

A Kinetic Scheme for an Amine-Epoxy Reaction with Simultaneous Etherification

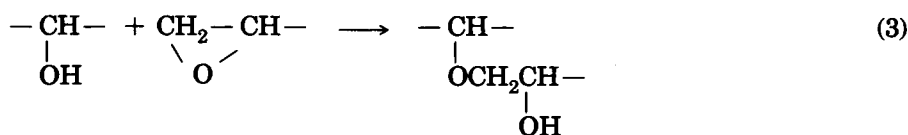
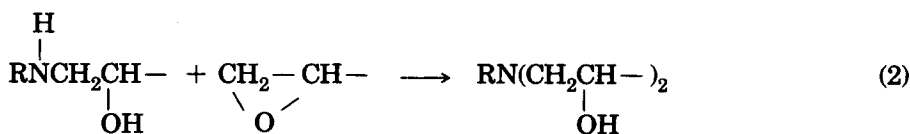
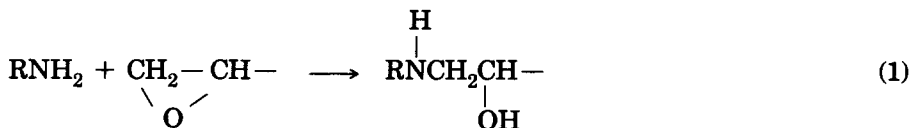
CARMEN C. RICCARDI and ROBERTO J. J. WILLIAMS,* *Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, (7600) Mar del Plata, Argentina.*

Synopsis

The curing reaction of an epoxy resin with a diamine is analyzed, taking into account the possibility of simultaneous etherification. A kinetic scheme is derived and fitted to experimental results for the reaction of commercial bisphenol A diglycidyl ether (BADGE) with diaminodiphenyl sulfone (DDS). Total reaction heat, vitrification curve, and reactivity ratio of secondary to primary amine hydrogens are experimentally characterized. It is shown that the etherification reaction is significant at $T > 150^\circ\text{C}$, at intermediate and high reaction extents when the primary amine has been sufficiently depleted.

INTRODUCTION

The reaction of a primary amine with an epoxide leads to the following possibilities¹



A fourth possibility, namely the homopolymerization of epoxy groups requires the presence of Lewis bases (i.e., tertiary amines), inorganic bases (i.e., NaOH), or Lewis acid catalysts (i.e., F_3B complexed with an amine).^{2,3} As the tertiary amine arising from step (2) is usually sterically hindered,

* To whom all correspondence should be addressed.

its catalytic effect toward the homopolymerization reaction will not be significant.¹ Thus, this possibility will be deleted from the analysis.

The relevance of step (3) with respect to the two other reactions depends very much on the nature of the diamines. There is plenty of experimental evidence indicating that, for stoichiometric mixtures of epoxy resins with aliphatic diamines, the etherification reaction may be neglected.^{1,4-7} However, for aromatic diamines this may no longer be the case. The reasons are the low reactivity of the secondary amine with respect to the primary one,⁸ and the higher temperatures needed to produce the curing. For example, for the curing of tetraglycidyl 4,4' diaminodiphenyl methane (TGDDM) with diaminodiphenyl sulfone (DDS), there is evidence of the presence of the etherification reaction.⁹⁻¹⁴ Rate constants for secondary amine-epoxy and hydroxyl-epoxy are reported to be equal and about one-tenth of the reaction rate constant for the primary amine-epoxy reaction.^{13,14} It is fair to point out, however, that the etherification reaction has not been found for other epoxy resin-aromatic diamine systems.^{15,16}

The aim of this paper is to derive a rate equation for the epoxide consumption, taking into account the possibility of etherification. Model predictions will be compared with experimental results arising from an epoxy-aromatic diamine system, and general trends will be discussed.

