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Kinetics of the curing reaction of a diglycidyl ether of bisphenol A with a modified polyamine

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Abstract

Differential scanning calorimetry (DSC) was used at different heating rates to study the cure kinetics of the diglycidyl ether of bisphenol A (DGEBA) with a polyaminophenolic product (PAP) derived from the modification of tetraethylenepentamine (TEPA). The activation energy (E_a) based on a single heating rate was compared with E_a based on multiple heating rates (Kissinger, isoconversional method).

Keywords: Epoxy resin; DSC; Isoconversional method

1. Introduction

Epoxy resins are converted into a three-dimensional, cross-linked, thermoset network during a cure reaction. The physical properties of the network depend on the structures of both resin and hardener [1,2], the extent of cure [3,4], the time of cure and the cure temperature [5,6]. Kinetic parameters related to network formation provide substantial information concerning the final structure of the network, properties and material processability [7,8]. Kinetic studies determine the activation energy (E_a) and reaction order (n), parameters, that can provide quantitative predictions about the degree of advancement of the reaction with time during a fixed thermal program and propose a reaction mechanism in agreement with the experimental data. Differential scanning calorimetry (DSC) provides rapid determination of the kinetics of epoxy system. In the present work, DSC is employed to study the cure reaction of a diglycidyl ether of bisphenol A (DGEBA) in the presence of a modified tetraethylenepentamine (TEPA) curing agent. The purpose is to compare three methods of data analysis.

The generally accepted scheme of an amino-epoxy cure involves three main reactions of the glycidyl ether: a primary amine group addition to the epoxy ring, a secondary amine group addition and the etherification (Fig. 1). This is an autocatalytic process because the hydroxylic molecules formed as one of the reaction products partly protonate the oxygen atom of the epoxy group, facilitating the ring-opening reaction [9,10].

The concentration of the hydroxyl groups increases as the reaction proceeds, so the cure rate steeply increases. The reactions of primary and secondary amines are described by two rate constants, k_1 and k_2. The ratio of the rate constants, k_1/k_2, depends on the electron-donating properties of the amines [11].

Normally, the secondary amine addition is not important in the beginning of the cure because the primary amine addition controls the overall rate.

2. Experimental

2.1. Materials

The epoxy resin was a diglycidyl ether of bisphenol A (Epon 828 from Shell), with epoxy equivalent of 190, specific gravity at 20 °C of 1160 kg m^{-3}, molecular mass of 380, viscosity at 20 °C of 0.13 Pa s.

The curing agent was a polyaminophenolic oligomer prepared from tetraethylenepentamine (supplied by Fluka) by reaction with phenol in the presence of formaldehyde [12] and characterized by the presence of two amino groups, a primary and a secondary amino group (Fig. 2). TEPA/CH_2OH/Phenol molar ratio was 1:1:0.8.

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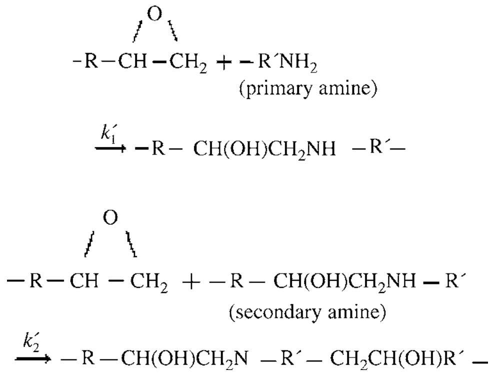

Fig. 1. Scheme of reaction in amine cured epoxy resins.

2.2. *Differential scanning calorimetry analysis*

Calorimetric measurements were performed by means of a Pyris 1 Perkin-Elmer DSC. The DSC was calibrated with an indium standard.

Resin and hardener were mixed at a weight ratio of 2:1 at room temperature. Samples of 10 ± 2 mg were enclosed in aluminium DSC pans and immediately scanned at heating rates of 5, 10, 15 and 20 K min^{-1} from 293 to 450 K. Three samples for each heating rate were scanned. An empty aluminium pan was used as reference. The experiments were carried out under a nitrogen atmosphere.

2.3. *Methods*

The temperature ramp varies linearly with time as:

$$T - T_\mathrm{i} = \beta t \tag{1}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ is the scanning rate, T the current temperature and T_i is the initial temperature. The rate, expressed by the Borchardt–Daniels equation [10] is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \tag{2}$$

where α is the fraction of the sample reacted, t the time, n the reaction order and k is the rate constant.

The temperature dependence of the reaction rate is specified as in Eq. (3)

$$k = Z\exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{3}$$

where Z is the pre-exponential constant, E_a the activation energy of the cure reaction, R the gas constant and T is the absolute temperature.

