

## Autocatalytic Cure Kinetics of DGEBA/MDA/PGE-AcAm System

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### DGEBA/MDA/PAGE-AcAm 계의 자촉매 반응 속도론

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**초 록** Diglycidyl ether of bisphenol A (DGEBA)/4, 4'-methylene dianiline (MDA) 계의 반응속도에 미치는 10 phr의 phenyl glycidyl ether (PGE)-acetamide (AcAm) 의 영향을 살펴보았다. PGE-AcAm이 첨가됨으로 인해서 승온적 DSC곡선에 서 최대 발열피크의 온도와 피크 시작 온도가 감소하였다. PGE-AcAm의 첨가 여부에 관계없이 전화를 곡선은 s-자 형상이었고, 이는 DGEBA/MDA 계와 DGEBA/MDA/PGE-AcAm계가 자촉매 반응을 한다는 것을 의미한다. 또한 PGE-AcAm이 10 phr 첨가됨으로 인해서 반응속도가 1.2~1.4배 증가하였는데, 이는 PGE-AcAm의 수산기가 촉매로 작용하기 때문이다.

**Abstract** The cure kinetics for diglycidyl ether of bisphenol A(DGEBA)/4, 4'-methylene dianiline(MDA) system with or without 10phr of phenyl glycidyl ether(PGE)-acetamide(AcAm) was studied by autocatalytic cure expression. On the dynamic DSC curves, the exothermic peak temperature and the onset temperature of reaction decreased with the addition of PGE-AcAm. Regardless of the addition of PGE-AcAm, the shape of the conversion curve showed sigmoid, and this meant that DGEBA/MDA and DGEBA/MDA/PGE-AcAm systems followed autocatalytic cure reaction. When PGE-AcAm was added to DGEBA/MDA system, the cure rate increased about 1.2~1.4 times due to the catalytic role of hydroxyl groups in PGE-AcAm.

### 1. Introduction

With the increasing demands for new applications of epoxy resins in the fields of space shuttle, aircrafts, automobiles, ships and structural components, many researchers have been reported about the cure reaction of epoxy resin systems. However, the detailed kinetics information for each new system should be studied, for it is very important to know the accurate cure rate of the epoxy system at different temperatures from the standpoint of working life and shelf life.<sup>1~8)</sup> If the exact cure rate is not known, the epoxy resin may be cured at the middle of the processings such as filament winding, pultrusion and laminating processes or not cured at the end of the processings. In addition, the epoxy system may be stored in vain, since the system is cured at the storage conditions. Therefore, the exact cure rate expressions should be investigated.

To study cure kinetics by DSC analysis, researchers have proposed many expressions which is divided into

two categories. One is simple n-th order expression<sup>6,7)</sup> and the other is autocatalytic expression.<sup>1~3)</sup> In this study, the latter was used to express the cure reaction more accurately. The autocatalytic cure rate equation<sup>2,8)</sup> was

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

where  $\dot{\alpha}$  : cure rate,  $\alpha$  : degree of cure,  $k_1, k_2$  : rate constants,  $m, n$  : reaction orders. The initial cure rate was not zero, so  $k_1$  can be readily obtained from  $\dot{\alpha}$  at  $t=0$  and the expression was

$$\left(\frac{d\alpha}{dt}\right)_{t=0} = k_1 \quad (2)$$

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

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

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

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

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

## 2. Experiment

Diglycidyl ether of bisphenol A (DGEBA) type (Epon 828) was supplied by Shell Co., 4,4'-methylene dianiline (MDA) and phenyl glycidyl ether (PGE)-acetamide (AcAm) were used as a curing agent and an additive, respectively.<sup>9-11)</sup>

To study cure kinetics, DGEBA was mixed with 30phr of MDA and various contents of PGE-AcAm under 80°C and stored at -13°C to stop the cure reaction. The samples were placed into DSC container and isothermal DSC analysis was performed at 80°C, 90°C, 100°C, 110°C and 120°C. The nitrogen flow rate was 40 ml/min. Assuming that the heat evolved during the cure is proportional to the extent of monomer conversion,<sup>12,13)</sup> a cure rate,  $\dot{\alpha}$  and a conversion,  $\alpha$  at a time can be directly obtained from the isothermal DSC curve. To get total heat 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.

