Kinetic of Epoxy Resin Formation by High-Performance Liquid Chromatography

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ABSTRACT: This article is focused on the following of the cure of an epoxy resin by high-performance liquid chromatography (HPLC) and the comparison of the data obtained with those obtained by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) techniques usually employed for characterize curing processes. A reversed-phase HPLC method with UV detection is developed to study the kinetic of the curing reaction of diglycidyl ether of bisphenol A (DGEBA) with 1,3-cyclohexanebismethylamine (1,3-BAC) at 60, 70, and 80°C, before and after gelation. The limits of quantification obtained permit the application of the proposed method until the last steps of the formation kinetic. HPLC and DSC analysis show a good correlation. The gel conversions obtained by HPLC and DMA agree well. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 497–504, 2003

Key words: curing of polymers; differential scanning calorimetry (DSC); high-performance liquid chromatography (HPLC); kinetics (polym.); resins

INTRODUCTION

Epoxy resins are superior in heat resistance, adhesion, corrosion resistance, and also mechanical properties among thermosetting resins, and are widely used for coatings, adhesives, electric insulating materials, and matrices. Epoxy resins exhibit during cure the same features as other polymeric systems such as extensive branching, passage through the gel point, and 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 isothermal reaction two phenomena of critical importance can occur: gelation and vitrification.

Gelation generally occurs first, and is characterized by the incipient formation of material of infinite molecular weight, and indicates the limiting conditions of processability of the material. Prior to gelation, the system is soluble, but after gelation both soluble and insoluble fractions are present. As gelation is approached, the 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 cure temperature.[1]

Although numerous studies[2–4] of curing kinetics of epoxy/diamines by DSC have appeared in the literature, less articles have appeared about cure processes by DMA,[5,6] and, in the last years, the high-performance liquid chromatography (HPLC) has been applied to the study of the first steps of the polymerization reactions.[7–10]

For the curing reaction of the diglycidyl ether of bisphenol A (DGEBA) with an aromatic diamine with a low reactivity, 4,4′-mehtylenebis(3-chloro-2,6-diethylaniline) in the presence of two thermoplastics polyetherimide (PEI) and polystyrene (PS) at 135°C, their kinetics have been studied until the gelation time starting from the area of the DGEBA chromatographic peak that has been obtained by HPLC using a reversed-phase C_{18} column, a mobile phase of mixture water : acetonitrile, and UV detector, set at 254 nm. The temperature was 20°C.[7,8]

The cure at 29, 50, 75, and 100°C of the epoxy prepolymer, which was based on DGEBA and 4,4′-diamine-3,3′-dimethyldicyclohexylmethane (3DCM), was controled until pregel time by size-exclusion chromatography (SEC), using a PL gel 1000, 500, 100, and 100 Å column, mobile phase of THF, UV, and IR detectors. The disappearance of epoxy monomer was

followed using the area of the DGEBA chromatographic peak.[9]

The kinetics of two phenolic resols synthesized under the same conditions but with different types of catalyst were studied. The evolution during synthesis at 80°C of the major components of the prepolymer was followed by reversed-phase HPLC, using a UV detector set at 280 nm.[10]

To be able to carry out this type of studies, the dissolving of monomer in the sample is necessary, and so different procedures are followed.

For DGEBA/PEI blends, the extraction of soluble products was conducted in two steps: first in dichloromethane, and thereafter in acetonitrile to make PEI precipitate. A complete extraction of residual epoxy monomers was then possible.[7,8]

The extraction of bisphenol A from water samples was carried out using solid-phase extraction (SPE). The compounds were desorbed by methanol. In samples of liver and muscle tissue, the extraction procedure was more complicated using microwave-assisted solvent extraction (MASE) followed by SPE.[11]

The stoichiometric mixtures DGEBA–3DCM are dissolved in tetrahydrofuran to follow the kinetic by HPLC.[9]

In samples of noncured epoxy resins Bisphenol A, Bisphenol B, DGEBA, and DGEBF were dissolved in methanol.[12]

Also, it is possible to determinate residual monomers in the finished products. Residual DGEBA from finished epoxy resins cured was extracted by refluxing epoxy amine formulations in a chloroform methanol (25 : 75) mixture.[13]

The aim of the present work is to study the complete kinetic of the curing reaction of DGEBA with 1,3-cyclohexanebismethylamine (1,3 BAC) by HPLC and to compare the kinetic data with those obtained by DSC. Also, the HPLC data of gelation times are compared with those obtained by DMA.

