Cure Kinetics of DGEBA/MDA System with Various Contents of NPG

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NPG 함량에 따른 DGEBA/MDA 계의 경화반응 속도론

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초   록   Neopentyl glycol(NPG)의 함량변화에 따른 diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline (MDA) 계의 등온적 경화거동을 DSC를 이용하여 분석하였다. DGEBA/MDA 계의 경화속도를 증가시키기 위하여 NPG를 첨가하였다. NPG 함량에 관계없이 전화율 곡선이 s-자 모양이었으며, 이것은 DGEBA/MDA/NPG 계의 경화반응이 자촉매 반응 메커니즘에 따른다는 것을 의미한다. NPG의 함량이 증가함에 따라 경화속도가 증가하였으며, 이것은 NPG가 가지고 있는 두 개의 hydroxyl 기가 촉매로 작용하기 때문이다.

Abstract   The isothermal cure behavior of diglycidyl ether of bisphenol A(DGEBA)/ 4,4'-methylene dianiline(MDA) system with various contents of neopentyl glycol(NPG) has been analyzed by differential scanning calorimetry(DSC). To increase the cure rate of DGEBA/MDA system, NPG was introduced as an accelerator. Regardless of the NPG content, the shape of the conversion curves showed sigmoid indicating that DGEBA/MDA/NPG system followed autocatalytic cure reaction. The cure reaction of DGEBA/MDA system increased with the increment of NPG content and it was due to the catalytic role of hydroxyl groups of NPG.

1. Introduction

It has been well known that there are many catalysts such as $-OH$, $-COOH$, $-SO_3H$ and $CONH_2$ which can donate hydrogen bonds to the amine-epoxide reaction. In this study, the catalytic effect of hydroxyl groups was investigated. To increase the cure rate of epoxy system, neopentyl glycol(NPG) was added.

It has been well known that the cure rate of epoxy/ diamine system is expressed by the multiplication of noncatalytic reaction and autocatalytic reaction as follows[1~11]

$$\dot{\alpha} = \frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (1)$$

where, $\dot{\alpha}$: cure rate, α : degree of cure, k_1, k_2 : rate constants and m, n : reaction orders. k_1 represents the rate constant associated with noncatalytic reaction between epoxide group and amine group and also associated with the catalytic reaction due to the existence of catalyst in the initial formulation. k_2 represents the rate constant associated with the autocatalysis by the hydroxyl groups generated from the reaction between epoxide group and amine group. From the first assump-

tion that the initial cure rate was not zero, k_1 was the same value of $\dot{\alpha}$ at $t=0$, which can be readily obtained from the DSC curve and it is

$$k_1 = \dot{\alpha}_{t=0} = (\frac{d\alpha}{dt})_{t=0} \qquad (2)$$

To get other kinetic parameters, the following equations were used.

$$m + n = 2 \qquad (3)$$

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

$$k_2 = \frac{(2-m)k_1\,\alpha_p^{1-m}}{m-2\alpha_p} \qquad (5)$$

where, α_p : degree of cure at maximum peak and $\dot{\alpha}$: cure rate at maximum peak. α_p and $\dot{\alpha}_p$ were easily obtained from the isothermal DSC curve.

2. Experiment

Diglycidyl ether of bisphenol A (DGEBA, Epon 828) was a commercial epoxy resin supplied by Shell Co. and curing agent was 4,4'-methylene dianiline(MDA) of Fluka Chemie AG. As a catalyst, neopentyl glycol

Table 1. Temperature Dependence of Cure Kinetics Variables for DGEBA/MDA/NPG(10 phr) System.

