Effect of modified rubber compound on the cure kinetics of DGEBA/MDA system by Kissinger and isoconversional methods

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Abstract

The cure kinetics of diglycidyl ether of bisphenol A (DGEBA)/4,4′-methylene dianiline (MDA) system with various contents of MDA-endcapped carboxyl-terminated butadiene acrylonitrile (CTBN) were studied by Kissinger and isoconversional methods. With increasing MDA-endcapped CTBN content, the exothermic heat decreased due to the diffusion control induced by rubber domain produced in the epoxy matrix, which disturbed the diffusion of functional groups, and the maximum exothermic peak value and the activation energy by Kissinger equation decreased due to the increasing content of amine group in rubber compound, which reacted with epoxy group and formed a hydroxyl group acted as a catalyst. In the isoconversional method, the activation energy decreased until minimum value in the initial stage and increased after that value. The decreasing in the initial stage was due to the autocatalytic cure reaction and the increasing after the minimum value was due to the increasing crosslink density and rubber domain. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The applications of the cured epoxy resins have been expanded in various fields such as coatings, adhesives, electrical insulators, matrices for fibrous composites, etc. However, the cured epoxy resins having high crosslink density are so brittle that they are easily broken by an instant impact. Therefore, many researchers have studied to enhance the toughness of the cured epoxy resins and one of the most well-known methods is to incorporate various

amounts of reactive liquid rubbers [1,2] and in this study, carboxyl-terminated butadiene acrylonitrile (CTBN) rubber was introduced to the epoxy system of diglycidyl ether of bisphenol A (DGEBA)/4,4′-methylene dianiline (MDA). When epoxy resin together with liquid rubber is cured, the rubber-rich domains are separated from the epoxy-rich matrix due to the incompatibility between epoxy resin and liquid rubber and the rubber domain improve the toughness by absorbing the impact energy [2].

Many useful methods and techniques are proposed to estimate the cure rate of epoxy system by differential scanning calorimetry (DSC) with the assumption that the heat evolved during the cure reaction is proportional to the monomer conversion [3–12].

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Kissinger equation [3,4], isoconversional equation [5,6], autocatalytic cure rate equation [7,8], fractional-life equation [9,10], etc. are well-known, and in this study the following Kissinger (Eq. (1)) and isoconversional (Eq. (2)) equations were used. Kissinger equation is

$$E_a = -R \frac{d(\ln(q/T_P^2))}{d(T_P^{-1})} \tag{1}$$

where q is the heating rate, T_P the maximum temperature of exothermic peak, E_a the activation energy, and R the gas constant. The relationship between $-\ln(q/T_P^2)$ and $1/T_P$ was obtained from the dynamic DSC curves of different heating rates, and activation energy could be calculated from the slope.

While only an overall activation energy could be obtained from Kissinger equation, a more complete accession of activation energy throughout the entire conversion could be calculated by isoconversional equation and it is

$$E_a = -R \frac{d(\ln q)}{d(T^{-1})} \tag{2}$$

where E_a, q and R are the same terms of Kissinger equation and T is the temperature to be a selected conversion, α at each heating rate. From the slope, activation energies could be obtained and the average activation energy from isoconversional equation was compared with the overall activation energy from Kissinger equation.

2. Experimental

Epoxy formulation was the complex mixture of DGEBA (Epon 828, Shell), MDA (Fluka Chemie AG) and CTBN (Hycar 1300×8, B.F. Goodrich). To enhance the compatibility between epoxy and CTBN, MDA-endcapped CTBN was synthesized by the reaction between MDA and CTBN at 160°C for 1 h [13].

DGEBA and MDA-endcapped CTBN (0, 10 and 20 phr) were vigorously mixed at 100°C for 5 min, and cooled to 70°C. Then, MDA (30 phr) was added and well-mixed at 70°C for 2 min, and the samples were stored at −5°C. The unit "phr" is the abbreviation of "part per one hundred base resin" and the base resin, in here, is DGEBA.

Dynamic curing was performed by DSC (Cahn 2121, USA) at 5, 10, 15 and 20 K/min under a purge of nitrogen (40 ml/min). Sample mass was 3 mg, and indium and benzoic acid were used as standards to calibrate the temperature and heat flow rate.