EXPERIMENTAL

Materials

Bisphenol A diglycidyl ether [2,2 bis-(4-hydroxyphenyl) propane-bis(2,3-epoxypropyl)ether (DGEBA) (Shell Epikote 828) was obtained from Shell Chemicals, St. Charles, LA; weight per epoxy equivalent = 192 g/eq). A stock solution was prepared containing 0.2340 g of DGEBA in 100 mL of HPLC grade methanol from Merck (Darmstadt, Germany). The working solution with a concentration of 46.8 mg/L was prepared by dilution of the stock solution. Both solutions were stored in the dark at 4°C. The compound 1,3-cyclohexanebis(methylamine) BAC 99%, C_6H_{10} $(CH_2NH_2)_2$ was supplied from Aldrich (Stein-

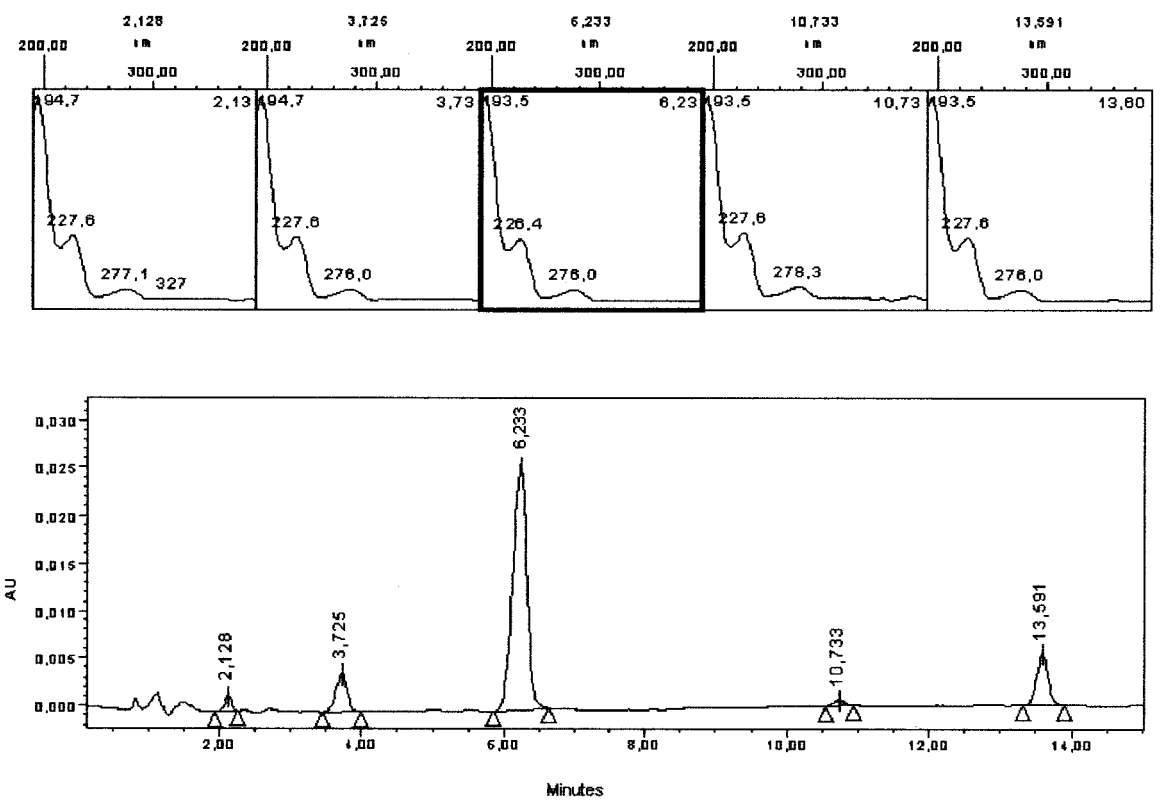

Figure 1 Chromatogram for a standard solution of DGEBA (7.49 mg/L in methanol). Monomer $n = 0$, retention time = 6.23 min. Column: Symmetry C_{18} . Guard Column: Symmetry C_{18}. Mobile phase: water–acetonitrile (gradient elution). $\lambda = 228$ nm. Injection: 20 μL.