KINETIC SCHEME

Two kinds of kinetic models may be found in the literature. On the one hand, pure phenomenological equations of the type

$$r = (K_A + K_B x^m) (1 - x)^p \quad (4)$$

have been used to describe the autocatalytic cure of various epoxy resins.^{12,17-26} K_A and K_B are specific rate constants, m and p adjustable parameters, and x and r are the conversion and rate of conversion of epoxy groups. Expressions of this type may be useful as constitutive equations for the reaction rate, although they do not provide any information about the reaction path. This knowledge is necessary for any study dealing with the analysis of the network structure.

On the other hand, models arising from proposed kinetic mechanisms have also been used, the most relevant being, perhaps, the one proposed by Horie et al.⁶ Only for the case of diamines with equal reactivity of primary and secondary amines, the rate equation derived by Horie et al. reduces to Eq. (4), with $m = 1$ and $p = 2$. We have recently used this model to analyze the curing of a commercial bisphenol A diglycidyl ether (BADGE) with ethylenediamine (EDA) in a broad temperature range.²⁷ In this case there was no need to consider the etherification reaction.

Zukas et al.¹¹ presented an approach to incorporate the etherification reaction into the model of Horie et al.,⁶ by assuming that, similarly to steps (1) and (2), step (3) may take place both by a noncatalytic path and by a reaction catalyzed by OH groups. Particular equations were obtained assuming a low conversion in the etherification reaction. This approach is

now extended without imposing any restriction on the amount of etherification.

By denoting, e = concentration of epoxy equivalents, a_1 = concentration of primary amine hydrogens, a_2 = concentration of secondary amine hydrogens, k = specific constant for the catalytic reaction rate, k' = specific constant for the noncatalytic reaction rate (subscripts 1, 2, and 3 indicate the possible reaction paths), the following kinetic equations may be written:

$$-de/dt = e\{[k'_1 + k_1(\text{OH})]a_1 + [k'_2 + k_2(\text{OH})]a_2 + [k'_3 + k_3(\text{OH})](\text{OH})\} \quad (5)$$

$$-da_1/dt = 2a_1e[k'_1 + k_1(\text{OH})] \quad (6)$$

$$da_2/dt = e\{[k'_1 + k_1(\text{OH})]a_1 - [k'_2 + k_2(\text{OH})]a_2\} \quad (7)$$

$$d(\text{OH})/dt = e\{[k'_1 + k_1(\text{OH})]a_1 + [k'_2 + k_2(\text{OH})]a_2\} \quad (8)$$

The ratio of specific reaction rates is assumed to be constant and independent of temperature:

$$k'_2/k'_1 = k_2/k_1 = n \quad (9)$$

$$k_1/k_3 = k'_1/k'_3 = \lambda \quad (10)$$

The parameter n gives the reactivity ratio between secondary and primary amine hydrogens. Its value may be obtained from an experimental determination of the critical gelation ratio of samples with a diamine excess.⁷ The parameter λ , which is obtained from the fitting of the kinetic model to experimental results, gives the reactivity ratio for the epoxy-primary amine reaction with respect to the etherification. When $\lambda \rightarrow \infty$, this last reaction may be neglected.

By introducing Eqs. (9) and (10) in Eqs. (5), (7), and (8), we get

$$-de/dt = [k'_1 + k_1(\text{OH})][a_1 + na_2 + (\text{OH})/\lambda]e \quad (11)$$

$$da_2/dt = [k'_1 + k_1(\text{OH})](a_1 - na_2)e \quad (12)$$

$$d(\text{OH})/dt = [k'_1 + k_1(\text{OH})](a_1 + na_2)e \quad (13)$$

From Eqs. (6), (12), and (13), (OH) may be related to a_1 and a_2 , through

$$(\text{OH}) = (\text{OH})_0 + (a_{10} - a_1) + (a_{20} - a_2) \quad (14)$$

In what follows it will be assumed that the epoxy-amine system is stoichiometric (i.e. $e_0 = a_{10}$; $a_{20} = 0$). If this is not the case, the procedure described below may be used to generate similar equations with e_0/a_{10} as a parameter. Equation (14) reduces to

$$(\text{OH})/e_0 = (\text{OH})_0/e_0 + 1 - (a_1 + a_2)/e_0 \quad (15)$$

An experimental determination of the initial ratio $(\text{OH})_0/e_0$ becomes necessary.

