

Isothermal Curing by Dynamic Mechanical Analysis of Three Epoxy Resin Systems: Gelation and Vitrification

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ABSTRACT: Times to gelation (t_{gel}) and times to vitrification (t_{vit}) during isothermal curing for the epoxy systems diglycidyl ether of bisphenol A (DGEBA)/1,3-bisaminomethylcyclohexane (1,3-BAC), tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)/4,4'-diaminodiphenylsulfone (DDS), and TGDDM/epoxy novolac (EPN)/DDS were measured at different curing temperatures. This article reports on a method to determine t_{gel} and t_{vit} by dynamic mechanical analysis (DMA). Gelation was determined at the onset of the storage modulus or by the peak of the loss factor. Vitrification was defined as the curve of the storage modulus as the curve reached a constant level (endset) in DMA tests. The experimental values obtained for t_{gel} and t_{vit} were compared with values obtained by other experimental methods and with theoretical values ($t_{\text{gel}}^{\text{t}}$'s) or indirect determinations ($t_{\text{vit}}^{\text{i}}$'s). From kinetic analysis by differential scanning calorimetry, conversions corresponding to gelation were obtained for the three systems; this yielded a constant value for each system that was higher than theoretical value. Values of the apparent activation energies of the DGEBA/1,3-BAC, TGDDM/DDS, and TGDDM/EPN/DDS epoxy systems were obtained from plots of t_{gel} 's against reciprocal temperatures. They were 53.2, 58.2, and 46.5 kJ/mol, respectively. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 78–85, 2002

Key words: gelation; curing of polymers

INTRODUCTION

Epoxy resins have superior heat resistance, adhesion, corrosion resistance, and also mechanical properties among thermosetting resins and are widely used for coatings, adhesives, electric insulating materials, and matrices. During curing, epoxy resins exhibit the same features, including extensive branching, passage through the gel point, and the formation of macromolecules, as other polymeric systems.

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

Gelation generally occurs first and is characterized by the incipient formation of a material of infinite molecular weight and indicates the conditions of the processability of the material. Prior to gelation, the system is soluble, but after gelation, both soluble and insoluble materials are present. As gelation is approached, viscosity increases dramatically, and the molecular weight goes to infinite; gelation does not inhibit the curing process.

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Vitrification is the transformation from liquid or rubbery material to glassy material. At vitrification, the material solidifies, and the chemical reactions can be stopped; T_g can, therefore, equal or exceed the curing temperature.¹

Although numerous studies²⁻⁴ of the curing kinetics of epoxy/diamines by differential scanning calorimetry (DSC) have appeared in the literature, few articles have appeared about curing processes by dynamic mechanical analysis (DMA).^{5,6}

Gelation and vitrification have been determined by several techniques, including DSC, solubility in tetrahydrofuran, rheological measurements, and DMA. Tung and Dynes⁷ proposed that the gelation is the point at which the storage and loss modulus curves cross on DMA tests. The gel times (t_{gel} 's) measured by this method correspond closely with those obtained with the standard ASTM D 2471.⁸ This method is only good for stoichiometric systems⁹ at temperatures well above their T_g .

The main objective of this study was to determine gelation and vitrification by isothermal DMA for three epoxy/amine systems. Previously, we reported for these systems the curing kinetics by DSC¹⁰⁻¹² and isothermal time-temperature transformation diagrams for diglycidyl ether of bisphenol A (DGEBA)/1,3-bisaminomethylcyclohexane (1,3-BAC)¹³ and tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)/epoxy novolac (EPN)/4-4'-diaminodiphenylsulfone (DDS)¹⁴ systems.

EXPERIMENTAL

Materials

One of the epoxy resin systems used was a commercial DGEBA (Shell Epikote 828, Shell Chemicals, St. Charles, LA; weight per epoxy equivalent = 192 g/eq). The hardener was a cycloaliphatic diamine 1,3-BAC from Mitsubishi Gas Chemical America Inc., New York, NY (molecular weight = 142.18, manufacturer purity value > 95%). The amine/epoxy ratio was 1. The mixture was stirred at room temperature.

The second of the systems used was the prepolymer TGDDM (Ciba-Geigy MY720, Ciba-Geigy, Basle, Switzerland; weight per epoxy equivalent = 130 g/eq). The curing agent was an aromatic amine DDS purchased from Fluka-Chemie (Milwaukee, WI). The hardener had a molec-

ular weight of 248.31 and purity greater than 96%, according to the supplier. The TGDDM/DDS samples were prepared with a stoichiometric ratio. They were mixed at 120°C for 8 min.