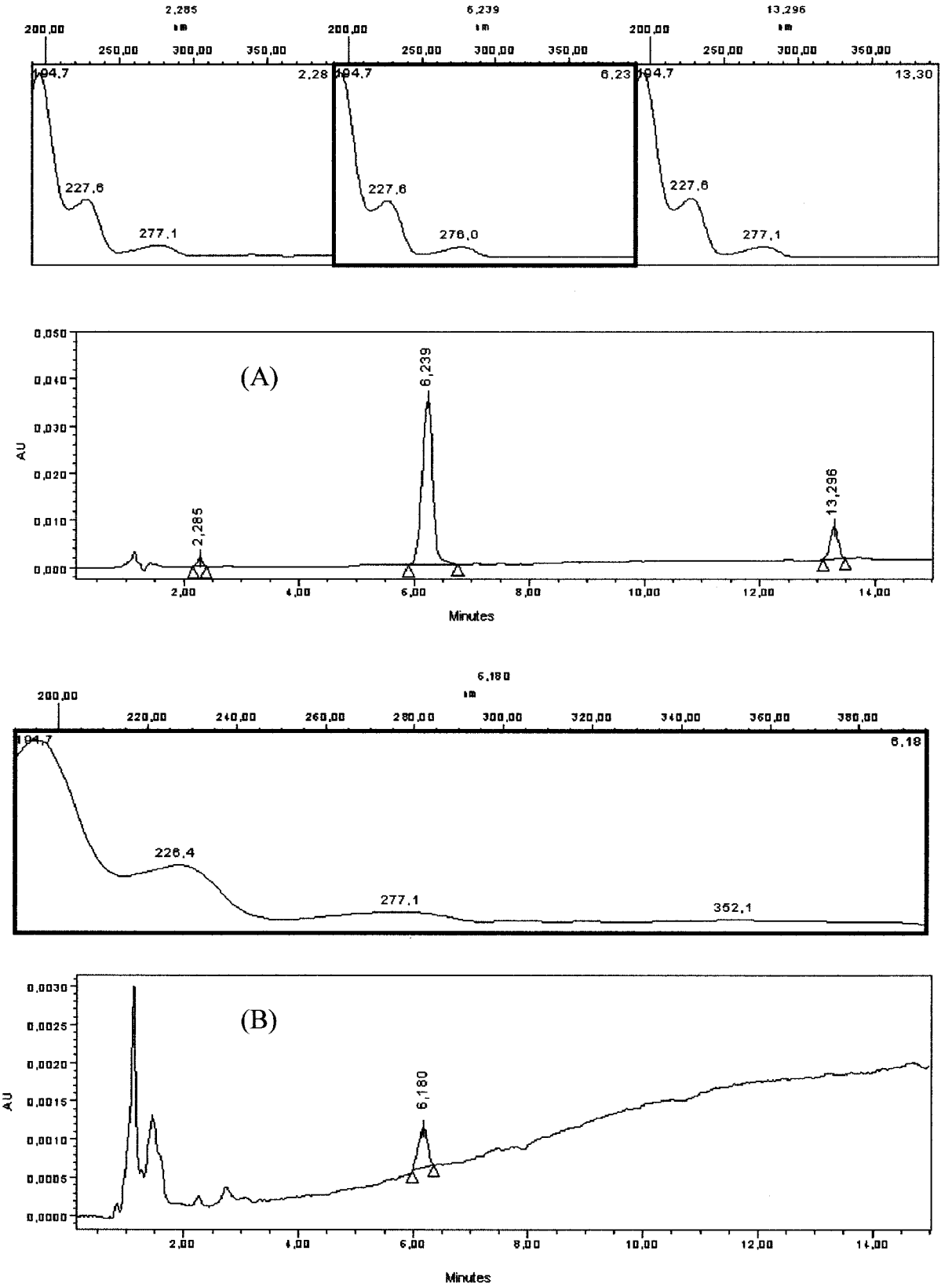

Figure 2 Chromatograms obtained during kinetic of epoxy resin formation at 60°C. (A) Reaction time 5 min. (B) Reaction time 60 min. Column: Symmetry C_{18}. Guard Column: Symmetry C_{18}. Mobile phase: water–acetonitrile (gradient elution). λ = 228 nm. Injection: 20 μL.

heim, Germany). Gradient HPLC grade acetonitrile was obtained from Panreac (Barcelona, Spain). Water used as HPLC solvent was purified with a Milli-Q water system (Millipore, Bedford, MA). Helium (N-50) from Carburos Metálicos (Barcelona, Spain) was used for degassing the mobile phases.

HPLC analysis

In this study we used a Waters 600 HPLC chromatograph (Waters Corporation, SA, Milford, MA) equipped with a HPLC Waters 600 quaternary pump, a Waters 600 organizer, a 7725i rheodyne valve injector (20 L loop), a Waters 996 diode array detector (DAD), which made it possible to collect data at a few wavelengths simultaneously and to take UV spectrum, and a software Millenium 32 (Waters Corporation, SA, Milford, MA).

The determination was performed with a Symmetry C_{18} (5 μm, 3.9 $\times$ 150 mm) column from Waters. Symmetry C_{18} (5 μm, 3.9 $\times$ 20 mm) guard columns from Waters were used to protecting the packing in analytical column. The mobile phase was composed of water and acetonitrile. The eluent flow rate was 1 mL/min. Gradient elution for DGEBA consisted of a 10-min linear gradient from water–acetonitrile (40 : 60) to 80% acetonitrile, 2-min isocratic elution at 80% acetonitrile, 1-min linear gradient to 60% acetonitrile and 2-min isocratic elution at 60% acetonitrile. The last step returns the column to the initial conditions and the column is ready for a new analysis.

The DGEBA spectrum shows three maxima, which set at 193, 228, and 276 nm. To reduce interferences, the wavelength 228 nm was selected although it has lower intensity than λ 193 nm.