3. Results and discussion

Fig. 1 shows DSC curves for DGEBA/MDA system without MDA-endcapped CTBN at four different heating rates. The cure reaction took place in one stage regardless of heating rate and the total exothermic heat was 117.0 ± 1.8 kJ/mol of epoxide group. The base line was taken as the tangent to the DSC curve at the locations proceeding and following the exotherm. The exothermic curve started from about 50°C for all curves, and the temperature of the maximum peak value increased with increasing heating rate as shown in Table 1. To use the Kissinger equation, the relationships between $-\ln(q/T_P^2)$ and $1/T_P$ were also listed on Table 1 and displayed in Fig. 2. The straight line was expressed as

$$-\ln \frac{q}{T_P^2} = 5.2 \times 10^3 \frac{1}{T_P} - 2.1$$

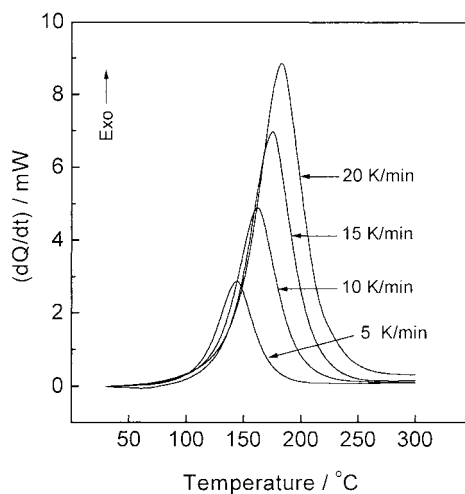The slope was corresponded to E_a/R, so the activation energy of cure reaction was 43.3 ± 1.7 kJ/mol.

Fig. 1. DSC curves for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system at various heating rates.

Table 1
The relationship between heating rate (q) and maximum temperature of exothermic peak (T_P) for DGEBA/MDA/MDA-endcapped CTBN (0 phr)

q (K/min)	T_P (K)	$-\ln(q/T_P^2)$	$1/T_P \times 10^3$ (K^{-1})
5	416.7 ± 1.2	10.6	2.40
10	434.8 ± 1.2	9.8	2.30
15	447.5 ± 0.8	9.5	2.23
20	455.4 ± 1.0	9.2	2.20

Fig. 2. Kissinger plot for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system.
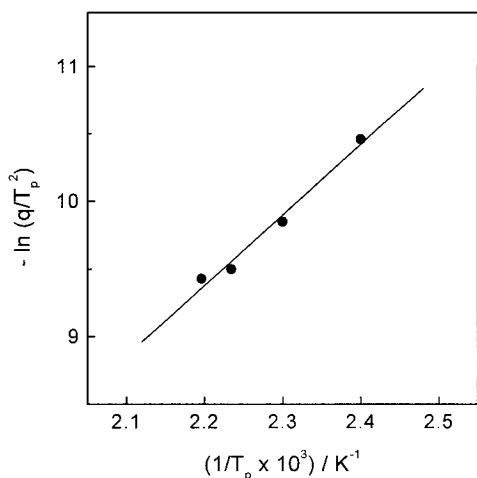

Fig. 3. Conversion curves at different heating rates for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system.

Fig. 3 shows the conversion curves for DGEBA/MDA system without MDA-endcapped CTBN at four heating rates, which could be obtained from the integrating the DSC curves of Fig. 1. On the curve of 5 K/min, the conversion increased very slowly in the initial stage and rose abruptly in the range 100–180°C, and it was almost constant in the final stage.
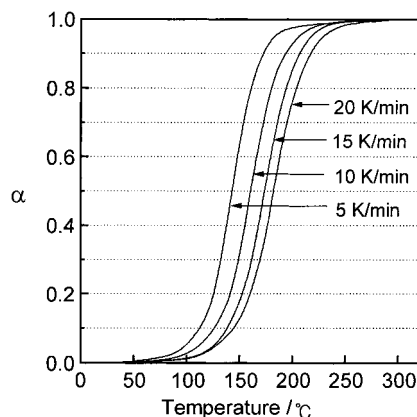
The abrupt increment of cure rate in the short temperature range could be explained by the autocatalytic cure mechanism [1,14]. All curves for other heating rates also showed the s-shape and they shifted to right-hand side with the increasing heating rate.

