PII: S0032-3861(97)00517-X

Polymer Vol. 39 No. 11, pp. 2247–2253, 1998

0032-3861/98/$19.00+0.00

Study of the kinetic and crosslinking reaction of novolak with epoxy resin

M. C. Gualpa, C. C. Riccardi and A. Vázquez*
Research Institute of Material Science and Technology (INTEMA)—Mar del Plata, University and National Research Council (CONICET), Juan B. Justo 4302 (7600), Mar del Plata, Argentina
(Received 7 February 1997; revised 20 May 1997)

Novolak and epoxy reaction was studied by means of differential scanning calorimetry. Two reactions can take place in the mixture: one between OH groups of the novolak and epoxy groups, and the other between secondary OH groups (coming from the opening of the epoxy ring by the first reaction) and epoxy groups. Since only one peak was detected in dynamic thermograms obtained at different heating rates, both reactions occurred simultaneously. A global kinetic model with two kinetic constants was developed. It agreed with dynamic and isothermal experiences. The reaction heat was determined by an average of several runs as 23.1 kcal equiv.$^{-1}$ (96.7 kJ/equiv.epoxy). The glass transition temperature was determined for different novolak/epoxy stoichiometric ratios from 0.04 to 2.2 The maximum glass transition was obtained for the 1:1 ratio and it was 99°C.

The activation energy obtained from gel–time measures was 15.8 kcal equiv.$^{-1}$ (66 kJ equiv.$^{-1}$).

A statistical structural model was used in order to describe the epoxy–novolak cure. Equal reactivity between OH groups of the novolak, equal reactivity between epoxy groups and no-substitution effect are taken into account. Intramolecular reaction in the pre-gel stage is neglected. Expression of the average molecular weight and gel conversion are derived. It is shown from the model that for the stoichiometric ratio of OH groups to oxirane groups, the predicted gel conversion agreed with the experimental value. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: novolak; epoxy; blends)

INTRODUCTION

Epoxy–phenolic resin is one of the most utilized types of coating in the beverage industry. This coating combines the properties of phenolic resin (low cost, high impact resistance, high hardness and high resistance to acid attack), and the properties of epoxy resin (high alkali resistance, flexibility and low shrinkage)[1–5]. Most of the work related to this type of resin has been patented[6–8], and fundamental studies on the route of polymerization remain largely unreported. One of the first works in the field was by Schechter and Wynstra[9]. They investigated the reaction between the epoxy and polyphenols and proposed the following steps: (i) the reaction between the phenol hydroxyl and the epoxy groups, and (ii) the reaction between the secondary hydroxyl generated from the opening of the oxirane group and the epoxy group (homopolymerization).

Smith and Ishida[10] investigated the reaction between bisphenol-A and diglycidyl ether of bisphenol A (DGEBA) by means of the application of Fourier transform infrared spectroscopy (FTIR). Lineal chain addition and branching were considered within a general model. Catalysis effects upon the branching reaction are found to be negligible for the stoichiometric mixture. The activation energy of the lineal reaction (between the OH from the bisphenol-A and oxirane ring) was found to be 18 ± 1 kcal mol^{-1}, while the activation energy of the branching reaction (between the secondary OH and the oxirane group) was 20 ± 1 kcal mol^{-1}. When higher-order terms in the representation of secondary alcohol concentration were taken into account, the activation energy became nearly equal at 18 ± 1 kcal mol^{-1} for both reactions. They proposed a model reaction with order 1 with respect to the epoxy concentration for the linear condensation reaction.

Doszlop *et al.*[11] reported that the solution reaction of phenol and diepoxy proceeds to a level of 50%. At this value the phenolic species activated the branching reactions, and as a consequence the material reached gelation time.

The aim of the present work is to study the kinetic reaction, gel conversion and the glass transition temperature of the epoxy and novolak resin blends without a catalyst. The application of the statistical structural model for the novolak–epoxy resins and the prediction of the gel conversion by this method is carried out.

EXPERIMENTAL SECTION

The diglycidyl ether of bisphenol A, DGEBA GY-250 was obtained from Ciba-Geigy. The equivalent epoxy was determined through acid titration and the average value was 190 g equiv.$^{-1}$. The resin was degassed under vacuum before using at 80°C for 4 h.

