

Blends of Acrylonitrile–Butadiene–Styrene with an Epoxy/Cycloaliphatic Amine Resin: Phase-Separation Behavior and Morphologies

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ABSTRACT: The phase-separation behavior and morphologies of a commercial epoxy resin based on diglycidyl ether of bisphenol A cured with the diamine hardener 1,3-bisaminomethylcyclohexane and blended with different amounts of acrylonitrile–butadiene–styrene thermoplastic were studied with dynamic mechanical analysis and other techniques. In comparison with the neat system, the modified systems reached before gelation and vitrification, events that were assigned to the onset and endset of the storage modulus signals in a dynamic mechanical analysis curve (storage modulus versus time). These results were explained by a phase-separation phenomenon induced by polymerization. Scanning electron microscopy and light transmission focused on phase separation revealed a sea-island morphology for low thermoplastic contents, a bicontinuous structure for intermediate thermoplastic contents, and an epoxy-nodular phase-inverted structure for high thermoplastic contents. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1277–1286, 2002

Key words: acrylonitrile–butadiene–styrene (ABS)/epoxy blends; dynamic mechanical analysis; morphology; polymerization-induced phase separation

INTRODUCTION

Among thermosetting resins, epoxy resins are superior in heat resistance, adhesion, corrosion resistance, and mechanical properties, and they are widely used as coatings, adhesives, electric insulating materials, and matrices for composites. Epoxy resin curing systems exhibit during cure the same features as other polymeric systems, such as extensive branching, passage through a gel point, and the formation of macromolecules.

As the chemical reaction proceeds, the glass-transition temperature (T_g) increases, and if the reaction is carried out isothermally below T_g of the fully reacted system, the polymer will reach a partial cure. During an isothermal reaction, two phenomena of critical importance can occur: gelation and vitrification.¹

Gelation generally occurs first and is characterized by the incipient formation of a material of infinite molecular weight and limited conditions for processability of the material. Before gelation, the system is soluble and fusible, but after gelation, both soluble and insoluble materials are present. As gelation is approached, the viscosity increases dramatically, the molecular weight becomes infinite, and gelation does not inhibit the curing process. Gelation can be like a phase-separating process with a soluble fraction or soluble

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phase and an insoluble fraction or gel phase with noticeable mechanical properties.

Vitrification is the transformation from a liquid or rubbery material to a glassy material. At vitrification, the material solidifies and chemical reactions can be stopped; T_g can, therefore, equal or exceed the cure temperature.

Although numerous studies^{2,3} of curing kinetics of epoxy/diamines by differential scanning calorimetry (DSC) have appeared in the literature, fewer articles have appeared about cure processes by dynamic mechanical analysis (DMA).⁴⁻⁶

With the aim of improving the low toughness of these materials due to the high degree of crosslinking, epoxy resins have been modified with different materials. They have been blended with liquid elastomers⁷ and later with thermoplastics. Thermoplastics have advantages over elastomers, in that T_g of the modified systems does not decrease drastically.^{8,9} The influence of the morphologies of the thermoset/thermoplastic mixtures on the toughness of some materials has been studied by various authors.^{10,11} A method for adding a modifier consists of dissolving the modifier and the epoxy prepolymer in a common solvent and inducing phase separation during cure; this is usually called *polymerization-induced phase separation*.

The main objective of this article is to study the curing evolution via DMA for an epoxy/amine system modified with different amounts of acrylonitrile-butadiene-styrene (ABS), the events that occur during cure (phase separation, gelation, and vitrification), and the final morphology. Previously, we reported for these systems the curing kinetics by DSC.¹²

EXPERIMENTAL

Materials

The resin used was a commercial diglycidyl ether of bisphenol A (DGEBA), Araldite GY 260 from Ciba-Geigy (Basle, Switzerland), with a weight per epoxy equivalent of 205.1 g equiv⁻¹. The neat epoxy resin and its blends with ABS (QI-300; weight-average molecular weight = 163,000, weight-average molecular weight/number-average molecular weight = 2.59; Polidux, REPSOL, Huesca, Spain) were cured with a cycloaliphatic diamine hardener, 1,3-bisaminomethylcyclohexane (1,3-BAC), from Aldrich Chemical (Milwaukee, WI), with a molecular weight of 142.25 and a

purity value of greater than 99% according to the supplier.