The quantification of the analysis was performed using total area of the DGEBA peak in the resulting chromatograms. The chromatogram obtained in this way is shown in Figure 1. With these working conditions the retention time for the DGEBA peak was 6.23 min, the lowest in regard to other chromatographic methods, where the value is 17 min,[13] 22 min,[11] and 9.45 min.[14]

The standard chromatogram shows five peaks with a similar UV spectrum, their retention times are 2.13, 3.73, 6.23, 10.7, and 13.6 min, respectively. These data agree with the study of Bisphenol A and DGEBA characterization by reversed-phase HPLC using a mass spectrometry detector.[9] Two impurities more polar than the DGEBA monomer at $n = 0$ are detected, and other two impurities less polar than the DGEBA monomer at $n = 0$ are shown. All of them are characterized by an organic structure derivative from DGEBA.

Kinetic study

Stoichiometric amounts of DGEBA and 1,3 BAC were weighed. The sample was divided in different fractions, which were extended on pieces of tinfoil, which were placed in a heater at reaction temperature. The fractions were removed every 5 min for the reactions at 60 and 70°C and every 2 min for the reaction at 80°C. The reaction was stopped by placing the samples in liquid nitrogen. They were kept at −20°C until analysis time.

An aliquot of about 1.0 mg of the sample was weighed into a 10-mL volumetric flask, and the flask was filled to the mark with methanol. A 1-mL amount of the sample solution was transferred into a 10-mL volumetric flask diluted to volume with methanol. Finally 20 μL of sample solution were injected. After the gelation time the sample was stirred in ultrasonic bath for 120 min at 20°C. Every sample was processed duplicated.

