Morphology of a Linear Polymer-Modified Epoxy-Amine Formulation Cured by Microwave Energy at Different Heating Rates

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ABSTRACT: Microwave energy was used to cure a bisphenol A diglycidyl ether-based epoxy resin with an aromatic diamine curing agent (4,4′-diaminodiphenylsulfone) in the presence of a rubber (epoxy-terminated butadiene–acrylonitrile copolymer) or a thermoplastic (polyetherimide). Because microwaves allow high flexibility in the choice of the cure schedule, samples were cured at different heating rates between 3 and 110°C/min. The morphologies of the systems were studied as a function of the cure schedule. Scanning and transmission electron microscopy and differential scanning calorimetry were used to characterize the generated morphologies. The influence of the heating rate on the particle size distribution, the volume fraction of the dispersed phase, and the composition of both phases are discussed. The generated morphologies were found to be conditioned by the time–temperature profile, no matter what kind of heating was used. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1118–1128, 2001

Key words: phase separation; morphology; microwave; epoxy-amine; rubber; thermoplastic

INTRODUCTION

Epoxy resins are often associated with a rubbery or thermoplastic secondary phase to remedy their inherent brittleness. This extra component, called the *modifier* or the *toughener*, is initially miscible with the resin and curing agent. Reaction-induced phase separation is caused by the reduction of solubility caused by the increasing average molar mass of the polymer. Phase separation starts *in situ* at the cloud-point conversion (x_{cp}), and when the matrix gels, this primary separation is practically finished.[1–2] After gelation, a secondary phase separation may continue inside the dispersed phase. The mechanical properties of toughened formulations depend on the morphology developed during the phase-separation process. Predominant parameters that affect the final morphology include the content of modifier, the reactivity of system, the cure temperature, and the cloud-point viscosity (η_{cp}). Several authors have investigated the influence of the cure schedule on the resulting morphology. Most of the time studies concerned cure temperature.[3–10] Conclusions about the influence of the cure temperature on morphological parameters are rather controversial and include the following:

- Particle size goes through a maximum,[4,7,9] or increases,[3,8,10] as temperature increases.
- The concentration of the dispersed phase decreases,[3–5,8,9] or goes through a minimum,[7] as temperature increases.
- The volume fraction of the dispersed phase (V_D) remains practically constant,[3,6,8–10] increases,[4,7] or decreases[5,10] as the temperature increases.

Some work has been reported on the effect of varying heating rates.[11,12] Fang et al.[12] elaborated on "sandwich" structures caused by the different heating rates between core and layers.

In this work, microwave energy was used to study the influence of the heating rate on the generated morphology. This way of curing offers a large range of heating rates compared with conventional heating. The influence of the initial input power was investigated by Srinivasan et al.[11] with amorphous phenolphthalein-based poly-(arylene ether)-modified cyanate ester networks. By varying both the rates of conversion and the thermoplastic compositions, they generated controlled morphologies. This article is devoted to bisphenol A diglycidyl ether (DGEBA)–4,4′-diaminodiphenylsulfone (DDS)–epoxy-terminated butadiene–acrylonitrile copolymer (ETBN) and DGEBA–DDS–polyetherimide (PEI) systems. In a previous article,[13] the kinetics of the reaction of the neat DGEBA–DDS and ETBN-modified formulations were analyzed for both kinds of heating (conventional and microwave). Two kinetic phenomenological models were proposed. We concluded that the kinetics of reaction were the same when microwaves or conventional heating was used and were only conditioned by the time–temperature profile. This kinetic investigation was very useful because it allowed the localization of the phase-separation process during the cure by microwave energy. The cure kinetics of the PEI-modified system are presented here.

For both ETBN- and PEI-modified DGEBA–DDS systems, phase separation occurred during the temperature plateau. There was only one exception, the rubber-modified formulation cured at 3°C/min. The effect of varying the initial input power under such conditions is discussed.

EXPERIMENTAL

Materials

The epoxy formulation investigated consisted of DGEBA epoxy resin (DER 332, Dow Chemicals) and DDS (Aldrich, Saint Quentin Fallavier, France) curing agent. The rubber used in this study was an epoxy-terminated butadiene–acrylonitrile random copolymer (ETBN13). The rubber was prepared by the reaction of the carboxyl groups of a carboxy-terminated butadiene acrylonitrile copolymer (CTBN13) with an excess of DGEBA in the presence of triphenylphosphine as a catalyst, as earlier described.[3] The CTBN used was Hycar 1300×13 (Goodrich, Brecksville, OH) with a 26% acrylonitrile content and a COOH functionality of 1.8. The thermoplastic modifier employed was a commercial-grade PEI (Ultem 1000) supplied by General Electric (Evry, France). Chemical structures of the different components are shown in Figure 1. The weight percentages of rubber and thermoplastic introduced in the modified system were 15 and 10%, respectively, with respect to the total weight of the mixture.