Novolak resin was synthesized with phenol (P) and formaldehyde (F). Phenol (PA grade, from Anedra) and formaldehyde (37%w, PA grade from Mallinckrod) were used without further purification. Oxalic acid from Merck was used as catalyst. Phenol and formaldehyde with a molar phenol/formaldehyde ratio of 0.75 were reacted under refluxing by adding 0.005 mol. of oxalic acid by mol. of phenol. The reaction condition was 90°C for 8 h. During the

---

* Author to whom correspondence should be addressed

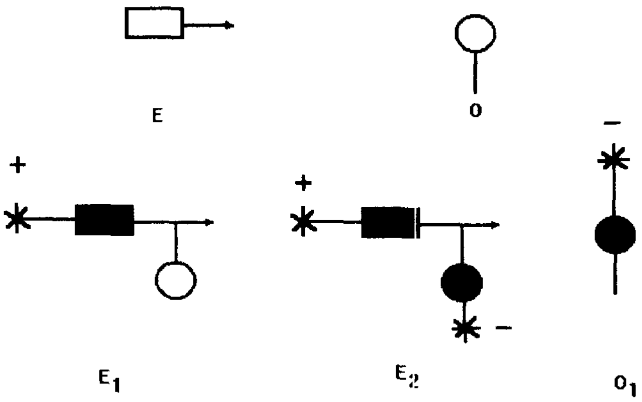


Figure 1 Structural fragment present during the cure of epoxy and novolak. Squares and circles represents epoxy and OH– groups respectively, and black symbols denoted reacted groups

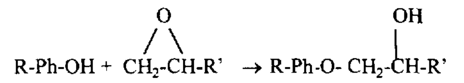
reaction the free formaldehyde was measured by the hydroxylamine method. The final content of formaldehyde was 1%, which corresponds with a conversion higher than 95%. After the reaction, the novolak resin was neutralized with OHNa 1 N and distillate under vacuum for 6 h. Characterization of the novolak was done by means of gel permeation chromatography (GPC Waters 244 with differential refractometer), and differential scanning calorimeter (DSC, Shimadzu S-50).

Samples of epoxy and novolak mixtures were prepared in bulk with different stoichiometric ratios, r = equiv.OH/ equiv.epoxy: 0.7, 1 and 1.5. Heating rates of 5, 10 and 20°C min^{-1} were used in the scanning DSC analysis and isothermal runs were done at 160, 170, 180, 200 and 210°C. In order to determine the gelation time, mixture with $r = 1$ was introduced into sealed ampoules in an oil bath at a constant temperature of 140, 150, 160 and 180°C, and the dissolution of reacted samples was tested in methyl ethyl ketone (MEK) and tetrahydrofuran (THF).

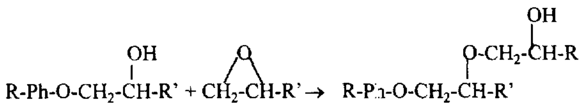
The gel conversion was determined by measuring the residual reaction heat evolved in each sample in the DSC equipment. The glass transition temperature was determined by the onset of DSC experience at a heating rate of 10°C min^{-1}.

THEORETICAL SECTION

The following reactions were taken into account:



$$\text{R-Ph-OH} + \overset{\text{O}}{\text{CH}_2\text{-CH}}\text{-R'} \rightarrow \text{R-Ph-O-CH}_2\text{-}\overset{\text{OH}}{\text{CH}}\text{-R'} \quad (1)$$



$$\text{R-Ph-O-CH}_2\text{-}\overset{\text{OH}}{\text{CH}}\text{-R'} + \overset{\text{O}}{\text{CH}_2\text{-CH}}\text{-R'} \rightarrow \text{R-Ph-O-CH}_2\text{-}\overset{\text{O-CH}_2\text{-}\overset{\text{OH}}{\text{CH}}\text{-R'}}{\text{CH}}\text{-R'} \quad (2)$$

where Ph = benzene ring.

The statistical structural model (SSM) was utilized for different non-ideal polymerization[13–17]. In the SSM, kinetically generated fragments are statistically combined. *Figure 1* shows different structural elements present during the reaction of novolak and epoxy resin. E are epoxy groups and O are initial OH groups. Implicit in this notation is the fact that for simplicity both the epoxy group of the same diepoxide molecule, and all initial hydroxyls (from novolak, epoxy or residual phenol) have equal reactivity, and substitution effects are not taken into account. Implicit in the calculation is the fact that cyclization reactions are considered negligible. The resulting network is built-up by joining arrows with arrows and positive asterisks with negative asterisks.