Kinetic equations may be written in terms of the reaction extent of epoxy groups,

$$x = (e_0 - e)/e_0, \quad (16)$$

and the reduced variable

$$\alpha = a_1/e_0 \quad (17)$$

Dividing Eq. (12) by Eq. (6), and integrating, we get

$$a_2/e_0 = (\alpha^{n/2} - \alpha)/(2 - n) \quad (18)$$

By defining,

$$K_1 = k_1 e_0^2 \quad (19)$$

$$K'_1 = k'_1 e_0 \quad (20)$$

and replacing Eqs. (15) to (20) in Eq. (11), we obtain

$$\begin{aligned} dx/dt = & [(1 - x)/(2 - n)] [K'_1 + K_1 F(\alpha)] \\ & [2(1 - n)\alpha + n\alpha^{n/2} + (2 - n) F(\alpha)/\lambda], \end{aligned} \quad (21)$$

where

$$F(\alpha) = 1 + (\text{OH})_0/e_0 - [(1 - n)\alpha + \alpha^{n/2}]/(2 - n) \quad (22)$$

The relationship between α and x may be obtained by introducing Eq. (17) in Eq. (6), dividing by Eq. (21), and integrating. This leads to

$$\begin{aligned} x = & \{(1 - \alpha)(1 - n)(2 - 1/\lambda) + 2(1 - \alpha^{n/2})(1 - 1/n\lambda) - \\ & - [(2 - n)/\lambda] [1 + (\text{OH})_0/e_0] \ln \alpha\} / 2(2 - n) \end{aligned} \quad (23)$$

Equation (21), together with Eq. (22) and (23), describe the kinetics of disappearance of epoxy groups. For the particular case of $n = 1$ and $\lambda \rightarrow \infty$, Eq. (21) leads to

$$dx/dt = \{K'_1 + K_1 [x + (\text{OH})_0/e_0]\} (1 - x)^2 \quad (24)$$

Equation (24) has been used to describe the cure of BADGE with EDA, a system in which n is close to one.^{6,27}

MATERIALS

The epoxy resin was a commercial BADGE, Araldit GY 250 (Ciba-Geigy) with an epoxy content of 5.34 eq/kg (weight per equivalent WPE = 187.3 g/eq) and $(\text{OH})_0/e_0 = 0.061$, as previously reported.²⁷ The amine was 4,4'

diaminodiphenyl sulfone (DDS), provided by Ciba-Geigy (HT 976). Stoichiometric mixtures of the epoxy-amine were prepared by heating the epoxy resin to 80°C and dissolving the diamine until a clear homogeneous solution was obtained. The reaction extent during the mixing time (5–10 min) is completely negligible, as may be corroborated by extrapolating the experimental cure kinetics.

HEAT OF REACTION

Figure 1 shows a dynamic run in the DSC, at 10°C/min, in a N₂ atmosphere at 650 psi. The heat of reaction arising from the area under the peak is $Q = 563 \text{ J/g} = 25.3 \text{ kcal/eq}$. This value agrees satisfactorily with results reported for the reaction of phenyl glycidyl ether with butylamine, taken as a model system.⁶ Close values have been reported for several epoxy-amine systems.^{25,26,28} This means that if the etherification reaction has any significance at all, its associated reaction heat must be close to the one reported for the epoxy-amine reaction. This enables us to obtain the overall kinetics of epoxy consumption from calorimetric information.

VITRIFICATION CURVE

In order to determine the reaction extent at vitrification, several stoichiometric samples were degassed, closed in glass tubes, and cured at a constant temperature in a thermostat. After several hours, one of the tubes was extracted from the bath and cooled to room temperature. The partially cured resin was pulverized to a very fine powder and the remaining epoxy groups were reacted with pyridinium chloride, followed by titration of the excess pyridinium chloride with standard base. A detailed description of this technique is reported by Bell.¹⁵ This procedure was repeated for the different tubes extracted from the thermostat at different times. When two determinations gave the same epoxy content it meant that the vitrification curve at the particular curing temperature had been attained, arresting the curing reaction.