Formulation and Cure

The reactants were used as received with a stoichiometric ratio (aminohydrogen over epoxy functions) equal to 1. DDS had to be mixed with the other components at 135°C until a clear solution was obtained. In the case of the rubber-modified formulations, ETBN, DGEBA, and DDS were mixed together at 135°C. For the thermoplastic-modified formulations, PEI was first dissolved at 140°C in the epoxy prepolymer. DDS was then added at 135°C. A low part of the epoxy-amine reaction occurred during mixing; this initial conversion was evaluated by chromatographic measurements. The initial conversion was equal to 5% for the DGEBA–DDS–ETBN system and 12.5% for the DGEBA–DDS–PEI system. The initial conversion was much higher because DDS was more difficult to dissolve in the DGEBA–PEI mixture than in the DGEBA–ETBN mixture.

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

For the kinetic study of the PEI-modified formulation, ramp-curing experiments at different heating rates were performed with differential scanning calorimetry (DSC) as previously described.[13]

The cure with microwave heating was conducted in an oversized rectangular waveguide, where the propagation mode remained fundamental transverse electric propagation mode
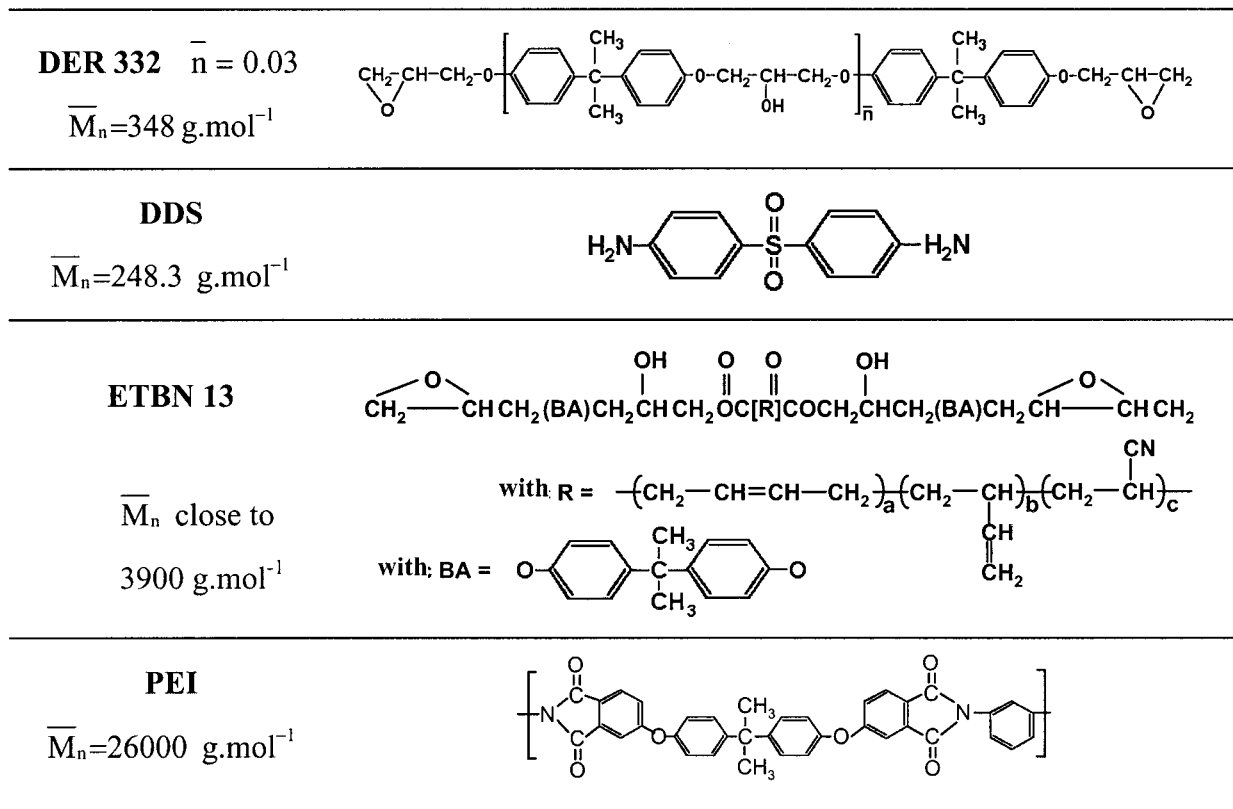
Figure 1 Chemical structures of the components used in the formulations.

(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 polyethylene (PE) honeycomb structure whose function was to insulate the sample and to ensure that the polymer mixture was in the area where the electric field was maximal. The largest dimension of the container was parallel to the electric field vector; its width was parallel to the wave path.

The heating rate was varied by the application of different initial powers ranging from 30 to 240 W. When 170°C was reached, a computer started to control the power to automatically maintain a constant temperature of 190°C.

Determination of the Cloud Point

The time when phase separation began was recorded with a light-transmission device as previously described.[14] Phase separation was observed by the change of the transmitted and scattered light intensity. This method, which uses light in the visible band, characterizes the start of the phase separation as the time when the dispersed

particles have a diameter of about 0.1 μm. Samples were removed from the cloud-point apparatus and quenched to permit the determination of x_{cp} by size exclusion chromatography.

Characterization of Morphologies

The morphologies of the samples were studied by scanning electron microscopy (SEM) or transmission electron microscopy (TEM).