In terms of structural fragments, the reaction scheme may be written as:

$$\mathrm{E} + \mathrm{O} \xrightarrow{k_a} \mathrm{E}_1 + \mathrm{O}_1 \qquad (3)$$

$$\mathrm{E}_1 + \mathrm{E} \xrightarrow{k_b} \mathrm{E}_1 + \mathrm{E}_2 \qquad (4)$$

where k_a is the kinetic constant for the reaction between initial OH groups and epoxy group, and k_b is the kinetic constant for the reaction of the secondary OH from the epoxy and the epoxy groups (homopolymerization).

The evolution of the concentration of each fragment in the course of polymerization is given by:

$$\frac{d[E]}{dt} = -k_a[E][O] - k_b[E_1][E] \qquad (5)$$

$$\frac{d[E_1]}{dt} = k_a[E][O] \qquad (6)$$

$$\frac{d[E_2]}{dt} = k_b[E_1][E] \qquad (7)$$

$$\frac{d[O]}{dt} = -k_a[E][O] \qquad (8)$$

$$\frac{d[O_1]}{dt} = k_a[E][O] \qquad (9)$$

Defining the dimensionless time as $t^* = k_a[E]_0 t$, dimensionless concentration of fragment I as $[E_1]^* = [E_1]/[E]_0$ where $[E]_0$ is the initial epoxy concentrations and $k = k_b/k_a$ dimensionless equations (5)–(9) become

$$\frac{d[E]^*}{dt^*} = -[E]^*[O]^* - k[E_1]^*[E]^* \qquad (10)$$

$$\frac{d[E_1]^*}{dt^*} = [E]^*[O]^* \qquad (11)$$

$$\frac{d[E_2]^*}{dt^*} = k[E_1]^*[E]^* \qquad (12)$$

$$\frac{d[O]^*}{dt^*} = -[E]^*[O]^* \qquad (13)$$

$$\frac{d[O_1]^*}{dt^*} = [E]^*[O]^* \qquad (14)$$

The system of equations (10)–(14) may be solved using a fourth-order Runge–Kutta method if k is known.

In order to calculate the weight average molecular weight, $\overline{M}_w$, let us define

W_F = average weight hanging from an arrow (→)
W_N = average weight hanging from a negative asterisk ($-*^-$)
W_P = average weight hanging from a positive asterisk ($-*^+$)which are calculated with following equations

$$W_F = \{M_{E\cdot}[E] + (M_{E1} + W_P)[E_1] + (M_{E2\cdot} + W_P + W_N)[E_2]\}/[E]_0 \qquad (15)$$

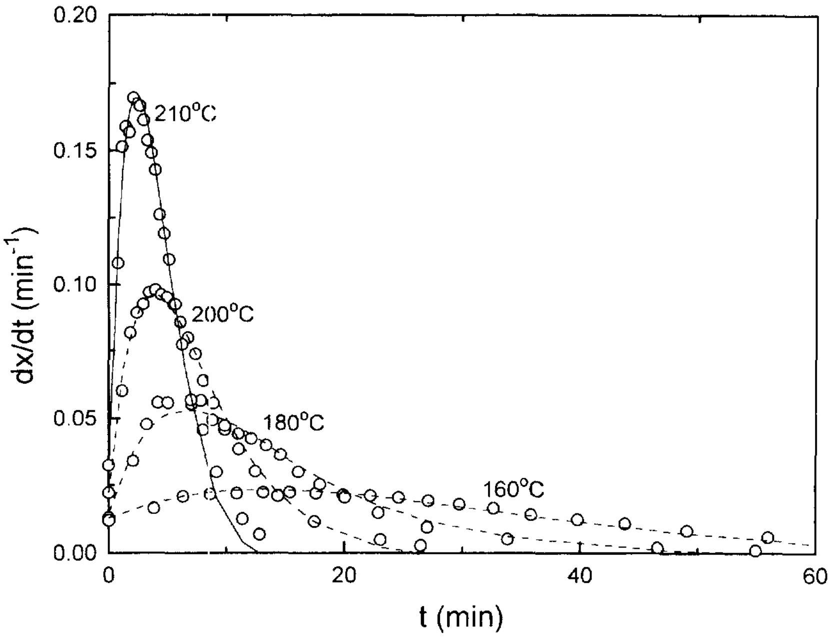


Figure 2 Model fitting for the isothermal runs of the stoichiometric novolak–epoxy mixture

$$W_P = \{(M_{E2\cdot} + W_P + W_F)[E_2] + M_{O1}[O_1]\}/([E_1] + [E_2]) \quad (16)$$

$$W_N = \{(M_{E1} + W_F)[E_1] + [E_2](M_{E2} + W_N + W_F)\} /([E_2] + [O_1]) \quad (17)$$

where M_I is the mass of fragment I and $[E]$.