Temp. (℃)	$\dot{\alpha}_p$ x 10^2	α_p	m	n	k_1 x 10^2 (min^{-1})	k_2 x 10^2 (min^{-1})	Ea (kcal/mol)		A (min^{-1})	
							Ea$_1$	Ea$_2$	A$_1$	A$_2$
80	1.76	0.26	0.80	1.20	1.20	3.92				
90	2.62	0.26	0.72	1.28	1.49	6.27				
100	3.80	0.23	0.61	1.39	1.78	8.90	4.61	10.89	8.76	22.2×10⁴
110	5.51	0.21	0.52	1.48	2.01	12.4				
120	8.16	0.20	0.48	1.52	2.37	18.5				

(NPG) was used. Firstly, various contents of NPG melted in DGEBA at 100℃ and 30 phr of MDA was added at 80℃ and stored at -13℃ to prevent the cure reaction during the storage. Isothermal experiment was conducted at 80℃, 90℃, 100℃, 110℃ and 120℃ in order to obtain both the cure rate and extent of cure as a function of time. The isothermal baseline was established at the pre-selected cure temperature and range setting by using a fully-cured sample. To get total heat, Q_T evolved during the complete cure, dynamic DSC analysis was carried out from 30℃ to 350℃ at the heating rate of 10 ℃/min. The degree of conversion is

$$\dot{\alpha} = \frac{d\alpha}{dt} = \frac{1}{Q_T} \cdot \frac{dQ}{dt} \quad \text{[1,12]}$$

3. Results and Discussion

Fig. 1 shows that isothermal cure rate curves for DGEBA/MDA/NPG(10 phr) at three different temperatures. With the increment of cure temperature, the cure reaction is accelerated at the early stage of cure, maximum exothermic peak temperature appeared at shorter time and the value was increased and falled down rapidly to the baseline after maximum cure rate. When $\alpha = 0$ at $t = 0$, the Eq.(1) became Eq.(2), and this equation indicated that kinetic rate constant k_1 was the initial cure rate. Values of k_1 at different cure tempera-
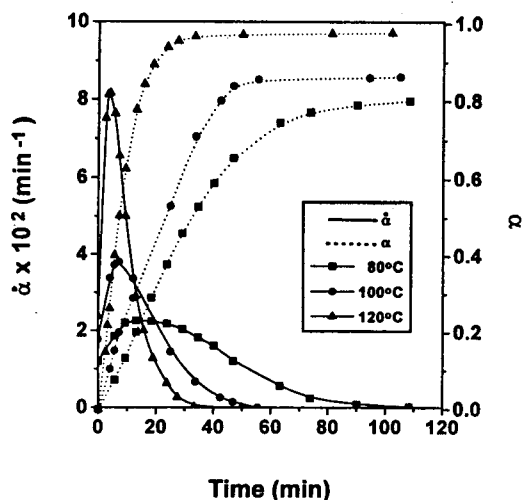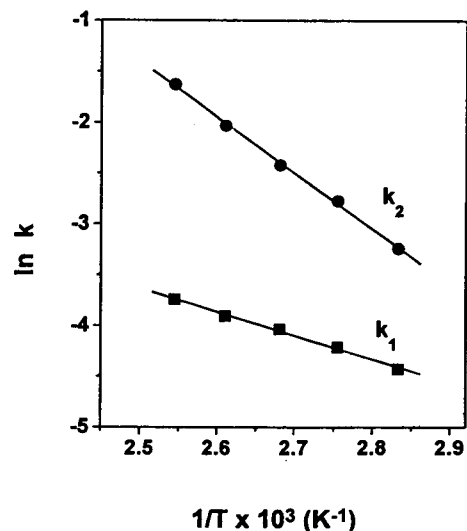

Fig. 2. Kinetic constants k_1 and k_2 as a function of reciprocal curing temperature for DGEBA/MDA/NPG(10 phr).

tures were obtained from the isothermal cure rate curves and were listed on Table 1. As the increment of cure temperature, k_1 was increased. The relationship between cumulative heat at a time, Q and the total exothermic heat, Q_T gave the conversion, α as a function of time, which was also plotted in Fig. 1. The sigmoid shape of the curves meant that the cure reaction of the system followed autocatalytic mechanism.