After cooling by liquid nitrogen, samples presenting an initial crack were broken. The fractured surfaces were coated with a gold sputterer and observed by SEM with a Philips XL20 apparatus. The crack trajectory was assumed to go through the equatorial planes of particles.[3] This led to an estimation of higher V_D's and concentrations of dispersed phase particles than were actually present. The region under analysis contained between 100 and 200 particles and was characterized by image-analysis software. Morphological parameters were thus determined as explained hereafter.

Particles of dispersed phases are commonly described in terms of average diameter or V_D's but

Table I Kinetics Parameters

System	k (s^{-1})	k' (s^{-1})	E (kJ/mol)	E' (kJ/mol)	m	n
DGEBA–DDS 10% diluted	3.78×10^8	5×10^2	105	46.9	0.81	1.84
DGEBA–DDS–PEI	3.47×10^8	4.23×10^2	105	46.9	0.81	1.84

E, E': activation energy of the rate constant K and K'.

more rarely in terms of particle size distribution. Different ways can be found in the literature to represent them, including the frequency,[1] the relative frequency,[2,7] or a distribution function.[15] The first two ways require the division of the population of particles into intervals. Consequently, the representation is highly dependent on the number of intervals. For this reason, we used a continuous law to describe the dispersed phase, the normal law also called the *Gauss statistic*.

For each sample, the particle diameters were sorted by increasing order, and a probability was assigned to each diameter. A classical estimator was used to calculate the experimental probability. A quantitative comparison of data requires a fit between the experimental and theoretical values. Good agreement was obtained when the normal law was used.

V_D is given by the following expression:

$$V_D = \frac{\pi}{4} \cdot \frac{\sum nD^2}{S} \tag{1}$$

where n is the number of particles having a diameter D and S is the area of the micrograph region under analysis.

Equation (1) assumes that the volume fraction is an isotropic property; hence, values measured in the plane are the same as in the volume.

The mass fraction of rubber dissolved in the matrix (W_R^M) can be obtained with the Fox[16] equation:

$$\frac{1}{T_g^M} = \frac{(1 - W_R^M)}{T_g^{EA}} + \frac{W_R^M}{T_g^R} \tag{2}$$

where T_g^M, T_g^{EA}, and T_g^R are the glass-transition temperatures of the matrix, the DGEBA–DDS pure network, and the ETBN pure rubber, respectively. If the samples are postcured to achieve full conversion, T_g^{EA} is known and equal to $T_{g\infty}$ of the pure epoxy network; hence, the value of W_R^M may

be obtained. This method is inappropriate with PEI because of equality between its T_g (210°C) and T_g^{EA} (214°C).

Another expression that allows for the determination of W_R^M from DSC experiments was proposed by Couchman:[17]

$$\ln T_g^M = \frac{W_R^M \cdot \Delta C_p^R \cdot \ln T_g^R + (1 - W_R^M) \cdot \Delta C_p^{EA} \cdot \ln T_g^{EA}}{W_R^M \cdot \Delta C_p^R + (1 - W_R^M) \cdot \Delta C_p^{EA}} \tag{3}$$

where ΔC_p^R and ΔC_p^{EA} are the isobaric capacity changes of the ETBN rubber and the DGEBA–DDS system, respectively. ΔC_p^{EA} is a decreasing function of the conversion of the epoxy network.

Through the consideration of the densities ($\rho_R = 0.96$ g/cm^3 of the ETBN rubber, and $\rho_{EA} = 1.23$ g/cm^3 of the DGEBA–DDS network), the volume fraction of rubber dissolved in the matrix (V_R^M) is given by

$$V_R^M = \frac{W_R^M / \rho_R}{W_R^M / \rho_R + (1 - W_R^M) / \rho_{EA}} \tag{4}$$
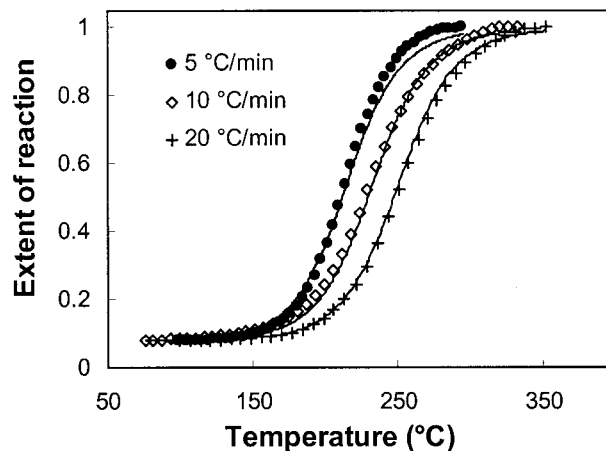

Figure 2 Experimental data of the dynamic measurements (symbols) and calculated extent of the reaction (—) for DGEBA–DDS–PEI.
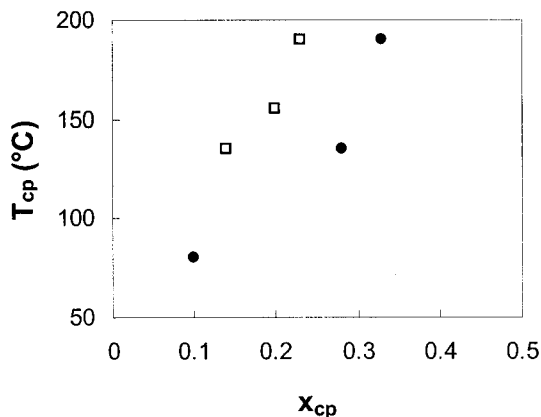
Figure 3 T_{cp} versus x_{cp} for ($\square$) DGEBA–DDS–ETBN and ($\bullet$) DGEBA–DDS–PEI.