Mathematical working of equations (15)–(17), taking into account that the total number of positive asterisks is equal to the total number of negative asterisks, enables us to obtain the following expressions

$$W_P = W_F \frac{[E_2]}{[E_1]} + M_{E2\cdot}[E_2] + M_{01\cdot}[O_1] \quad (18)$$

$$W_N = W_F\left(1 + \frac{[E_2]}{[E_1]}\right)\left(\frac{M_{E1\cdot}[E_1] + M_{E2\cdot}[E_2]}{[E_1]}\right) \quad (19)$$

$$W_F = \frac{(M_{E\cdot}[E] + M_{E1\cdot}[E_1] + M_{E2\cdot}[E_2]) + W_P([E_1] + [E_2]) + W_N[E_2]}{[E]_0} \quad (20)$$

The $\overline{Mw}$ may be calculated as follows:

$$\overline{Mw} = \sum w_{I\cdot} Mw_I \quad (21)$$

where w_I and Mw_I are the mass fraction and the molecular weight of fragment I, respectively. Gelation conversion, x_{gel}, is the reaction extent at which $\overline{M_w} \rightarrow \infty$. This condition is verified when W_F, W_P or $W_N \rightarrow \infty$, and the gelation condition obtained is the following

$$1 - 2\frac{[E]_1] + [E_2]}{[E_1]}[E_2] = 0 \quad (22)$$

RESULTS AND DISCUSSION

Characterization of the novolak resin

Gel permeation chromatography of the novolak was carried out. The assigned volume of elution was the following: (1) phenol, 50.81; (2) dimers, 48.87; and (3) trimers, 47.11. This assignation agreed with the result obtained in the same device for a similar system by Oyanguren[12]. Weight- and number-average molecular weights were determined by a calibration curve as 1134 and 462.7, respectively. Including the phenol in excess (not reacted) and assuming complete conversion of formaldehyde, the number average molecular weight can be calculated by the following equation

$$\overline{Mn} = \frac{12(F/P) + 94}{1 - (F/P)} = 412$$

The experimental value is close to the theoretical one. The difference could be attributed to the incomplete reaction of formaldehyde in the novolak. The number of repetitive units in the structure was 2.478 and the equivalent of OH per mol de novolak was 4.478 equiv.OH/mol. The equivalent weight of the novolak is 254.13 g/equiv.OH. This value was taken for the formulation of the epoxy–novolak mixtures. The content of free phenol was 11.8%. The 'onset' glass transition temperature of the novolak obtained by the second run of the DSC was 65°C.

Reaction of novolak and epoxy resins

The simplified model represented by the following equation

$$dx/dt = (1 - x)(K_2\sqrt{x} + K_1) \quad (23)$$

where x is the epoxy conversion, fitted the experimental isothermal and dynamic runs for stoichiometric mixture, as shown in *Figure 2* and *Figure 3*, respectively. *Figure 4* shows values of kinetic constants, K_1 and K_2 by means of an Arrhenius expression. The activation energy and pre-exponential values are shown in *Table 1*. It was possible to proposed a reaction mechanism (see Appendix A) to obtained the ratio $k = k_b/k_a$ from K_1 and K_2 values:

$$k = 1.736\ 10^{-8}\exp(-7133.4/T)$$

The average reaction heat was 23.1 kcal/equiv. (96.7 kJ/equiv. epoxy). The reaction heat value is similar to that of

