Curing Kinetic of the Epoxy System BADGE *n* = 0/1,2 DCH by Fourier Transform Infrared Spectroscopy (FTIR)

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ABSTRACT: The curing reaction of an epoxy system consisting of a diglycidyl ether of bisphenol A (BADGE *n* = 0) and 1,2-diaminocyclohexane (DCH) was studied by Fourier Trasform Infrared Spectroscopy (FTIR). From the infrared spectra using a peak-height method, that was based on the ratio of the height of the characteristic to reference absorbance peak, degree of conversion at different isothermal temperatures were calculated. From a kinetic study, the Horie et al. model was used; parameters such as rate constants and activation energies were determined. The results were compared to those obtained for same epoxy systems using scanning differential calorimetry (DSC). © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3366–3372, 2001

Key words: FTIR; kinetic parameters; BADGE (*n* = 0); epoxy resins

INTRODUCTION

Epoxy resins are of great commercial importance for elastic, abrasion-resistant and chemical-resistant paints and coatings, and for casting and impregnation resins. On account of their excellent adhesion to most types of surfaces they are also employed as adhesives and sealing agents.

The curing of epoxy resin passes from the liquid state through its gel point, where it is transformed into a rubber, then through the vitrification point, at which it is converted into a glass.

Various techniques are used to follow the kinetic of curing of epoxy resins. Fourier transform infrared spectroscopy (FTIR) is one of the technique used, because it is possible to detect the variation of functional groups if FTIR spectra were checked at consecutive periods of times. This is based on the fact that, if the degree of conver-sion increases, the intensity of the absorption bands of terminal groups decrease. For quantitative analysis a reference band is used. In this study we use the absorption band at 915 cm^{-1} of the terminal epoxy groups.

The model proposed by Horie et al.,[1] assuming equal reactivity for all amine hydrogens, is used to determinate the rate constants. Once one knows the rate constants, and using Arrhenius law, the activation energies for two mechanisms, *n*th order and autocatalyzed can be determined.