Miscibility Studies

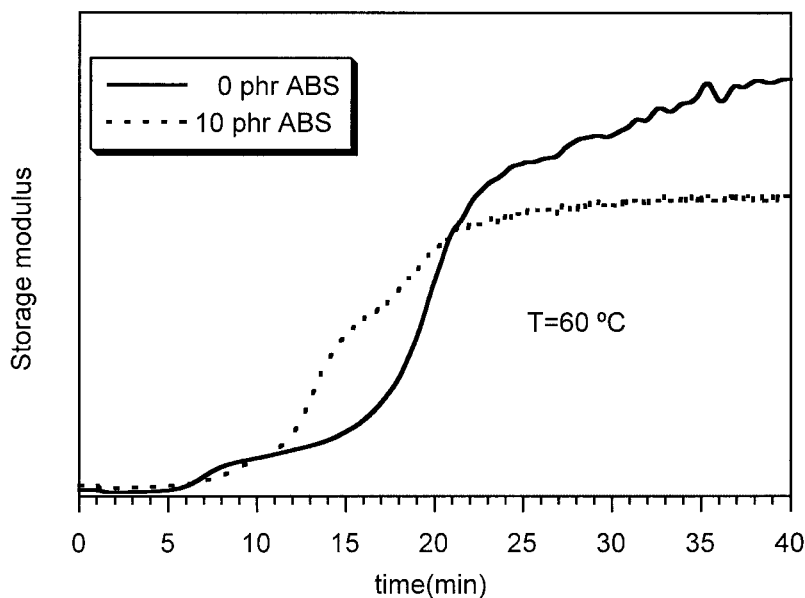
Initial miscibilities of DGEBA/ABS mixtures were studied. ABS was held in an oven at 70°C to dry. Then, it was dissolved in dichloromethane, and the resulting polymer solution was mixed with 100 g of the epoxy resin at room temperature. The solvent in the mixture was removed in a thermal bath at 80°C. The samples were quenched at -30°C and then were tested by DSC at a heating rate of 5°C min⁻¹ to 300°C. T_g was determined by the onset of the DSC experiment. To check reproducibility, we repeated the procedure several times.

DMA Measurements

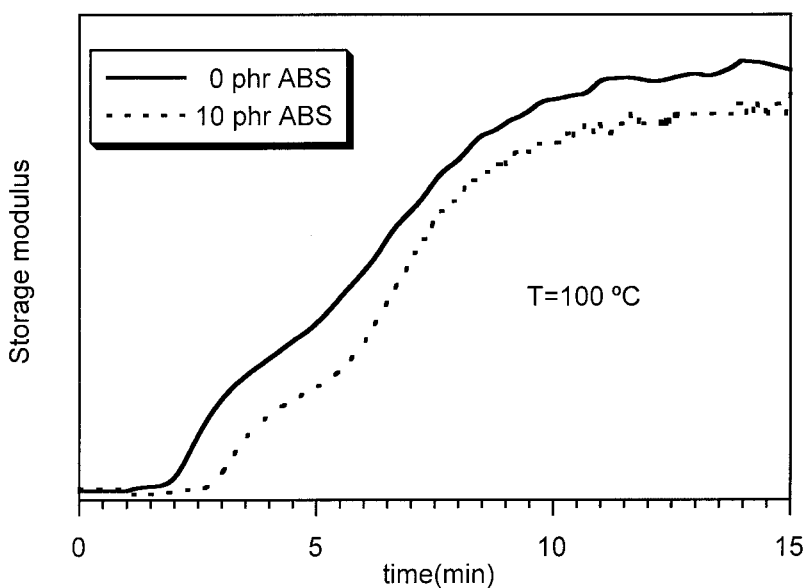
A DMA-7 dynamic mechanical analyzer from PerkinElmer, equipped with an intracooler and supported by a PerkinElmer computer for data acquisition and analysis, was used to characterize the time dependence of the dynamic storage modulus (E') and loss factor ($\tan \delta$) of the samples at various temperatures. DMA measurements were made in the isotherm mode.

A stoichiometric amount of 1,3-BAC was added to the DGEBA/ABS mixture to obtain the final blends. The mixture was poured into aluminum capsules and covered, the DMA probes were placed over the covers, and a static force of 150 mN was placed on top of a dynamic force of 100 mN; that is, the mode of deformation was compression. About 15 mg of the mixture was prepared over fiber glass to maintain the thickness of the samples. The measurement system was similar to parallel plates with cylindrical geometry for the sample.