The other epoxy resin system used was a mixture of three components. The main component, TGDDM, and the hardener, DDS, were described previously, and the third component was a multifunctional novolac glycidyl ether resin (Ciba-Geigy EPN 1138, Ciba-Geigy; weight per epoxy equivalent = 189 g/eq). The composition of the mixture was 43.3% TGDDM, 35.7% EPN, and 21.0% DDS, which yielded an amine/epoxy ratio of 0.64. We prepared the material by mixing the components in an oven at 120°C and stirring continuously until a homogeneous mixture was obtained.

The weights per epoxy equivalent of the three epoxies were determined by hydrochlorination in our laboratory. All the components were commercial products and were used as received without further purification. Some of specifications¹³ given by the suppliers were proved by ¹H-NMR.

DMA Measurements

A DMA-7 dynamic mechanical analyzer from PerkinElmer was used to characterize the time dependence of the dynamic storage modulus (E') and the loss factor ($\tan \delta$) of the samples at various temperatures. DMA measurements in isotherm mode were used.

The mixture was poured into aluminum capsules and covered; the probe of the DMA was placed over the cover, and a static force of 150 mN was put on top a dynamic force of 100 mN; that is, the mode of deformation was compression. About 15 mg of mixture were prepared over fiberglass to retain the thickness of the samples. The system of measurement was similar to parallel plates with cylindrical geometry of the sample. The tests were realized at a frequency of 1 Hz over different temperature ranges according to the studied system, with a 10°C temperature increment and times up to 300 min. A dry helium flow of 40 mL/min 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.

DSC Measurements

A differential scanning calorimeter (PerkinElmer DSC 7, equipped with an intracooler and sup-

ported by a PerkinElmer computer for data acquisition/analysis) was used for the isothermal cure experiments and data analysis. The calorimeter was calibrated with the enthalpy of fusion and the

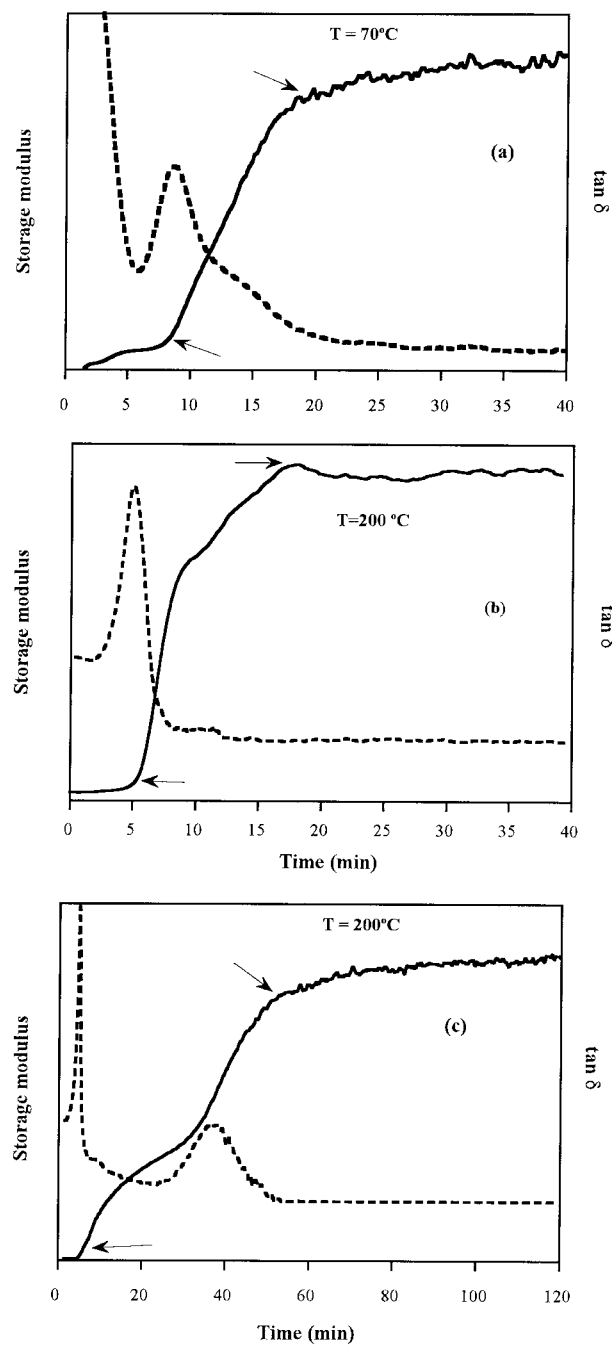


Figure 1 E' (—) and $\tan \delta$ (---) during isothermal curing for (a) DGEBA/1,3-BAC, (b) TGDDM/DDS, and (c) TGDDM/EPN/DDS. Arrows indicate gelation and vitrification.

