

## 합성된 PGE-AcAm이 에폭시 수지 계의 반응속도에 미치는 영향

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### Effect of Synthetic PGE-AcAm on the Reaction Rate of Epoxy System

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**초 록** Diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA) 계의 경화반응 속도에 미치는 phenyl glycidyl ether(PGE)-acetamide(AcAm)의 영향을 연구하였다. 반응성 첨가제로 사용된 PGE-AcAm는 PGE와 acetamide를 2:1의 몰 비로 혼합한 후 180°C에서 1시간 반응시켜서 합성하였으며, PGE의 에폭사이드기와 AcAm의 아민기가 반응함으로써 수산기를 형성함에 의해 진행되었다. 이 때 생성된 수산기는 DGEBA와 MDA의 반응에서 촉매로 작용하여 반응속도를 크게 증가시켰으며, 활성화 에너지 값을 감소시켰다. PGE-AcAm이 첨가되지 않은 DGEBA/MDA 계의 활성화 에너지는 11.11 kcal/mol이었고, 30 phr의 PGE-AcAm이 첨가된 계의 활성화 에너지는 7.91 kcal/mol이었다.

**Abstract** The effect of phenyl glycidyl ether(PGE)-acetamide(AcAm) on the cure kinetics of diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA) system was studied. The synthetic PGE-AcAm as a reactive additive was prepared by the reaction of PGE : AcAm = 2 : 1 (molar ratio) at 180°C for 1hr. An epoxide group of PGE reacted with an amine group of AcAm and formed a hydroxyl group which was acted as a catalyst on the cure reaction of DGEBA and MDA. Therefore, the cure rate became very fast and activation energy was lowered by the addition of PGE-AcAm. The activation energy of DGEBA/MDA system without PGE-AcAm was 11.11 kcal/mol and that of the system with 30 phr of PGE-AcAm was 7.91 kcal/mol.

### 1. Introduction

With the increasing demands for epoxy composites in the fields of space shuttle, aircrafts, automobiles, ships and structural components, many researchers have studied to develop matrices having good physical, mechanical and thermal properties<sup>1~8)</sup>. To improve these properties, epoxy resins or/and curing agents are modified<sup>1, 2)</sup>, various species of reactive liquid rubbers are incorporated<sup>3, 4)</sup>, reactive additives are added<sup>5~8)</sup>, and different epoxy and curing agent are mixed. In this study, synthesized

phenyl glycidyl ether(PGE)-acetamide(AcAm) as a reactive additive was used to improve the mechanical properties of diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA) system.

It is very important to know the cure rate to improve the processibility of the epoxy system in pultrusion process, filament winding process, laminate process, encapsulation process, etc., and the cure rate is strongly dependent upon the degree of cure, which affects the mechanical properties of the cured epoxy resin<sup>9~11)</sup>. Therefore, many expressions and techniques to

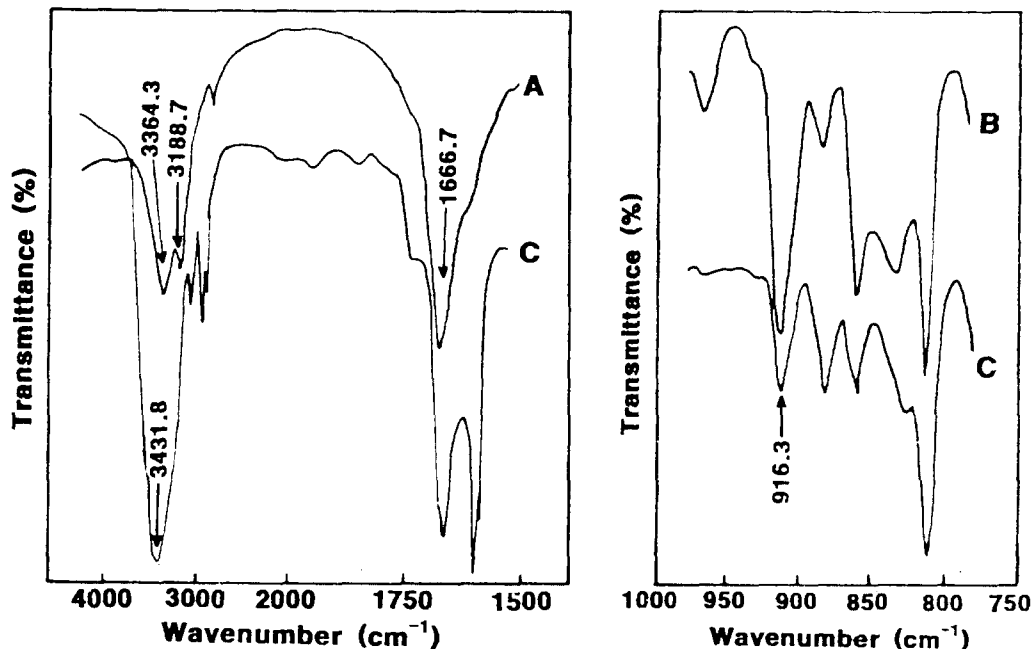


Fig. 1. FT-IR spectra of (A) AcAm, (B) PGE and (C) synthesized PGE-AcAm.

