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Kinetic studies of an epoxy cure reaction by isothermal DSC analysis

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Abstract

Autocatalytic cure kinetics for an epoxy system was studied by isothermal DSC analysis. The system used in this study was the diglycidyl ether of bisphenol A(DGEBA)/4,4′-methylene dianiline (MDA) system with various contents of phenyl glycidyl ether (PGE)-acetamide (AcAm). Regardless of the PGE-AcAm content, the shape of the conversion curves was sigmoid, and this meant that DGEBA/MDA/PGE-AcAm system underwent an autocatalytic cure reaction. When the PGE-AcAm content increased, the cure rate increased due to the catalytic role of hydroxyl groups of PGE-AcAm. From the comparison between theoretical prediction and experimental data, it was found that the autocatalytic expression correctly represented to analyze the cure kinetics of these systems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Epoxy; Cure kinetics; DSC analysis; Autocatalytic reaction

1. Introduction

The previous studies of Bajaj et al. [1], Dutta and Ryan [2,3] relating to the cure rate of epoxy/diamine system have found that the autocatalytic cure rate expression is well agreed with the experimental results. It is expressed by the multiplication of non-catalytic reaction and autocatalytic reaction as follows [1–4]:

$$\dot{\alpha} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^m)(1-\alpha)^n, \tag{1}$$

where $\dot{\alpha}$ is the cure rate, α is the degree of cure, k_1, k_2 are the rate constants, and m, n are the reaction orders. k_1 represents the kinetic rate constant associated with noncatalytic reaction between epoxide group and amine group and the catalytic reaction due to the existence of catalysts in the initial formulation. k_2 represents the kinetic rate constant associated with the autocatalysis by the –OH groups generated from the reaction between the former noncatalytic or catalytic reactions. The initial cure rate was not zero, so k_1 is the value of $\dot{\alpha}$ at $t = 0$, which can be readily obtained from the DSC curve and it is

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{t=0} = k_1. \tag{2}$$

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To determine the other kinetic parameters, the DSC results were introduced to the following equations [2–4]:

$$m + n = 2, \tag{3}$$

$$m = \frac{\ln\left(\dfrac{\dot{\alpha}_p/(1-\alpha_p)^{2-m} - k_1}{(2-m)k_1\alpha_p^{1-m}/(m-\alpha_p)}\right)}{\ln\alpha_p}, \tag{4}$$

$$k_2 = \frac{(2-m)k_1\alpha_\mathrm{p}^{1-m}}{m-2\alpha_\mathrm{p}}, \tag{5}$$

where α_p is the degree of cure at exothermic peak and $\dot{\alpha}_\mathrm{p}$ is the cure rate at the exothermic peak. α_p and $\dot{\alpha}_\mathrm{p}$ were easily obtained from the isothermal DSC curve.

Epoxy resins are used in the fields of adhesives, coatings, electrical insulators, encapsulants, structural applications, automobiles, aircrafts, etc. and many researchers have investigated to develop new epoxy resins of high performance [5–7]. To improve the mechanical, thermal and electrical properties, epoxy resins or/and curing agents are modified by the following methods: (1) introduction of reactive additives, (2) incorporation of reactive liquid rubbers, and (3) mixing with different epoxy and curing agent. In this study, epoxy resin was modified by phenyl glycidyl ether (PGE)-acetamide (AcAm) as a reactive additive and the effect of –OH group in PGE-AcAm on the cure rate of diglycidyl ether of bisphenol A(DGEBA)/4,4′-methylene dianiline (MDA) system was investigated.

2. Experimental

The epoxy resin was diglycidyl ether of bisphenol A(DGEBA) type Epon 828 supplied by Shell and the curing agent was 4,4′-methylene dianiline (MDA). Phenyl glycidyl ether (PGE)-acetamide (AcAm) was used as an additive [5,6].