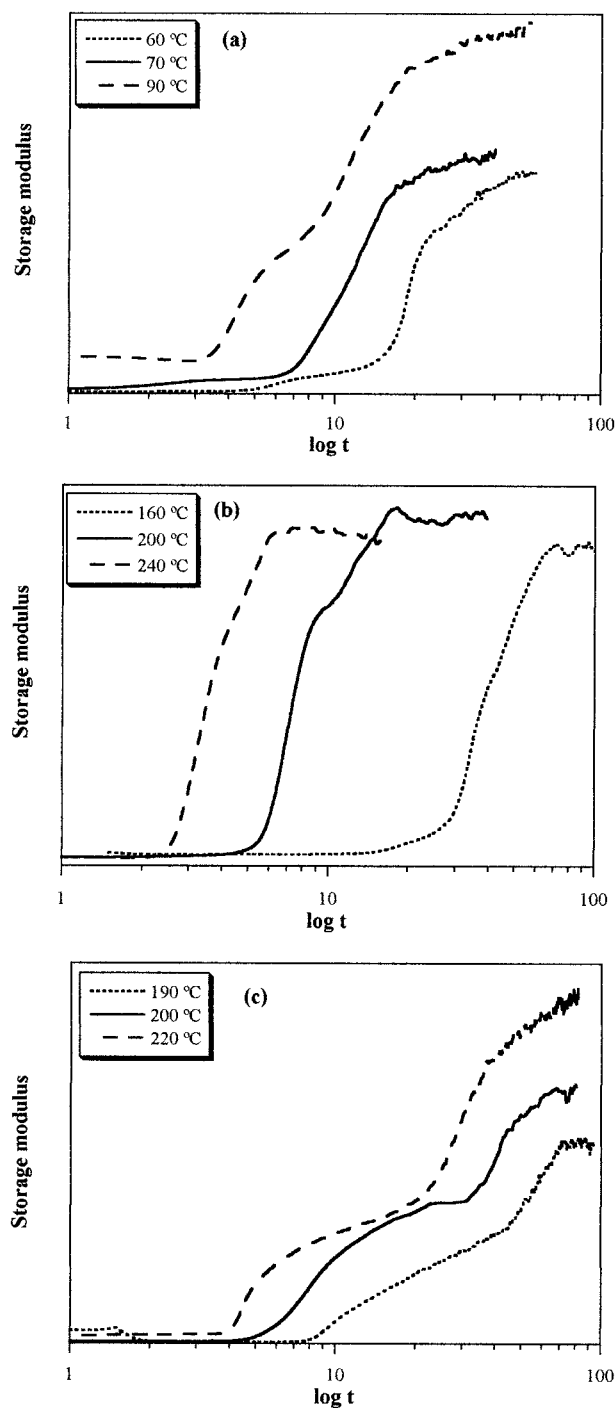


Figure 2 E' during three isothermal runs for (a) DGEBA/1,3-BAC, (b) TGDDM/DDS, and (c) TGDDM/EPN/DDS.

melting point of pure indium. A dry nitrogen flow of 40 mL/min was used as a purge gas. Samples of about 10 mg were enclosed in aluminum DSC capsules.

Table I t_{gel} 's and t_{vit} 's at Different Isothermal Cures for DGEBA/1,3-BAC

	Temperature (°C)				
	60	70	80	90	100
t_{gel} (s)	1032	486	396	210	120
t_{vit} (s)	1362	1080	960	840	570

RESULTS AND DISCUSSION

Isothermal measurements by DMA between 60 and 100°C for the DGEBA/1,3-BAC, 140 to 250°C for TGDDM/DDS, and 170 and 240°C for TGDDM/EPN/DDS with 10°C temperature increment were used for the characterization of the curing processes of each system. The basis for the determination of the range of temperatures were mentioned in previous works.

