

Kinetics Modeling of a Modified Epoxy–Amine Formulation Cured by Thermal and Microwave Energy

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ABSTRACT: The reaction kinetics of a rubber-modified epoxy formulation cured by microwave or thermal energy were investigated. Two phenomenological models were developed to predict the time and temperature dependence of the conversion for the neat and the modified systems. Good agreement was observed between the kinetic models and experimental results generated by chromatographic and calorimetric techniques. The same kinetic behavior was observed whatever the curing process (conventional or microwave heating). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 543–552, 1998

Key words: kinetics; modeling; microwave; phase separation; epoxy–amine

INTRODUCTION

Epoxy resins are nowadays widely used for composite materials in industry where properties such as high modulus, low creep, and reasonable elevated temperature performance are required. This extensive use of epoxy resins has resulted in an increased interest in modeling their processing. With a good model it is possible to predict how the system will behave during curing and what its final properties will be. However, the chemistry involved in the epoxy curing process is rather complex so that developing the models always involves certain assumptions and approximations.

The rather high levels of crosslinking required in epoxy networks to obtain satisfactory properties lead to brittle materials. The incorporation of a reactive rubber that phase separates upon curing in the epoxy network has often been used as

a way to improve the toughness of epoxy resins.^{1–3} The replacement of rubbers by thermoplastics such as polyethersulphone (PES) or polyetherimide (PEI) was developed in the 80s.⁴ This extra component, reactive rubbers or thermoplastics, called the modifier, is initially miscible with the resin and the curing agent. Reaction-induced phase separation is caused by the reduction of solubility due to the increasing average molar mass of the polymer. Phase separation starts *in situ* at the “cloud-point” conversion and when the matrix gels, this primary separation is practically finished.^{5,6} After gelation, a secondary phase separation may continue inside the dispersed phase.

The mechanical properties of the final heterogeneous material are reported to be affected by the type and content of the modifier and the curing agent, the solubility parameter of the modifier, its end group, and the cure temperature.⁷ Recently, microwave processing of polymers and polymer composites has been studied as an alternative to conventional thermal processing.^{8–11} Microwaves, offering a large range of heating rates compared to conventional heating, appear to be an

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useful way of varying the cure schedule. During microwave curing process energy is directly supplied inside the materials allowing more efficient and faster heating. The smaller the thermal conductivity of the system, the more efficient heating from microwave energy is because of low thermal transfers occurring with the external medium.

Hence, to investigate the influence of the cure schedule on the resulting morphology of a rubber-modified epoxy-amine system, the first step of this study is to understand the kinetic behavior of such systems cured in a microwave apparatus and then to identify the beginning of the phase separation and gelation. We will first study the kinetics of the reaction of the neat system DGEBA-DDS and the ETBN-modified system during a conventional heating cure cycle. Two phenomenological kinetic models will be proposed to calculate the extent of reaction from any time-temperature cycle. Then a similar study with a microwave circuit will be conducted with the aim of comparing epoxy-amine reaction rates in these two curing methods. Model prediction and experimental values of the reaction extent will be compared to check the validity of the models in the case of a microwave curing process.

EXPERIMENTAL

Materials

The epoxy formulation investigated consisted of the diglycidyl ether of bisphenol A (DGEBA) epoxy resin (DER 332, Dow Chemicals) and 4,4'-diaminodiphenylsulfone (DDS, Aldrich) curing agent. The reactants were used as received with a stoichiometric ratio (aminohydrogen over epoxy functions) $a/e = 1$.

The rubber used in this work was an epoxy terminated butadiene-acrylonitrile random copolymer (ETBN). The latter was prepared by reacting the carboxyl groups of a CTBN with an excess of DGEBA, in the presence of triphenylphosphine as a catalyst, as earlier described.¹² CTBN used was Hycar 1300 × 13 (Goodrich) with a 26% acrylonitrile content and a COOH functionality of 1.8. Chemical structures of the different components are shown in Figure 1. The weight percentage of rubber introduced in the modified system was 15% with respect to the total weight of the mixture. DDS had to be mixed with DGEBA at 135°C until a clear solution was obtained; ETBN was added at the same time. A low part of the

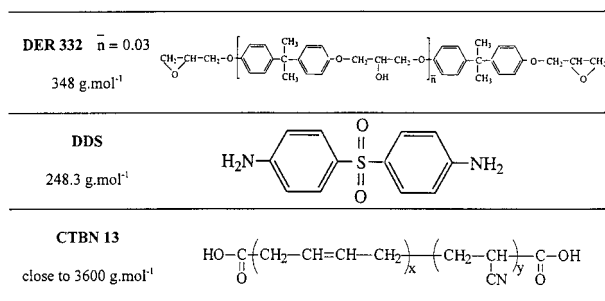


Figure 1 Chemical structures of the components used in the formulations.

epoxy-amine reaction occurred during mixing, this initial conversion was evaluated by chromatographic measurements. For the samples elaborated for the thermal processing, the initial conversion is equal to 3% for the DGEBA/DDS system and to 5% for the DGEBA/DDS/ETBN system. For the samples elaborated for the microwave processing, the initial conversion is equal to 5% for the DGEBA/DDS system and to 8% for the DGEBA/DDS/ETBN system. As a result of this epoxy-amine reaction the initial concentration of hydroxyl groups is no longer equal to zero, and this needs to be taken into account in the kinetics modeling in the case of a mechanistic study.