Isothermal measurements by DMA between 60 and 110°C for DGEBA/1,3-BAC/ABS mixtures with 0, 5, 10, and 15 phr ABS (where phr represents the number of parts by mass quantity of ABS per hundred parts of DGEBA epoxy resin), with 10°C temperature increment, were realized for the characterization of the curing process of each system. The tests were performed at a frequency of 1 Hz. A dry helium flow of 40 mL min⁻¹ was used as a purge gas. The DMA calibration had different routines. These automatic routines allowed calibration of the height, furnace, temperature, and force. The temperature calibration was made with the melting point of pure indium.



(a)



(b)

Figure 1 E' during the isothermal cure of the neat epoxy resin (solid line) and 10 phr ABS-modified epoxy resin (dashed line) at (a) 60 and (b) 100°C.

DSC Measurements

A PerkinElmer DSC 7 differential scanning calorimeter equipped with an intracooler and supported by a PerkinElmer computer for data acquisition and analysis was used for the isothermal cure experiments and data analysis. The calorimeter was calibrated with the enthalpy of fusion and melting point of pure indium. A dry nitrogen

flow of 40 mL min^{-1} was used as a purge gas. Samples of about 10 mg were enclosed in aluminum DSC capsules.

Isothermal measurements by DSC between 80 and 110°C for DGEBA/1,3-BAC/ABS mixtures with 0, 5, 10, and 15 phr ABS, with 10°C temperature increments, were made for the characterization of the curing process of each system.¹²

Table I Times at Which E' Began to Increase, Taken as the Onset of $E'-t$ Curves for the Neat and Modified Systems During Different Isothermal Runs

ABS (phr)	Time (s)					
	60°C	70°C	80°C	90°C	100°C	110°C
0	1032	486	396	210	120	108
5	672	445	294	228	156	124
10	660	415	292	224	167	120
15	651	408	256	171	121	96

Light Transmission (LT)

Isothermal measurements at 70 and 80°C of LT through samples with 5, 10, and 15 phr ABS permitted us to determine the beginning of the phase-separation process. The light source was a laser, and the receptor device was a conventional luxometer.

Morphology

The morphology of the blends was studied with scanning electron microscopy (SEM) with a JEOL JXA-6400 apparatus. Samples of 0, 5, 10, 15, and 30 phr ABS were cured for 4 h at 80°C and post-cured for 2 h at 110°C. Each sample was etched with dichloromethane before examination by SEM for 24 h. The electromicrographs of the modified epoxy systems showed the development of domains due to the curing process.

RESULTS AND DISCUSSION

First, the binary blends of ABS with DGEBA resin exhibited a single glass transition in the range of temperatures studied. Therefore, we can assume that the blends constitute homogeneous systems, which indicate complete miscibility over the entire composition range.¹²

It was discovered with DSC that the reaction enthalpy per epoxy equivalent was over 105 kJ equiv⁻¹, so we must admit two conclusions: first, the activation energy for the modified systems is not affected by the presence of the thermoplastic, and second, gelation will take place with equal degrees of conversion for the neat and modified systems.

Figure 1(a,b) shows the signals for E' obtained with the dynamic mechanical analyzer for isothermal tests carried out at 60 and 100°C for the

neat system and the system modified with 10 phr ABS. The shapes of these signals are similar for both systems.

For the neat system, we have associated the onset and endset of the curves with the characteristic events of cure process, gelation and vitrification, respectively. The gelation and vitrification times, when conversions were reached, agreed with those obtained by other techniques and those expected theoretically.⁶ However, in the modified systems, such assignments could not be made in that way because the incorporation of the thermoplastic to the resin led, when the cure advanced, to the appearance of two separated phases.

During the cure, with only the information supplied by DMA, we cannot know if the phenomenon that takes place when E' increases is due to phase separation or gelation. Gelation is conducted by chemical kinetics, and phase separation is conducted by thermodynamic factors,^{13,14} both phenomena contribute to a modulus increase.

Tables I and II show the onset and endset times taken of E' -time (t) curves for the analyzed isothermals corresponding to the neat and modified systems.

According to Table I, in the range of temperatures below the maximum use temperature, the values of which are usually 20 or 30°C below T_g of a pure thermoplastic, the increase in modulus occurs in the modified systems before it occurs in the neat resin, and in the range of temperatures around or higher than T_g of a pure thermoplastic, the increase in modulus occurs at approximately the same time in the neat and modified systems. Figure 2 shows this for the neat and 5 phr ABS-modified systems.

