

# Application of the half-width kinetic method on the amine-initiated cross-linking of an epoxy resin with cyclic anhydrides

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The utility of a non-isothermal kinetic method—the half-width method—is demonstrated in the determination of the activation energy for amine-initiated cross-linking reactions of the epoxy resin diglycidylether of bisphenol-A with three different cyclic anhydrides: succinic, maleic and *cis*-1,2-cyclohexanedicarboxylic anhydrides. Triethylamine was employed as an initiator. The cross-linking reactions were kinetically followed by differential scanning calorimetry at various temperature scanning rates. The half-width method furnished values for the energy of activation in the range 60–100 kJ mol<sup>-1</sup>. These values are similar to those obtained by applying the well-known non-isothermal multiple-scanning rate methods of Kissinger and Osawa but differ significantly from the ones obtained by applying the single-rate method of Barret. © 1997 Elsevier Science Ltd.

(Keywords: epoxy system; half-width method; curing processes)

## INTRODUCTION

Over a long period much controversy on the validity of non-isothermal kinetics arose in the thermal analysis literature<sup>1–6</sup>. Criticism was mainly focused on the mathematical description of non-isothermal kinetic rate equations. On the other hand it was clearly demonstrated that isothermal kinetic equations can be extended to non-isothermal reactions<sup>3</sup>. From the practical standpoint, the determination of kinetic parameters implies the application of a convenient model and that of Arrhenius has been the most frequently applied one. In the field of epoxy resins, non-isothermal kinetics has found widespread use due mainly to the convenience of rapid access to kinetic parameters, as for example the energy of activation which can be determined by carrying out a single kinetic run. Recent implications of non-isothermal kinetics in the study of epoxy resins can be found in various journals<sup>7–11</sup>.

This work intends to show the application of the half-width method<sup>7,8,12</sup>, a non-isothermal method, to the study of the cross-linking kinetics of diglycidylether of bisphenol-A (DGEBA) with three different cyclic anhydrides: succinic, maleic and *cis*-1,2-cyclohexanedicarboxylic anhydrides in the presence of triethylamine as initiator.

## EXPERIMENTAL

Maleic and succinic anhydrides were both purified by recrystallization in chloroform. *cis*-1,2-cyclohexanedicarboxylic (CH) anhydride was distilled under vacuum.

Triethylamine was refluxed under potassium hydroxide and distilled under an inert atmosphere. The epoxy resin DGEBA (Ciba-Geigy) had an epoxy equivalent of 190 with 82–92% of monomeric material (data furnished by the supplier). Prior to the measurements, DGEBA was dried at 130°C. Epoxy resin and anhydride were mixed in a 1:1 molar ratio, then heated to the melting point of the anhydride and again homogenized. After cooling to room temperature, triethylamine was added in the molar ratio 3.7% (with respect to the epoxy resin). Subsequently about 5 mg of the samples was accurately weighed into small d.s.c. aluminium pans. The d.s.c. thermograms were obtained from 50 to 300°C using Perkin Elmer DSC-4 equipment. The temperature scanning rates employed were 5, 10, 20 and 30°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

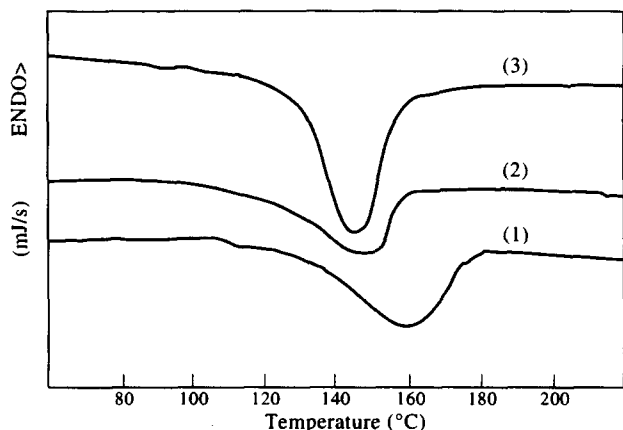
The activation energy of the cross-linking reactions of the epoxy resin DGEBA with the three different anhydrides in the presence of triethylamine was determined by applying the multiple scanning-rate methods of Kissinger<sup>13</sup>, Osawa<sup>14</sup>, half-width<sup>7,8,12</sup> as well as the single rate method of Barret<sup>15</sup>. The basic equations of each method are collected in *Table 1*. *Figure 1* shows typical thermograms for all three systems studied at the same scanning rate. Heat is evolved during the curing reaction of an epoxy resin, and the exothermic peaks shown in *Figure 1* are characterized by a minimum temperature  $T_{\min}$ . It was observed that  $T_{\min}$  values increase with the scanning rate for all systems under investigation. Similar behaviour was previously reported for other epoxy systems<sup>16–18</sup>.