The kinetic was followed by decreasing of the area of the DGEBA monomer chromatographic peak (Fig. 2).

The conversion[7–9] was obtained by,

$$x = 1 - (A_t/A_o)^{1/2} \quad (1)$$

where x is the conversion degree or extent of reaction, A_o is the DGEBA monomer peak area for 0 s, and A_t is the DGEBA monomer peak area for t s.

The gelation time obtained during HPLC measurements was considered to be the time at which the presence of an insoluble fraction was first observed.[7–9]

DSC analysis

A differential scanning calorimeter (Perkin-Elmer DSC 7, equipped with an intracooler and supported

TABLE I
Repeatability (r) (n = 9)

DGEBA concentration	Peak area (arbitrary units) Mean	SD	RSD (%)	r[a]	Retention time (min) Mean	SD	RSD (%)	r*
7.49 mg/L	357056	10688	2.99	29925	6.08	0.280	4.60	0.784
0.856 mg/L	35711	656.81	1.84	1839	6.12	0.126	2.06	0.353

[a] $r = 2.8\ SD_R$.

TABLE II
Reproducibility (R) $n = 15$

DGEBA concentration	Peak area. (arbitrary units) Mean	SD	RSD (%)	R	Shewhart: Warning limits Mean − 2 SD	Mean + 2 SD	Action limits Mean − 3 SD	Mean + 3 SD
7.49 mg/L	359,151	7781.33	2.17	21,787.8	343,589	374,714	335,807	382,495
0.856 mg/L	35,523	585.26	1.65	1638.7	34,352	36,693	33,767	37,279

$R = 2.8\ SD_R$.

by a Perkin-Elmer 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 melting point of pure indium. A dry nitrogen flow of 40 mL/min was used as purge gas. Samples of about 10 mg were enclosed in aluminium DSC capsules. Isothermal runs at cure temperatures of 60, 70, and 80°C were carried out.

Kinetic study

Differential scanning calorimetry assumes a proportionality between the heat evolved during cure and the extent of reaction that implies that the rate of heat evolved during cure and the rate of extent of reaction or the rate of conversion are proportional also. This last magnitude is obtained directly in the DSC signal, and is the starting print in almost all kinetic analysis by DSC. The conversion reached in an isothermal run with time is given by the expression

$$x = Qt/Q_T \quad (2)$$

where Qt is the heat evolved during time t, and Q_T is the total heat of reaction evaluated in a dynamic run.

DMA analysis

A DMA-7 dynamic mechanical analyzer from Perkin-Elmer was used to characterize the time dependence of the dynamic storage modulus, E', and the loss factor, tan δ, of the samples at various temperatures. DMA measurements in isotherm mode were used.

Samples of about 15 mg were prepared over Fiberglas. The mixture was poured in aluminium capsules and covered; the probe of DMA was placed over the cover and a static force of 150 mN put on top a dynamic force of 100 mN. This system of measurement is similar to parallel plates with cylindrical geometry of the sample. The tests have been realized at a frequency of 1 Hz for curing temperatures of 60, 70, and 80°C. A dry helium flow of 40 mL/min was used as purge gas. The DMA calibration has different routines. These automatic routines allow calibrating the height, furnace, temperature, and force. The temperature calibration was made using the melting point of pure indium.

Dynamic mechanical analysis assumes a dependence between elastic modulus and the increasing of cure. Dynamic mechanical signal can detect certain changes in the physical state of the analyzed sample like the sol-gel transition.

RESULTS AND DISCUSSION

Monomer dissolution after the gelation time

Soxhlet,[15,16] refluxing extraction[13] and ultrasonic extraction[17] have been applied to extract residual monomers or additives from polymers in most of studies. Usually, soxhlet extraction and refluxing method have been rejected by being very slow methods with extraction times between 12 and 16 h.[15,16] However, a shorter extraction time about 1 h has been obtained by ultrasonic methods.[17]

Mixtures of chloroform and methanol,[13] dichloromethane, and acetonitrile[7,8] were used by different authors. In this work, the methanol has been chosen by its compatibility with the chromatographic method.