To determine if the phenomenon that takes place at the onset of the $E'-t$ curves is gelation

Table II Times at Which E' Levelled Off, Taken as the Endset of $E'-t$ Curves for the Neat and Modified Systems During Different Isothermal Runs

ABS (phr)	Time (s)					
	60°C	70°C	80°C	90°C	100°C	110°C
0	1362	1080	960	840	570	507
5	1281	894	745	592	525	398
10	1326	1047	652	600	540	756
15	1232	906	724	481	442	532

(kinetic phase separation) or phase separation (thermodynamic phase separation), other techniques are needed.

With the data given in the Table I and with previous kinetic studies of the system,¹² we can determine the conversions at different isothermals. They are indicated in Table III. According to the Flory hypothesis,¹⁵ the theoretical conversion at the gel point is 0.58.

For the neat resin, the conversion at the times registered in Table I corresponds to an isoconversional state characteristic of gelation, slightly above the theoretical value, due basically to the difference between macroscopic experimental gelation and theoretical molecular gelation that take place under certain conditions for the ideal formation of crosslinking networks. For the modified systems, the average conversions reached at those times increase with temperature until val-

ues are obtained near those obtained for the neat system. Conversions measured by DSC correspond to an average value of disperse and continuous phases, the conversions of the epoxy-rich phase being higher than those of the thermoplastic-rich phase.

To detect phase separation experimentally, we used LT and SEM. Figure 3 shows the results with LT for three samples cured isothermally with 5, 10, and 15 phr ABS at two temperatures. The times at which LT falls appreciably, characteristic of the appearance of an opalescence phase that prevent LT, are shorter than the times corresponding to the onset of E' in the DMA curves.

Electron microscopy also confirms the initially homogeneous appearance of two phases in the system. Figure 4 illustrates the morphology developed in samples cured isothermally at 80°C with 0, 5, 10, 15, and 30 phr ABS.

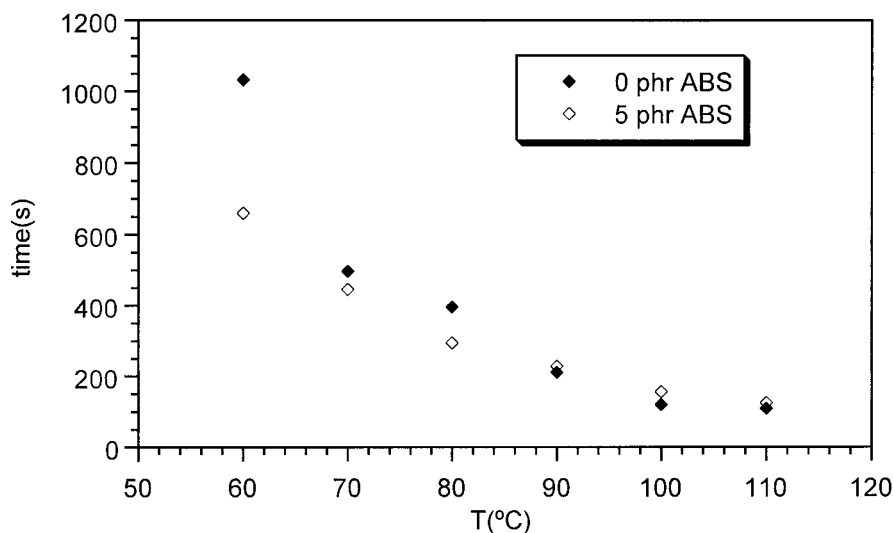
**Figure 2** Times at which E' began to increase, taken as the onset of $E'-t$ curves for the neat epoxy resin and 5 phr ABS-modified epoxy resin during different isothermal runs.

Table III Experimental and Theoretical Conversions for the Neat and Modified Systems at Different Temperatures

ABS (phr)	Conversions			
	80°C	90°C	100°C	110°C
0	0.62	0.61	0.63	0.62
5	0.39	0.46	0.52	0.62
10	0.45	0.50	0.59	0.62
15	0.38	0.38	0.47	0.54

Theoretical = 0.58.