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**Table 1** Differential methods used in non-isothermal kinetic analysis (linear plots:  $y = mx + c$ )

Method	y	x	Slope (m)	Ref.
Kissinger	$\ln[\phi/(T_{min})]^2$	$1/T_{min}$	$-E/R$	13
Osawa	$\ln \phi$	$1/T_{min}$	$-E/R$	14
Half-width	$\ln t_{1/2}$	$1/T_{min}$	$E/R$	7, 8, 12
Barret	$\ln k^a$	$1/T$	$-E/R$	15

<sup>a</sup>  $k = dH/dt(H_T - H)$



**Figure 1** D.s.c. typical thermograms of all three systems cured with (1) succinic, (2) maleic and (3) CH anhydrides measured at  $5^\circ\text{C min}^{-1}$

*Application of the Barret method*

The classical kinetic Barret method<sup>15</sup> constitutes a useful way to investigate the cross-linking epoxy process and calculate kinetic parameters. This method assumes a first-order reaction. For amine-initiated epoxy-anhydride reactions, it was verified that the order of reaction varies between 1.0 and 1.5<sup>19-21</sup>. When deviations from linearity occur in the plot  $\ln k$  versus  $1/T$ , Barret method provides additional information about network formation, i.e. on initiation, gelation and vitrification processes. When the behaviour is linear, activation energies can be estimated using the Barret method. However, it has often been verified that single-rate methods provide superestimated values for the energy of activation<sup>20,22</sup>. In this work the Barret method was applied to determine the activation energies for the three systems studied at all temperature scanning rates measured. Table 2 shows the results obtained. One can observe that for different temperature scanning rates the activation energy behaves nearly constantly for each epoxy system. When CH anhydride is used as the curing agent, the energy of activation is considerably higher than in the case of maleic or succinic anhydride. This behaviour suggests that structural peculiarities with respect to each anhydride influence the reactivity

towards the cross-linking process. The values obtained by multiple scanning-rate methods are also higher for CH (Table 3), although the increase in this case is not so accentuated. Literature data for the same systems are available only for the cross-linking with CH: Patel *et al.*<sup>19</sup> report a value for the energy of activation of  $116 \text{ kJ mol}^{-1}$  obtained by applying the Barret method at a scanning rate of  $10^\circ\text{C min}^{-1}$ . This value lies near those obtained by multiple-scanning methods (Table 3) but it is approximately half of that obtained by applying the Barret method (Table 2). Except for the fact that the sample prepared by Patel *et al.* was obtained by solvent casting while ours was prepared in bulk, we see no explanation for this discrepancy. On the other hand, our results also indicate that the anhydride structure affects the cross-linking reaction mentioned by Patel *et al.*<sup>19</sup>.

In Figure 2 the system cured with succinic anhydride demonstrates similar behaviour with increasing temperature scanning rate. A shift of the  $\ln k$  values to higher temperatures (lower  $T^{-1}$  values) is observed. However, the  $30^\circ\text{C min}^{-1}$  curve shows two different stages. The same behaviour is obtained in Figure 3, where an initiation stage can be identified from 0.05 until about 0.40 extent of reaction; this part of the reaction range is displaced to higher temperatures at higher temperature scanning rates. The second, where the vitrification process occurs, includes until about 0.95 extent of reaction. The obtained rate constant values show that the smaller the temperature scanning rates the smaller the rate constant values, if the same extent of reaction is taken into account.