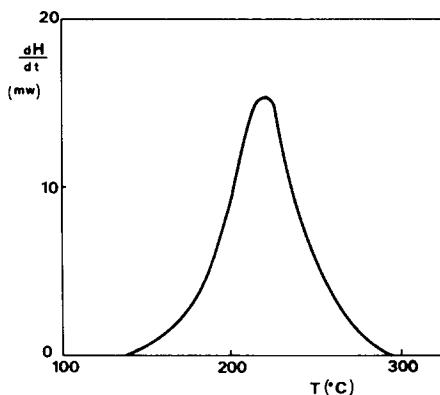


Fig. 1. Curing of BADGE with DDS in the dynamic mode of the DSC, at a 10°C/min heating rate (sample mass = 10 mg).

Figure 2 shows the vitrification curve for the BADGE-DDS system in a conversion versus curing temperature diagram. Results reported by Barton²² and Enns and Gillham²⁹ for a similar system are plotted with a dotted line.

The glass transition of the vitrified samples was checked by TMA runs at 10°C/min (Du Pont 943 Thermal Mechanical Analyzer). The resulting value was very close to the curing temperature (in every case the difference was less than 5°C).

The information plotted in Figure 2 (i.e. maximum reaction extent x_T), for a particular curing temperature, is necessary for the interpretation of the isothermal kinetic runs.

REACTIVITY RATIO OF AMINE HYDROGENS

Dušek et al.⁷ derived statistical parameters of the network resulting from the cure of an epoxy resin with a diamine, including the effect of the different reactivity of primary and secondary amines. This analysis may be used to find the reactivity ratio of secondary to primary amine hydrogens, by curing formulations with an excess of amine, $a_{10}/e_0 > 1$, and finding the critical a_{10}/e_0 ratio leading to gelation at full epoxy conversion.

Equations derived by Dušek et al.⁷ are plotted in Figure 3 as a_{10}/e_0 vs. n [Eq.(9)]. Curing with a high excess of amine and at not very high temperatures, enables one to neglect the etherification reaction, making possible the use of Figure 3.

The experimental determination of a_{10}/e_0 was performed as follows. Samples with a_{10}/e_0 values lying between 2 and 3 were prepared by dissolving appropriate amounts of DDS in the epoxy resin, at 80°C. After a heating period of 3 h at 120°C, they were cooled and the sol fraction was extracted with MEK or dioxane (both solvents gave the same results). It was found that, for $a_{10}/e_0 = 2.57$ a gel fraction was present while for $a_{10}/e_0 = 2.63$ the sample was completely soluble. Thus, the critical ratio is located between these values. Using Figure 3, a reactivity ratio lying between 0.38 and 0.46 is found. The value selected for the kinetic model was $n = 0.40$, in good agreement with values quoted in the literature for aromatic diamines.⁸

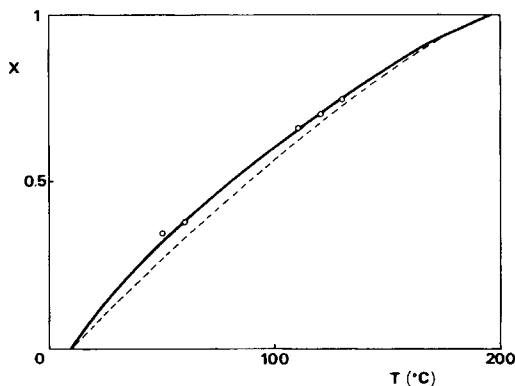


Fig. 2. Reaction extent for vitrification as a function of the curing temperature. The dotted line is the functionality reported by Barton²² and Enns and Gillham²⁹ for a similar system.