DGEBA was well mixed with both 30 phr of MDA and various contents of PGE-AcAM, where the unit phr is an abbreviation of ‘‘part per one hundred base resin’’, and here DGEBA is a base resin. They were stored at −13°C to prevent the cure reaction during the storage. To measure the total heat, Q_T, evolved during the complete cure, dynamic DSC analysis was carried out from 30°C to 350°C at the heating rate of 10°C/min and to measure cumulative heat, Q, at a time, isothermal DSC analyses were performed at 80°C, 90°C, 100°C, 110°C and 120°C. Based upon the assumption that the heat evolved at any time during the cure reaction is directly proportional to the extent of monomer conversion, the degree of conversion is $\alpha = Q/Q_\mathrm{T}$ and the differential cure rate is $\dot{\alpha} = \mathrm{d}\alpha/\mathrm{d}t = (1/Q_\mathrm{T})(\mathrm{d}Q/\mathrm{d}t)$ [7,8].

3. Results and discussion

Isothermal cure rate curves for DGEBA/MDA/PGE-AcAm (5 phr) at five different temperatures are shown in Fig. 1. With the increment of cure temperature, the maximum point appears at shorter time and the value of differential cure rate at this point is increased. The maximum in the cure rate curve means that the cure reaction follows an autocatalytic mechanism, therefore cure kinetics should be investigated by Eq. (1) in this system [2,3]. Initially when $t = 0$ and $\alpha = 0$, Eq. (1) is simplified to Eq. (2), and this equation indicates that kinetic rate constant k_1 is the initial cure rate. k_1 at different cure temperatures were calculated from the isothermal cure rate curves and are listed in Table 1. The relationship between cumulative heat at a time, Q, and the total exothermic heat, Q_T, gives the conversion, α, as a function of time,

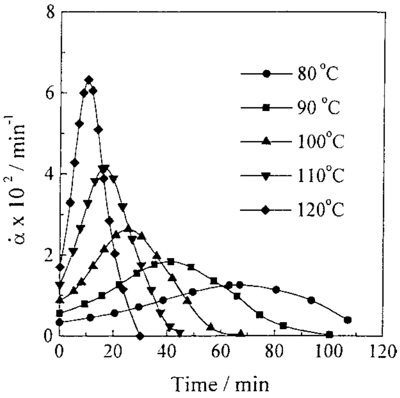


Fig. 1. Cure rate vs. time for DGEBA/MDA/PGE-AcAm (5 phr), where the unit phr is an abbreviation of part per one hundred base resin.

Table 1
Temperature dependence of cure kinetic variables for the DGEBA/MDA/PGE-AcAm (5 phr) system

Temperature (°C)	$\dot{\alpha}_p \times 10^2$ (min^{-1})	α_p	m^a	$k_2 \times 10^2$ (min^{-1})	$k_1 \times 10^2$ (min^{-1})
80	1.26	0.55	1.17	0.34	4.22
90	1.84	0.51	1.11	0.56	6.46
100	2.64	0.44	0.99	0.88	8.64
110	4.15	0.45	1.00	1.27	13.51
120	6.33	0.41	0.90	1.71	21.68

[a] $n = 2 - m$ (Eq. (3)).

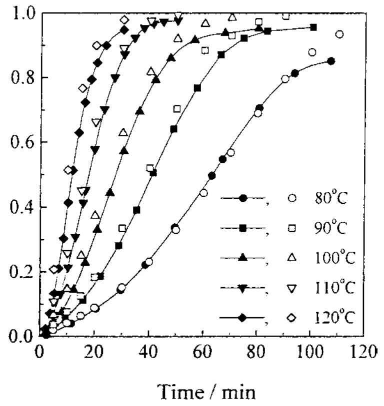


Fig. 2. Conversion vs. time for DGEBA/MDA/PGE-AcAm (5 phr). The solid symbols represent the experimental data and the open symbols represent the theoretical predictions.

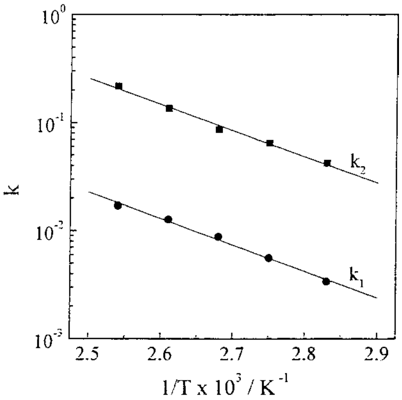


Fig. 3. Kinetic constants, k_1 and k_2, as a function of reciprocal cure temperature for DGEBA/MDA/PGE-AcAm (5 phr).

which is plotted in Fig. 2. All curves are typical sigmoid shape and it is also meant that this system could be interpreted by autocatalytic cure rate expression. The times to reach $\alpha = 0.6$ at 80°C, 90°C, 100°C, 110°C, and 120°C were 71.4, 46.8, 32.0, 20.6 and 13.7 min, respectively. Therefore, relative cure rates at 90°C, 100°C, 110°C and 120°C were about 1.52, 2.23, 3.47 and 5.21 times faster than the cure rate at 80°C, respectively.