In Figures 4 and 5 it can be seen that the system cured with maleic anhydride behaves differently from the system cured with succinic anhydride, when the temperature scanning rate is varied; the cure reactions show three stages. The first stage can be identified from 0.05 until about 0.40 extent of reaction; this range corresponds to the initiation cure process. The second stage, identified from 0.40 until about 0.85, can be assigned to the gelation process. At extents of reaction higher than 0.90, the last stage, the rate constants suffer a deeply accentuated decrease. In this range the vitrification process takes place, and this behaviour is more evident at small temperature scanning rates such as  $5^\circ\text{C min}^{-1}$  where the diffusional effects are marked by d.s.c. measurements.

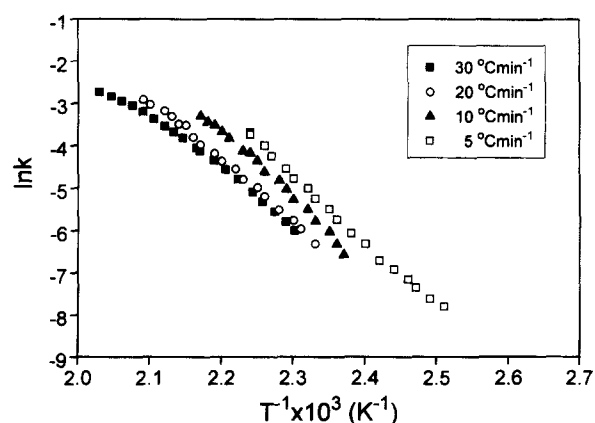
In Figures 6 and 7, the system cured with CH anhydride behaves qualitatively differently from the previous systems, when the temperature scanning rate is varied. However, the cure reactions show again three stages: initiation, gelation and vitrification processes. The difference between the system cured with maleic anhydride and the system cured with CH anhydride can be noticed in the shape of the curves in the Barret

**Table 2** Energies of activation for the cross-linking reactions of DGEBA with three different cyclic anhydrides in the presence of triethylamine as determined by the single-rate method of Barret at various scanning rates (calculations were performed for the linear part of the plot, where diffusional effects are not detectable)

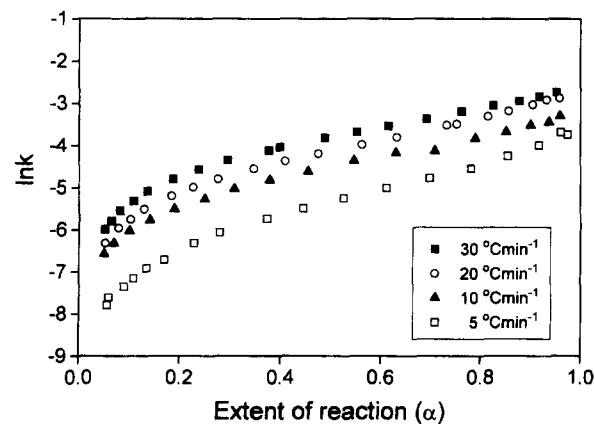
Anhydride	Energy of activation ( $\text{kJ mol}^{-1}$ )			
	$5^\circ\text{C min}^{-1}$	$10^\circ\text{C min}^{-1}$	$20^\circ\text{C min}^{-1}$	$30^\circ\text{C min}^{-1}$
Succinic	$121 \pm 2$	$146 \pm 1$	$121 \pm 1$	$114 \pm 2$
Maleic	$111 \pm 3$	$100 \pm 4$	$88 \pm 4$	$92 \pm 4$
cis-1,2-Cyclohexane dicarboxylic	$192 \pm 7$	$224 \pm 5$	$212 \pm 1$	$205 \pm 3$