Figure 4 Heating rate versus initial input power for ($\square$) DGEBA–DDS–ETBN and ($\bullet$) DGEBA–DDS–PEI.

The initial volume fraction of rubber added to the formulation (V_R^0) can be decomposed as follows:

$$V_R^0 = V_D \cdot V_R^D + (1 - V_D) \cdot V_R^M \qquad (5)$$

The volume fraction of the epoxy network in the dispersed phase (V_{EA}^D) may be obtained by:

$$V_{EA}^D = 1 - V_R^D \qquad (6)$$

RESULTS AND DISCUSSION

Kinetic Study

Because the purpose of this study was to predict the evolution of the conversion during the microwave processing by measuring only the *in situ* temperature, a phenomenological approach to modeling the reaction kinetics was considered. Furthermore, a mechanistic study in the case of the modified system is complex because of the reaction-induced phase separation. Because the materials cured by microwave heating undergo a nonisothermal history, DSC experiments were carried out on DGEBA–DDS–PEI systems in scanning mode at three different heating rates within a range of 5–20°C/min. The DSC signal (dH/dt) was assumed to be proportional to the
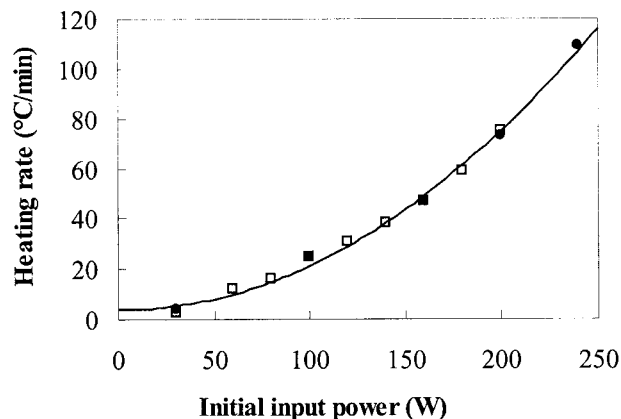
Table II Solubility Parameters, δ, in MPa$^{1/2}$

DGEBA	DDS	ETBN	PEI
20.9	23.2	17.9	22.9

rate of conversion (dx/dt). The total heat production (ΔH) was found to be 105 $\pm$ 5 kJ/mol (of reacted epoxy groups) for the neat formulation[13] and 102 $\pm$ 1 kJ/mol for the PEI-modified system, when the initial conversion of epoxy groups was taken into account. These values show a good agreement with the results of Horie et al.,[18] Kamal and Sourour,[19] and Klute and Viehmann[20] for epoxide cured with primary amines.

Kamal and Sourour[19,21] developed the phenomenological model used here. The rate of conversion and the extent of reaction x are related to one another as follows:

$$\frac{dx}{dt} = (K + K'x^m)(1 - x)^n \qquad (7)$$

where the sum of m and n represents the overall reaction order and K and K' are constants depending on temperature according to an Arrhenius law.

The different parameters of this model were determined for each formulation by the best agreement between the experimental and calculated values of conversion. Further details about the method used and results obtained for the DGEBA–DDS and DGEBA–DDS–ETBN formulations can be found in a previous article.[13]

It has been reported that the introduction of PEI at a low concentration does not affect cure kinetics.[22] Before phase separation, the reaction kinetics of the PEI-modified formulation differ from the neat formulation only because of the dilution of reactive functions.

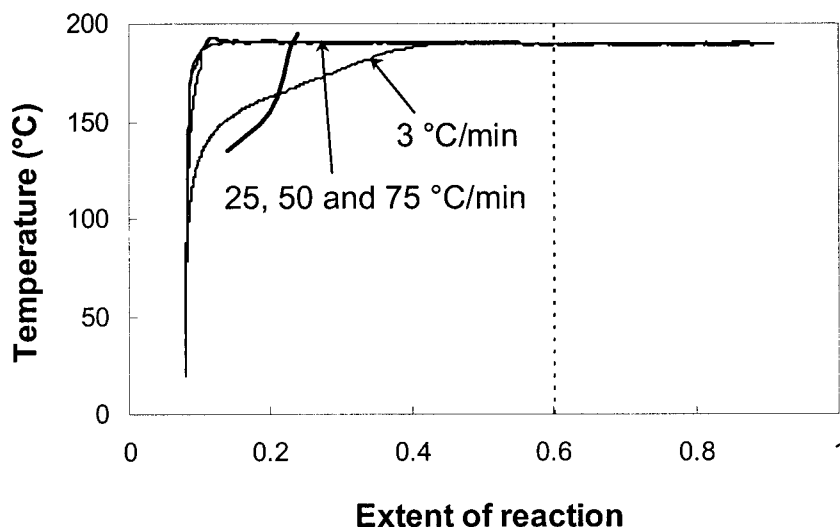This dilution effect can be calculated by expressing the kinetic equation as a function of the