The mixture was then poured in a PTFE mold (12.5 g) for the microwave processing or in glass vials (500 mg) for the kinetic study realized with conventional heating.

Processing

Thermal Processing

The kinetic studies during the isothermal cure were conducted in a regulated oil bath at various temperatures ($T = 155$ and 180°C). A thermocouple (K type Chromel-Alumel) was introduced into a sample to record the *in situ* temperature during the cure. Samples were removed from the bath and quenched at set time intervals then analyzed by chromatography and calorimetry. Ramp-curing experiments were performed by means of DSC as will be explained later.

Microwave Processing

The cure with microwave heating was conducted in a rectangular oversized waveguide in which the propagation mode remains TE_{01} , at a 2.45 GHz frequency. The temperature inside the sample was monitored by a Luxtron Model 755 fluoroptic

thermometer to the nearest 1°C. The PTFE container was set into a PE honeycomb structure whose function is to insulate the sample and to ensure the polymer mixture was in the area where the electric field is maximal. The largest dimension of the container is parallel to the electric field vector; its width is parallel to the wave path.

The initial power applied to the system applicator sample was 100 W, then when a 170°C temperature has been reached, a computer controlled the power to automatically maintain a constant temperature of 190°C. Different samples were cured for different set times, ranging from 0 to 3 h, after which they were removed from the applicator and quenched to avoid further curing.

Techniques

Size exclusion chromatography (SEC) was employed to follow the extent of reaction of the two systems up to gelation. A Waters apparatus was used with double detection (UV at $\lambda = 254$ nm and a differential refractometer). The elution solvent used was tetrahydrofuran (THF) and the separation was carried out on two styrene-divinyl benzene columns (Macherey-Nagel) with a flow rate of 1 mL min⁻¹. The extent of reaction, x , was determined by following the epoxy monomer disappearance. If the lack of substitution effect is assumed, the conversion in epoxy functions x is given by eq. (1):

$$x = 1 - \left(\frac{h_t}{h_0} \right)^{1/2} \quad (1)$$

where h_t/h_0 is the ratio of the actual height of the DGEBA peak on the chromatogram with respect to the initial one.

Differential scanning calorimetry (DSC) analyses were conducted using a Mettler TA3000 apparatus in an argon atmosphere. DSC was used on one hand to estimate the degree of conversion of DGEBA-DDS samples by measuring the glass transition temperature, T_g , at a heating rate equal to 10°C/min. T_g was correlated to x with the reevaluated DiBenedetto equation,¹³ which gives a convenient relationship between the extent of reaction x and T_g :

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad (2)$$

where T_{g0} and $T_{g\infty}$ are, respectively, the glass transition of the unreacted monomers ($x = 0$), the one of the fully cured network ($x = 1$), and $\lambda = \Delta C_{p\infty} / \Delta C_{p0}$,¹⁴ where $\Delta C_{p\infty}$ and ΔC_{p0} are, respectively, the isobaric capacity changes of the fully reacted network and the initial unreacted mixture. The values of T_g were taken at the onset of the glass transition. Parameters involved in eq. (2), for the system DGEBA-DDS, refer to the work of Girard-Reydet et al.,¹⁵ conducted in the INSA laboratory, and are

$$T_{g0} = -7^\circ\text{C}, \quad T_{g\infty} = 214^\circ\text{C} \quad \text{and}$$

$$\lambda = \Delta C_{p\infty} / \Delta C_{p0} = 0.35$$

The DiBenedetto equation cannot be used any more to evaluate the conversion of epoxy group in the rubber-modified system because the material exhibits a two-phase structure and, therefore, two glass transition temperatures: T_{gR} , at low temperature, is due to the rubbery nodular structure, and T_{gM} , at high temperature, is due to the glassy epoxy matrix. As the phase separation is not total a part of the ETBN rubber remains soluble in the epoxy matrix, thus lowering the value of $T_{g\infty}$. As a result, conversions of the modified system were measured only by SEC, that is to say, before gelation.

Also, DSC was used to develop a kinetic model by measuring the heat flux as a function of time and temperature.