To get m, n and k_2, α and $\dot{\alpha}$ were also listed on Table 1 and they were introduced to Eqs.(3~5). The values of kinetic parameters were also listed on Table 1.

To get activation energy and pre-exponential factor for k_1 and k_2, Arrhenius equation was used and Arrhenius plots in Fig. 2 were expressed as follows.

$$\ln k_1 = 2.17 - 2.32 \times 10^3/T$$
$$\ln k_2 = 12.3 - 5.48 \times 10^3/T$$

The activation energy was calculated from the slope and pre-exponential factor was obtained from intercept. The activation energy and pre-exponential factor for k_1 were 4.61 kcal/mol and 8.76 min^{-1} and those values for k_2 were 10.89 kcal/mol and 2.22×10⁵ min^{-1}. As

Fig. 1. Cure rate vs. time and conversion vs. time for DGEBA/MDA/NPG(10 phr).
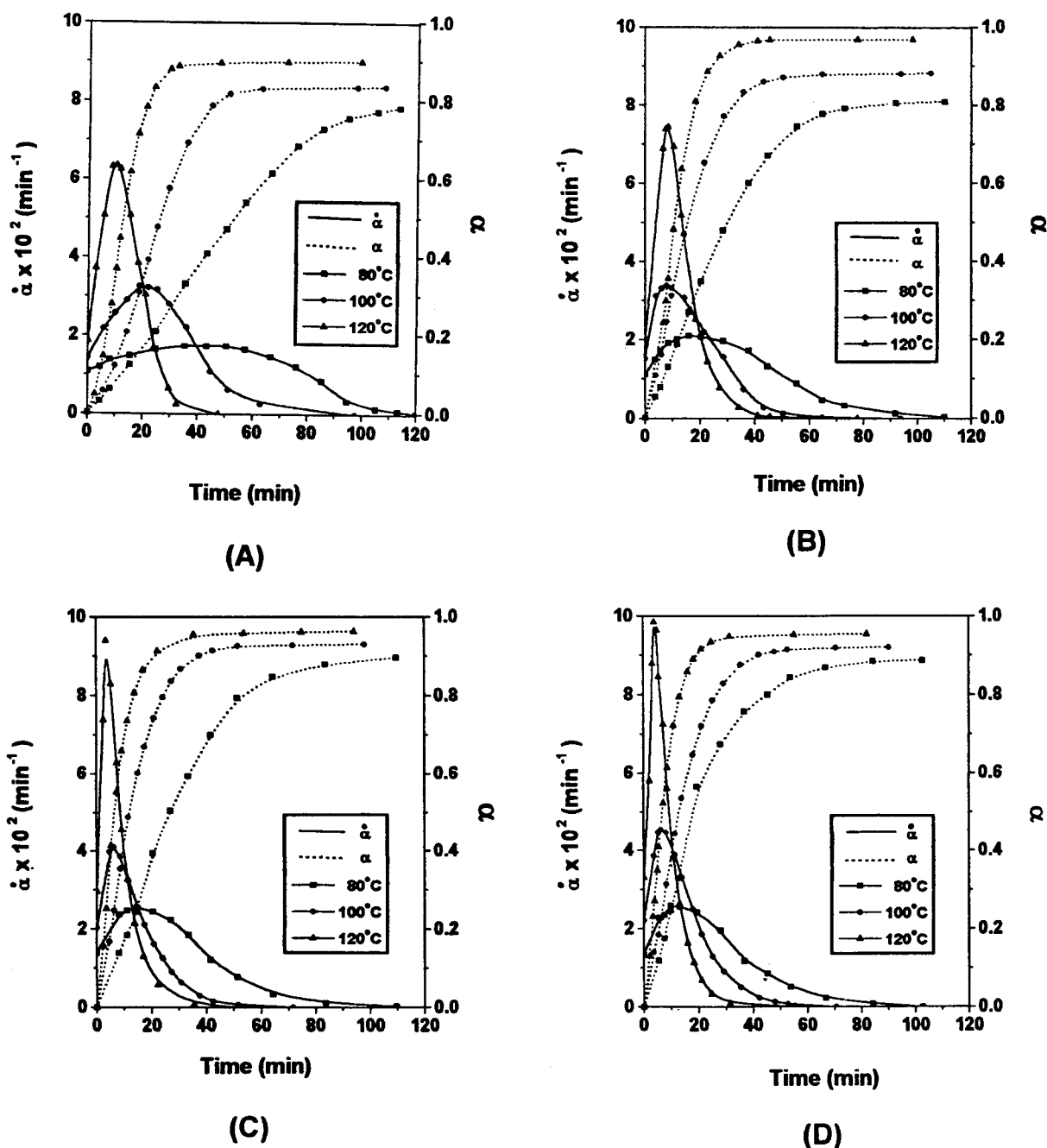
Fig. 3. Cure rate vs. time and conversion vs. time for DGEBA/MDA system with different contents of NPG.
(A) 0 phr, (B) 5 phr, (C) 15 phr and (D) 20 phr