Figure 5 Conversion–temperature profiles undergone by DGEBA–DDS–ETBN samples (microwave heating). The bold and dotted lines are the cloud-point and gelation curves, respectively.

concentrations of epoxy groups and hydroxyl (OH) groups. The pre-exponential factors of K and K' (k and k') of the kinetic model described previously for the neat system [eq. (7) and Table I] can be then 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 and ρ_M (the densities of the neat and the modified system, respectively) by

$$f = \left(1 + \frac{\Phi_w}{1 - \Phi_w} \frac{\rho_N}{\rho_M} \right)^{-1} \tag{8}$$

where $\Phi_w = 0.1$, $\rho_N = 1.23$, and $\rho_M = 1.27$, leading to $f = 0.9$ for the PEI-modified formulation.

The new parameters k_d and k'_d (Table I) obtained were correlated with the parameters k and k' as follows:
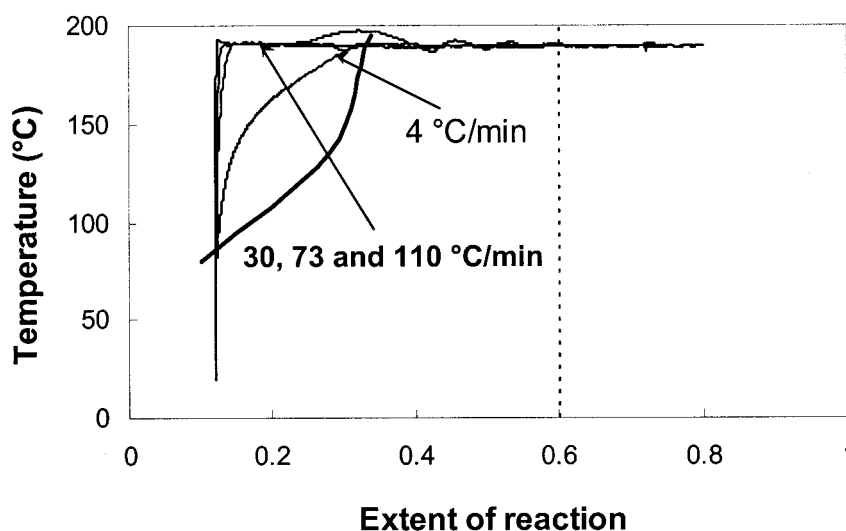
$$\frac{k_d}{k} = f^{n-1} \tag{9}$$

Figure 6 Conversion–temperature profiles undergone by DGEBA–DDS–PEI samples (microwave heating). The bold and dotted lines are the cloud-point and gelation curves, respectively.

Table III x_{cp} and T_{cp}

System	Heating Rate (°C/min)	x_{cp}	T_{cp} (°C)
ETBN-modified	3	0.22	165
	25, 50, 75	0.24	190
PEI-modified	4, 30, 73, 110	0.34	190

$$\frac{k'_d}{k'} = f^{n+m-1} \qquad (10)$$

where m and n are the exponents of eq. (7).

In Table I, the final results of the fitting are summarized, and Figure 2 shows the experimental and calculated curves for the DGEBA–DDS–PEI formulation. The model agrees well with the experimental DSC results. This model allows the extent of reaction during microwave processing to be estimated.

Localization of Phase Separation During Microwave Cure

Phase separation starts at a given extent of the reaction x_{cp} at a cloud-point temperature (T_{cp}).

Figure 3 shows the cloud-point curves of the DGEBA–DDS–ETBN and DGEBA–DDS–PEI systems. The intersection of these curves with the time–temperature profiles realized during microwave curing allowed us to locate phase separation for any profile that was performed with microwave heating. Data obtained from former works in the laboratory were completed by cloud-point measurements (see the Experimental section). Both formulations exhibited upper-critical-solution-temperature behavior; that is, miscibility increased with temperature. This miscibility behavior is most frequently observed. Figure 3 also reveals a higher solubility of the thermoplastic modifier than that of rubber. The difference between the solubility parameter, δ, of the epoxy-amine system and the modifier was indeed much lower for the PEI than for ETBN. Values of the solubility parameters of the different components are given in Table II.

