On the other hand, the E/P relationship affects the rheokinetics parameters at least at the larger stoichiometric imbalance. As the E/P ratio decreases from 1 to 0.25 (novolac excess), the k value at 150°C decreases, indicating that the cure reaction is slower. Notice that the relatively low value of the activation energy obtained for this sample was also calculated from the gel times measured by the ''tube'' technique. The observed decrease of the rate of reaction is ascribed to the much lower value of the pre-exponential factor. Since the sample was prepared in phenolic excess, differences in the rate of development of the network structure with respect to that of the stoichiometric network were to be expected. In par-

TABLE V
Values of Rheokinetics Fitting Parameters

System	TPP (wt %)	A (s^{-1})	E'_a (kJ/mol)	k' ($T = 150°C$)	m	n
			Equation (9)			
E–P(67/33)	0.1	856,090	63.1	0.01396	0.96	2.03
E–P(67/33)	0.3	9,835,800	65.4	0.08258	1.02	2.31
E–P(50/50)	0.1	2,462,100	67.2	0.01230	0.97	1.98
E–P(35/65)	0.1	56,220	57.3	0.00473	0.91	1.76
			Equation (10)			
E–P(67/33)	0.1	1,413,000	63.6	0.01997	1	2
E–P(67/33)	0.3	9,066,000	65.8	0.06825	1	2
E–P(50/50)	0.1	3,339,700	67.2	0.01663	1	2
E–P(35/65)	0.1	129,290	57.5	0.01033	1	2

ticular, and according to the solubility results (Fig. 2), major differences occur when the phenolic resin is added in excess.

Figures 7 and 8 show a comparison of the experimental and predicted values of β and $d\beta/dt$ versus time for the system E/P = 1 with 0.1% TPP. The figures show agreement between experimental and calculated data for the rheological conversion, as well as for the derivative with respect to time. Similar results for E/P ratios 0.5 and 0.25 were also obtained.

In spite of the simplicity of the model and the fact that it was derived from rheological properties, the trends observed for the kinetic parameters closely match previously reported calorimetric studies.[2,33] The activation energy varies with the stoichiometric ratio but is almost independent of the catalyst concentration. The effect of this last variable appears in values of the pre-exponential factor. The agreement between previous calorimetric measurements and the rheology study presented here derives from the relation that exists between the measured modulus and the growing density of crosslinks during the curing reaction. This in turn is related to the growing conversion of the system. The rate of increase of the material modulus accelerates after the gel point, and the model follows this rapid change accurately. Thus, the model may be useful for predicting the development of mechanical properties of the material, which can be utilized to determine piece demolding times.

CONCLUSIONS

The curing process of an epoxy–phenolic matrix can be followed by the changes in the rheological behavior of the crosslinking system. The knowledge of the polymerization kinetics is critical when the knowledge of the rate of development of the network structure is needed to control the process.

The criteria of using the crossover of G' and G'' to determine the gel time is a simple technique, which

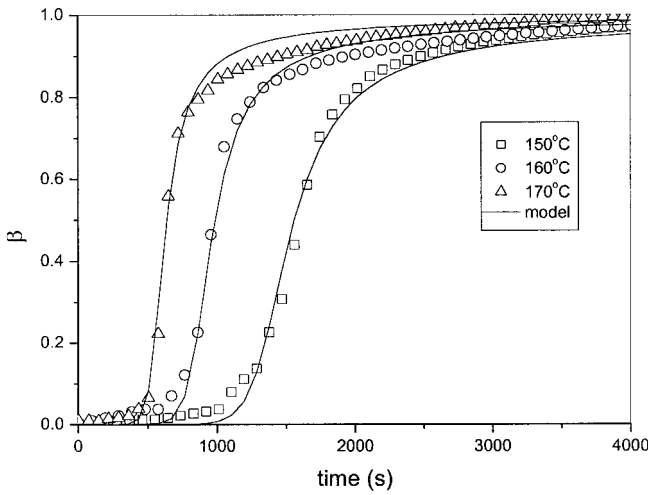

Figure 7 Comparison of experimental and predicted value of β versus time for the system E–P (67/33) with 0.1% of TPP.

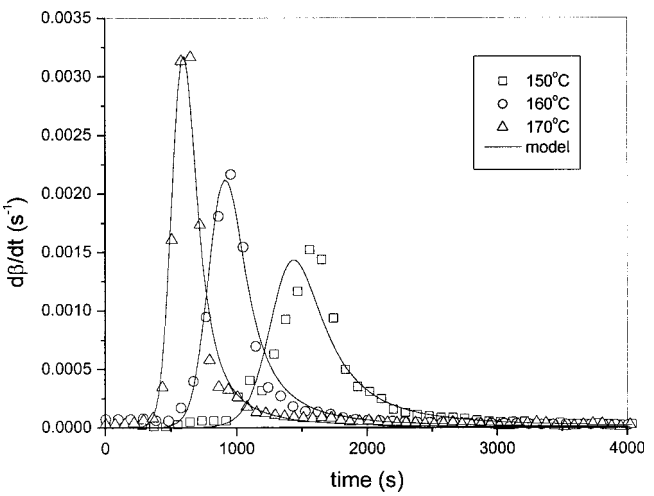

Figure 8 Comparison of experimental and predicted value of $d\beta/dt$ versus time for the system E–P (67/33) with 0.1% of TPP.

resulted consistent with the criteria developed by Winter and the wire/tube technique for this particular system and accepting the small time differences existing between the different techniques. The simplicity of the crossover technique makes it the chosen one for this particular system. On the other hand, the use of wire/tube technique is validated as a simple method to measure gel time if expensive rheometers are not available.

An autocatalytic model used to fit the normalized storage modulus development, yielded predictions that agree very well with the experimental results. This simple phenomenological model predicts successfully the rapid acceleration of the G' increase (β conversion) around the gel point, even at different curing temperatures and with a single set of kinetic parameters. The model can be used in similar systems as a processing tool to calculate the time at which the modulus of the material is high enough to allow handling without piece deformation. The activation energy values are consistent with the values calculated from gel times.

Understanding and predicting the kinetics of these materials is of practical interest both in the manufacturing process and in end-product performance and reliability.

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