study the cure kinetics of epoxy resins have been proposed by many scientists<sup>7, 12~15</sup>. In this study, Kissinger equation<sup>7, 12</sup>) as a sort of dynamic DSC analysis was used and it is

$$-\ln(q/T_p^2) = E_a/RT_p^2 - \ln(AR/E_a)$$

where  $q$ : heating rate,  $T_p$ : exothermic peak temperature,  $E_a$ : activation energy,  $R$ : gas constant,  $A$ : pre-exponential factor.

## 2. Experiment

### 2.1 Synthesis of PGE-AcAm

To synthesize PGE-AcAm, phenyl glycidyl ether(Fluka Chemie AG.) and acetamide(Hayashi Pure Chemical Ind. Ltd.) were mixed at the molar ratio of 2:1 in three-neck flask equipped with stirrer, condenser and thermometer. The mixture was reacted at 180°C for 1hr and the synthesized PGE-AcAm was stored at -13°C. To study the reaction mechanism between PGE and AcAm, FT-IR analysis was carried out and the consumption of epoxide group was calculated by the hydrohalogenation method<sup>16</sup>).

### 2.2 DSC Analysis

To study cure kinetics, DGEBA, 30 phr of MDA and various contents of PGE-AcAm were mixed under 80°C, and this mixtures were stored at -13°C to stop the cure reaction. The samples were placed into DSC container and DSC analysis was performed from 30°C to 350°C at 5, 10, 15 and 20 °C/min. The nitrogen flow rate was 40 ml/min.

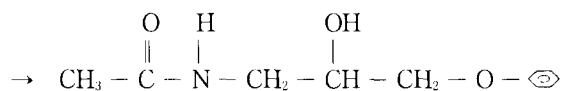
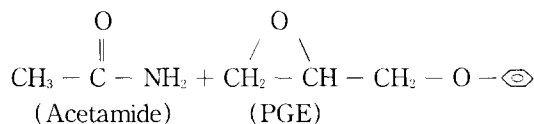
## 3. Results and Discussion

### 3.1 Synthesis of PGE-AcAm

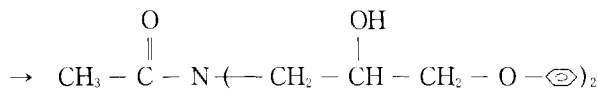
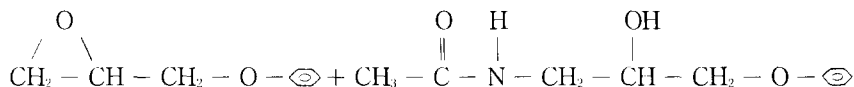
To investigate the reaction mechanism between PGE and AcAm, FT-IR analysis was carried out and the FT-IR spectra were shown in Fig.1. Two sharp bands at 3188.7  $\text{cm}^{-1}$  and 3364.3  $\text{cm}^{-1}$  on the AcAm spectrum(A) disappeared, which were for amine group( $-\text{NH}_2$ ) and the band at 916.3  $\text{cm}^{-1}$  of PGE spectrum (B) decreased, which was for epoxide group ( $\text{C}-\text{C}-\text{O}$ ). However a new band at 3431.8  $\text{cm}^{-1}$  appeared on the spectrum(C) of synthesized PGE-AcAm, which was for hydroxyl group ( $-\text{OH}$ ). From these spectra, it was apparent

that an epoxide group of PGE was reacted with a primary amine group of AcAm and a new hydroxyl group was formed by the opening of the epoxide group, and this reaction was shown in Scheme 1. The formed secondary amine in Scheme 1 successively was reacted with another epoxide group and another

hydroxyl group and tertiary amine were formed, as shown in Scheme 2. These two mechanisms have been well known in the epoxy system cured with amine compound<sup>8, 17</sup>. But, the band of  $>C=O$  at  $1666.7\text{ cm}^{-1}$  was almost the same intensity and this group did not take part in the reaction.



Scheme 1. The reaction of primary amine and epoxide groups.