The isoconversional temperatures at four different heating rates could be obtained from the cross points of the conversion curves and the dotted lines at various selected conversion α, and $1/T \times 10^3$ according to $\ln(q)$ were listed in Table 2. To get activation energy at each conversion, the relationships of the two variables at the conversion of 0.1–0.9 are displayed in Fig. 4, and the linear expression for each straight line is listed in Table 3. All the slopes were corresponded to E_a/R at these particular conversions and activation energies were also listed in Table 3. The values changed slightly in the range 51.7 ± 2.2 to 64.9 ± 2.2 kJ/mol at different degree of conversion. The value decreased with the increasing conversion in the initial stage and showed minimum value at $\alpha = 0.4$. The decrement

Table 2
The data for isoconversional temperature and the relationship between $\ln(q)$ and T^{-1} for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system

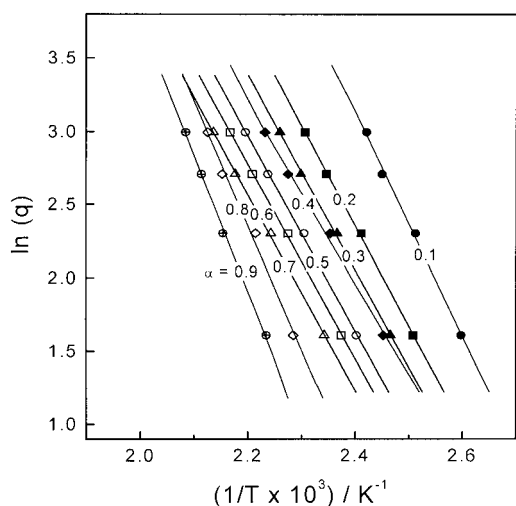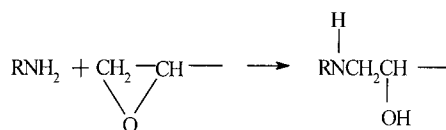| $\ln(q)$	$1/T \times 10^3$ (K^{-1})								
	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.4$	$\alpha = 0.5$	$\alpha = 0.6$	$\alpha = 0.7$	$\alpha = 0.8$	$\alpha = 0.9$
1.61	2.60	2.51	2.47	2.45	2.40	2.37	2.34	2.28	2.23
2.30	2.51	2.41	2.37	2.35	2.30	2.27	2.24	2.21	2.15
2.71	2.45	2.35	2.30	2.27	2.24	2.21	2.18	2.15	2.11
3.00	2.42	2.31	2.26	2.23	2.20	2.17	2.14	2.13	2.08

Fig. 4. Isoconversional plots at various conversions for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system.

Scheme 1.

of activation energy was due to the autocatalytic role of hydroxyl group in the cure reaction [1,14]. One hydroxyl group was generated by the reaction between an epoxide group and an amine group (Scheme 1) and the generated hydroxyl group acted as a catalyst for the reaction between another epoxide group and amine group (Scheme 2). As the cure reaction proceeded, the concentration of hydroxyl group increased, so the cure rate steeply increased. However, the activation energy value increased at final conversion due to the increased viscosity and crosslink, which reduced the mobility of the unreacted functional groups [15].

The average activation energy was 57.1 ± 2.3 kJ/mol which was somewhat higher than 43.3 ± 1.7 kJ/mol obtained by the previous Kissinger equation. The T_P values in Kissinger equation appeared at $\alpha = 0.52$, 0.53, 0.52 and 0.51 for 5, 10, 15 and 20 K/min, respectively. So, it was reasonable that the activation energy by Kissinger equation was compared to that by isoconversional method at $\alpha = 0.5$, which was 55.4 ± 2.4 kJ/mol. It was also higher than that of Kissinger equation and it was due to the different mathematical approach. So, it would be good to consider the activation energies by autocatalytic rate equation [7].

Fig. 5 shows DSC curves for DGEBA/MDA system with MDA-endcapped CTBN (A: 10 phr and B: 20 phr) at four different heating rates. All curves showed only one exothermic peak and the temperature at the maximum exothermic peak value increased with increasing heating rates, which were similar to those of Fig. 1. However, the maximum peak temperature decreased with increasing MDA-endcapped CTBN as tabulated in Table 4. T_P value at each heating rate was introduced to the Kissinger equation and activation energies could be calculated from the slopes. The effect of MDA-endcapped CTBN content on the activation energy was compared in Table 5, which showed that E_a decreased with increasing MDA-endcapped CTBN content. The decrement of T_P and E_a

Table 3
Activation energy for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system by isoconversional equation