To dissolve all residual monomer, the stirring time has been studied after settling the solvent and its volume. Initially, the sample was stirred for 180 min,

TABLE III
Regression Analysis

Linear range	Slope	Intercept	r^2	DL: Peak area	DL: mg/L	QL: Peak area	QL: mg/L
0.468–9.36 mg/L	4.61×10^4	-4.482×10^3	0.9999	1.66×10^3	0.133	1.60×10^4	0.444
1.87×10^{-2}–0.281 mg/L	3.6915×10^4	484	0.9855	1.94×10^3	3.93×10^{-2}	5.32×10^3	0.131

an aliquot of the sample solution was removed each 15 min, which was injected. The main rise of chromatographic peak was observed initially and the response was more regular after 90 min of stirring. A new extraction was carried out removing the first aliquot at 90 min and a stirring time of 120 min was selected

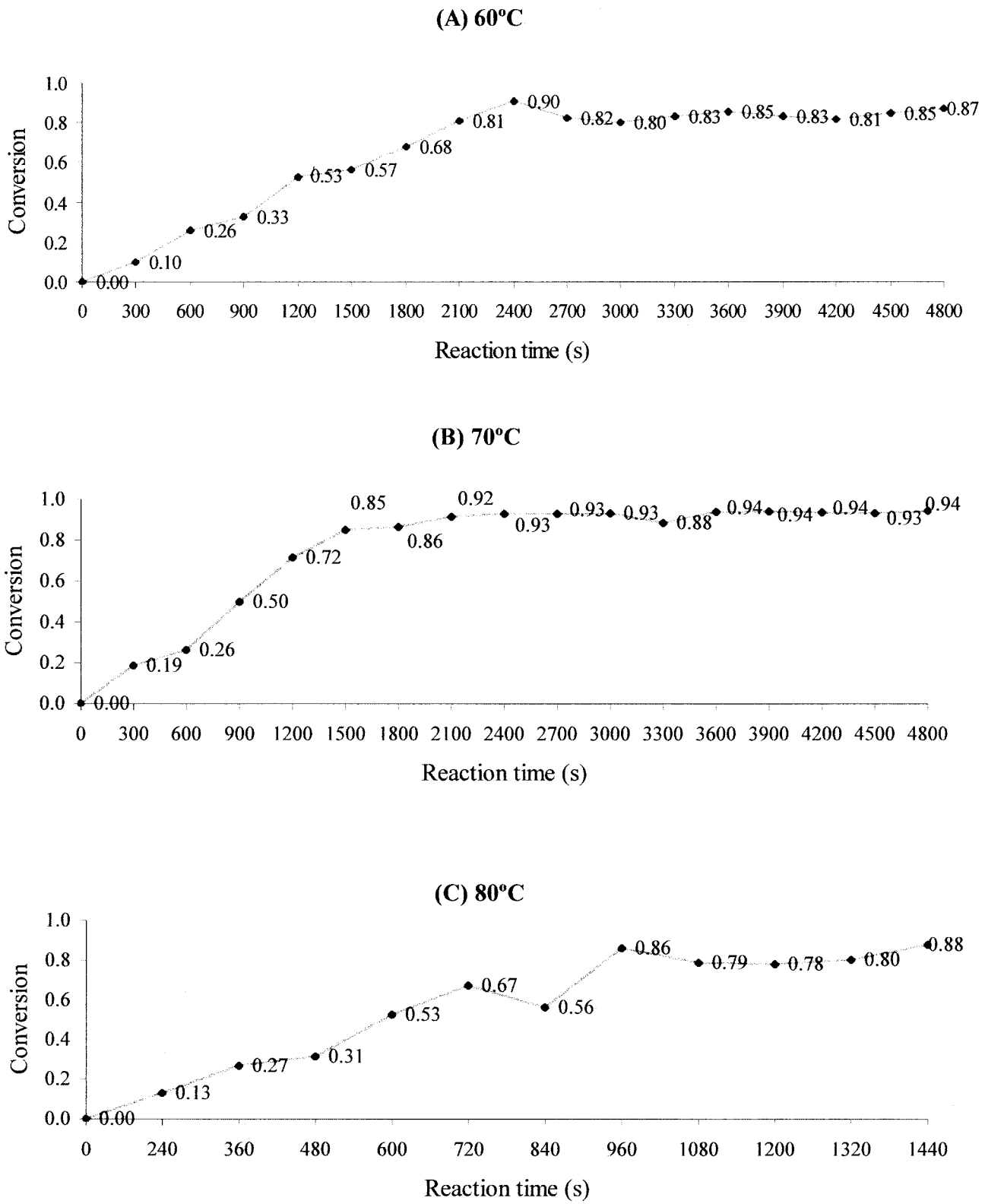

Figure 3 Evolution of conversion during formation of epoxy resin. (A) Kinetic of formation at 60°C. (B) Kinetic of formation at 70°C. (C) Kinetic of formation at 80°C.

because a relative standard deviations of 19.9 and 2.97% were obtained when the stirring times were below and above 120 min, respectively.

Analytical performance

Repeatability and reproducibility

The analytical method was studied for solutions of different concentrations 7.49 mg/L of DGEBA in methanol and 0.856 mg/L.

The repeatability was carried out performing nine replicate injections of each solution in the same day. For peak area, the relative standard deviation (RSD) was 2.99 and 1.84%, corresponding to the 7.49 and 0.856 mg/L solution, respectively (Table I). Retention time repeatability was evaluated from the same set of injections (Table I).