An objective of this study was to obtain kinetic data (degree of conversion, reaction rates, and activation energies) for the curing reaction of the epoxy system diglycidyl ether of bisphenol A *n*=0/1,2 diaminocyclohexane using quantitative analysis of Fourier transform infrared spectra (FTIR). Kinetic data are compared with those obtained using DSC in previous studies.[2–5] Another objective of this study was to check the applicability of FTIR analysis to analyze the curing kinetic of epoxy resins.
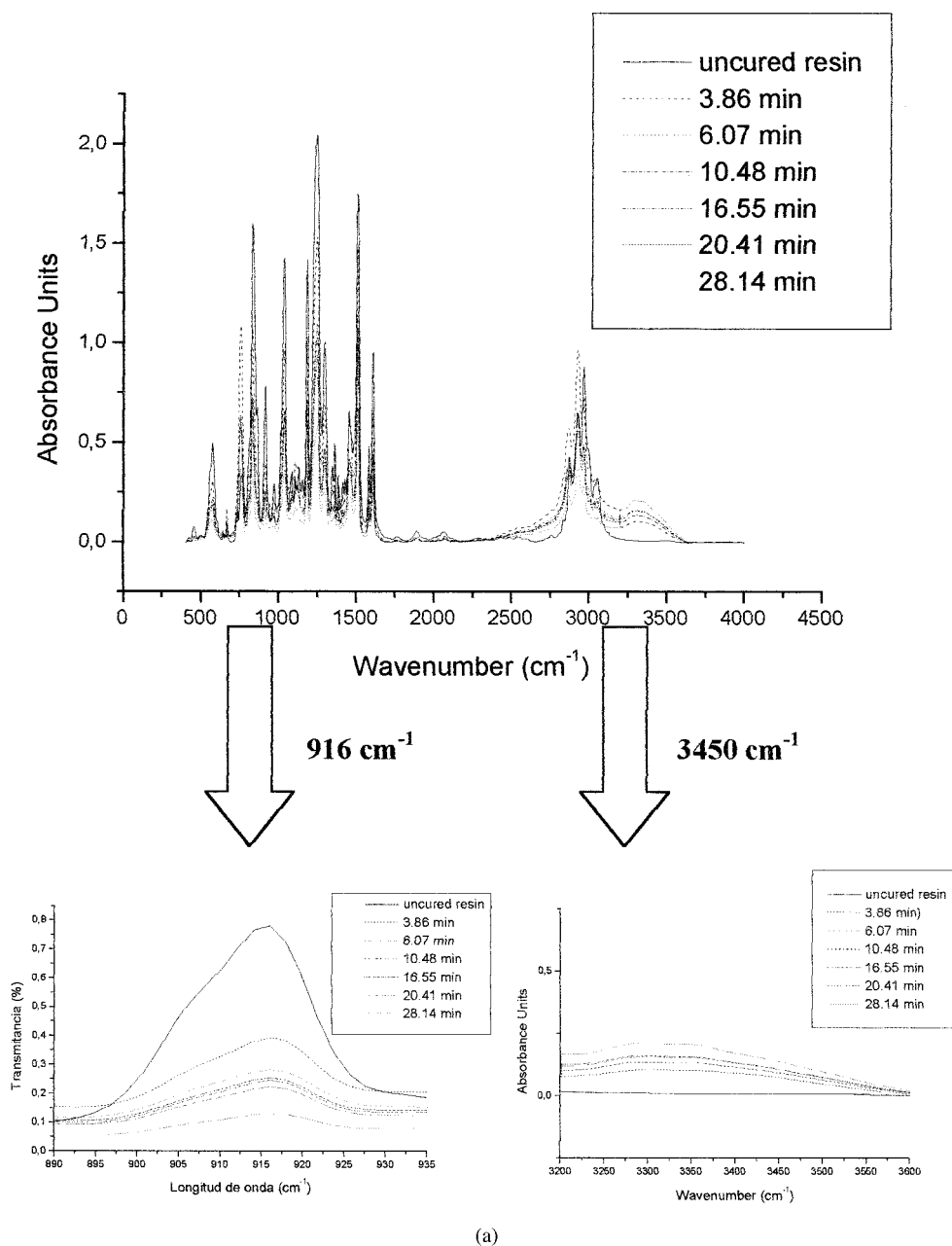
Figure 1 (a) FTIR spectra for different cure times at 60°C. (b) FTIR spectra for different cure times at 70°C. (c) FTIR spectra for different cure times at 80°C. (d) FTIR spectra for different cure times at 90°C.

EXPERIMENTAL

Materials

BADGE ($n = 0$) was the epoxy resin used (Resin 332, Sigma Chemical Co, St. Louis, MO), and 1,2 diamine cyclohexane (DCH, Fluka) was the curing agent. The epoxide equivalent weight of the resin was 173.6, as determined by wet analysis,[6,7] and that of the diamine was taken as 28.5.[2]