Figure 1 illustrates typical experiments by DMA for each system. E' and $\tan \delta$ were determined in an isothermal test. Gelation was defined as the onset of the storage modulus or by the peak of $\tan \delta$, where the material began to develop mechanical properties characteristic of the elastic solids. Vitrification was defined on the curve of the storage modulus at the moment where E' became constant or almost constant and represented the maximum state of cure at a determined isothermal run. These events are indicated with arrows in the Figure 1. Figure 2 shows a partial set of isothermal runs with the storage modulus versus time for each system. Gelation and vitrification can be clearly appreciated in the onset and the endset of each curve.

Tables I, II, and III give the t_{gel} 's and vitrification times (t_{vit} 's) at different curing temperatures (T_c 's) for DGEBA/1,3-BAC, TGDDM/DDS, and TGDDM/EPN/DDS, respectively. The values of t_{gel} for TGDDM/DDS agreed with those obtained by other researchers using rheological techniques;¹⁵ moreover, the obtained values for

DGEBA/1,3-BAC and TGDDM/EPN/DDS were similar to those determined by solubility in tetrahydrofuran.^{14,16}

The t_{gel} can be used to calculate the activation energy,¹⁷⁻¹⁹ the precise determination of which would enable a more accurate kinetic cure model to be available. The assumption typically made is that cure kinetics involves only a single reaction with a single activation energy. Although this is often not the case, the single activation energy value so obtained can be considered to be representative of the multiple reactions in progress.

The rate of a kinetically controlled reaction may be expressed by an equation of the following type:

$$\frac{d\alpha}{dt} = kf(\alpha) = A \cdot f(\alpha) \exp\left(\frac{-E}{RT_c}\right) \quad (1)$$

where α is the conversion; k is the conversion rate constant, which is assumed to be a function of temperature based on an Arrhenius-type equation; $f(\alpha)$ is a function of conversion independent of temperature; A is a preexponential factor; E is the apparent activation energy for the overall function; and R the Boltzman constant. Rearrangement and integration give the following equation:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \exp\left(\frac{-E}{RT_c}\right) \int_{t=0}^{t=t_\alpha} dt = A \exp\left(\frac{-E}{RT_c}\right) t_\alpha \quad (2)$$

where t_α is the time at which the conversion reaches α . The natural logarithm can be taken as follows:

$$\ln\left(\int_0^\alpha \frac{d\alpha}{f(\alpha)}\right) = \ln A - \frac{E}{RT_c} + \ln t_\alpha \quad (3)$$

or

Table II t_{gel} 's and t_{vit} 's at Different Isothermal Cures for TGDDM/DDS

	Temperature (°C)											
	140	150	160	170	180	190	200	210	220	230	240	250
t_{gel} (s)	3900	2760	1740	1140	780	540	330	252	240	192	168	132
t_{vit} (s)	7560	5220	3840	2700	2040	1500	1140	960	780	780	390	348

Table III t_{gel} 's and t_{vit} 's at Different Isothermal Cures for TGDDM/EPN/DDS

	Temperature (°C)							
	170	180	190	200	210	220	230	240
t_{gel} (s)	882	636	498	348	270	252	186	156
t_{vit} (s)	9000	6120	4260	3180	2700	2460	1860	600

$$\ln t_{\alpha} = \frac{E}{RT_c} + \left[\ln \left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \right) - \ln A \right] \quad (4)$$

As gelation is a phenomenon that happens at a given constant degree of conversion, t_{gel} follows an Arrhenius relationship with temperature.²⁰ Figure 3 shows experimental values of $\ln t_{\text{gel}}$ plotted versus T^{-1} .

From the slopes of the straight lines represented in Figure 3, activation energies equal to 53.2; 58.2, and 46.5 kJ/mol were obtained for the DGEBA/1,3-BAC; TGDDM/DDS, and TGDDM/EPN/DDS systems, respectively. Excellent linearity was observed for the three systems, which confirmed that the criterion used for the determination of t_{gel} throughout curing by the DMA method used represents a point of constant frac-

tional conversion. This allows for prediction of the t_{gel} 's for curing temperatures outside of the studied range. The obtained values of the activation energies by DMA showed good agreement with the values obtained by DSC.

Isothermal DSC tests were conducted for the three systems, and the experimental values of the conversion versus time were plotted. Figure 4 shows this plot for the TGDDM/DDS system. The plots for the other systems can be found in our other works.^{10,11} These plots were used to determine the respective conversion from the t_{gel} obtained by DMA.