explained above, k_2 for the autocatalytic mechanism was higher than k_1 for the noncatalytic mechanism.

Fig. 3 shows isothermal cure rate curves for DGEBA /MDA system with various contents of NPG at three different cure temperatures. Values of k_1 for various contents of NPG at different cure temperatures were also obtained from the isothermal cure rate curves and were listed on Table 2. k_1 was increased with the increment of cure temperature and NPG content. It can be clearly explained by the role of two hydroxyl groups in

NPG acting as a catalyst for DGEBA/MDA system. Conversion vs. time for the systems with various contents of NPG were obtained from the relationship between Q and Q_T for each system and were also shown in Fig. 3. All systems showed sigmoid shape and this meant that the cure reactions of the systems followed autocatalytic mechanism regardless of NPG content.

m, n, k_1, α and $\dot{\alpha}$ listed on Table 2 were obtained from Fig. 3, and were introduced to Eqs. (3~5). The values of kinetic parameters were also listed on Table 2.

Table 2. Temperature Dependence of Cure Kinetics Variables for DGEBA/MDA/NPG System with Various NPG Content.

NPG Content (phr)	Temp. (℃)	$\dot{a}_p \times 10^2$	α_p	m	n	$k_1 \times 10^2$ (min⁻¹)	$k_2 \times 10^2$ (min⁻¹)	Ea (kcal/mol)		A (min⁻¹)	
								Ea_1	Ea_2	A_1	A_2
0	80	1.09	0.39	1.16	0.84	1.09	2.79	3.80	12.7	2.39	18.3×10^4
	90	1.65	0.38	1.09	0.91	1.24	3.76				
	100	2.53	0.37	0.95	1.05	1.42	6.93				
	110	3.81	0.36	0.86	1.14	1.66	11.3				
	120	5.25	0.34	0.80	1.20	1.86	16.0				
5	80	1.54	0.36	1.04	0.96	1.14	3.53	4.14	10.9	3.46	3.76×10^4
	90	2.30	0.27	0.75	1.25	1.31	5.58				
	100	3.39	0.25	0.64	1.36	1.53	8.44				
	110	4.96	0.20	0.49	1.51	1.80	11.4				
	120	7.44	0.19	0.45	1.55	2.02	17.5				
15	80	2.55	1.33	0.75	1.25	1.33	4.87	5.52	10.0	35.2	7.69×10^4
	90	2.83	1.62	0.70	1.30	1.62	6.62				
	100	4.10	2.03	0.63	1.37	2.03	9.70				
	110	4.91	2.14	0.60	1.40	2.42	15.1				
	120	9.40	2.96	0.48	1.52	2.96	19.9				
20	80	2.30	1.38	0.72	1.28	1.38	5.31	5.88	9.52	63.4	4.30×10^4
	90	3.54	1.86	0.65	1.35	1.86	8.29				
	100	4.44	2.21	0.62	1.38	2.21	10.4				
	110	7.03	2.74	0.55	1.45	2.74	16.8				
	120	8.90	3.32	0.52	1.48	3.32	21.0				