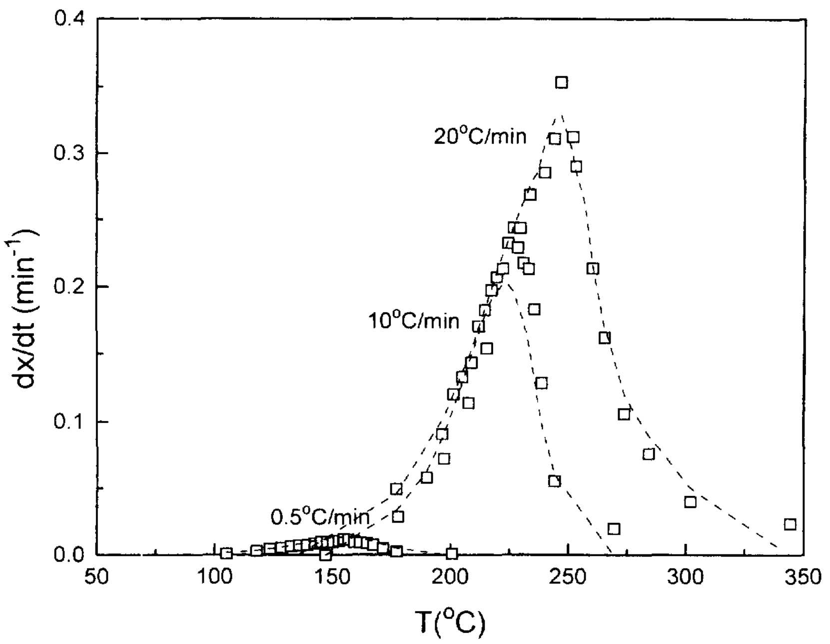


Figure 3 Model fitting for the dynamic runs of the stoichiometric novolak–epoxy mixture

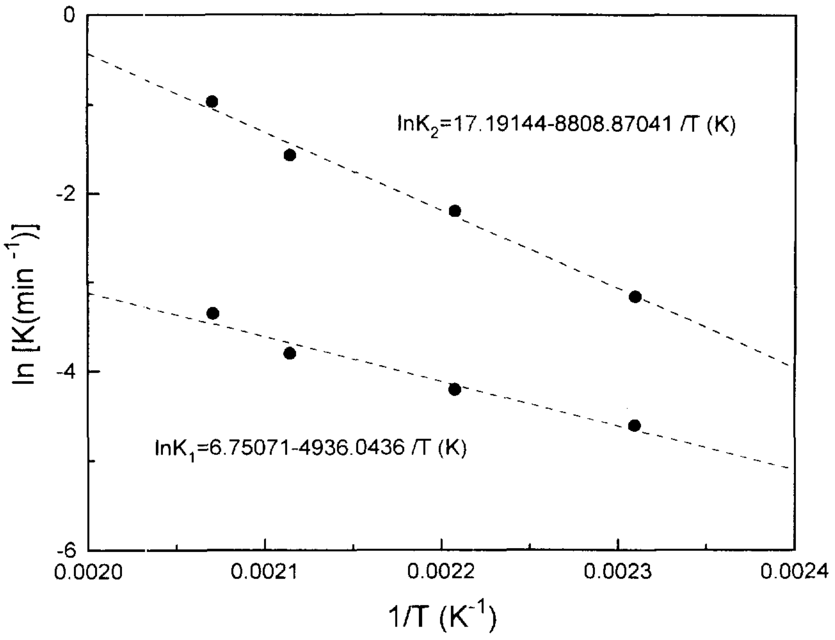


Figure 4 Lineal regression of the Arrhenius expression for the kinetic constants

the system *o*-cresyl glycydyl ether and *m*-cresol with imidazol as initiator (20 kJ/equiv. (86.5 kJ/equiv. epoxy))[18].

Gel condition

Figure 5 shows the ln (t_{gel}) *versus* 1/T and the activation energy obtained is 15.8 kcal/equiv. (66.2 kJ/equiv.). This value is within the order of magnitude of the activation energy value for the autocatalytic kinetic constant (K_2), and it is related to the crosslinking reaction.

Table 1 Activation energy and pre-exponential factor

	E (kJ mol^{-1})	A (min^{-1})
K_1	41.04 (9.8 kcal/mol)	8.54 10^2
K_2	73.2 (17.5 kcal/mol)	2.92 10^7

Table 2 shows the comparison between the gelation conversion obtained from experimental gelation time by means of the equation (23), and the experimental gelation conversion obtained by the residual heat of reaction in DSC.

Figure 6 shows the gel conversion predicted by using the SSM statistical model and experimental points. The results show that higher gel conversion could be obtained for a lower reaction temperature. Its means that linear reaction is more important than the branching reaction if the reaction temperature decreases.