The time when phase separation began (i.e., the cloud-point conversion for a particular sample and cure cycle), was recorded with a light transmission device previously described.¹⁶ Phase separation was observed by the change of the transmitted and scattered light intensity. This method, using light in the visible band, characterizes the start of phase separation as the time when the dispersed particles have a diameter of about 1 μm .

Samples were removed from the cloud-point apparatus and quenched to permit the determination of the cloud-point conversion x_{cp} by SEC.

Among the different techniques allowing dielectric measurements, the method known as "small perturbation of a resonant cavity" is probably the most accurate.¹⁷ In this method the perturbations caused by a sample to frequency and amplitude of cavity electromagnetic resonance are compared to standards to determine its complex permittivity. The cavity resonant frequency tracking is obtained by frequency tuning instead of the mechanical adjustment generally used. To

carry out this frequency tracking, a microcomputer continuously monitors the microwave frequency applied to the cavity, in a closed loop circuit, by measuring at regular intervals the cavity perturbations with a fast frequency sweep (50 ms) around the resonance maximum. These perturbations are compared to standards (aliphatic alcohols from methanol to decanol, water, or more convenient solid standards) to determine the dielectric constants ϵ' and ϵ'' of the sample. Because of the dependence of dielectric constants on temperature, the sample temperature is fixed precisely (see Fig. 7).

RESULTS AND DISCUSSION

Thermal Processing

The curing reactions of epoxy-amine systems have been widely investigated, and several rate expressions have been proposed in the literature.^{15,18–25} Two principal reactions take place: the reaction of the primary amine hydrogen with the epoxy group (k_1 and k'_1) and the reaction of the secondary amine hydrogen with the epoxy group (k_2 and k'_2). The epoxy-amine reaction appears as a competition between a catalytic (k_1 and k_2) and a noncatalytic (k'_1 and k'_2) mechanism. The etherification reaction does not occur in a system such as a stoichiometric DGEBA/DDS mixture.^{15,26}

Kinetics Modeling

Because the purpose of this work was not to account for the epoxy-amine reaction mechanisms but to allow us to predict the evolution of the conversion during the microwave processing by measuring only the *in situ* temperature, a phenomenological approach to modeling the cure of the neat and ETBN-modified DGEBA-DDS systems was considered. Furthermore, a mechanistic study in the case of the modified system is complex because of the reaction-induced phase separation. It involved performing calorimetric measurements assuming that the DSC signal (dH/dt) is proportional to the rate of conversion (dx/dt). Because the materials cured by microwave heating undergo a nonisothermal history, DSC experiments were carried out in scanning mode at five different heating rates within a range 5–12°C/min, as

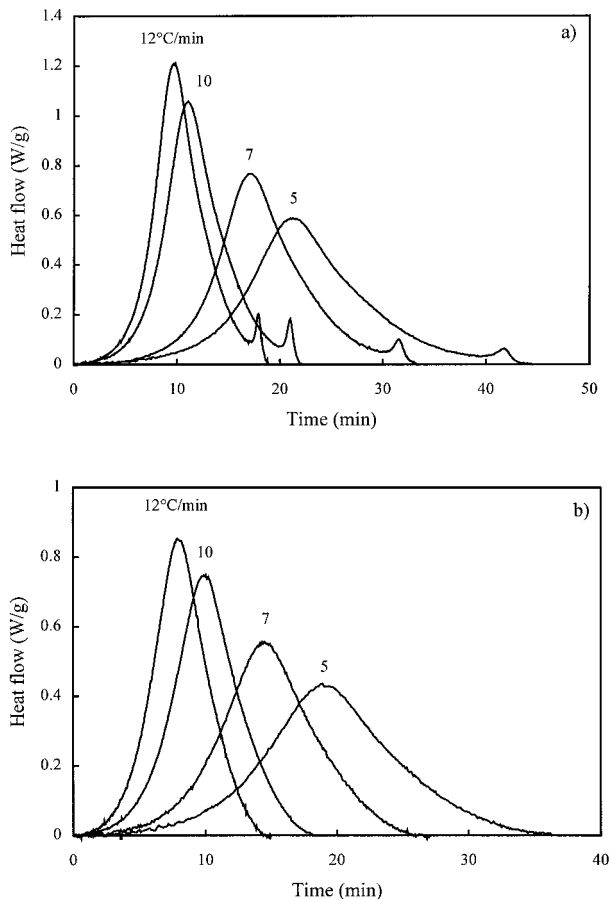


Figure 2 Heat flow measured by DSC during cure at constant heating rates: 5, 7, 10, and 12°C/min for DGEBA-DDS (a) and DGEBA-DDS-ETBN (b).

shown in Figure 2. The DSC signal of the neat formulation presents a small peak at the end of the reaction [Fig. 2(a)]. The corresponding heat production is negligible and represents about 1% of the total reaction heat. A study conducted by Wei et al.²⁷ on the DGEBA-DDS system exhibits the same result. This peak is unassigned and was not taken into account in calculations. The fact that it is not observed for the ETBN-modified formulation is derived from the low temperature shift of the reaction peak.