Sample Preparation

Epoxy resin and cure agent were carefully and homogeneously mixed at the stoichiometric ratio before being introduced into the flasks. Curing reac-
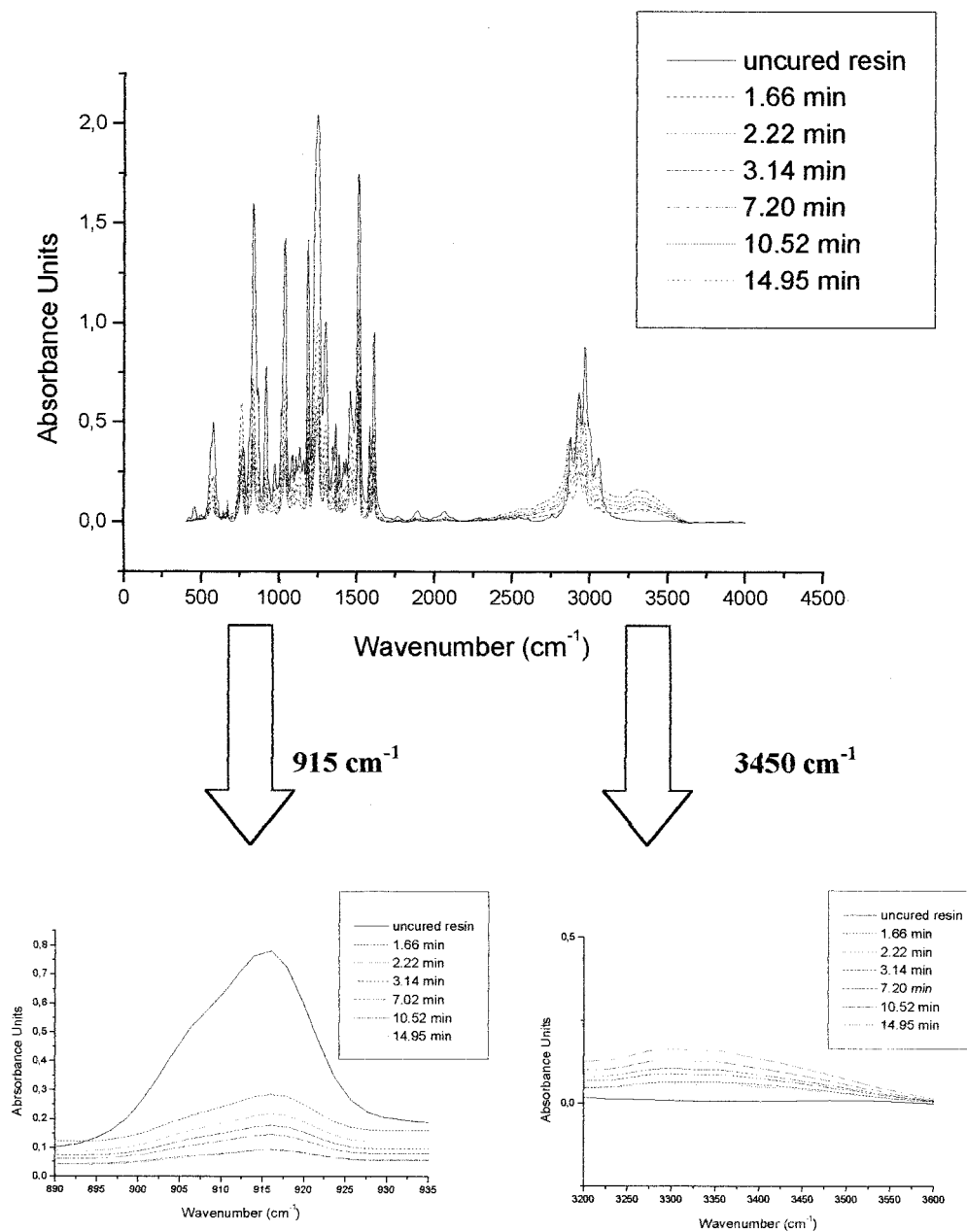
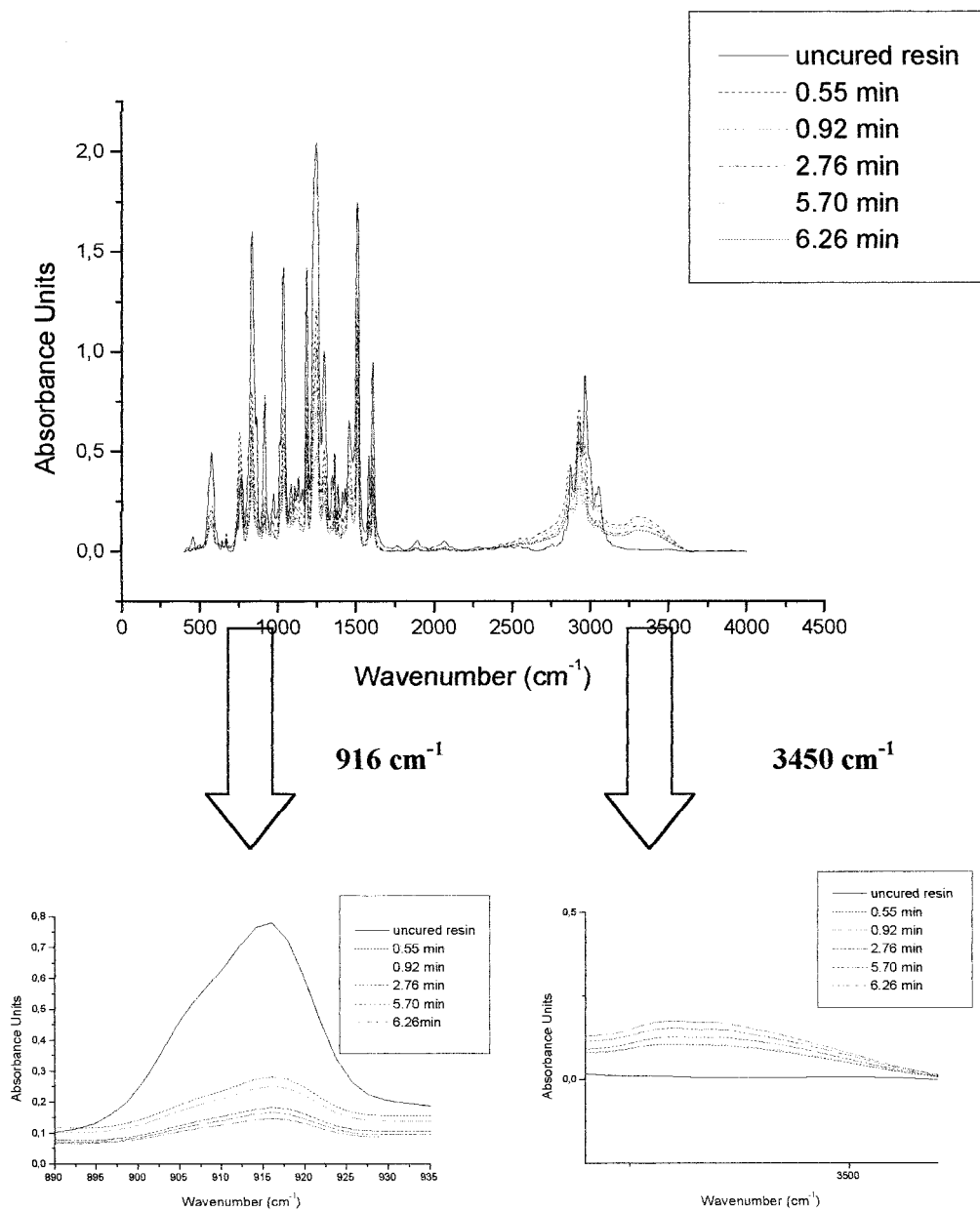**Figure 1**   (*Continued from the previous page*)