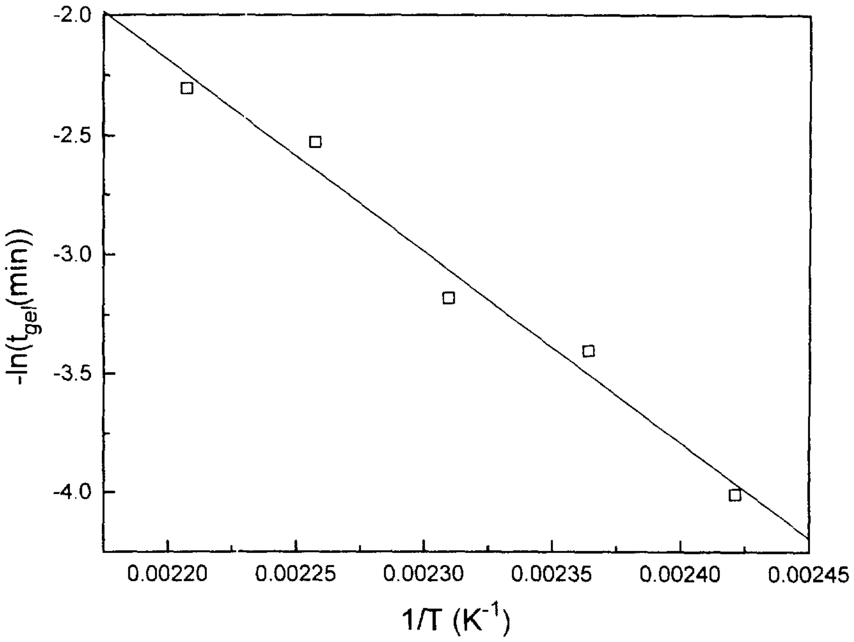


Figure 5 Lineal regression of the gel time as a function of the temperature

Table 2 Comparison of gelation conversion

Temperature (°C)	$x_{\text{experimental}}$	x_{model}
140	0.50	0.51
150	0.48	0.424
160	0.56	0.505
180	0.42	0.45

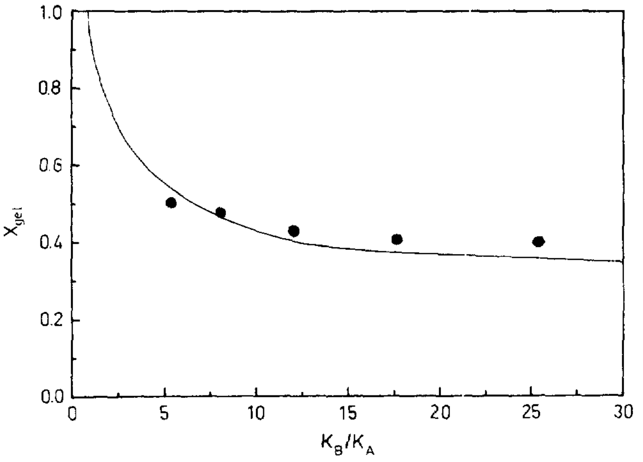


Figure 6 Comparison between experimental gel conversion value and predicted gel conversion by SSM: (a) — model, (b) ● experimental

Glass transition temperature of the formed network

Figure 7 shows the second run of the isothermal measurements. There is no residual heat after the isothermal runs and the complete conversion was obtained after the heating. *Table 3* shows the glass transition temperatures (T_g) for different novolak–epoxy stoichiometric ratios. As expected, the T_g values show a maximum for the stoichiometric ratio. However, the values are not very different and could be an indication that the formed network has a high level of crosslinking.

CONCLUSIONS

A simple kinetic model related to the reaction mechanism was found. This kinetic model proposed fitted the dynamic and the isothermal runs. As a consequence, it is a good model for using in processing this material. From the dynamic runs in DSC, only one peak was detected and both reactions occurred simultaneously between the secondary OH coming from the opening of the epoxy group and the epoxy ring and the initial OH of the novolak and the epoxy ring. The experimental gelation conversion agrees with that obtained from the model, and the activation energy obtained was 15.8 kcal/equiv. (66 kJ/equiv.epoxy) The maximum T_g value obtained was 99°C for the stoichiometric ratio.

A statistical structural model (SSM) was developed to describe the epoxy–novolak cure. An expression for the pre-gel parameter was derived by reflecting intramolecular reactions in the pre-gel stage. It was shown that the gelation conversion increased when the temperature decreased. However, these values are slightly dependent on temperature, within the studied range.