In the neat resin, no kind of dual structure can be observed [Fig. 4(a)]. For 5 and 10 phr ABS [Figs. 4(b,c)], a disperse phase is observed that is rich in thermoplastic etched by solvent surrounded by a continuous phase or epoxy matrix; the morphology is the sea-island type, in which a disperse phase is immersed in a continuous phase. The dimensions of domains of the thermoplastic phase increase with the thermoplastic proportion, ranging from 0.3 to 0.8 μm for 5 and 10 phr ABS, respectively. This morphology is formed by nucleation and a growth mechanism. A sample with 15 phr ABS [Fig. 4(d)] has a bicontinuous structure, and its composition is near the critical composition. For 30 phr ABS, phase inversion occurs with a disperse phase rich in epoxy and a continuous phase rich in thermoplastic. A nodular structure is observed [Fig. 4(e)] in which the

epoxy-rich phase forms spherical nodules and the ABS-rich phase forms the matrix. Morphologies obtained by other researchers for similar systems present analog structures.^{16,17}

The previous observations confirm experimentally that during the cure of the modified resin thermodynamic factors compete with kinetic factors¹⁴ to cause phase separation.

Figure 5 represents a conversion–temperature diagram for a modified polymer with a fixed thermoplastic concentration. In this diagram are given vitrification curves for both phases [disperse ($T_{g\text{ disp}}$) and continuous ($T_{g\text{ cont}}$)], a phase-separation curve (T_{ps}), and gelation of the continuous phase.

Taking into account previous results, we propose an explanation for the evolution of the studied systems with temperature. For curing temperatures below the thermoplastic T_g , in the beginning of a cure, comonomers constitute a single or homogeneous phase. When curing progresses, the mixture reduce its miscibility until the system becomes thermodynamically unstable and two phases appear [Fig. 5(a)]. One phase is epoxy-rich, and the other is thermoplastic-rich. The epoxy-rich phase or continuous phase increases its average molecular weight because of crosslinking. The thermoplastic phase or dispersed phase will contain increased proportions of thermoplastic with the progress of the reaction and phase separation. Both phases contribute to the viscosity increase of the system. When point a is exceeded,

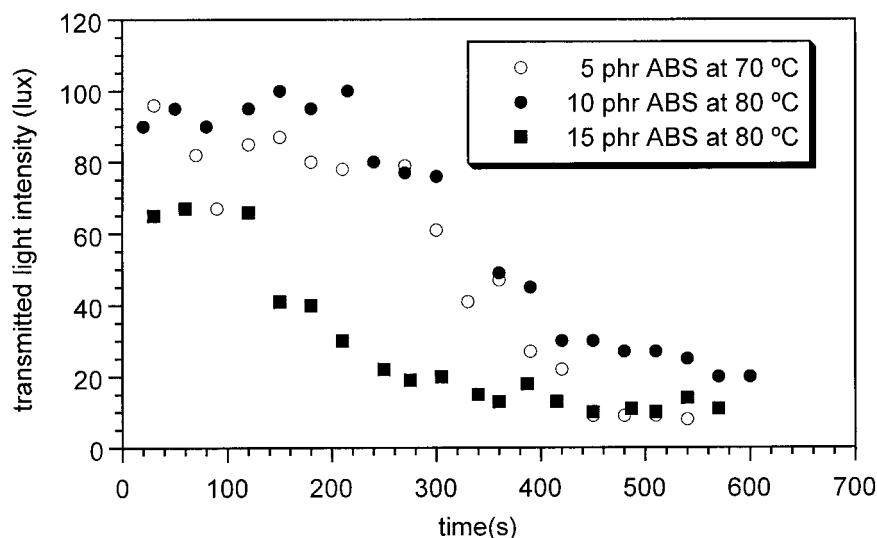
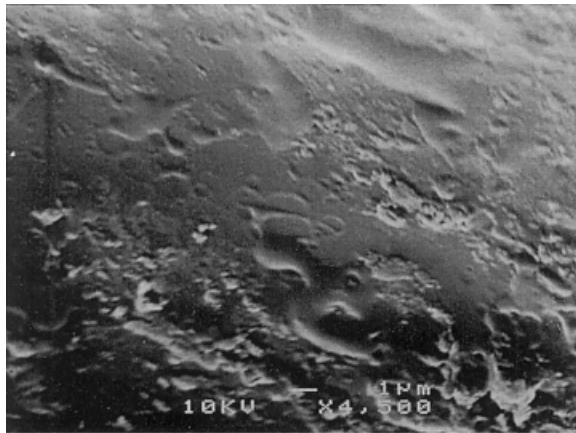
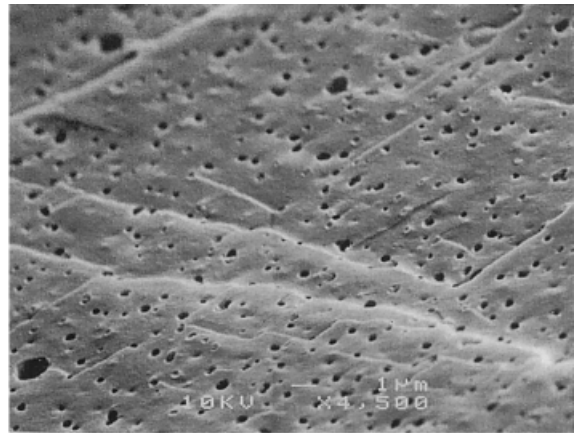