**Table 3** Energies of activation for the cross-linking reactions of DGEBA with three different cyclic anhydrides in the presence of triethylamine as determined by Kissinger<sup>13</sup>, Osawa<sup>14</sup> and half-width<sup>7,8,12</sup> multiple scanning-rate methods

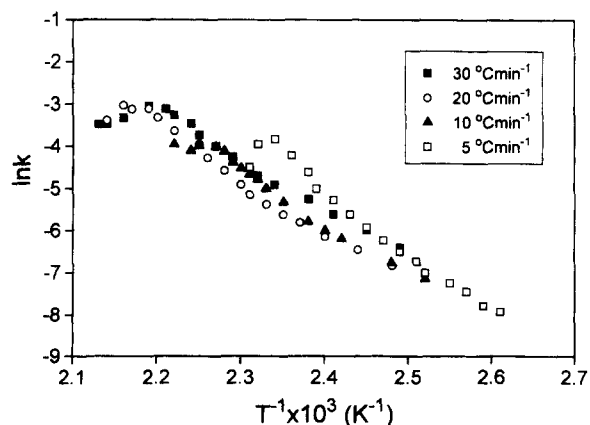
Anhydride	Energies of activation (kJ mol <sup>-1</sup> )		
	Kissinger	Osawa	Half-width
Succinic	73 ± 3	80 ± 3	60 ± 6
Maleic	64 ± 10	72 ± 10	58 ± 5
cis-1,2-Cyclohexane dicarboxylic	95 ± 12	102 ± 12	97 ± 11



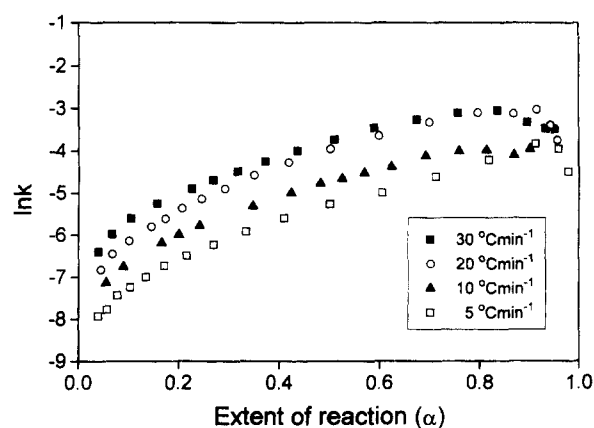
**Figure 2** Plot of  $\ln k$  versus  $T^{-1}$  (K<sup>-1</sup>) (Barrett method) for the system cured with succinic anhydride at 5, 10, 20 and 30°C min<sup>-1</sup>



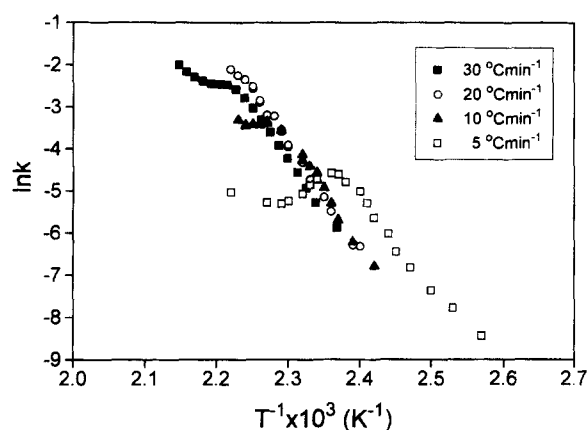
**Figure 3** Plot of  $\ln k$  versus extent of conversion (Barrett method) for the system cured with succinic anhydride at 5, 10, 20 and 30°C min<sup>-1</sup>