Peak area reproducibility and retention time reproducibility were examined by performing 15 injections on different dates (Table II). The obtained results were used to fix the Shewhart graphic parameters (Table II).

Linear range and limits

A very different response was observed between samples corresponding to the initial points and the last points of the kinetic study. Therefore, the linearity was examined for two concentration ranges (Table III).

Detection and quantitation limits were calculated by using calibration curve, detection limit (*DL*), $DL = y_B + 3\ S_B$; quantitation limit (*QL*), $QL = y_B + 10\ S_B$. y_B (blank signal) = a {intercept of the calibration graph [S_B (standard deviation of the blank) = Sy/x (standard deviation)]}.[18]

These limits provided a good enough performance to follow the kinetic reaction until the last steps. The lower limits were obtained by using other detectors, but they were removed in this work because the analytical procedures were more elaborated.

Parameter	Intercept	Slope
Value	-0.04027	1.010
Standard Error	0.02852	0.03920

Correlation Coefficient = 0.9889

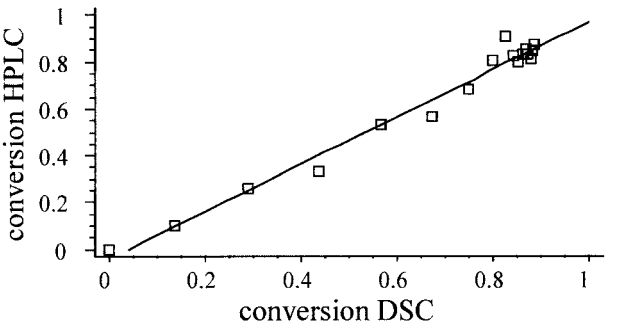

Figure 5 Relationship between HPLC and DSC data.

HPLC, DSC, and DMA analysis

The experimental kinetic data at 60, 70, and 80°C are shown in Figure 3. Two complementary methods to follow the cure and to compare the results obtained in respect to the HPLC analysis were carried out with differential scanning calorimetry and dynamic mechanical analysis in the isothermal mode at the same isothermal temperatures that were examined in HPLC.

The experimental values of conversion by DSC computed taking into account the heat evolved during cure are presented in Figure 4, together with the data obtained by HPLC.