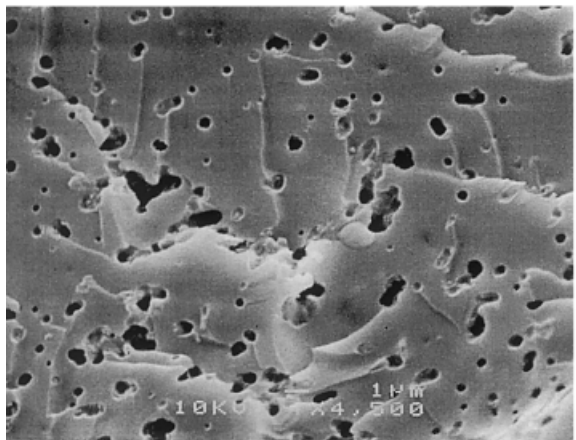
Figure 3 LT results for samples cured at 70°C with 5 phr ABS, at 80°C with 10 phr ABS, and at 80°C with 15 phr ABS.



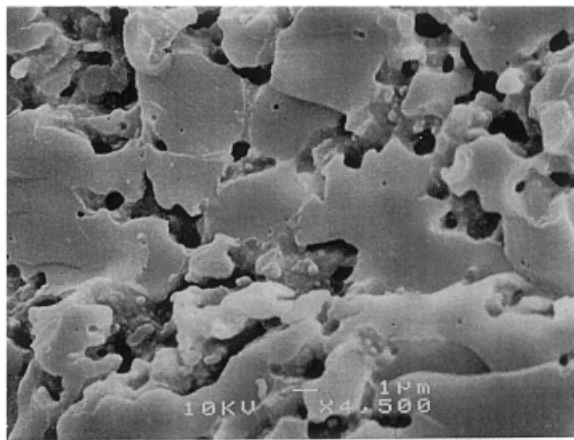
(a)



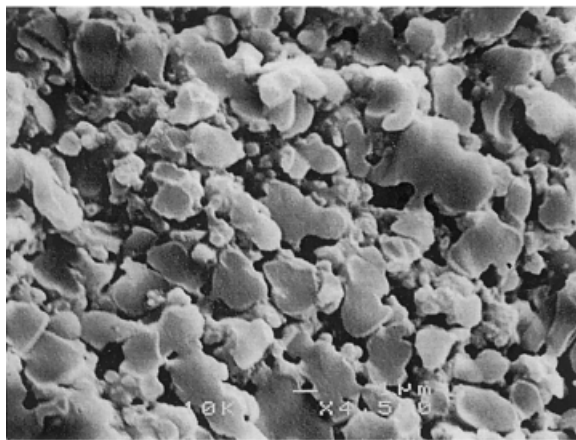
(b)



(c)



(d)



(e)

Figure 4 SEM micrographs for samples of DGEBA cured isothermally at 80°C with 1,3-BAC blended with various percentages of ABS: (a) neat, (b) 5 phr, (c) 10 phr, (d) 15 phr, and (e) 30 phr.