To determine m, n and k_2, α and $\dot{\alpha}$ were obtained from Figs. 1 and 2 and listed in Table 1. By substituting them into Eqs. (3)–(5), the values of kinetic parameters were calculated and also listed in Table 1.

The rate constants k_1 and k_2 exhibit Arrhenius behavior, as shown in Fig. 3. The activation energy, E_a, and pre-exponential factor, A, for k_1 are 49.23 kJ/mol and 7.42×10^4 min^{-1}and those values for k_2 are 46.06 kJ/mol and 26.94×10^4 min^{-1}.

Fig. 4 shows isothermal cure rate curves for DGEBA/MDA system with various contents of PGE-AcAm at five different cure temperatures. As in Fig. 1, as the cure temperature increases, the maximum points also appear at shorter time and the value of differential cure rate at the point is increased. k_1 values for various contents of PGE-AcAm at different cure temperatures were determined from the isothermal cure rate curves and are listed in Table 2. Conversion vs. time curves for the systems containing various contents of PGE-AcAm were obtained from $\alpha = Q/Q_T$ by integrating Fig. 4. All systems show sigmoid shaped curves evidenced that the cure reaction of the system followed autocatalytic mechanism regardless of PGE-AcAm content.

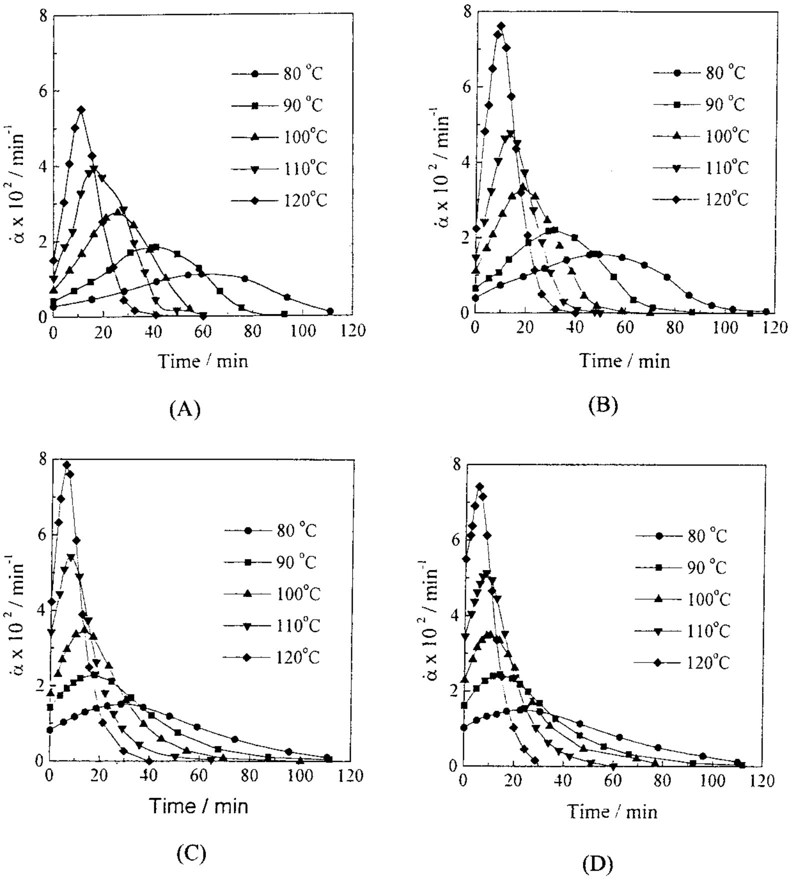


Fig. 4. Cure rate vs. time for DGEBA/MDA system with different contents of PGE-AcAm: (A) 0 phr, (B) 10 phr, (C) 15 phr and (D) 20 phr.