For kinetic studies by means of DSC, the following expression is applied:

$$\frac{dx}{dt} = \frac{1}{\Delta H} \cdot \frac{dH}{dt} \quad (3)$$

where ΔH is the total heat production generated to reach full conversion.

The phenomenological model used in this article,

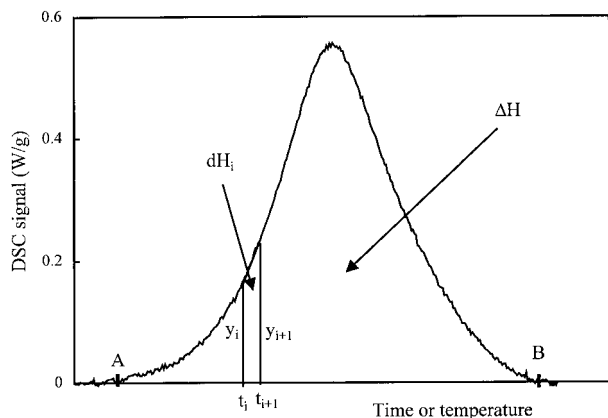


Figure 3 Method of determination of the conversion from DSC data.

which is also widely used in the literature for epoxy systems,^{28–33} has been developed by Kamal and Sourour.^{34,35} The rate of conversion and the extent of reaction x are related to one another as follows:

$$\frac{dx}{dt} = (K + K'x^m)(1 - x)^n \quad (4)$$

where the sum of m and n represents the overall reaction order.

The rate constants K and K' depend on temperature according to an Arrhenius law:

$$K = k \exp\left(\frac{-E}{RT}\right) \quad (5)$$

$$K' = k' \exp\left(\frac{-E'}{RT}\right) \quad (6)$$

Figure 3 explains the method that allowed us to determine the conversion from the DSC data.

ΔH was calculated by making the summation from A to B of dH_i (trapezoidal area). ΔH has been found to be 440 ± 20 J/g for the neat formulation and 300 ± 25 J/g for the ETBN-modified system, taking into account the initial conversion of epoxy groups. The total heat production obtained for the neat system shows a good agreement with the results of Horie and al.,²¹ Kamal and Sourour,³⁵ or Klute and Viehmann³⁶ for epoxide cured with primary amines. In the case of the modified formulation, the measured value of ΔH (83 kJ/ee) is somewhat lower than the theoretical value but has been proved to correspond to a com-

plete reaction. Two more scans were performed for every heating rate to ensure that the glass transition temperature of the sample has reached its maximal value, i.e., that the reaction is complete at the end of the first scan.

The inaccuracy (± 25 J/g) of the value of ΔH is not a real problem, because for every heating rate the calculated areas are normalized by the associated total reaction heat ΔH . The reaction is complete when the DSC signal reaches its initial value again and the ratio

$$\sum_A^B dH_i / \Delta H$$

always equal 1.

The experimental function $x(t)$ is determined, for the five heating rates, from eq. (3).

For elaborating the phenomenological models, eq. (4) was solved with a four-order Runge Kutta integration technique. The values of time and temperature used here are those previously measured during the DSC experiments. Fitting the theoretical prediction and experimental $x(t)$ function (Fig. 4) allowed the kinetic parameters k , k' , E , E' , m , and n to be determined. This fitting was realized by minimizing the sum

$$\sum (x_{\text{theor}} - x_{\text{exp}})^2.$$

In Table I are summarized the final results of the fitting. Because the exponents m and n found are not integers, no physical meaning will be assigned to them.

Isothermal cures (at 155 and 180°C), in the range of temperature used in microwave experiments, were also conducted. On both systems, the models turned out to agree well with experimental SEC and/or DSC results, as shown in Figure 5. These models will allow the extent of reaction during the microwave processing to be estimated.