APPENDIX A: REACTION MECHANISM

The evolution of the concentration of each fragment in the course of the polymerization is given by

$$\frac{d[E]}{dt} = -k_a[E][O] - k_b[E_1][E] \qquad \text{(A1)}$$

$$\frac{d[E_1]}{dt} = k_a[E][O] \qquad \text{(A2)}$$

$$\frac{d[E_2]}{dt} = k_b[E_1][E] \qquad \text{(A3)}$$

$$\frac{d[O]}{dt} = -k_a[E][O] \qquad \text{(A4)}$$

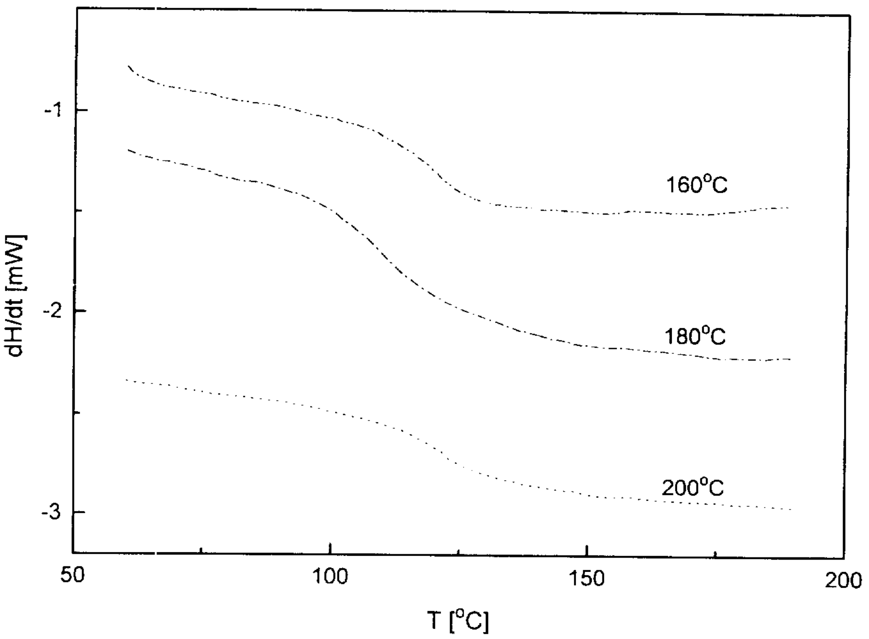


Figure 7 Second runs after the DSC isothermal runs measured at 10°C min^{-1} heating rate

Table 3 Glass transition temperature for different stoichiometric ratios

r^*	T_g (°C)
0.04	82 ± 2
0.7	93 ± 4.5
1.0	99.5 ± 3.2
1.5	93.5 ± 2.5
2.2	89 ± 2

* r = equiv.OH.epoxi:

$$\frac{d[O_1]}{dt} = k_a[E][O](A5) \qquad (A5)$$

Dividing equation (A1) by equation (A4)

$$\frac{d[E_1]}{d[O]} = -1$$

and integrating this expression, the following equation is obtained

$$[E_1] = [O]_0 - [O] \qquad (A6)$$

where $[O]_0$ is the initial concentration of the fragment O Dividing equation (A1) by equation (A4)

$$d[E]/d[O] = 1 + k_b/k_a[E_1]/[O] \qquad (A7)$$

By replacing equation (A1) in equation (A7)

$$\frac{d[E]}{d[O]} = 1 - k + k\frac{[O]_0}{[O]} \qquad (A8)$$

where $k_b/k_a = k$, rearranging it results in

$$d[E] = k[O]_0\left\{k'd[O] - \frac{d[O]}{[O]}\right\} \qquad (A9)$$

where $k' = (1-k)/k[O]_0$.