Different initial powers were applied to samples, ranging from 30 to 240 W. In such a way, heating rates ranging from 3 to 110°C/min were obtained. The correlation between initial input power and the heating rate for both systems is presented in Figure 4. Variations were not linear and were about the same for both modifiers.
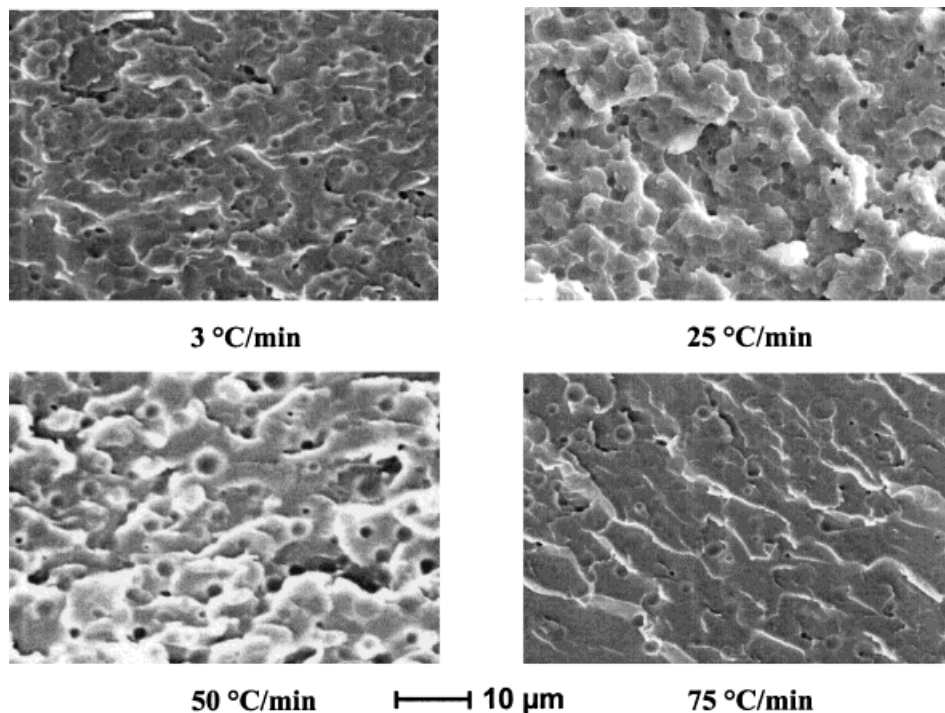

Figure 7 SEM micrographs obtained for DGEBA–DDS–ETBN samples cured at different heating rates.
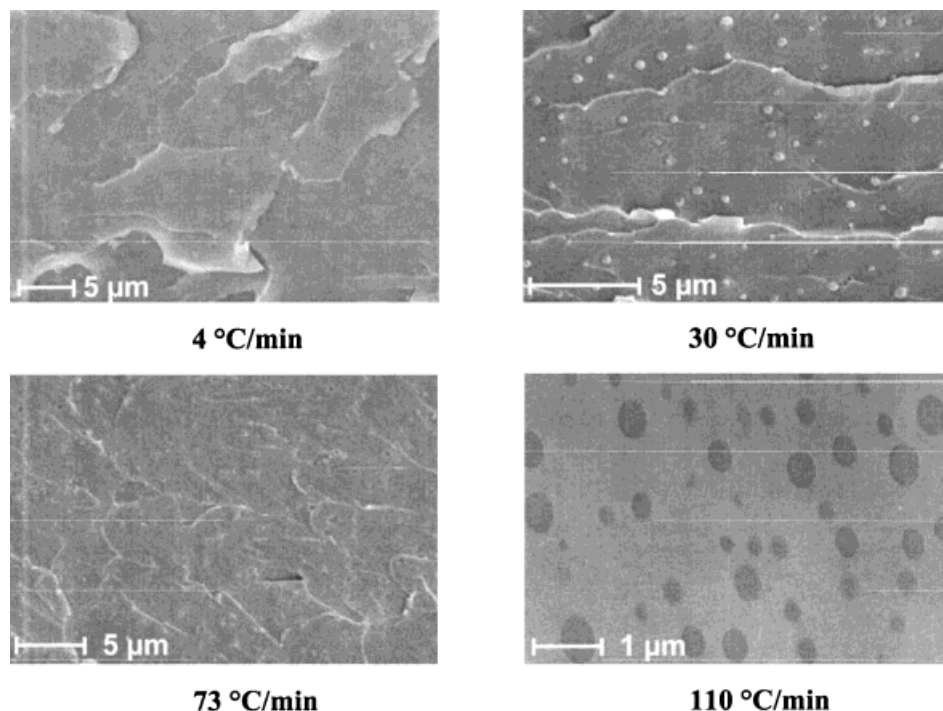
Figure 8   SEM and TEM micrographs obtained for DGEBA–DDS–PEI samples cured at different heating rates.

Time–temperature profiles could be turned into conversion–temperature (Figs. 5 and 6) profiles with the kinetic model available for any time–temperature history. By reporting the cloud points (Fig. 3) on the conversion–temperature profiles, we were able to locate phase separations for every heating rate (Table III). x_{cp}'s of about 0.23 and 0.34 were determined for the DGEBA–DDS–ETBN and the DGEBA–DDS–PEI systems, respectively. A T_{cp} independent of the heating rate was found for both formulations. Phase sep-

aration started at 190°C and occurred during the temperature plateau, except for the rubber-modified formulation cured at 3°C/min. For this formulation, $x_{cp} = 0.22$ and $T_{cp} = 165$°C.