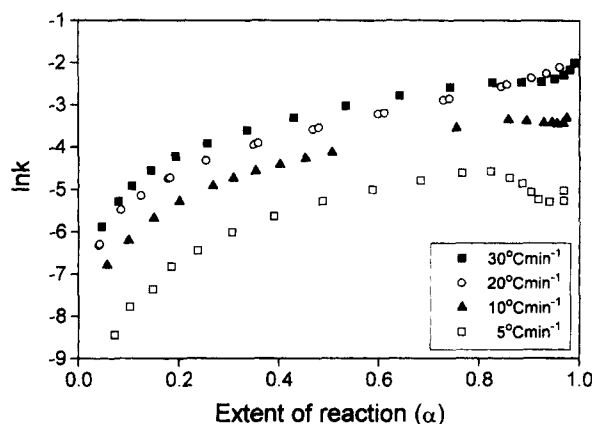
**Figure 4** Plot of  $\ln k$  versus  $T^{-1}$  (K<sup>-1</sup>) (Barrett method) for the system cured with maleic anhydride at 5, 10, 20 and 30°C min<sup>-1</sup>



**Figure 5** Plot of  $\ln k$  versus extent of conversion (Barrett method) for the system cured with maleic anhydride at 5, 10, 20 and 30°C min<sup>-1</sup>

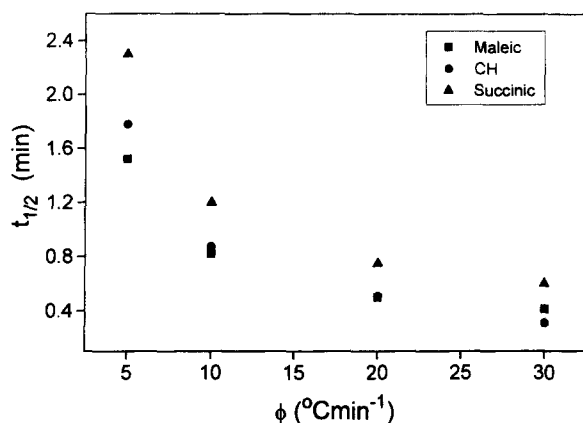


**Figure 6** Plot of  $\ln k$  versus  $T^{-1}$  (K<sup>-1</sup>) (Barrett method) for the system cured with CH anhydride at 5, 10, 20 and 30°C min<sup>-1</sup>



**Figure 7** Plot of  $\ln k$  versus extent of conversion (Barrett method) for the system cured with CH anhydride at 5, 10, 20 and 30°C min<sup>-1</sup>

studies. In the gelation–vitrification path, at extents of reaction higher than 0.50, a maximum in the constant rate is followed by a deep decrease, and finally the vitrification process tends smoothly to a constant rate plateau. This behaviour is more accentuated at smaller temperature scanning rates such as 5°Cmin<sup>-1</sup> where diffusional effects are more noticeable by d.s.c. measurements. In the system cured with CH anhydride the singular gelation–vitrification processes can not be described through Arrhenius-type kinetics.



**Figure 8** Half-width time ( $t_{1/2}$ ) versus scanning rate  $\phi$  ( $^{\circ}\text{Cmin}^{-1}$ ) for all three systems cured with succinic, maleic and CH anhydrides at 5, 10, 20 and  $30^{\circ}\text{Cmin}^{-1}$

The fact that the Barret method furnishes values too high for the energy of activation may be assigned to the invalidity of assuming the order of reaction as 1.0, but it may also have its origin in the difficulties of excluding the influence of diffusional effects. The half-width method circumvents these difficulties.

#### Application of Kissinger, Osawa and half-width methods

The half-width method consists of plotting the natural logarithm of the half-width time versus the inverse of  $T_{\min}$  (see Table 1). The half-width time is obtained from the d.s.c. thermogram as follows. At the peak temperature  $T_{\min}$  one locates the half-height. At the half-height, the half-width is measured in temperature units. By multiplying this half-width by the scanning rate one obtains the half-width in time units, i.e. the 'half-width time'. Figure 8 shows the behaviour of the half-width time. If the scanning rate is increased, the half-width time becomes shorter. An exponential dependence is observed. Similar behaviour was reported recently<sup>8</sup> for the cross-linking reaction of the same epoxy resin with 4,4'-diaminodiphenylmethane. Taking into account the Arrhenius equation for the temperature dependence of the rate constant of an activation controlled reaction,