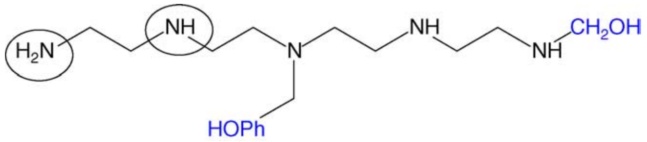

Fig. 2. PAP curing agent with primary and secondary amino groups.

By combining Eqs. (1)–(3), we obtain:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = Z\exp\left(-\frac{E_\mathrm{a}}{RT}\right)(1-\alpha)^n \tag{4}$$

or, in linear form:

$$\ln\left[\beta\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\right] = \ln(Z) - \frac{E_\mathrm{a}}{RT} + n\ln(1-\alpha) \tag{5}$$

The value of α can be obtained from the area under the DSC curve:

$$\alpha = \frac{Q_n}{Q_\mathrm{tot}} \tag{6}$$

where Q_n is given by the fractional peak area and Q_tot by the total peak area obtained as a mean of the values at different heating rates. This method is based on the Kissinger equation. The kinetic parameters are obtained by the variation of the exotherm peak temperature, T_p, with respect to the heating rate β [13]:

$$E_\mathrm{a} = -R\left[\frac{\mathrm{d}(\ln(\beta/T_\mathrm{p}^2))}{\mathrm{d}(1/T_\mathrm{p})}\right] \tag{7}$$

where T_p is the maximum temperature of the exothermic peak.

By means of an isoconversional method [14–16], it is possible to obtain a more complete evaluation of activation energy throughout the whole conversion. The basic idea of this method is that the reaction rate at a constant conversion depends only on the temperature.

$$E_\alpha = -R\left[\frac{\mathrm{d}(\ln(\beta)_\alpha)}{\mathrm{d}(1/\mathrm{T})_\alpha}\right] \tag{8}$$

where E_α is the activation energy value at a given conversion degree and T is the temperature of a selected conversion degree at each heating rate.

3. Results

Fig. 3 shows the DSC curves recorded at 5, 10, 15 and 20 K min^{-1}.

The DSC curves all show a single exothermic peak. As a first approximation, this allows that the reactions of primary and

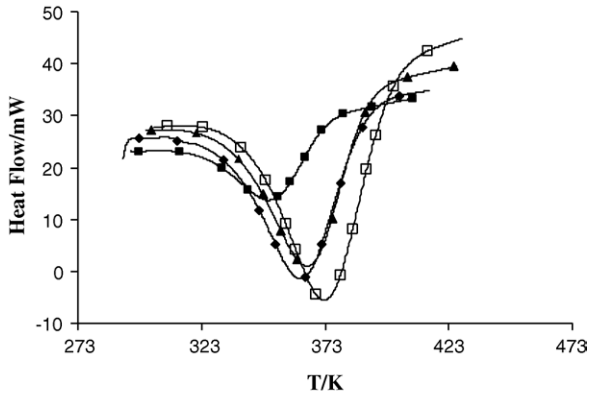

Fig. 3. DSC curves at different heating rates: (△) 20 K min^{-1}; (□) 15 K min^{-1}; (■) 10 K min^{-1}; (◆) 5 K min^{-1}.

Table 1
Curing characteristics of the epoxy system evaluated from DSC curves

β (K min^{-1})	ΔH_r (J g^{-1})	T_o (K)	T_p (K)	T_i (K)	T_{end} (K)
5	389 ± 3	320	351 ± 1	308 ± 2	374 ± 2
10	396 ± 3	330	364 ± 1	306 ± 1	389 ± 2
15	368 ± 4	332	367 ± 1	304 ± 2	390 ± 2
20	374 ± 3	338	373 ± 1	310 ± 2	400 ± 2

Table 2
Kinetics of the epoxy curing reaction

β (K min^{-1})	E_a (kJ mol^{-1})	ln Z (s^{-1})	n
5	74 ± 1	20.2 ± 0.2	1.01 ± 0.01
10	73 ± 1	19.6 ± 0.3	1.01 ± 0.02
15	72 ± 1	19.5 ± 0.3	0.95 ± 0.02
20	71 ± 2	19.2 ± 0.3	0.99 ± 0.02

secondary amine hydrogen atoms of polyaminophenolic product (PAP) with epoxy occur simultaneously.

The total heat of reaction, ΔH_r, the initial curing temperature, T_i, the onset temperature, T_o, the peak exothermic temperature, T_p, and temperature of complete cure, T_{end} were calculated from the DSC curves of all four samples. The baseline was taken as the tangent to the DSC curve at the locations preceding and following the exothermic peak. The average values of the three samples registered for each heating rate are summarized in Table 1.