The theoretical conversion reached at t_{gel} was calculated by the following equation:²¹

$$\alpha_{\text{gel}} = \left[\frac{r}{(f-1)(g-1)} \right]^{1/2} \quad (5)$$

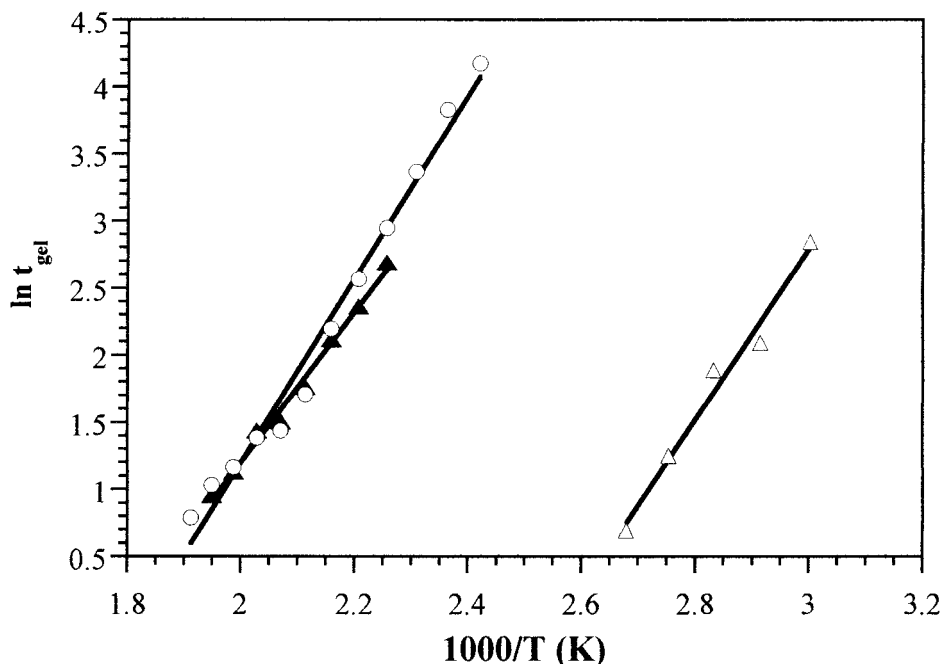


Figure 3 t_{gel} 's and curve fit for (▲) DGEBA/1,3-BAC, (○) TGDDM/DDS, and (△) TGDDM/EPN/DDS.

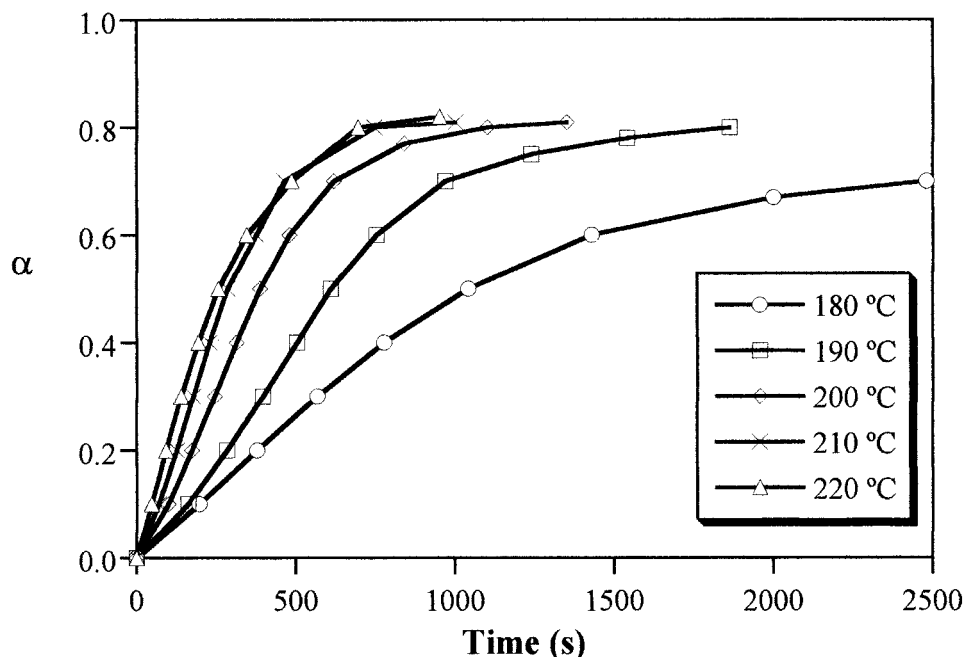


Figure 4 Experimental data of conversion versus time for TGDDM/DDS at different temperatures.