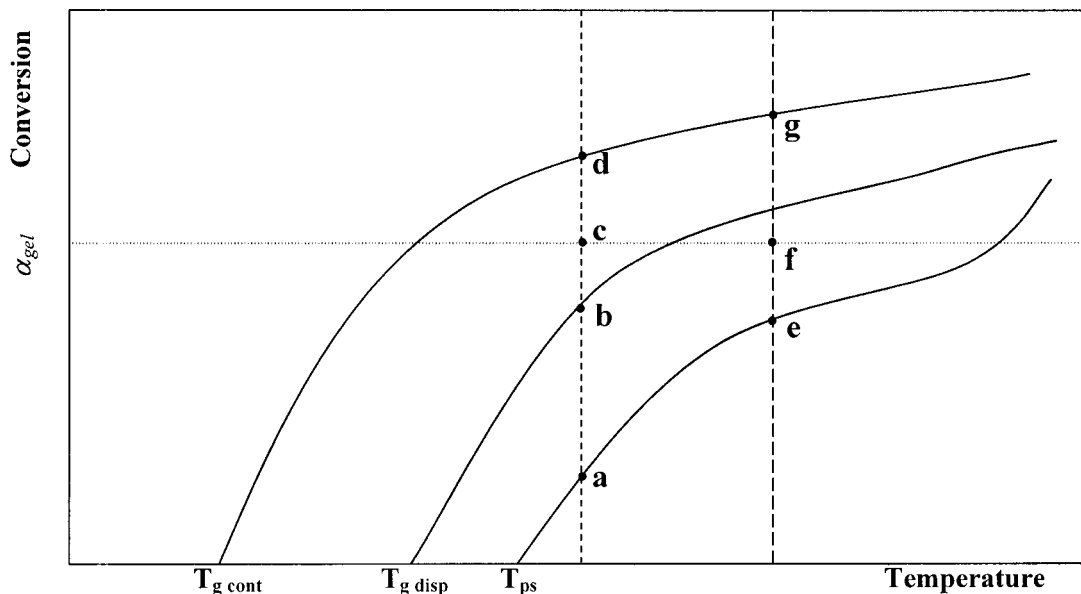


Figure 5 Conversion–temperature diagram representing qualitatively the evolution of the curing system with time and temperature and the physical state transformations that can take place.

the disperse phase progressively increases its T_g until it reaches the cure temperature, at which point vitrification begins [Fig. 5(b)]. Starting from the phase separation, the disperse phase will concentrate lighter oligomers of the resin. The continuous phase will progressively concentrate the heavier oligomers and will gel [Fig. 5(c)].

Gelation of the continuous phase is reflected in a change in mechanical properties by the rising value of E' measured by DMA. In this way, we can justify that the appearance of significant mechanical properties in the modified systems, a phenomenon associated with phase separation, occurs earlier in the neat system when the modulus increase is due to gelation.

However, an increase in the solubility of the thermoplastic with temperature will cause phase separation to take place at increasing conversions, as shown in Table III.

For curing temperatures equal or above the maximum T_g reached by the thermoplastic, the appearance of appreciable mechanical properties in DMA signals takes place equally for the modified and neat systems. However, the conversions reached correspond to conversions near the gel point.

An analysis by SEM of a sample cured at 115°C with 10 phr ABS shows that the morphology is analogous to that obtained with curing at 80°C; this proves that phase separation occurs before

gelation [Fig. 5(e,f) and Fig. 6]. In this range of temperatures, the disperse phase does not vitrify; there will be gelation, the phenomenon observed in the DMA signal when the modulus begins to rise. Because the reaction is slower than for the neat system on account of the dilution effect of the epoxy, gelation takes place later in the modified systems.

With respect to vitrification, Table II lists the endset times in the E' – t curves measured by DMA for the studied systems at different temperatures.

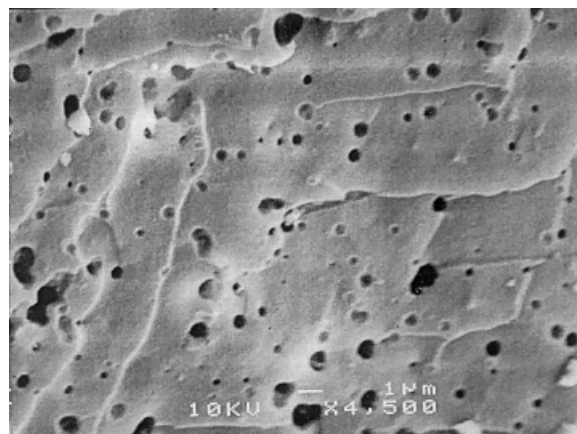


Figure 6 SEM micrograph for a sample of DGEBA cured isothermally at 115°C with 1,3-BAC blended with 10 phr ABS.

Table IV Experimental and Critical Conversions for the Neat and Modified Systems at Different Temperatures

ABS (phr)	Conversions ($\alpha_{\text{exp}}/\alpha_c$)			
	80°C	90°C	100°C	110°C
0	0.73/0.71	0.82/0.79	0.85/0.86	0.87/0.85
5	0.74/0.77	0.78/0.79	0.86/0.87	0.91/0.90
10	0.70/0.74	0.81/0.81	0.86/0.84	0.91/0.89
15	0.71/0.71	0.74/0.80	0.81/0.83	0.90/0.89

Table IV shows the conversions obtained from thermal analysis.¹² We denominated experimental conversions (α_{exp}) to the conversions corresponding to times obtained by DMA according to DSC conversion–time curves. The critical conversion (α_c) is the conversion when the reaction passes from kinetic control to diffusion control. α_c can be considered the beginning of theoretical vitrification and is calculated by the application of diffusional considerations to a kinetic model.¹⁸ Values obtained by both methods agree satisfactorily; this seems to support our criteria.