$$k = A \exp(-E/RT) \quad (1)$$

one assumes an inverse proportionality between the rate constant and the half-width time  $t_{1/2}$ . So the equation above can be rewritten as

$$\ln(1/t_{1/2}) = \ln A - E/RT \quad (2)$$

or simply as

$$\ln t_{1/2} = E/RT - \ln A \quad (3)$$

where all parameters have the usual Arrhenius significance and  $T$  is the absolute temperature. Table 3 lists the results of the energy of activation ( $E$ ) by the half-width method, which are comparable to those furnished by the Osawa and Kissinger methods with the exception of the reaction with succinic anhydride, whose value of  $E$  as determined by the half-width method differs by about

20% in comparison with  $E$  determined by the Osawa method.

## CONCLUDING REMARKS

The Barret method provided values too high for the energy of activation. This fact may be assigned to the invalidity of assuming the order of reaction as 1.0 but it may also have its origin in the difficulties of excluding the influence of diffusional effects. However, the Barret method provided information on the different stages of the network formation. By applying the half-width method, the difficulties mentioned above can be circumvented. The half-width method furnished values for the energy of activation in the range  $60\text{--}100 \text{ kJ mol}^{-1}$ . These values are similar to those obtained by applying the well-known non-isothermal multiple-scanning rate methods of Kissinger and Osawa.

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## REFERENCES

- Holba, P. and Sesták, J., *Z. Phys. Chem.*, 1972, **80**, 1.
- Simmons, E. L. and Wendlandt, W. W., *Thermochim. Acta*, 1972, **3**, 498.
- Sesták, J., *J. Thermal Anal.*, 1979, **16**, 503.
- Criado, J. M., *Thermochim. Acta*, 1981, **43**, 111.
- MacCallum, J. R., *Thermochim. Acta*, 1982, **53**, 375.
- Blazejowsky, J., *Thermochim. Acta*, 1984, **76**, 359.
- Ojeda, T., Liberman, S., Amorim, R. and Samios, D., *J. Polym. Eng.*, 1996, **16**, 105.
- Miranda, M. I. G., Tomedi, C., Bica, C. I. D. and Samios, D., *Polymer*, 1997, **38**, 1017.
- Samios, D., Castiglia, S., Silveira, N. P. and Stassen, H., *J. Polym. Sci. B: Polym. Phys.*, 1995, **33**, 1857.
- Miranda, M. I. G. and Samios, D., *Eur. Polym. J.* (in press).
- Parekh, J. K. and Patel, R. G., *Angew. Makromol. Chem.*, 1995, **227**, 1.
- Bica, C. I. D., Samios, D., Miranda, M. I. G., Tomedi, C. and Diel, F., *Proceedings of 6th International Macromolecular Colloquium, 2nd Ibero-American Polymer Symposium and 4th Latin American Polymer Symposium, Gramado-RS, Brasil*, 1994, vol. 1, p. 306.
- Kissinger, H. E., *Anal. Chem.*, 1957, **29**, 1702.
- Osawa, T., *Bull. Chem. Soc. Jpn*, 1965, **38**, 1881.
- Barret, K. E. J., *J. Appl. Polym. Sci.*, 1967, **11**, 1617.
- Fava, R. A., *Polymer*, 1968, **9**, 137.
- Yilgör, I., Yilgör, E., Bantia, A. K., Wilkes, G. L. and McGrath, J. E., *Polym. Bull.*, 1981, **4**, 323.
- Shim, J. S., Lee, W. and Jang, J., *Polym. Bull.*, 1991, **25**, 669.
- Patel, R. D., Patel, R. G. and Patel, V. S., *Angew. Makromol. Chem.*, 1987, **155**, 57.
- Soprana, J., M.Sc. thesis, Porto Alegre, 1990.
- Fidalsky, G., M.Sc. thesis, Porto Alegre, 1992.
- May, C. A., (ed.), *Epoxy Resins-Chemistry and Technology*. Marcel Dekker, New York, 1988.