Influence of Heating Rate on Generated Morphologies

Figures 7 and 8 show SEM and TEM micrographs obtained for samples cured at different heating rates. A spherical dispersed phase was observed
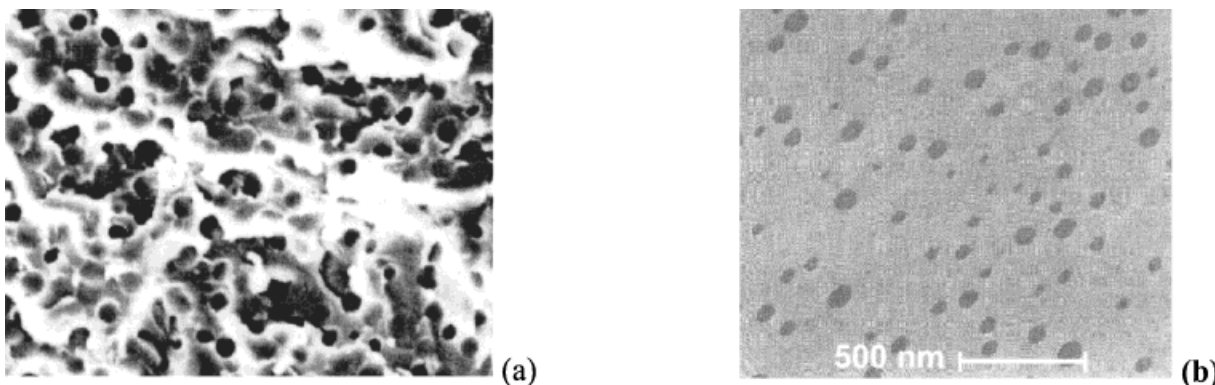

Figure 9   Micrographs obtained for samples cured in an oven (heating rate $\sim$ 7°C/min): (a) DGEBA–DDS–ETBN (SEM) and (b) DGEBA–DDS–PEI (TEM).

Table IV   Comparison of Average Diameters Generated in Conventional and Microwave Ovens (Heating Rate = 7°C/min)

	Average Diameter	
System	Conventional Oven	Microwave Oven
ETBN-modified	2.6 μm	2.7 μm
PEI-modified	670 nm	800 nm

in every case. Figure 9 presents micrographs obtained with DGEBA–DDS–ETBN and DGEBA–DDS–PEI[23] samples cured with conventional heating (an oven) at a heating rate of about 7°C/min followed by a temperature plateau of 190°C. Table IV summarizes the average diameters of the dispersed-phase particles that were generated by both types of heating (oven and microwave) at similar heating rates. The same morphologies (same type and same size) were produced with both conventional and microwave heating. A variety of specific effects have been attributed to microwave heating: acceleration of the reaction kinetics,[24–26] a decrease in the rate of reaction,[27] and incomplete phase separation.[28,29] According to our results, the differences observed were the result of a comparison of samples that did not have the same time–temperature history. We showed in a previous article that the kinetics of the epoxy-amine reaction are completely independent of the type of heating used.[13] Furthermore, micrographs and particle sizes obtained for both types of heating confirmed that the controlling factors were the temperature and the heating rate.

Figures 10 and 11 show particle size distributions for samples cured at different heating rates. In Table V, morphological parameters (average diameter and V_D) obtained with SEM and TEM techniques for DGEBA–DDS–ETBN and DGEBA–DDS–PEI formulations are summarized. No reasonable influence of the heating rate on generated morphologies could be demonstrated. The particles from the dispersed phase had diameters between 2 and 4 μm for ETBN-modified samples and less than 1 μm for PEI-modified samples. The V_D's also seemed to be independent of the heating rate. For reasons of experimental inaccuracy, it is reasonable to give an average value of V_D = 15 $\pm$ 3 for DGEBA–DDS–ETBN and 7 $\pm$ 3 for DGEBA–DDS–PEI.
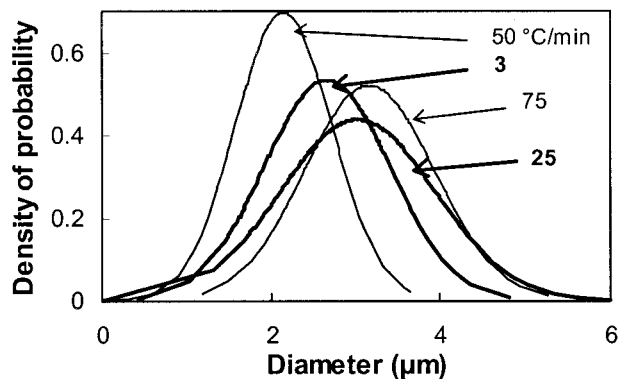
Figure 10   Particle size distribution: density of probability (normal law) for DGEBA–DDS–ETBN samples cured at different heating rates.