tion was programmed at different isothermal temperatures (60, 70, 80, and 90°C) for different times. After curing, samples were dissolved in chloroform, and one droplet of this mixture was placed on a CsI plate. After evaporation of solvent a thin film was formed on the CsI plate. The thickness of the film was optimized to provide the best absorbance unit. For the infrared measurements the sample was covered with another CsI plate.

FTIR Spectroscopy

The FTIR spectra were obtained on a BRUKER IFS-66V. The resolution of this equipment was of $0.250 \ cm^{-1}$. The vacuum purge was of 2 mbar.

RESULTS AND DISCUSSION

Figure 1(a)–(d) shows the infrared spectra of epoxy system at different temperatures of 60, 70, 80,

(c)

Figure 1 (*Continued from the previous page*)

and 90°C for different periods of times of the vibration bands of the epoxy groups (760, 915, and 970 cm^{-1}) for the infrared analysis the reference band at 915 cm^{-1}, is used, which decreases during the curing reaction. In these figures we see that the intensity of the vibration band of the terminal epoxy groups decreases during the cure reaction; at the same time ν(OH) at 3450 cm^{-1} increases in intensity. The band ν_{as}(C—O—C) at

1245 cm^{-1} can be assigned to the aliphatic-aromatic ether linkage, and the bands at 1510 and 830 cm^{-1} can be assigned to p-phenylene groups. These last bands are not appropriate to kinetic analysis because of overlapping of the spectra at the same temperature for different periods of times.