To magnitudes of m, n and k_2, α and $\dot{\alpha}$ listed in Table 2 were again substituted to Eqs. (3)–(5) and the values of kinetic parameters are also listed in Table 2.

The rate constants k_1 and k_2 for every system fit Arrhenius behavior as shown in Fig. 5. From the slope, the activation energy is obtained and from the y-intercept, the pre-exponential factor is calculated, and they are shown in Table 2. All systems give values of k_2 that are higher than k_1 and E_{a_2} is lower than E_{a_1}.

To ascertain the kinetic parameters determined by theoretical equations, the curves of conversion vs. time calculated by the numerical integration of Eq. (1) through the Runge–Kutta method [9] were compared to those obtained by experimental method and these were shown in Fig. 2. Very good agreement is observed confirming that the kinetic parameters have been chosen correctly.

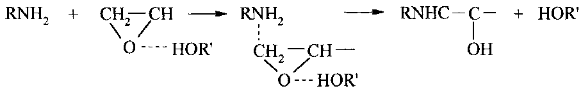
Fig. 6 shows the effect of PGE-AcAm content on the cure rate at 80°C. With the increment of PGE-AcAm content, the value of $\dot{\alpha}$ at $t = 0$, that is k_1 increases and the maxima $\dot{\alpha}$ appear at shorter times. k_1 is the kinetic constant associated with noncatalytic reaction (here, primary amine-epoxide and secondary-epoxide reactions) [10,11] and the catalytic reaction due to the pre-existent hydroxyl group in PGE-AcAm as a catalyst, which was produced by the reaction between epoxide group of PGE and amine group of AcAm. So, the effect of catalytic reaction increases with the increasing PGE-AcAm content. The role of this hydroxyl group as a catalyst is explained by the

Table 2
Temperature dependence of cure kinetic variables for DGEBA/MDA system with various contents of PGE-AcAm

PGE-AcAm content (phr)	Temperature (°C)	$\dot{\alpha}_p \times 10^2$ (min^{-1})	α_p	m[a]	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	E_a (kJ/mol)		A × 10^{-4} (min^{-1})	
							E_{a_1}	E_{a_2}	A_1	A_2
0	80	1.11	0.42	0.92	0.28	4.03	49.12	44.41	5.34	16.41
	90	1.84	0.52	1.09	0.42	6.76				
	100	2.76	0.47	1.01	0.71	9.57				
	110	3.95	0.42	0.92	1.03	12.97				
	120	5.51	0.41	0.90	1.51	20.00				
10	80	1.55	0.50	1.08	0.40	5.40	48.96	45.33	7.63	26.97
	90	2.20	0.48	1.01	0.66	7.48				
	100	3.33	0.43	0.96	1.12	10.82				
	110	4.78	0.43	0.95	1.48	16.55				
	120	7.62	0.42	0.92	2.24	26.19				
15	80	1.51	0.35	0.90	0.82	4.14	47.12	45.29	8.20	21.45
	90	2.29	0.34	0.91	1.42	5.95				
	100	3.47	0.36	0.89	1.79	9.85				
	110	5.42	0.30	0.84	3.42	13.28				
	120	7.85	0.30	0.79	4.23	20.02				
20	80	1.49	0.29	0.86	1.20	3.41	47.37	47.12	10.75	34.11
	90	2.44	0.28	0.82	1.62	5.76				
	100	3.48	0.28	0.82	2.28	8.09				
	110	5.13	0.30	0.88	3.45	12.22				
	120	7.42	0.29	0.81	5.50	18.06				

[a] $n = 2 - m$ (Eq. (3)).

formation of termolecular transition state with the epoxide group of DGEBA and amine group of MDA as follows [12,13]:



Therefore, the effect of catalytic cure reaction is increased by the increment of PGE-AcAm content at the early stage. The times for reaction to reach $\alpha = 0.6$ for the systems with 0, 10 and 20 phr of PGE-AcAm content are 76.0, 56.1 and 46.3 min and the order of cure rate is 20 phr > 10 phr > 0 phr. The relative cure rates for 10 and 20 phr are 1.35 and 1.64 times faster than the cure rate for 0 phr. However, above $\alpha = 0.84$, the order of conversion is 10 phr > 20 phr > 0 phr, which is different from the result at early stage. This is caused by the effect of increasing diffusion control due to the rising viscosity and cross-link structure as a result of the developing within the reacting mixture.