These results are not surprising if one remembers that phase separation was found to occur during the temperature plateau for any heating rate. Morphologies were then generated at the same temperature (190°C) and for the same conversion (0.23 and 0.34, respectively, for DGEBA–DDS–ETBN and DGEBA–DDS–PEI). The rubber-modified sample cured at 3°C/min presented, however, a particular behavior because phase separation started at a temperature of 165°C and for a conversion of 0.22. The value of x_{cp} was almost the same, but T_{cp} was different in comparison to the other heating rates. A difference of 15°C did not seem to be enough to affect the size of the particles of the dispersed phase. An average diameter of 2.7 μm was indeed obtained for a heating rate of 3°C/min. The independence of the morphological parameters and the fact that phase
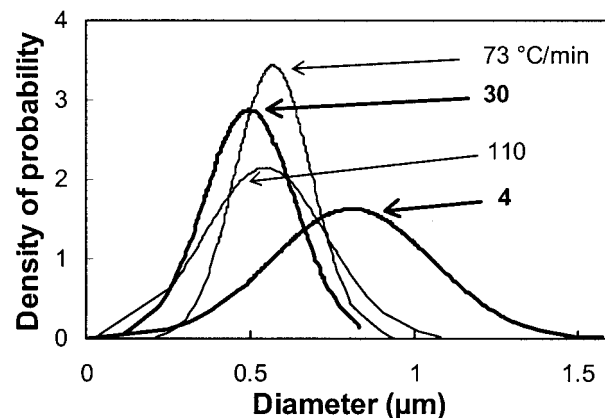

Figure 11   Particle size distribution: density of probability (normal law) for DGEBA–DDS–PEI samples cured at different heating rates.

Table V   Average Diameter and V_D Generated in a Microwave Oven at Different Heating Rates

System	Heating Rate (°C/min)	Average Diameter (μm)	V_D (%)
ETBN-modified	3	2.7	15
	25	3	17
	50	2.2	14
	75	3.2	13
PEI-modified	4	0.81	9
	30	0.5	4
	73	0.57	7
	110	0.7	10

separation occurred during the temperature plateau seemed to be in good agreement. The temperature of 190°C needed to cure the DGEBA–DDS–ETBN and DGEBA–DDS–PEI formulations did not seem to allow any control of the morphology. This aim would be achieved when either the temperature or the heating rate was increased. Nevertheless, in both cases these systems became hardly regulatable. As will be discussed in a future article, the control of morphology can be realized when the reactivity of the formulation and the conditions of cure are adapted so that phase separation occurs before the temperature plateau.

Samples were postcured to achieve full conversion, and their T_g's and Δ_{cp}'s were measured. As previously explained, we used the expressions developed by Fox and Couchman to determine the phase compositions of the DGEBA–DDS–ETBN samples. Details of the calculations can be found in Table VI. These measurements and calculations were realized for all samples, and the same value was obtained for every heating rate. Because a particular behavior was found for the sample cured at 3°C/min, it is given separately for this heating rate. However, the same value was obtained for other all heating rates; phase composition was independent of the heating rate:

- The matrix was composed of 5% in a volume of dissolved rubber and 95% in a pure network.
- Particles were composed of 90% rubber and 10% pure network.

Results obtained were coherent with values found in the literature. Grillet[30] determined a value of $7 \pm 1\%$ for the fraction of rubber dissolved in a 2,2′ bis(caminophenoxy)phenyl propane (DGEBA–DDS–BAPP) matrix. For an ETBN-modified 3,3′-dimethyl-4,4′-diamino dicyclohexylmethane (DGEBA–3DCM) system, Verchère et al.[3] obtained a value of 6% for W_R^M.

CONCLUSIONS

The generated morphologies of linear polymer-modified epoxy-amine formulations were studied

Table VI   Details of the Phase Composition Calculations for the ETBN-Modified Samples

Heating Rate (°C/min)	T_g^{EA} (°C)	ΔC_p^{EA} (J g^{-1} K^{-1})	T_g^R (°C)	ΔC_p^R (J g^{-1} K^{-1})	T_g^M (°C)	W_R^M Fox	W_R^M Couchman
25, 50, 75	214	0.189	−43	0.58	195	0.04	0.02
3	214	0.189	−43	0.58	192	0.04	0.02

	ρ_{EA} (g cm^{-3})		ρ_R (g cm^{-3})			V_R^M Fox	V_R^M Couchman
	1.23		0.96			0.05	0.02

Heating Rate (°C/min)	V_R^0	V_D	V_R^D Fox	V_R^D Couchman	V_{EA}^D Fox	V_{EA}^D Couchman
	0.18	0.15	0.92	—	0.08	—

as a function of heating rate. We showed in a previous article[13] that the kinetics of the epoxy–amine reaction depended only on the time–temperature history. Here, we also showed that the controlling factor for the generated morphology did not differ because of the use of microwave energy.

Kinetics modeling and cloud-point measurements allowed us to locate phase separation during microwave curing. With the DGEBA–DDS–ETBN and DGEBA–DDS–PEI formulations, phase separation was found to occur during the temperature plateau at 190°C. The characterization of the generated morphology did not reveal any strong influence of the heating rate. This fact is not surprising because phase separation was found to occur, for every heating rate, at the same temperature (190°C) and for the same x_{cp}. We will present in a future article that with well-chosen thermal kinetics, another system allows control of the morphology through the variation of the heating rate.

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