From the spectra we used a method derived on Beer's law[8,9] that was based on the ratio of
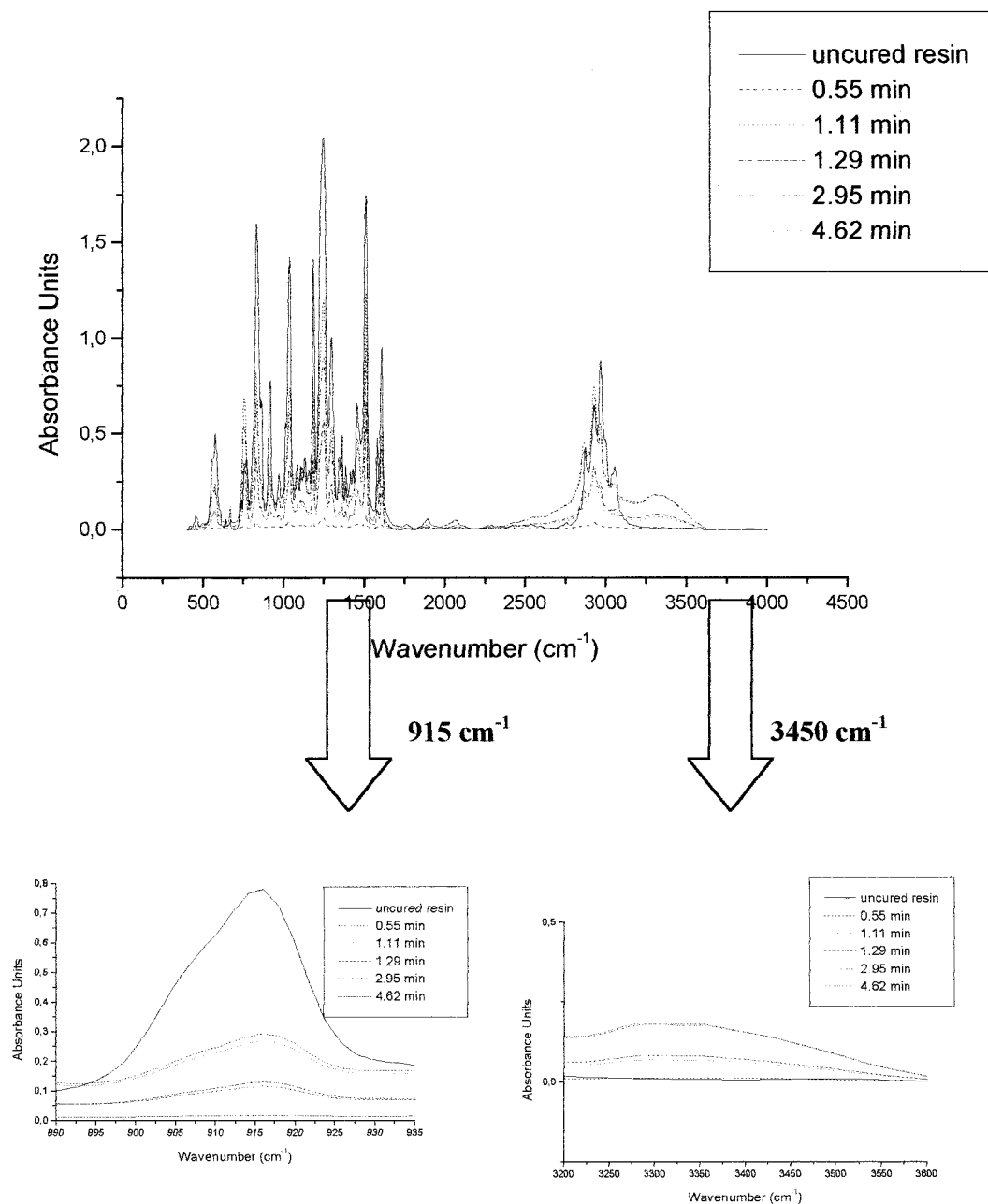
Figure 1 (*Continued from the previous page*)