where α_{gel} is the conversion at the gelation, r is the amine/epoxy ratio, and, f and g are the functionalities of the epoxy and amine, respectively. For TGDDM/EPN/DDS, where the ratio was not stoichiometric, both epoxides contributed proportionality to eq. (5).

Table IV shows experimental and theoretical values calculated by eq. (5) of the conversion reached at t_{gel} for different curing isotherms. The table shows that experimental values were higher than theoretical. This difference can be explained by several reasons. The main one is that DMA measures macroscopic gelation (experimental ge-

lation), usually posterior to molecular gelation (theoretical gelation), which takes place at a defined conversion in a perfectly growing network, which is not the case for real networks due to the presence of hanging chains or intramolecular reactions of the epoxy ring. This difference can be also due to experimental differences between both techniques. Meanwhile, small amounts of samples are needed in DSC, and they quickly reach the cure temperature; in DMA, the samples are larger, and the time to reach the cure temperature is higher. This mean that the reaction rate is different.

Table IV Experimental and Theoretical Conversions at the Gel Point for the Epoxy Systems Studied

DGEBA/1,3-BAC ^a		TGDDM/DDS ^b		TGDDM/EPN/DDS ^c	
Temperature (°C)	Experimental Conversion (%)	Temperature (°C)	Experimental Conversion (%)	Temperature (°C)	Experimental Conversion (%)
60	0.58	180	0.41	210	0.28
70	0.65	190	0.43	220	0.27
80	0.65	200	0.42	230	0.28
90	0.61	210	0.44	240	0.33
100	0.63	220	0.48		

^a Theoretical conversion = 0.58%.

^b Theoretical conversion = 0.33%.

^c Theoretical conversion = 0.28%.

Table V Experimental and Theoretical Conversions at the Vitrification Point for the Epoxy Systems Studied

	Temperature (°C)	Conversion	
		Experimental (%)	Theoretical (%)
DGEBA/1,3-BAC	60	0.64	0.66
	70	0.68	0.68
	80	0.73	0.71
	90	0.82	0.79
	100	0.85	0.86
TGDDM/DDS	180	0.65	0.66
	190	0.75	0.74
	200	0.80	0.80
	210	0.84	0.85
	220	0.81	0.95
TGDDM/EPN/DDS	210	0.75	0.75
	220	0.80	0.80
	230	0.83	0.80
	240	0.78	0.90

Conversions achieved during t_{vit} or at the experimental conversion at the vitrification point can be compared with the conversion at the theoretical vitrification, that is, the critical conversions when the kinetic model is corrected by diffusion phenomena, which take into account in the reaction model both chemical and diffusion control. Table V shows this comparison. A good correlation was observed between experimental and theoretical values. On the other hand, as expected, vitrification did not correspond to an isoconversional state but increased with T_c , corresponding to higher degree of cure.

CONCLUSIONS

We studied an epoxy system based on DGEBA and two others based on TGDDM, all cured by diamines.

A wide range of isothermal cures was performed by DMA and DSC to go on the curing process. Gelation and vitrification were the studied events. Gelation was determined on the onset of the storage modulus or by the peak of $\tan \delta$, and vitrification was defined on the curve of the storage modulus as the curve reached a constant level in DMA isothermal runs. Experimental conversions at gelation constituted an isoconversional state, which seemed to confirm our criteria for the selection of t_{gel} , and it was used to evaluate the activation energies. The values of E obtained from

t_{gel} 's were 53.2, 58.2, and 46.5 kJ/mol for DGEBA/1,3-BAC, TGDDM/DDS, and TGDDM/EPN/DDS, respectively. These values were comparable with the values of the activation energies calculated by other procedures and showed good agreement. Also, we compared the experimental conversions at vitrification with the theoretical ones and obtained similar results. These results seem to support our criterion of vitrification time. So, although more works in this sense are necessary to make a good contrast with the data, this method to determine t_{gel} 's and t_{vit} 's by DMA were coherent with other methods.

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