The rate constants k_1 and k_2 for every system follow Arrhenius behavior as shown in Fig. 4.[13~19] Activation energy and pre-exponential factor were obtained from the slope and intercept and those values are shown in Table 2. As explained above, all systems showed that k_2 was higher than k_1. k_1 and k_2 were increased with the increment of NPG content. These results gave a good account for the catalytic role of hydroxyl groups which were added or generated. The role of hydroxyl group as a catalyst has been well known. Water, isopropanol and phenol which have hydroxyl group can act as a catalyst. Hydrogen atom of hydroxyl group and oxygen of the epoxide formed a hydrogen bond, followed by the epoxide ring opening via a termolecular transition state, and it was found that the hydroxyl group in NPG could act as a catalyst in the reaction between amine group of MDA and epoxide group in DGEBA.

The degree of cure at the peak, α_p was plotted against curing temperature in Fig. 5. For a given formulation, α_p decreased with the increment of the curing temperature. At any given temperature, the value, α_p decreased with the increment of the content of NPG. Fig. 5 also showed that the shift of α_p was decreased with the increment of NPG content. It meant that with the increment of NPG content, the effect of two hydroxyl groups of NPG was higher than that of the

hydroxyl group from DGEBA/MDA. Maximum rate of cure occurs at 20~45% epoxy conversion in the temperature range examined, even though the autocatalyzed reactions were generally characterized by the maximum rate at approximately 30~40% epoxy conversion.

The reaction time required to attain this maximum rate, t_p was plotted against curing temperature in Fig. 6 and it was shown that the increment of temperature made the time required to reach the peak, t_p decreased in all systems and t_p was decreased with the increment of NPG content in the same temperature. It was good evidence that two hydroxyl of groups NPG acted as catalyst in the DGEBA/MDA system.

4. Conclusions

Regardless of the NPG content, the shape of the conversion curves showed sigmoid indicating that DGEBA/MDA/NPG system followed autocatalytic cure reaction. The kinetic constant with noncatalytic reaction, k_1 was increased with the increment of NPG ocntent, and this was the effect of catalytic role of NPG. The kinetic constant for autocatalytic reaction, k_2 was also increased with the increment of NPG content. k_2 was larger than k_1, and α_p and t_p were decreased with the increment of NPG content.
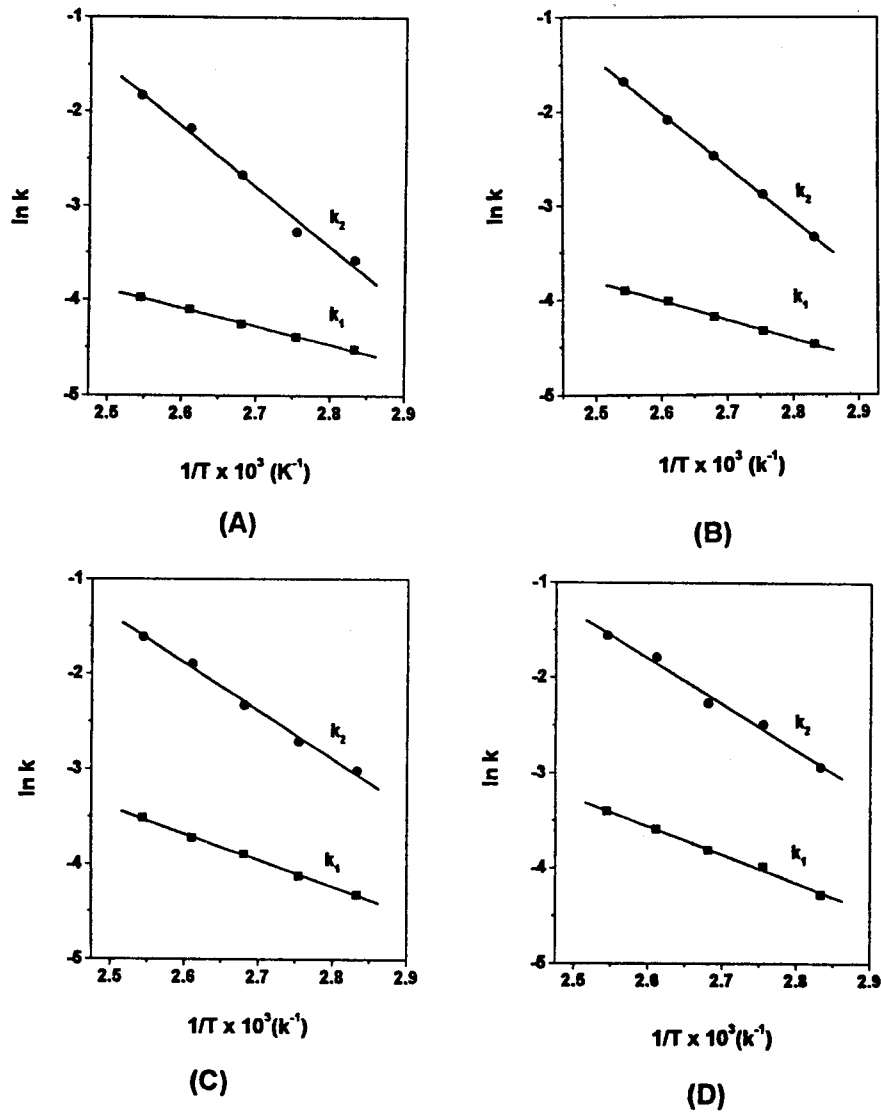
(A)