the height of the characteristic to reference absorbance peak. The reference peak used as a internal standard for the normalization of epoxy peak absorbance is phenylene at 830 cm^{-1}. The degree of conversion at different isothermal temperatures can be calculated. This FTIR method should be a more precise indicator of extent of cure than DSC, as it directly measures the

chemistry taking place, rather than the heat evolved.[9] Figure 2 shows the degree of conversion vs. time at different isothermal temperatures. The initial slope of the curves is steeper for higher temperatures. Next to that the slope gets very small after a certain amount of time, which can be assigned to a diffusion-controlled reaction. At all temperatures, the degree of con-
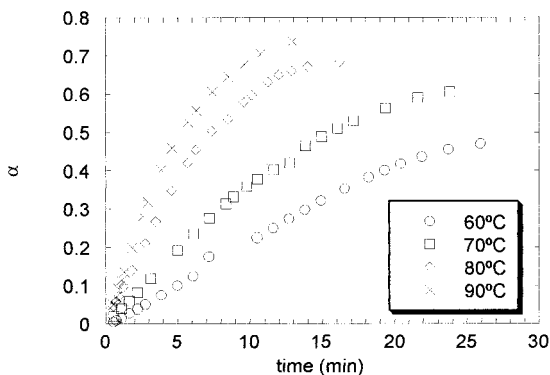
Figure 2 Degree of conversion vs. time at different isotheraml temperatures.

Figure 4 Reaction rates vs. time at different temperatures.

version shows autoacceleration in the initial stages, indicated by the slight positive curvature. Sewell et al.,[10] Nuñez et al.,[3,5] and Barton[11] showed autoacceleration for similar epoxy systems. Figure 3 shows the correlation of the results from two methods at different isothermal temperatures. Comparison of the values obtained using the IR method with those obtained using DSC show a slightly increase. This behavior is in good agreement with Sewell et al.[10] for similar systems.

In previous articles[2,3] it was concluded that for this epoxy system, the reaction rate, using a model proposed by Horie et al.[1] could be expressed as:

$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha)(1 - \alpha)^2 \qquad (1)$$

where K_1' and K_1 are constants proportional to rate constants for autocatalytic and nth order paths, respectively.
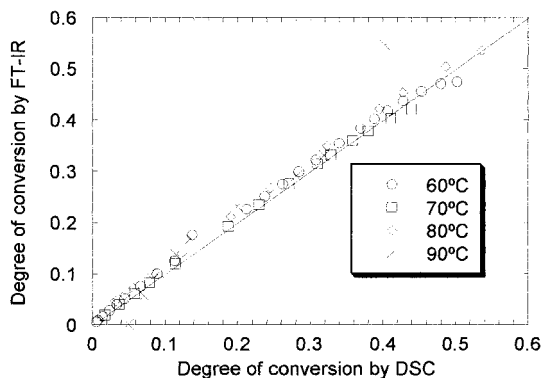

Figure 3 Plot of degree of conversion by DSC vs. degree of conversion by FTIR at different isothermal temperatures.
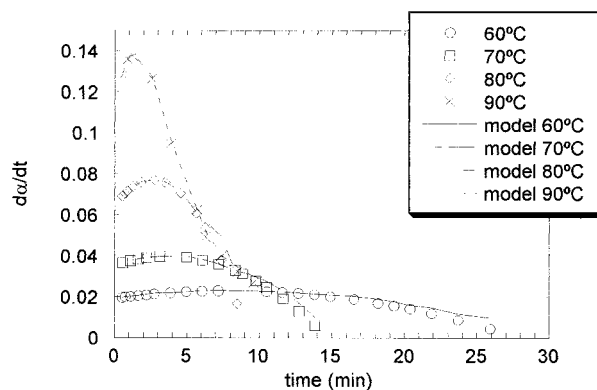
The reduced rate is defined as

$$\alpha^0 = \frac{\frac{d\alpha}{dt}}{(1 - \alpha)^2} = K_1' + K_1\alpha \qquad (2)$$

Figure 4 shows the reaction rates vs. time at different isothermal temperatures. It can be seen that the reaction rate increases with temperature, but drops faster with increasing temperatures. The experimental results are compared with those obtained using a chemical kinetic model. At all temperatures the agreement between experimental and model results mainly for small times. This may be because at high conversions the reaction is controlled by a diffusion mechanism.