## 3. Results and Discussion

Based upon the assumption between evolved heat and conversion, the degree of cure,  $\alpha$  could be expressed by the relationship between the total exothermic heat,  $Q_T$  and the cumulative heat at a time,  $Q$ .  $Q_T$  was obtained from the dynamic DSC curve, and the relationship was written as follows.

$$\alpha = \frac{Q}{Q_T} \quad (6)$$

$$\dot{\alpha} = \frac{d\alpha}{dt} = \frac{1}{Q_T} \cdot \frac{dQ}{dt} \quad (7)$$

Fig. 1 shows dynamic DSC curves for DGEBA/MDA system with and without PGE-AcAm(10phr) at the heating rate of 10°C/min. The cure reactions for the systems took place in one stage, and the peak temperature for the system without PGE-AcAm was 164.1°C and that of the system with PGE-AcAm was 160.5°C. The exothermic peak temperature and the reaction starting temperature of the system with PGE-AcAm were lower than those of the system without PGE-AcAm. From these results, the cure rate might be increased by the addition of PGE-AcAm, however exact cure rate was to be studied continuously in the follow-

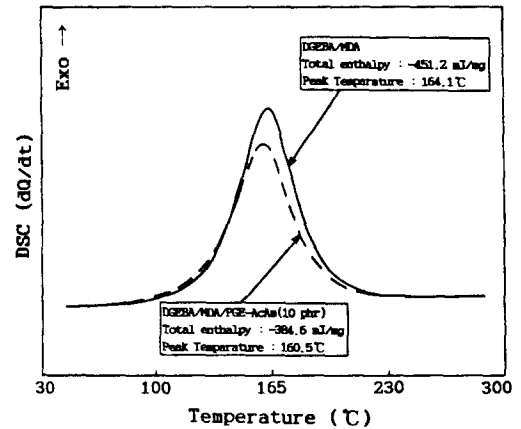


Fig. 1. Dynamic DSC curves for DGEBA/MDA system with and without PGE-AcAm(10phr).

ing autocatalytic cure expression.  $Q_T$  of the system with PGE-AcAm was 384.6 mJ/mg and that of the system without PGE-AcAm was 451.2 mJ/mg.

Fig. 2 shows the observed cure rate,  $\dot{\alpha}$  as a function of time for DGEBA/MDA system at different temperatures. As was expected, curing reaction readily took place as cure temperature increased and the reaction time was reduced. The cumulative heat at a time,  $Q$  corresponded to the area under the isothermal cure curves and the conversion,  $\alpha$  as a function of time was plotted in Fig. 3. The sigmoid shape of the curves meant that the cure reaction of the system followed autocatalytic mechanism. The time to be a conversion is inversely proportional to the cure rate and if a conversion was 0.6, the times at 80°C, 90°C, 100°C, 110°C and 120°C were 76.0 min, 45.8 min, 30.7 min, 21.5 min and 15.7 min, respectively. Therefore the cure rates at 90°C, 100°C, 110°C and 120°C were about 1.7, 2.5, 3.5 and 4.8

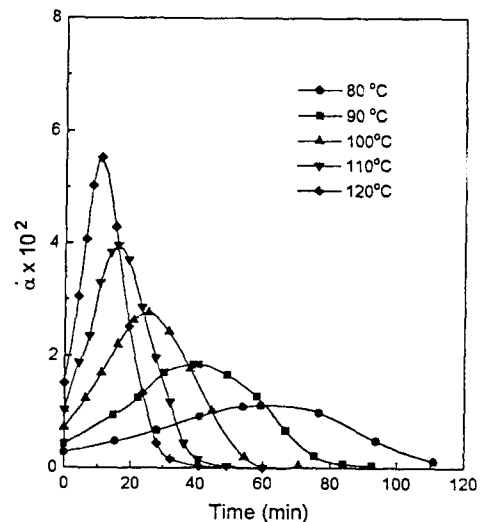


Fig. 2. Cure rate vs. cure time for DGEBA/MDA system at different temperatures.