The validation of HPLC method for the kinetic study was carried out by comparing with reference DSC method by applying a linear regression analysis for kinetic data at 60°C. The principal interest will be the identification of systematic mistakes. The conversion degree results obtained by DSC were settled as independent variable being the reference procedure while the conversion degree results obtained by HPLC were settled as a dependent variable.

Figure 5 shows that the calculated slope and intercept do not differ significantly from the values of 1 and 0, respectively, and thus, that there is no evidence

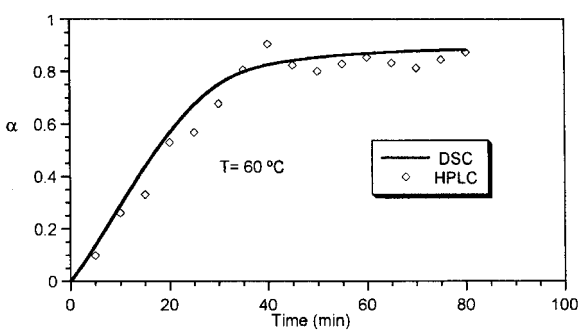

Figure 4 Isothermal run by DSC with the data obtained by HPLC at 60°C.

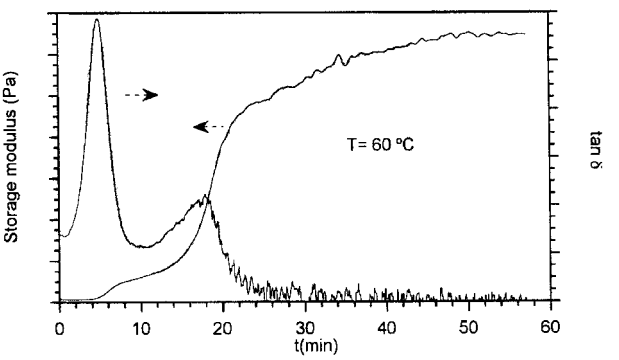

Figure 6 Isothermal run at 60°C by DMA.

TABLE IV
Comparison of Data Obtained by HPLC and DMA

	HPLC		DMA	
T (°C)	Gel time (s)	Gel conversion	Gel time (s)	Gel conversion (Indirect measurement)
60	1200	0.53	1030	0.59
70	900	0.50	490	0.55
80	600	0.53	400	0.62

for systematic differences between the two sets of results. The correlation coefficient shows a statistically significant relationship between both variables.

DMA curve (Fig. 6) represents the evolution of cure by following the storage modulus, E', the stored energy during a stress–strain cycle, and the tangent delta, that is, a ratio between the energy dissipated to energy stored in each cycle. Gelation time is assigned at the onset of E', vs. time curve or in the maximum of tan δ of the tan δ vs. t, and corresponds to the time where an abrupt change in mechanical properties take place when the material is transformed from a viscous liquid to an elastic solid infusible and insoluble.[6]

Table IV shows the gel conversion data obtained by HPLC and DMA for all isothermals considered. The data agree well, and they are in good agreement with the theoretical conversion proposed by Flory for an ideal network forming, where the value is 0.58 for a diamine and a difunctional epoxy resin. Also, are presented in this table the data of gel time determined by HPLC and DMA. The results are comparable with deviations due basically to the differences introduced by the techniques employed. The gel times obtained by DMA when are introduced into the DSC curves, conversion vs. time, showed that the values of gel conversion agree well with the data obtained with HPLC. By this indirect procedure the gel conversion values at 60, 70, and 80°C determined with the data of gel times obtained by DMA were respectively 0.59, 0.55, and 0.62.

CONCLUSIONS

We can conclude that the curves for cure development by HPLC and DSC are very similar, although there were difference due to the technique employed, so an HPLC carries out an analysis for each point of the curve with a certain dispersion around a "smoothed" curve mean while DSC can follow cure in one run, without the erratic appearance of the HPLC curve. The linear regression analysis between DSC and HPLC shows a good correlation coefficient value. Also, the comparative analysis by DMA and HPLC of times of gelation is satisfactory.

The proposed methodology is a good alternative to DSC and DMA for the study of the kinetic of the curing reactions, before and after gelation time.

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