The peak temperature, the onset temperature and the final cure temperature shift to higher values with increasing heating rate, while ΔH_r values undergo changes about 10%.

A multilinear regression procedure is performed with $\ln(\beta(d\alpha/dt))$, $-1/T$ and $\ln(1-\alpha)$ as variables to solve for Z, E_a and n in Eq. (5). Results are shown in Table 2.

A decreasing trend of E_a and ln Z is observed with increasing β. Despite relatively constant values of the activation energy and the reaction order, the cure reaction is not a single mechanism and no physical meaning can be attributed to the E_a and n values [17]. Kinetic parameters were than obtained by the proposed Kissinger method.

Fig. 4 shows the plot of the heating rate against $1/T_p$, where the data are linear and the slope is equal to $-E_a/R$. The E_a value thus obtained is 66 ± 3 kJ mol^{-1}.

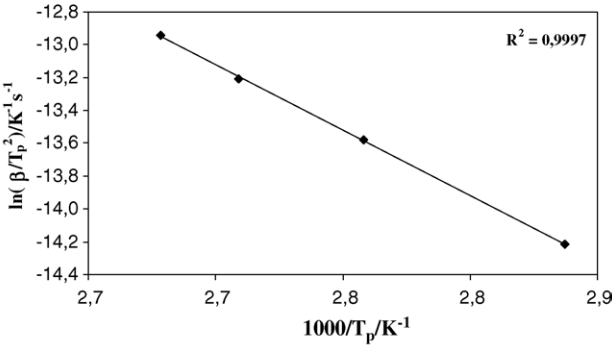

Fig. 4. Plot of the Kissinger equation: heating rate vs. 1000/T_p.

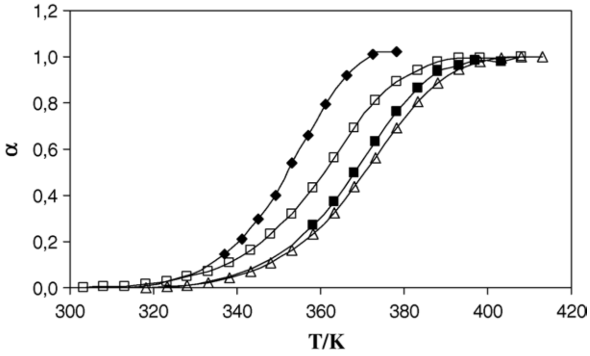

Fig. 5. Plot of the conversion degree vs. temperature: (♦) 5 K min^{-1}; (□) 10 K min^{-1}; (■) 15 K min^{-1}; (△) 20 K min^{-1}.

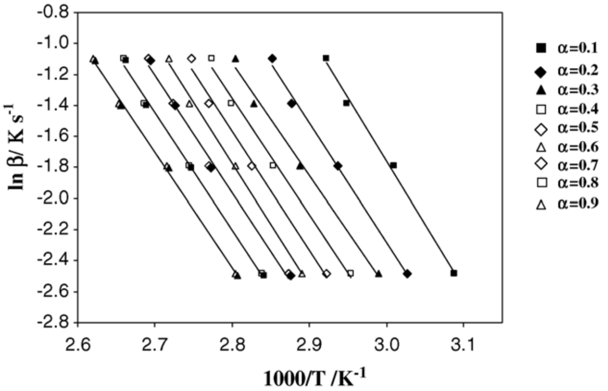

Fig. 6. Relationship between the conversion degree α and $1/T$.

To perform isoconversional analysis, the original DSC data (Fig. 1) were transformed into the form α_i versus T_i for each ith heating rate (Fig. 5).

For each degree of conversion, the logarithm of the heating rate was plotted against the inverse of the temperature (Fig. 6). The plots show systematic deviations from the fitted lines at $\beta = 10$ K min^{-1}. A reasonable explanation has not been found yet. For each experimental curve, the slope ($E\alpha$) of the corresponding plot was calculated.

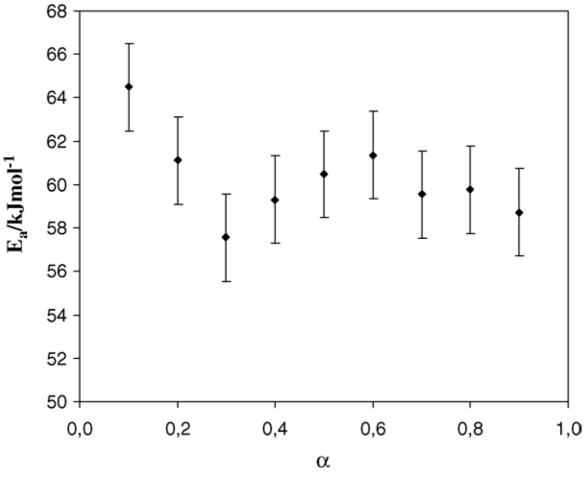

Fig. 7. Dependence of the activation energy on the conversion degree.