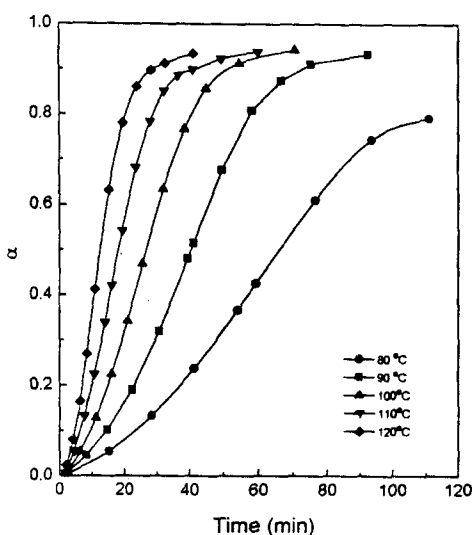


Fig. 3. Conversion vs. cure time for DGEBA/MDA system at different temperatures.

times faster than the cure rate at 80 °C, respectively.

To get kinetic parameters,  $\alpha$  and  $\dot{\alpha}$  are obtained from Fig. 1 and 2, and they are listed in Table 1. The initial cure rate at  $t=0$  was not necessarily zero in the autocatalytic cure reaction, and the rate constants,  $k_1$

are calculated by Eq. (2) and were listed in Table 1. Reaction orders,  $m$  and  $n$  and another rate constant,  $k_2$  are obtained from Eqs.(3~5) and are also listed in Table 1.

To get activation energy,  $E_a$  and pre-exponential factor,  $A$  for the system from the Arrhenius equation,  $-\ln k$  vs.  $1/T$  was plotted in Fig. 4. As can be seen in this figure,  $k_1$  and  $k_2$  followed Arrhenius dependence on cure temperature which was expressed as follows.

$$\ln k = A \ln(-E_a/RT) \tag{8}$$

Activation energy was calculated from the slopes of the straight lines in Fig. 4 and pre-exponential factor was obtained from the y-intercepts, and these values were listed in Table 1. Activation energy for  $k_1$  was 11.78 kcal/mol and that for  $k_2$  was 10.65kcal/mol.  $E_{a2}$  was smaller than  $E_{a1}$  and  $k_2$  was larger than  $k_1$ . These results were well agreed that  $k_1$  is the cure constant for noncatalytic reaction and  $k_2$  is for catalytic reaction and in this system, the hydroxyl groups produced during the cure reaction of DGEBA and MDA acted as a catalyst.<sup>14, 15)</sup>

Table 1. Temperature Dependence of Cure Kinetics Variables for DGEBA/MDA System.

Temp. (°C)	$\dot{\alpha} \times 10^2$	$\alpha_p$	m	n	$k \times 10^2$ (min <sup>-1</sup> )		Ea (kcal/mol)		$A \times 10^{-4}$ (min <sup>-1</sup> )	
					$k_1$	$k_2$	$E_{a1}$	$E_{a2}$	$A_1$	$A_2$
80	1.11	0.42	0.92	1.08	0.28	4.03				
90	1.84	0.52	1.09	0.91	0.42	6.76				
100	2.76	0.47	1.01	0.99	0.71	9.57	11.78	10.65	5.34	16.41
110	3.95	0.42	0.92	1.08	1.03	12.97				
120	5.51	0.41	0.90	1.10	1.51	20.00				

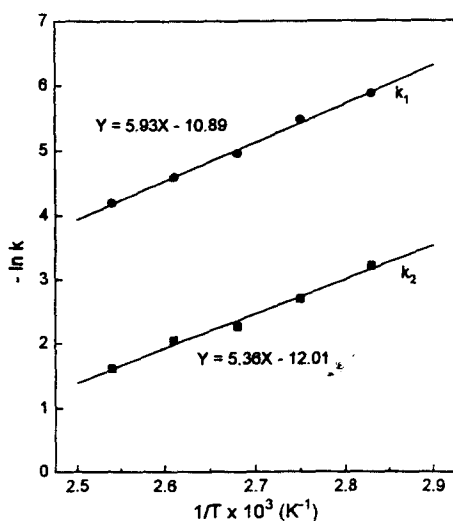


Fig. 4.  $-\ln k$  vs.  $1/T \times 10^3$  for DGEBA/MDA system.