Equation (2) was used to determine values of K_1' and K_1. From the straight lines resulting from linear fitting, values of K_1' and K_1 can be derived. Values of the rate constants for the infrared method and the DSC method are listed in Table I. As can be seen, the values obtained for IR method are very close to the DSC data.[2,3]

The activation energies corresponding to the two kinetic mechanisms (nth order and autocatalyzed) were obtained from Arrhenius plot of ln K vs. $1000/T$. Values of activation energies for infrared method and the DSC method are shown in Table II. These values are very similar for both methods. This fact shows the applicability of the infrared method to study the curing kinetics of thermosets. As expected, activation energy corresponding to the autocatalyzed reaction was slower than corresponding to nth order path.

Table I   Values of Rate Constants Calculated Using FTIR and DSC[(2–5)] Methods at Different Isothermal Temperatures

	FTIR		DSC[(2)]	
T (°C)	K'_1 nth-Order (min^{-1})	K_1 Autocatalyzed (min^{-1})	K'_1 nth-Order (min^{-1})	K_1 Autocatalyzed (min^{-1})
60	0.0193	0.0894	0.0177	0.0944
70	0.0368	0.1137	0.0385	0.1392
80	0.0635	0.2677	0.0636	0.2750
90	0.1239	0.3689	0.1115	0.3368

CONCLUSIONS

The kinetic parameters (degree of conversion, reaction rates, and activation energies) obtained using FTIR method are very close to those obtained using the calorimetric method. Thus, FTIR spectroscopy is a powerful tool to monitor the kinetic reaction of this epoxy. The intensity of the band at 915 cm^{-1} is suitable for quantitative analysis. As can be seen at all temperatures, the degree of conversion increases when the intensity of the band at 915 cm^{-1} decrease. The band at 3450 cm^{-1} can be also used for kinetic analysis, because the intensity of this band increases while the degree of conversion increases.

REFERENCES

1. Horie, K.; Kambe, H.; Sawada, M.; Mita, I.; Kambe, H. J Polym Sci 1970, 8, 1357.
2. Núñez, L.; Fraga, F.; Fraga, F.; Castro, A. J Appl Polym Sci 1997, 63, 635.
3. Núñez, L.; Taboada, J.; Fraga, F.; Núñez, M. R. J Appl Polym Sci 1997, 66, 1377.
4. Núñez, L.; Fraga, F.; Núñez, M. R.; Villanueva, M. J Appl Polym Sci 1998, 70, 1931.
5. Núñez, L.; Fraga, F.; Castro, A.; Núñez, M. R.; Villanueva, M. J Appl Polym Sci 2000, 75, 291.
6. Lee, H.; Neville, K. Handbook of Epoxy Resin; McGraw-Hill: New York, 1967.
7. May, C. A. Epoxy Resins: Chemistry and Technology; Marcel Dekker: New York, 1988.
8. Conley, R. T. Infrared Spectroscopy; Allyn and Bacon Inc.: Boston, 1972.
9. Hummel, D. O.; Solti, A. Atlas of Polymer and Plastics; VCH Publishers: New York, 1988, vol. I and II.
10. Sewell, G. J.; Billingham, N. C.; Kozielski, K. A.; George, G. A. Polymer 2000, 41, 2113.
11. Barton, J. M. Adv Polym Sci 1985, 72, 111.

Table II   Activation Energies Calculated using FTIR and DSC Methods for nth-Order and Autocatalyzed Mechanisms

	(kJ/mol)	
	FTIR	DSC[(2)]
nth-Order	61.51	61.19
Autocatalyzed	51.27	47.67