Vitrification times for the modified systems are below those of the neat system in the range of temperatures analyzed, except for experimental deviation (see Fig. 7). These results can be interpreted in the following way. In the beginning of the cure, the modified system is homogeneous. When curing advances, the system becomes thermodynamically unstable, and two phases develop: a continuous phase

rich in epoxy species with a high molecular weight and a disperse phase or growing phase rich in thermoplastic and epoxy oligomers with a low molecular weight. As a result, the continuous phase of the modified system will reach the curing temperature before that of the neat system, and so it will vitrify before the neat resin. Figure 5(d,g) shows the vitrification of the continuous phase for the modified systems at curing temperatures above and below T_g of the pure thermoplastic.

CONCLUSIONS

We have studied diglycidyl ether of bisphenol A (DGEBA) cured with the cycloaliphatic amine 1,3-BAC and modified with 5, 10, and 15 phr thermoplastic ABS.

A number of different isothermal tests of the curing process were performed with DMA and

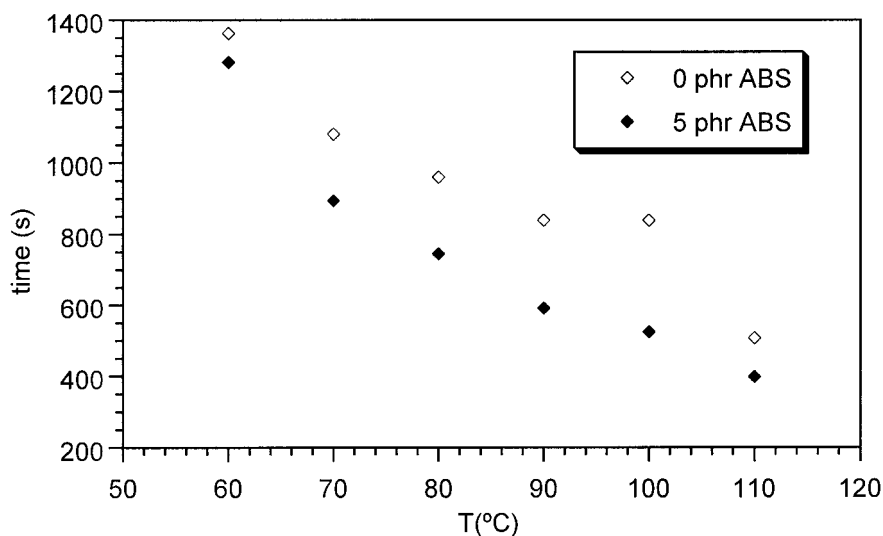


Figure 7 Times at which E' leveled off, taken as the endset of $E'-t$ curves for the neat system and 5 phr ABS-modified epoxy resin during different isothermal runs.

DSC. The study was completed with LT and SEM, which permitted us to determine the phase-separation behavior.

Gelation and vitrification are limiting and controlling factors of phase separation, which appears in the modified systems during the progression of the cure.

We propose that the appearance of significant mechanical properties in the modified resins measured by DMA coincides with gelation of the continuous phase, rich in resin and containing the heavier oligomers. This fact justifies the total conversion for both phases being lower than would correspond to gelation of the neat resin. Experimentally, the times and total conversions at which dynamic mechanical properties of the modified resin are found are lower than those corresponding to the neat resin. A significant decrease in LT intensity is observed in modified systems before gelation takes place.

Maximum values for E' (endset) measured by DMA have been assigned to vitrification of the continuous phase. Times for this event are shorter than for the neat resin because the continuous phase segregates light oligomers to the disperse phase.

Morphological analysis by SEM of cured materials shows a homogeneous phase for the neat resin and two phases for the modified systems. For compositions with 5 and 10 phr ABS, a sea-island morphology appears in which the domain size of the disperse phase increases with the thermoplastic. For compositions with 15 phr ABS, a bicontinuous morphology is developed. For compositions with 30 phr ABS, a phase inversion is observed with a nodular epoxy-rich phase immersed in a continuous ABS-rich phase.

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