Fig. 5 shows the observed cure rate,  $\dot{\alpha}$  as a function of time for DGEBA/MDA/PGE-AcAm(10phr) system

at five different temperatures. From the relationship between  $Q_T$  and  $Q$ , Fig. 6 was plotted. This system also showed the sigmoid shape, which meant the cure reaction followed autocatalytic mechanism. When conversion was 0.6, the times at 80 °C, 90 °C, 100 °C, 110 °C and 120 °C were 56.4min, 38.2min, 24.0min, 17.7min and 12.4min, respectively. Therefore the cure rates at 90 °C, 100 °C, 110 °C and 120 °C were about 1.5, 2.4, 3.2 and 4.6 times faster than that at 80 °C, respectively. The cure rate was increased by the addition of PGE-AcAm (10phr) about 1.2~1.4 times at each temperature and this result can be explained by the catalytic role of hydroxyl groups in PGE-AcAm.<sup>14, 15)</sup>

Kinetic parameters were calculated from Fig. 7 and Eqs.(3~5), and they were listed in Table 2. Activation energy for  $k_1$  was 11.74 kcal/mol and that for  $k_2$  was 10.87 kcal/mol. In this system,  $k_2$  was also larger than  $k_1$  and  $E_{a2}$  was smaller than  $E_{a1}$ .

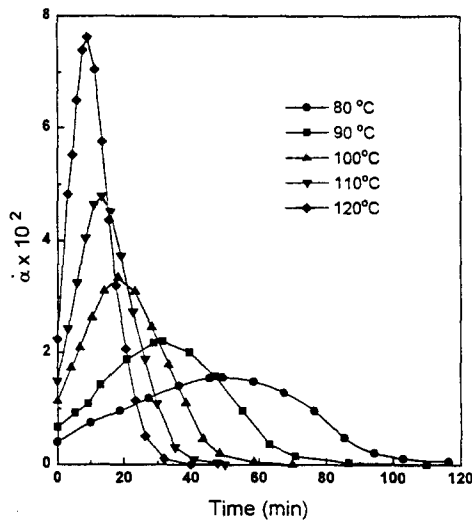


Fig. 5. Cure rate vs. cure time for DGEBA/MDA/PGE-AcAm (10phr) system at different temperatures.

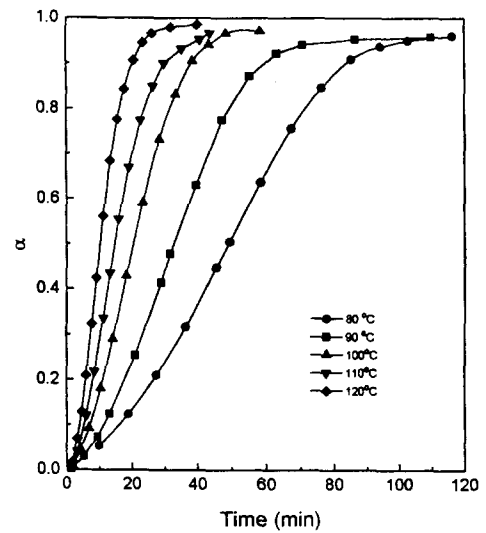


Fig. 6. Conversion vs. cure time for DGEBA/MDA/PGE-AcAm(10phr) system at different temperatures.

Table 2. Temperature Dependence of Cure Kinetics Variables for DGEBA/MDA/PGE-AcAm(10phr) System.