Fig. 7 shows the E_a values obtained by the proposed isoconversional method against the conversion degree (α).

Each point corresponds to E_a/R at each value of the conversion degree. The values vary between 58 ± 3 and $64 \pm 3\,\mathrm{kJ\,mol^{-1}}$.

4. Discussion

According to the hypothesized mechanism of an amino-epoxy, it seems reasonable to expect higher values of E_a at lower conversion where the non-autocatalyzed reaction occurs [11,15,18] followed by a decrease of E_a values.

The activation energy values most likely represent some average values between the activation energies of non-autocatalyzed and those of autocatalyzed reactions. For $\alpha \to 0$, E_a appears to match the activation energy value of the non-autocatalyzed reaction. At higher conversions, the value of E_a is determined by the k_1/k_2 ratio [19].

Consequently, the isoconversional kinetic method evidenced decreasing dependencies of E_a on α in the studied system.

The E_a values for $\alpha \to 0$ are not much higher than the values of E_a at higher conversions. Activation energies of the primary and secondary amine addition were found to be similar for different amines [11], so it is reasonable to suppose that E_1 and E_2 values are not so different [20].

The average activation energy is $60 \pm 3\,\mathrm{kJ\,mol^{-1}}$. The T_p values correspond to $\alpha = 0.60$, 0.66, 0.55 and 0.58 for 5, 10, 15 and $20\,\mathrm{K\,min^{-1}}$, respectively. So it seems reasonable to compare the activation energy value obtained by the Kissinger method with that from the isoconversional method at $\alpha = 0.60$, which is $63 \pm 2\,\mathrm{kJ\,mol^{-1}}$. The values agree with each other as well as with those reported in the literature for various epoxy-amine systems [6,21–23].

E_a values obtained by B–D method disagree by the isoconversional method because the B–D equation treats the curing reaction as a single step process.

5. Conclusions

This study confirms the effectiveness of the methods based on different heating rates (Kissinger, Isoconversional), and demonstrates the limitations of those based on single heating rate measurements.

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References

[1] P. Jain, V. Choudhary, I.K. Varma, Eur. Polym. J. 39 (2003) 181.
[2] D.J. Liaw, W.C. Shen, Polym. Eng. Sci. 34 (1994) 1297.
[3] N. Sbirrazzuoli, S. Vyazovkin, Thermochim. Acta 388 (2002) 289.
[4] S. Monserrat, J. Malek, Thermochim. Acta 228 (1993) 47.
[5] S. Monserrat, J. Therm. Anal. 40 (1993) 553.
[6] D. Rosu, F. Mustata, C.N. Cascaval, Thermochim. Acta 370 (2001) 105.
[7] L.E. Nielsen, R.F. Landel, Mechanical Properties of Polymers and Composites, Marcel Dekker, New York, 1994 (Chapter 2).
[8] R. Thiagarajan, P.V. Reddy, S. Sridhar, M.C. Ratra, J. Therm. Anal. 36 (1990) 277.
[9] C.A. May, Epoxy Resins: Chemistry and Technology, second ed., Marcel Dekker, New York, 1988.
[10] H.J. Borchardt, F.J. Daniels, J. Am. Chem. Soc. 79 (1956) 41.
[11] J. Mijovic, J. Wijaya, Macromolecules 27 (1994) 7589.
[12] G. Rinaldi, Ind. Eng. Chem. 36 (9) (1997) 3778.
[13] H.E. Kissinger, J. Res. Natl. Bur. Stds. 57 (4) (1956) 217.
[14] J. Malek, Thermochim. Acta 355 (2000) 239.
[15] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 20 (1999) 387.
[16] S. Vyazovkin, Thermochim. Acta 355 (2000) 155.
[17] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Stray, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.-R. Li, T.B. Tang, B. Roduit, J. Malek, T. Mitsuashi, Thermochim. Acta 355 (2000) 125.
[18] S. Sourur, M.R. Kamal, Thermochim. Acta 14 (1976) 41.
[19] K. Pielichowski, P. Czub, J. Pielichowski, Polymer 41 (2000) 4381.
[20] A.C. Grillet, J. Galy, J.P. Pascault, I. Bardin, Polymer 30 (1989) 2094.
[21] J.M. Salla, A. Cadenato, X. Ramis, J.M. Morancho, J. Therm. Anal. Calorim. 56 (1999) 771.
[22] R.M.V.G.K. Rao, A. Padma, H.S. Patel, High Perform. Polym. 4 (1) (1992) 41.
[23] R. Jenkins, L.J. Karre, J. Appl. Polym. Sci. 10 (1966) 303.