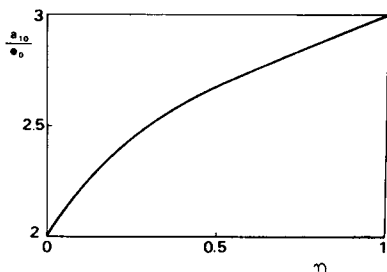


Fig. 3. Critical ratio of primary amine to epoxy equivalents leading to gelation at full epoxy conversion, as a function of the reactivity ratio between secondary and primary amine hydrogens.

CURING KINETICS

Stoichiometric samples were cured in the isothermal mode of a Du Pont 990 Thermal Analyzer, provided with a DSC pressure cell. Calibration of the device and operation conditions were described in a previous paper.²⁷ The temperature range which could be covered varied from 110°C to 200°C.

Figure 4 shows there typical runs for 10 mg samples. For a given time, the conversion was calculated as

$$x = x_T A(t)/A(\infty) \quad (25)$$

where $A(t)/A(\infty)$ is the relative fraction of the total area under the peak, and x_T is the maximum reaction extent at the particular curing temperature, obtained from Figure 2.

The reaction rate arises from

$$dx/dt = (dH/dt) x_T/A(\infty) \quad , \quad (26)$$

where $A(\infty)$ is expressed in energy units. (Notice that $A(\infty)/x_T$ represents the total heat of reaction Q , arising from dynamic runs.)

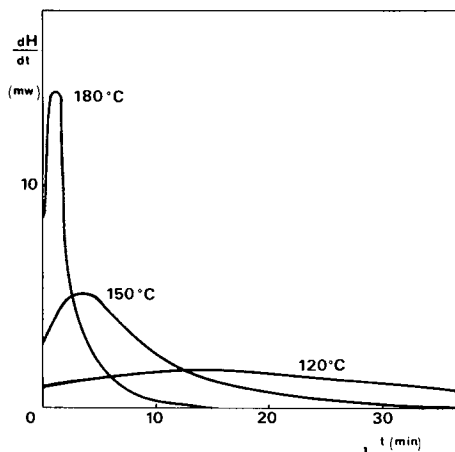


Fig. 4. Isothermal DSC runs for 10 mg samples of BADGE/DDS with stoichiometric composition.

In order to check the fitting of the proposed kinetic scheme with experimental results, Eqs. (21) to (23) are written for the particular case of $n = 0.4$ and $(\text{OH})_0/e_0 = 0.061$.

$$dx/dt = (1-x)[K_1' + K_1F(\alpha)] [0.75\alpha + 0.25\alpha^{0.2} + F(\alpha)/\lambda] \quad (27)$$

$$F(\alpha) = 1.061 - 0.375\alpha - 0.625\alpha^{0.2} \quad (28)$$

$$x = \{(1.2 - 0.6/\lambda)(1 - \alpha) + (2 - 5/\lambda)(1 - \alpha^{0.2}) - (1.6976/\lambda) \ln \alpha\} / 3.2 \quad (29)$$

By defining

$$Y = (dx/dt) / \{(1-x) [0.75\alpha + 0.25\alpha^{0.2} + F(\alpha)/\lambda]\} \quad (30)$$

Equation (27) may be written as

$$Y = K_1' + K_1F(\alpha) \quad (31)$$

The λ value giving the best linear regression between Y and $F(\alpha)$ was selected. Figure 5 shows the kind of regression obtained for every temperature. The proposed kinetic model fits the experimental results in almost all the conversion range; only for reaction extents approaching the glass transition there is a significant drop in the reaction rate. This behavior has already been described for aliphatic diamines.^{6,27}

Table I shows the kinetic parameters arising from the best linear regression. Below 150°C the etherification reaction may be neglected ($\lambda \rightarrow \infty$). At higher temperatures the formation of ether linkages has to be taken into account. In the 180–200°C temperature range, the model predicts that the specific rate constant for etherification is 6–9 times smaller than the corresponding constant for the reaction with primary amines. These values