Influence of ETBN Rubber on Kinetics

The evolution of the epoxy conversion, measured by SEC and/or DSC, as a function of the time of reaction at 180 and 155°C, is plotted in Figure 5 for the neat and the modified systems. At 180°C there is no significant difference between the evolution of conversion with time except that it appears that the sigmoidal curve, characteristic of an autocatalytic mechanism, is no longer observed in the modified system. The higher values of con-

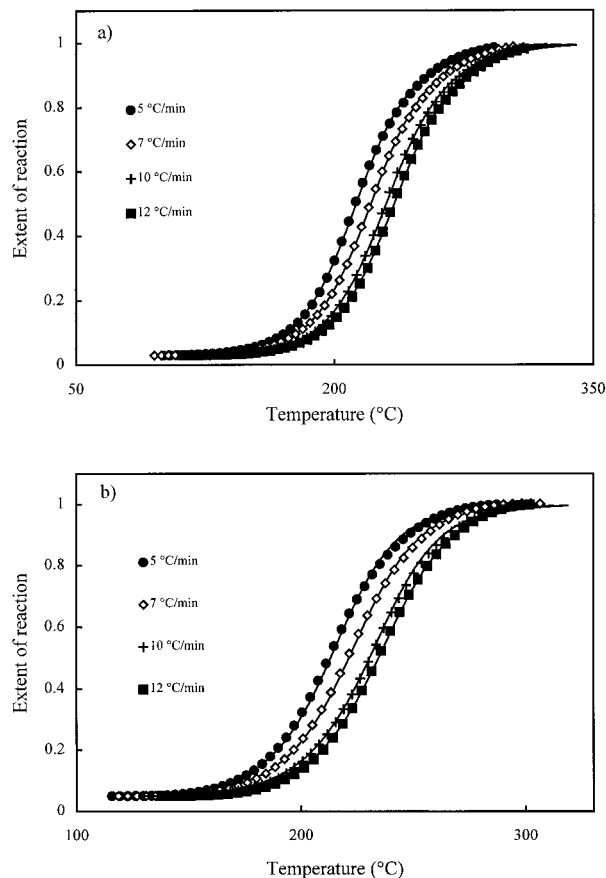


Figure 4 Experimental data of dynamic measurements (symbols) and calculated extent of reaction (—) for DGEBA–DDS (a) and DGEBA–DDS–ETBN (b).

version observed for the modified system during the first 3 min of the reaction are only due to the difference between the initial conversion of our two systems (3% for the neat system and 5% for the modified system, as explained in the Experimental Section). At the beginning of the reaction, a linear increase in the conversion with time is noticed for the modified system cured isothermally at 180°C. However, at a lower temperature (i.e., 155°C) an autocatalytic behavior is slightly observed.

At a given time of the reaction, the conversion is always lower for the formulation with ETBN.

Table I Kinetics Parameters

System	k (s ⁻¹)	k' (s ⁻¹)	E (kJ/mol)	E' (kJ/mol)	m	n
Neat	3.78×10^8	5×10^2	105	46.9	0.81	1.84
15% diluted	3.19×10^8	3.51×10^2	105	46.9	0.81	1.84
Modified	7.34×10^9	5×10^2	118	46.8	0.87	1.57

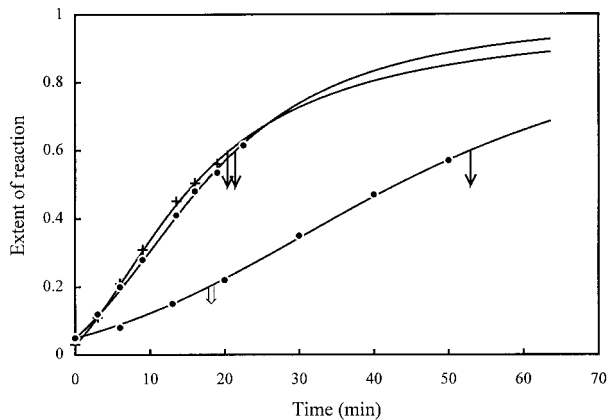


Figure 5 Experimental epoxy conversion versus reaction time at 180°C and/or 155°C for DGEBA–DDS (+) and DGEBA–DDS–ETBN (●). Lines represent the models prediction and arrows indicate gelation (↓) and cloud point (⊥).

This fact is not surprising, as the content of epoxy groups is lower by 15% by mass in the modified system. The kinetic equation can be expressed as a function of the concentration of epoxy groups $[e]$ and of hydroxyl groups $[OH]$ as follows:

$$-\frac{d[e]}{dt} = (\alpha + \alpha'[OH]^m)[e]^n \quad (7)$$

where α and α' are the kinetic constants of the model considering only a dilution effect.

The epoxy conversion is given by

$$x = \frac{[e]_0 - [e]}{[e]_0} = \frac{[OH]}{[e]_0} \quad (8)$$

where $[e]_0$ is the initial concentration of epoxy groups.

The relations between the constants K , K' and α , α' are

$$K = [e]_0^{n-1} \alpha \quad (9)$$

$$K' = [e]_0^{m+n-1} \alpha' \quad (10)$$

If the addition of the ETBN rubber modifier only leads to a dilution of reactive functions, the temperature dependence of the neat system and of the diluted system must be the same.