Temp. (°C)	$\dot{\alpha} \times 10^2$	$\alpha_p$	m	n	$k \times 10^2$ (min <sup>-1</sup> )		Ea (kcal/mol)		$A \times 10^{-4}$ (min <sup>-1</sup> )	
					$k_1$	$k_2$	Ea <sub>1</sub>	Ea <sub>2</sub>	A <sub>1</sub>	A <sub>2</sub>
80	1.55	0.50	1.08	0.92	0.40	5.40				
90	2.20	0.48	1.01	0.99	0.66	7.48				
100	3.33	0.43	0.96	1.04	1.12	10.82	11.74	10.87	7.63	26.97
110	4.78	0.43	0.95	1.05	1.48	16.55				
120	7.62	0.42	0.92	1.08	2.24	26.19				

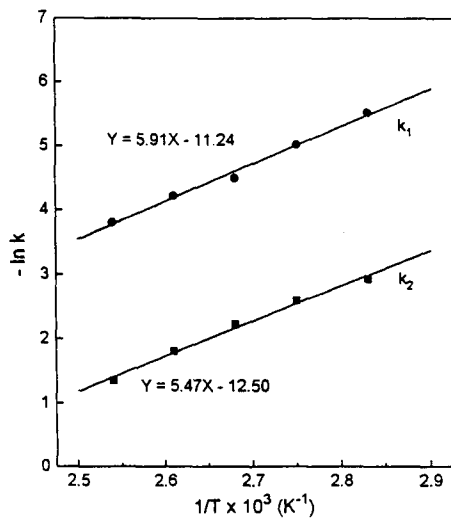


Fig. 7.  $-\ln k$  vs.  $1/T \times 10^3$  for DGEBA/MDA/PGE-AcAm (10phr) system.

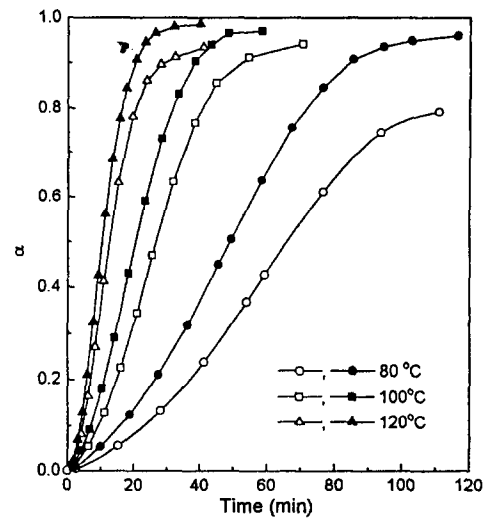


Fig. 8. Comparison of conversion for DGEBA/MDA system with (solid) and without (open) PGE-AcAm(10phr) at different temperatures.

Fig. 8 shows the comparison of cure rate for the system with or without PGE-AcAm(10phr). As was explained above, the cure rate increased with the addition of PGE-AcAm having hydroxyl groups. The autocatalytic cure mechanism was explained by the follows. An epoxide group reacted with an amine group

and produced a hydroxyl group and now, the produced hydroxyl group acted as a catalyst on the reaction between another epoxide group and another amine group. So, the hydroxyl group acted as an autocatalyst. When hydroxyl group, which was formed by the reaction be-

tween PGE and AcAm was mixed into epoxy and amine system from the exterior, the hydroxyl group was also acted as a catalyst and made the cure reaction increased. Therefore, cure reaction became faster by the addition of PGE-AcAm.

#### 4. Conclusions

From these results, the following conclusions were obtained.

1) On the dynamic DSC curves, the exothermic peak temperature and reaction starting temperature were decreased by the addition of PGE-AcAm.

2) Regardless of the addition of PGE-AcAm(10phr), the shape of the conversion curve showed sigmoid, and this meant that DGEBA/MDA system with and without PGE-AcAm(10phr) followed autocatalytic cure reaction.

3) Due to the role of hydroxyl group in PGE-AcAm as a catalyst, the cure rate of the system with PGE-AcAm was faster than that of the system without PGE-AcAm.

4)  $E_{a2}$  for catalytic reaction was smaller than  $E_{a1}$  for noncatalytic reaction, and  $k_2$  for catalytic reaction was larger than  $k_1$  for noncatalytic reaction.

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