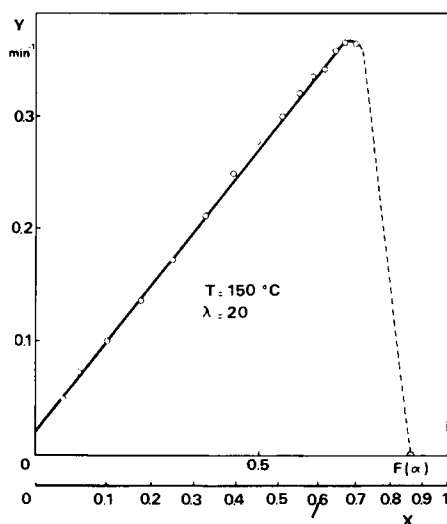


Fig. 5. Linear regression of the kinetic model for the run at 150°C, taking $\lambda = 20$.

TABLE I
Kinetic Parameters Arising from the Best Linear Regression

T (°C)	K_1' (min ⁻¹)	K_1 (min ⁻¹)	λ	Corr. Coef.	x_T
110	0.0044	0.0755	∞	0.997	0.66
120	0.0053	0.1468	∞	0.999	0.71
140	0.0304	0.2943	∞	0.999	0.79
150	0.0167	0.5251	20	0.999	0.85
180	0.0351	1.6369	6	0.998	0.96
190	0.0391	2.3538	7	0.999	0.985
200	0.1838	3.1908	9	0.999	0.99

are very close to the factor 10 reported by Morgan et al.^{13,14} for the cure of TGDDM with DDS. The epoxy-hydroxyl reaction is found to be 2.4–3.6 times slower than the epoxy–secondary amine reaction. The range of variation is the result of the rather low sensitivity of the best regression to the λ value. The activation energy of the epoxy-amine reaction catalyzed by OH groups is obtained from the Arrhenius plot depicted in Figure 6. This leads to

$$K_1(\text{min}^{-1}) = 2.307 \cdot 10^7 \exp - [7461.4/T(K)] \quad (32)$$

The activation energy is $E = 14.8$ kcal/mol, in excellent agreement with corresponding values reported for the curing of aliphatic diamines.^{6,27}

The corresponding activation energy for the noncatalytic epoxy-amine addition could not be obtained in the explored temperature range due to the low significance of this mechanism in the curing reaction (i.e., slight variations of the best K_1' affect strongly the ordinate intercept, K_1'). As the relative importance of the noncatalytic mechanism increases with temperature,²⁷ it is interesting to represent both the noncatalytic and the catalytic epoxy-amine reaction rates at the highest temperature of the range (i.e., 200°C). The noncatalytic reaction rate is proportional to K_1' while the catalytic one is proportional to $K_1 F(\alpha)$. Figure 7 shows both values as a function of the reaction extent at 200°C. While both mechanisms have similar im-

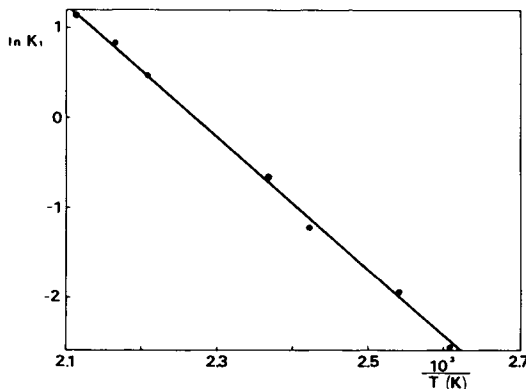


Fig. 6. Arrhenius plot of the specific rate constant for the epoxy-amine reaction catalyzed by OH groups.