The parameters k and k' of the kinetic model described previously for the neat system [eqs. (5) and (6) and Table I] can then be corrected by a dilution factor f equal to the ratio of the initial concentration of epoxy groups in the modified formulation with respect to the initial concentration of epoxy groups in the neat one. The ratio f can be expressed as a function of Φ_w (the mass fraction of the additive) and ρ_N , ρ_M (the densities of the neat and the modified system respectively) by

$$f = \left(1 + \frac{\Phi_w}{1 - \Phi_w} \frac{\rho_N}{\rho_M} \right)^{-1} \quad (11)$$

where $\Phi_w = 0.15$, $\rho_N = 1.23$ and $\rho_M = 0.96$ leading to $f = 0.816$.

The new parameters k_d and k'_d (Table I) obtained are correlated with the parameters k and k' as follows:

$$\frac{k_d}{k} = f^{n-1} \quad (12)$$

$$\frac{k'_d}{k'} = f^{n+m-1} \quad (13)$$

where m and n are the exponents of eq. (4).

Equations (12) and (13) allow us to plot (Fig. 6) the theoretical curve $x = f(t)$ of a 15% diluted DGEBA–DDS system cured at 155 and 180°C. When the system has reached a conversion of about 30%, the experimental values of conversion are higher than what can be predicted by only taking into account a dilution effect of the reactive functions. At this step of the reaction the ETBN-modified system have phase separated and its kinetics are no longer the same as in the neat formulation. This augmentation may be due to the higher concentration of reactive functions in the continuous phase. The influence of rubber on kinetics of epoxy–amine systems is a little controversial in the literature. A higher reactivity at the first stages of the reaction has been observed by Verchère et al.¹² with the system DGEBA–3DCM–ETBN compared to the neat system DGEBA–3DCM. Verchère et al.¹² incorporate a dilution effect in their modeling while wondering whether the dilution effect has a physical sense after phase separation.

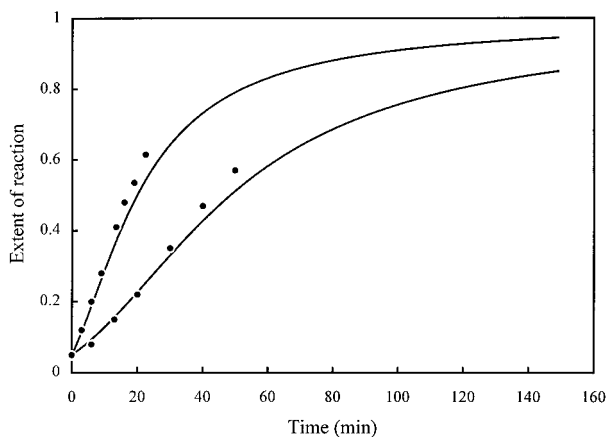


Figure 6 Experimental epoxy conversion versus reaction time at 180°C and/or 155°C for DGEBA–DDS–ETBN (●) and theoretical conversion (—) in the case of a simple effect of dilution of reactive functions.

A gel conversion x_{gel} equal to 60% for the neat formulation was found in perfect agreement with the mean field theory. The same value was measured in the case of the rubber-modified formulation.

The cloud point is observed for a conversion x_{cp} and a reaction time of 17 min for the system cured at 155°C. The value of x_{cp} , measured by SEC, can be compared with the one given by the kinetic model described previously. This model is valid because it leads to a cloud-point conversion equal to 20%. For the curing temperature of 180°C, cloud point occurs before the sample has reached 180°C. For this reason, no experimental value of x_{cp} can be given for this curing temperature.

Microwave Processing

The present section intends to compare the kinetic behavior of the DGEBA–DDS and DGEBA–DDS–ETBN systems cured by thermal and microwave energy. The time–temperature history of samples cured by microwave heating were used in the kinetic models reported previously [eq. (4)] to account for the kinetic behavior of our systems during a conventional curing.

The capability of a polymer thermoset to absorb microwave energy is highly conditioned by its dielectric constants ϵ' and ϵ'' . A high value of ϵ' will indeed lead to a high concentration of the electric field in the sample and the absorption of microwave energy is proportional to the value of ϵ'' . Nevertheless, the consequence of high ϵ' is also an important fraction of the applied power