By integrating equation (A9) the expression for epoxy concentration may be written as

$$[E] - [E]_0 = k[O]_0\{k'([O] - [O]_0) + (\ln[O] - \ln[O]_0)\} \qquad (A10)$$

Using a Taylor series and taken into account the second term

$$\ln[O] = \ln[O]_0 + \frac{[O] - [O]_0}{[O]_0} - \frac{([O] - [O]_0)^2}{2[O]_0^2} \qquad (A11)$$

By replacing equation (A11) in equation (A10)

$$[E] - [E]_0 = k[O]_0\left\{k'([O] - [O]_0) + \frac{[O] - [O]_0}{[O]_0} - \frac{([O] - [O]_0)^2}{2[O]_0^2}\right\} \qquad (A12)$$

and rearranging

$$[E] - [E]_0 = k[O]_0\left\{([O] - [O]_0)\left(k' + \frac{1}{[O]_0}\right) - \frac{([O] - [O]_0)^2}{2[O]_0^2}\right\} \qquad (A13)$$

working mathematically

$$[E] - [E]_0 = k[O]_0\left\{([O] - [O]_0)\left(\frac{1}{k[O]_0}\right) - \frac{([O] - [O]_0)^2}{2[O]_0^2}\right\} \qquad (A14)$$

If $k_b \gg k_a \Rightarrow k \ggg 1$ and $1/k \lll 1 \rightarrow 0$

The equation (A14) becomes

$$E] - [E]_0 = -k\frac{([O] - [O]_0)^2}{2[O]_0} \qquad (A15)$$

and

$$[O] = \sqrt{\frac{2([E]_0 - [E])[O]_0}{k}} + [O]_0 \qquad (A16)$$

By replacing equation (A16) in equation (A6)

$$[E_1] = \sqrt{\frac{2([E]_0 - [E])[O]_0}{k}} \qquad (A17)$$

and replacing equation (A16) and equation (A17) in equation (A1)

$$\frac{\mathrm{d}[E]}{\mathrm{d}t} = -[E]\left\{\sqrt{\frac{2([E]_0 - [E])[O]_0}{k}}(k_a - k_b) + k_a[O]_0\right\} \tag{A18}$$

As the epoxy conversion is defined as

$$x = \frac{[E]_0 = [E]}{[E]_0}$$

equation (A18) can be rewritten as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = (1 - x)\{K_2\sqrt{x} + K_1\} \tag{A19}$$

where $K_1 = k_a[E]_0$ and $K_2 = \sqrt{\frac{2}{k_b/k_a}}[E]_0(k_a - k_b)$ taking into account that for a stoichiometric system $[E]_0 = [O]_0$.

REFERENCES

1. Palackharry, P. J., *Polym. Mat. Sci. Eng.*, 1991, **65**, 277.
2. Bauer, R. S., *Polym. Mat. Sci. Eng.*, 1991, **65**, 315.
3. Can lining and white enamels based on araldite–epoxy resins. Technical Note, Ciba-Geigy.
4. Tess, R. W., in *Epoxy Resins: Chemistry and Technology*, 2nd edn, ed. C.A. May. Marcel Dekker, New York, 1988.
5. Good, R. H., *Am. Chem. Soc.*, 1988, **7**, 00.
6. Ellis, B., in *Chemistry and Technology of Epoxy Resins*, ed. B. Ellis, Blackie Academic, Chapman and Hall, 1993, p. 24.
7. Mika, T. F. and Bauer, R. S., in *Epoxy Resins: Chemistry and Technology*, 2nd edn., ed. C. A. May, Marcel Dekker, New York, 1988, p. 465.
8. Chen, X. M. and Ellis, B., in *Chemistry and Technology of Epoxy Resins*, ed. B. Ellis, Blackie Academic, Chapman and Hall, 1993, p. 303.
9. Schechter, L. and Wynstra, J., *Ind. Eng. Chem.*, 1956, **48**(1), 86.
10. Smith, M. E. and Ishida, H., *Macromolecules*, 1991, **27**, 2701.
11. Doszlop, S., Vargha, V. and Horkay, F., *Polym. Chem. Eng.*, 1978, **22**, 253.
12. Oyanguren, P., Ph.D. thesis, Mar del Plata University, 1992.
13. Aranguren, M. I., Borrajo, J. and Williams, R. J. J., *Ind. Eng. Chem., Prod. Res. Dev.*, 1984, **23**, 270.
14. Vazquez, A., Adabbo, H. E. and Williams, R. J. J., *Ind. Eng. Chem., Prod. Res. Dev.*, 1984, **23**, 375.
15. Riccardi, C. C. and Williams, R. J. J., *Polymer*, 1986, **27**, 913.
16. Williams, R. J. J., Riccardi, C. C. and Dusek, K., *Polym. Bull.*, 1987, **17**, 515.
17. Moschiar, S. M., Piacentini, C. A. and Williams, R. J. J., *Polymer*, 1994, **29**, 914.
18. Hale, A., Ph.D. thesis, Minnesota University, 1988.