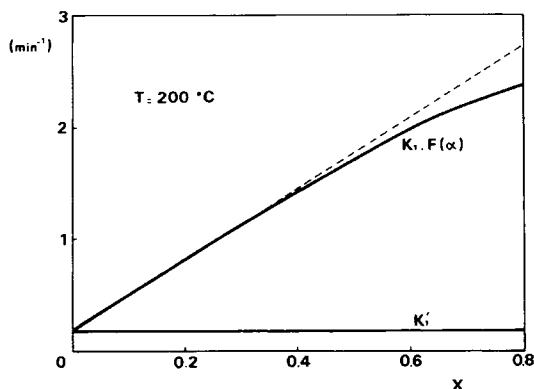


Fig. 7. Relative importance of the noncatalytic (proportional to K_1) and catalytic (proportional to $K_1F(\alpha)$) epoxy-amine reaction rates at 200°C, as a function of the reaction extent.

portance at the beginning of the reaction, the production of hydroxy groups by the epoxy-amine addition leads to a steep increase of the catalytic mechanism. Note, however, the departure of $K_1F(\alpha)$ from a straight line, resulting from the presence of the etherification reaction. This last reaction becomes significant at intermediate and high reaction extents.

From Eq. (27), the relative importance of the etherification with respect to the epoxy-amine reaction rate may be visualized by plotting $F(\alpha)/\lambda$ and $G(\alpha) = 0.75\alpha + 0.25\alpha^{0.2}$, as a function of the reaction extent. Figure 8 represents such a plot for $T = 180^\circ\text{C}$, showing again that the etherification mechanism becomes significant at high conversions. In this range, secondary amines and hydroxyls compete for the remaining epoxy groups.

INFRARED SPECTRA

Infrared (IR) spectra of stoichiometric samples reacted to the maximum possible conversion, x_T , at a particular temperature, were obtained by pulverizing the cured products, making pellets with KBr and monitoring on a Perkin-Elmer 599 IR spectrophotometer.

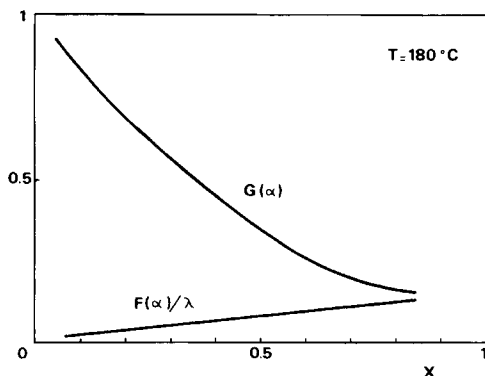


Fig. 8. Relative importance of etherification (proportional to $F(\alpha)/\lambda$) and epoxy-amine addition (proportional to $G(\alpha)$), at 180°C, as a function of the reaction extent.

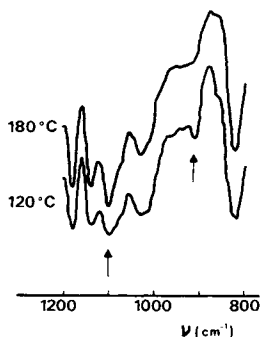


Fig. 9. IR spectra of BADGE/DDS samples with stoichiometric compositions, reacted to the maximum possible conversion at 120°C and 180°C.

Figure 9 shows IR spectra of samples cured at 120°C and 180°C. According to Mones et al.,¹⁰ epoxy groups show an IR band at 910 cm^{-1} while ether bands are expected in the region of 1120 cm^{-1} . Unreacted epoxy groups remain in the sample cured at 120°C ($x_T = 0.71$), while their presence is not significant in the product cured at 180°C ($X_T = 0.96$). The band at ca. 1100 cm^{-1} is enhanced in the sample cured at 180°C, giving extra evidence of the presence of the etherification reaction.

CONCLUSION

A kinetic scheme for an amine-epoxy reaction with simultaneous etherification has been proposed and found suitable to adjust experimental results for a BADGE/DDS system.

The etherification reaction becomes significant at $T > 150^\circ\text{C}$ and at intermediate and high reaction extents, when there are enough OH groups and the primary amine has been sufficiently depleted.

A statistical analysis of the network formation taking into account the etherification reaction is under way.

The authors wish to thank both the financial support and a scholarship given to C.C.R. by the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires. The financial support provided by the Secretaría de Ciencia y Tecnología, Argentina, is also acknowledged. Ciba-Geigy Argentina has kindly supplied the Araldit GY 250 and the HT 976 for this study.

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Received November 1, 1984

Accepted July 1, 1985