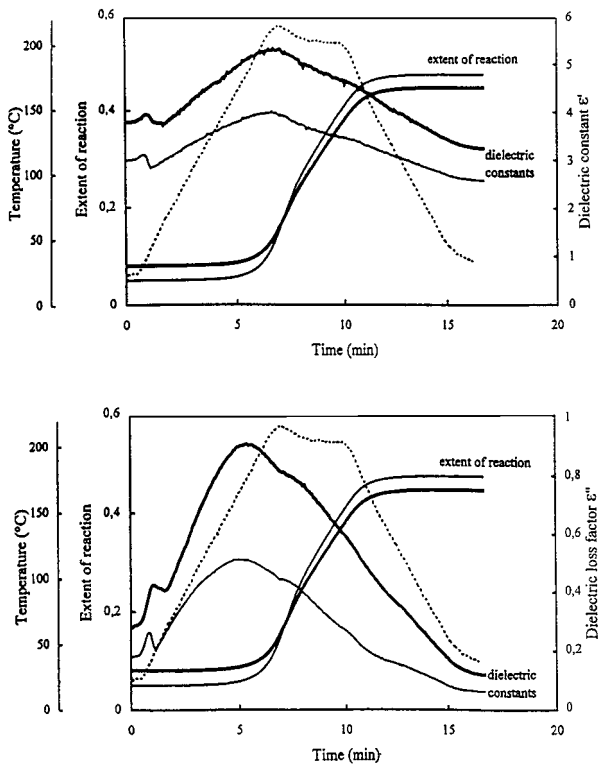


Figure 7 Dielectric constants, calculated extent of reaction versus time for DGEBA-DDS (—) and DGEBA-DDS-ETBN (—). Dotted line represents the sample temperature.

that is reflected, that is to say, a low absorbed power. The knowledge of the variations and the amplitude of the dielectric constants of our systems is a first approach to their microwave processing.

The recordings of ϵ' and ϵ'' and T during cross-linking were performed as a function of time and transformation, as shown in Figure 7. The time-temperature profile undergone by the samples during these dielectric experiments was used in the kinetic models described in this article and gave the evolution of the reaction extent during the experiment. A short plateau (200 s) at 200°C allows further curing of the system until the conversion reaches respectively 48 and 45% for the neat system and the modified system. For an identical cure cycle, the conversion is lower for the modified system. This result is in agreement with our previous observations (Fig. 5).

The small deviation at the beginning of the dielectric curves corresponds to a change of shape of the mixture as its viscosity decreases. During the first temperature ramp, dielectric constants increase with temperature. This increase of ϵ'

and ϵ'' corresponds to a constant conversion equal to the initial conversion. At this stage the temperature is the only parameter that influences the dielectric constants. A maximum is observed for ϵ' because the temperature stops to increase. The extent of reaction increases during the temperature plateau leading to the decrease of ϵ' . ϵ'' exhibits a maximum at 152 and 167°C, respectively, for the neat and modified formulation, while the conversion remains constant. At the end of the experiment, when the temperature is the same as at the beginning, lower values of ϵ' and ϵ'' are measured. It shows the influence of the reaction extent on the dielectric behavior.

The elimination of the time parameter allows the characterization of the change of ϵ' and ϵ'' with temperature directly, as shown in Figure 8. The introduction of ETBN into the epoxy network leads to higher dielectric constants, due to the introduction of the polar group —CN from the acrylonitrile. It is interesting to compare the temperature dependence of ϵ' and ϵ'' and the heating rate of both systems.

The time-temperature and time-power profiles used for kinetic studies with microwave energy are shown in Figure 9. Moreover, the neat system, which has lower dielectric constants than the modified system, has a higher heating rate. The total reaction heat for the neat system is higher than for the modified system. It seems that, for the systems studied in this article, the influence of the heat produced by the reaction on the heating rate predominates over the influence of the capability of the systems to absorb the microwave energy.

The fraction of the applied power that is ab-

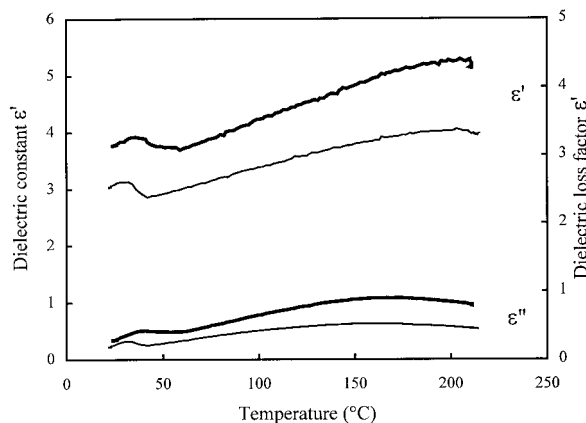


Figure 8 Dielectric constants as a function of temperature (and transformation) for DGEBA-DDS (—) and DGEBA-DDS-ETBN (—).