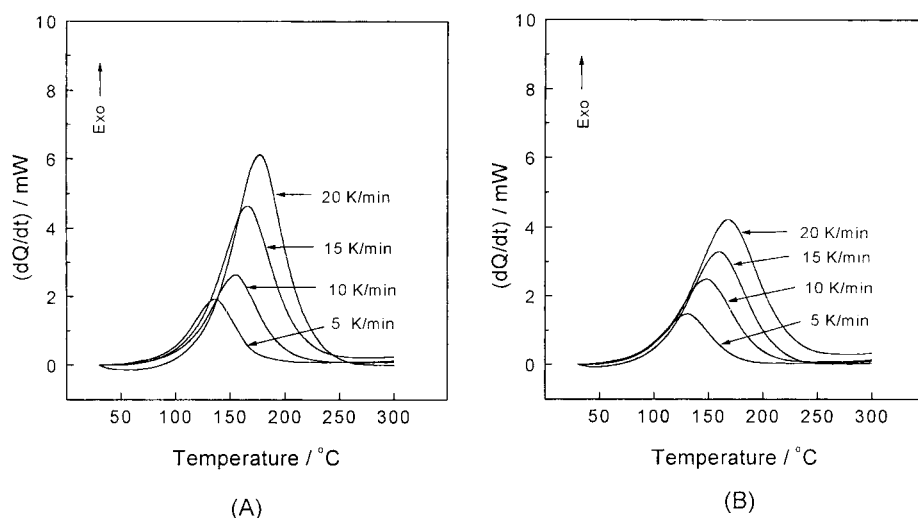| α	Linear expressions of Fig. 4	Activation energy (kJ/mol)
0.1	$Y = -7.1X + 19.4$	59.3 ± 2.4
0.2	$Y = -6.8X + 18.8$	56.9 ± 2.2
0.3	$Y = -6.7X + 18.1$	55.4 ± 1.8
0.4	$Y = -6.2X + 17.6$	51.7 ± 2.2
0.5	$Y = -6.7X + 17.6$	55.4 ± 2.4
0.6	$Y = -6.7X + 17.5$	55.4 ± 2.4
0.7	$Y = -6.7X + 17.2$	55.4 ± 2.7
0.8	$Y = -7.1X + 16.9$	59.1 ± 2.3
0.9	$Y = -7.8X + 17.0$	64.9 ± 2.2
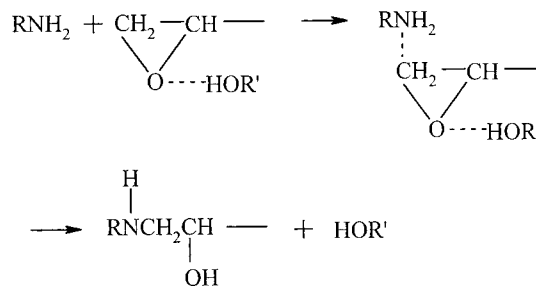
Scheme 2.

Fig. 5. DSC curves for DGEBA/MDA system with MDA-endcapped CTBN (A: 10 phr and B: 20 phr) at various heating rates.

with increasing rubber content said that MDA-end-capped CTBN made the cure rate of DGEBA/MDA system fast, and it was explained by the increasing content of end functional amine group in the modified rubber compound. The amine group also reacted with epoxy group and formed a hydroxyl group as shown in mechanism (I), and the hydroxyl group also could be acted as a autocatalyst as displayed in the mechanism (II).

Figs. 1 and 5 and Table 5 show another clue about the diffusion control by rubber domain produced in the cure procedure [2,14]. The exothermic area of DSC curve apparently decreased with MDA-endcapped CTBN content and the smaller reaction heat was due to the dilution by the rubber and the diffusion control by rubber domain. If it were only due to the former, the total heat generation in the unit, kJ/mol of

epoxide group, should have the same value regardless of rubber content. However, it also decreased with MDA-endcapped CTBN content, as shown in Table 5. Therefore, the final conversion of Fig. 6 showed smaller values. As cure reaction proceeded, CTBN domains were produced in the epoxy matrix, so the functional groups, epoxides, primary and secondary amines, and hydroxyl groups could not diffuse effectively. As a result, the functional groups finally quenched without reaching to the theoretical conversion.