(B)

(C)

(D)

Fig. 4. Kinetic constants k_1 and k_2 as a function of reciprocal curing temperature for DGEBA/MDA system with different contents of NPG. (A) 0 phr, (B) 5 phr, (C) 15 phr and (D) 20 phr
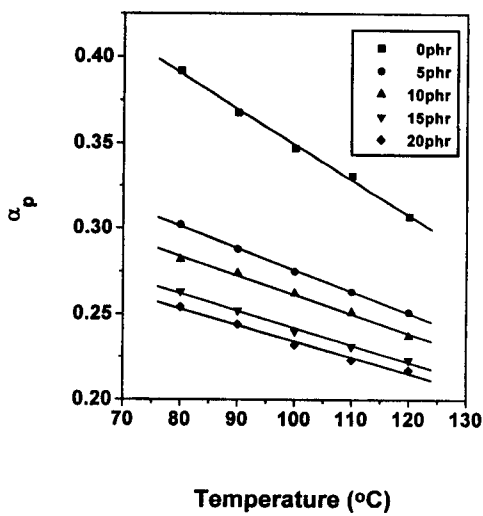

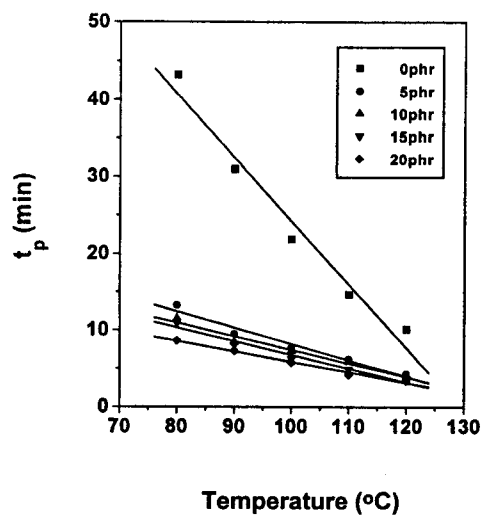Fig. 5. Variation of cure degree at the peak point, α_p with temperature.

Fig. 6. Variation of time at the peak point, t_p with temperature.

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