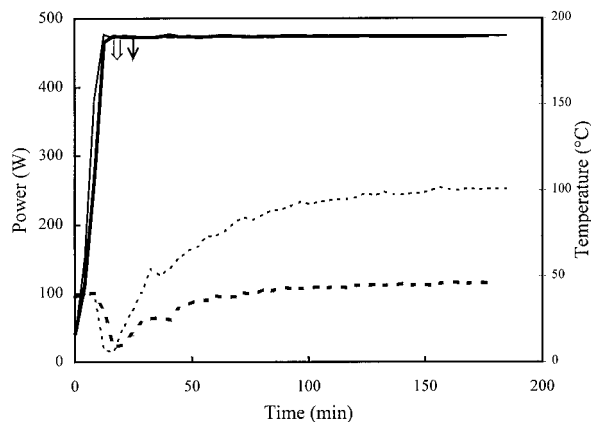


Figure 9 Time-temperature (solid line) and time-power (dotted line) profiles for DGEBA-DDS (—) and DGEBA-DDS-ETBN (---). Arrows indicate the localization of gelation (\downarrow) and cloud point (\downarrow).

sorbed by the polymer decreases as the extent of reaction increases (as the dielectric constants decrease). This is why the power undergoes a gradual increase during the temperature plateau. As may be seen in the Figure 9, the applied power necessary to maintain the temperature constant, is higher for the neat system. Moreover, the value of ε'' is lower for the neat system than for the modified system, and then the neat system leads to a lower fraction of the applied power that is absorbed.

Figure 10 shows the conversion, determined experimentally, of both systems cured by microwave energy and compared with the model prediction [eq. (4)] in the case of conventional heating. The conversion remains constant during the first 10 min of the cure and then increases drastically between 10 and 50 min. Then the reaction rate decreases because of vitrification that arises when the glass transition temperature, T_g , of the mixture becomes equal to the curing temperature, namely for a 96% conversion with DGEBA-DDS cured at 190°C.

For the neat and the modified systems, gelation occurs for a conversion of about 60%, in good agreement with the values previously measured for conventional curing. An *in situ* determination of gelation and cloud-point conversion x_{cp} was not possible. The time-temperature profile used in the microwave curing process is reproduced in the cloud-point apparatus. A value of x_{cp} equal to 26% is measured. A close value of 28% is obtained by simulation. Both gelation and phase separation occur during the temperature plateau (Fig. 9) and are separated by 35% of reaction extent.

To the extent that a little part of reaction continues during the quenching, it may be assumed that measured conversions are close to calculated ones, using the kinetic models developed for a conventional way of curing. Agreeing well with the study conducted by Mijovic et al.^{11,37} on the DGEBA-MDA system, or Jordan et al.¹⁰ on the DGEBA-3DCM system, the kinetic behavior of the neat DGEBA-DDS system are the same whatever the cure process used. Moreover, the same conclusion has been reached on the DGEBA-DDS-ETBN system in which phase separation occurs upon curing.

CONCLUSION

Kinetic studies were conducted to compare the behavior of the epoxy-amine DGEBA-DDS and the ETBN-modified systems during a cure using microwave or thermal heating. A phenomenological approach allowed us to propose two kinetic models that fitted the experimental results perfectly. It was also demonstrated that the kinetics of the modified system could not be described by considering only a dilution effect due to the ETBN rubber. Measured conversions of samples cured by microwave energy were compared with the model predictions and found to be independent of the curing method. For our experimental microwave conditions, both phase separation and gelation occurs during the temperature plateau for the system DGEBA-DDS-ETBN. To be able to vary the morphology generated by different cure

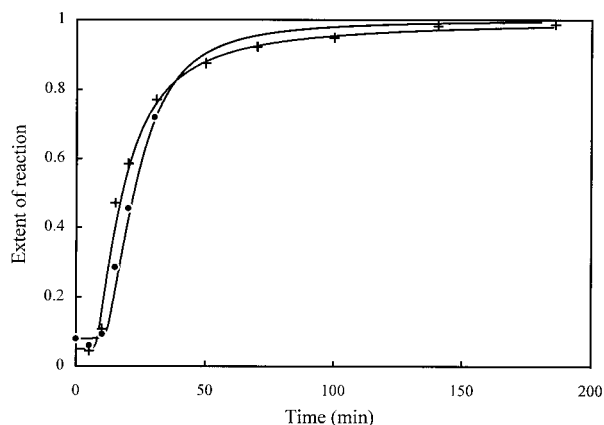


Figure 10 Conversion versus time for DGEBA-DDS (+) and DGEBA-DDS-ETBN (●) samples cured by microwave heating. Lines represent the models prediction.

cycles, it would be probably more efficient to use a system for which phase separation occurs during the heating ramp. The variation of the heating rate would then lead to the variation of the time during which the morphology could develop. With such a procedure we expect to be able to generate different sizes of dispersed particles when applying a different power. This relationship between morphology and microwave curing cycles will be reported in a future article.

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