The conversion curves for the systems with 10 and 20 phr of MDA-endcapped CTBN in Fig. 6 were obtained from the dividing partial exothermic heat by theoretical heat. By the same method of the iso-conversional equation, the activation energies were calculated from the linear relationship between $\ln(q)$

Table 4
T_P values for DGEBA/MDA system modified with various contents of MDA-endcapped CTBN

q (K/min)	T_P (K) (for various contents of MDA-endcapped CTBN)		
	0 phr	10 phr	20 phr
5	416.7	408.8	404.0
10	434.8	427.6	421.5
15	447.5	439.1	433.0
20	455.4	450.0	442.0

Table 5
Total exothermic heat and activation energy by Kissinger for DGEBA/MDA system modified with various contents of MDA-endcapped CTBN

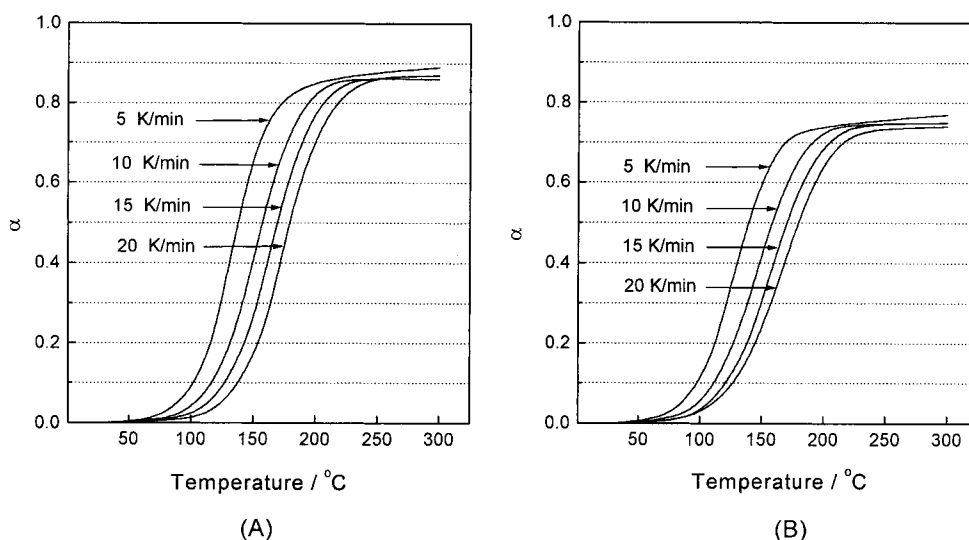| Contents of MDA-endcapped CTBN (phr)	Total exothermic heat (kJ/mol of epoxide group)	Activation energy (kJ/mol)
0	117.0±1.8	43.3 ± 1.7
10	107.7±1.2	44.9 ± 6.3
20	87.9±1.3	47.3 ± 4.6

Fig. 6. Isoconversional plots at various conversions for DGEBA/MDA system with MDA-endcapped CTBN (A: 10 phr and B: 20 phr).

and T^{-1} and they were compared with those of the system without MDA-endcapped CTBN in Table 6. The value decreased with increasing conversion in the initial stage and then inverted to increasing due to the autocatalytic role of hydroxyl group in the cure reaction [1,14]. With the increasing MDA-endcapped CTBN content, in the initial stage the activation energy decreased due to the increasing content of end functional amine group in the modified rubber compound and in the final stage the activation energy increased due to the producing rubber domain in the matrix.

Table 6
Activation energy for DGEBA/MDA system with various contents of MDA-endcapped CTBN by isoconversional equation

α	Activation energy (kJ/mol) (for various contents of MDA-endcapped CTBN)		
	0 phr	10 phr	20 phr
0.1	59.3 ± 2.4	52.3 ± 4.3	48.9 ± 3.1
0.2	56.9 ± 2.2	52.3 ± 2.22	48.3 ± 1.9
0.3	55.4 ± 1.8	51.2 ± 2.6	48.9 ± 2.7
0.4	51.7 ± 2.2	51.2 ± 2.9	52.7 ± 2.3
0.5	55.4 ± 2.4	53.8 ± 3.7	53.2 ± 3.1
0.6	55.4 ± 2.4	54.3 ± 2.7	55.0 ± 2.8
0.7	55.4 ± 2.7	56.3 ± 4.2	58.3 ± 2.7
0.8	59.1 ± 2.3	58.8 ± 3.3	–
0.9	64.9 ± 2.2	–	–

4. Conclusions

With increasing MDA-endcapped CTBN content, the exothermic heat decreased due to the diffusion control induced by rubber domain produced in the epoxy matrix, which disturbed the diffusion of functional groups, and the maximum exothermic peak value and the activation energy by Kissinger equation decreased due to the increasing content of amine group in rubber compound, which reacted with epoxy group and formed a hydroxyl group acted as a catalyst. In the isoconversional method, the activation energy decreased until minimum value in the initial stage and increased after that value. The decrease in the initial stage was due to the autocatalytic cure reaction and the increase after the minimum value was due to the increasing crosslink density and rubber domain.

Acknowledgements

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