4. Conclusions

From these results, the following conclusions were drawn:

1. With the increment of PGE-AcAm, the cure rate increased due to the catalytic role of hydroxyl groups in PGE-AcAm, which come from the reaction between epoxide group of PGE and amine group of AcAm.
2. E_{a_2} for catalytic reaction was smaller than E_{a_1} for noncatalytic reaction, and k_2 for catalytic reaction was larger than k_1 for noncatalytic reaction.
3. Regardless of the PGE-AcAm content, the conversion curves were sigmoid indicating that the cure reactions of the systems were autocatalytic.
4. From the comparison between theoretical prediction and experimental data, it was found that the autocatalytic kinetic expression was correct to analyze the cure kinetics of these systems.

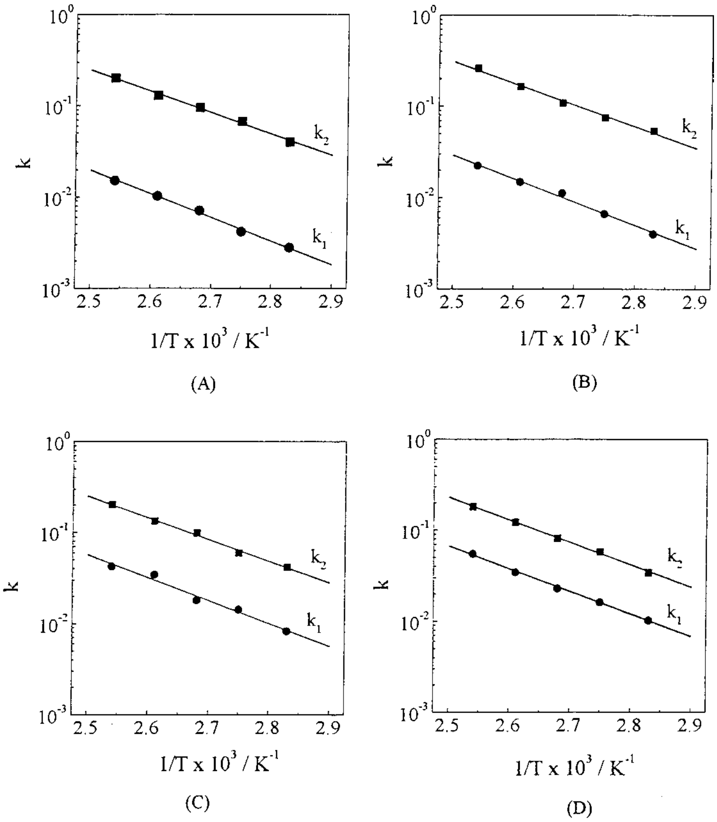


Fig. 5. Kinetic rate constant, *k*, as a function of reciprocal cure temperature for DGEBA/MDA system with different contents of PGE-AcAm: (A) 0 phr, (B) 10 phr, (C) 15 phr and (D) 20 phr.

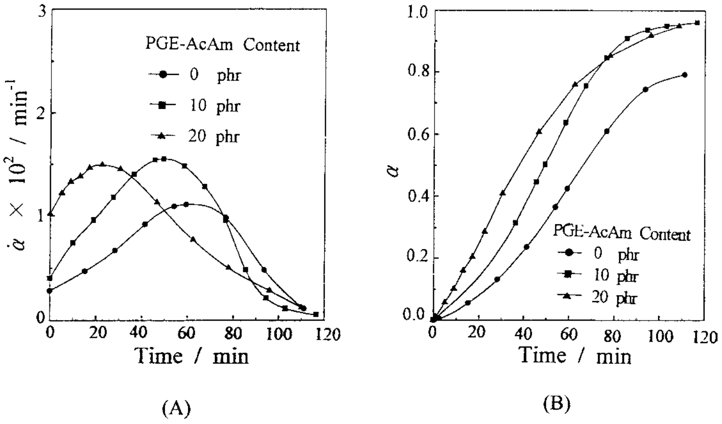


Fig. 6. The effect of PGE-AcAm on the cure rate at 80°C. Cure rate (A) or conversion (B) vs. time.

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