Scheme 2. The reaction of secondary amine and epoxide groups.

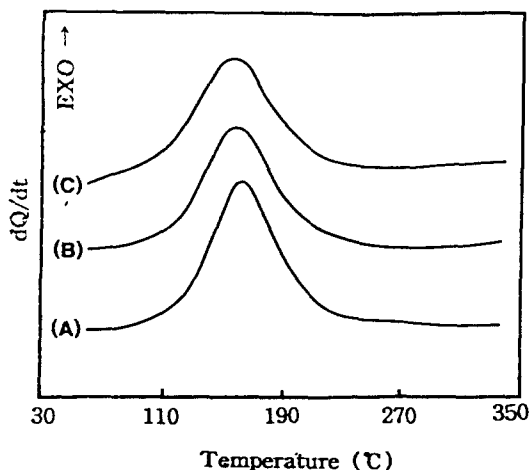


Fig. 2. DSC thermograms for DGEBA/MDA with various contents of PGE-AcAm at  $10^\circ\text{C}/\text{min}$ . (A) 10 phr, (B) 20 phr and (C) 30 phr.

The conversion of epoxide group was calculated by the chemical titration. Before the reaction between PGE and AcAm, the epoxy content in equivalents per 100 gram was 55.65

$\times 10^{-2}$  mol/g. However, after the reaction, that value was  $8.93 \times 10^{-2}$  mol/g. Putting the FT-IR analysis and chemical titration together, it was found that 84% of epoxide group in PGE was reacted with amine group and was converted to hydroxyl group, but unreacted epoxide group (16%) was not converted. It would be linked to the crosslink structure of DGEBA/MDA system by the cure reaction.

### 3.2 Cure Kinetics

It has been well known that the reaction between epoxide and amine groups is accelerated by the addition of hydrogen donor compounds acted as a catalyst, such as alcohols, water, hydroquinone, etc., and the reaction was also accelerated by the hydroxyl groups generated by the opening of epoxide group<sup>18, 19</sup>. As was shown above, the synthesized PGE-AcAm had hydroxyl groups and these groups would also take part in the cure reaction between epoxide-amine groups as a catalyst and the accelera-

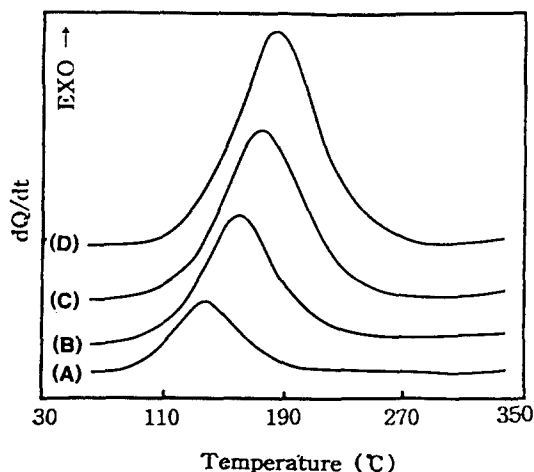


Fig. 3. DSC thermograms for DGEBA/MDA/PGE-AcAm(20 phr) at different heating rates. (A)5°C/min, (B)10°C/min, (C)15°C/min and (D)20°C/min

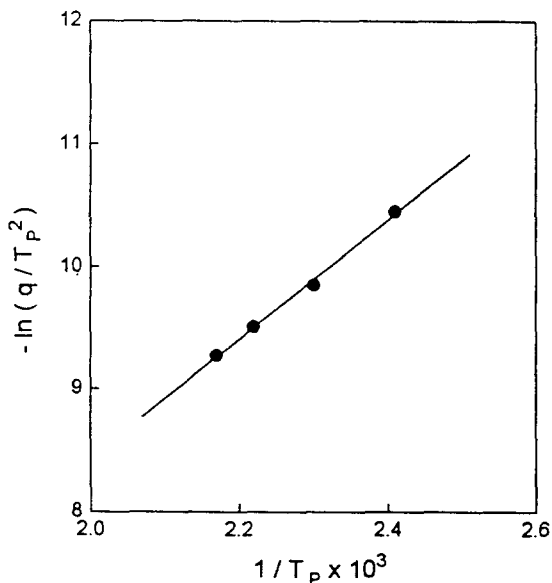


Fig. 4. Kissinger equation for DGEBA/MDA/PGE-AcAm(20 phr) system.

tion effect should be investigated.

The DSC thermograms for DGEBA/MDA system with various contents of PGE-AcAm at 10°C/min were shown in Fig. 2. The exothermic heat was directly proportional to the consumption reaction of epoxide group and the velocity of the heat generation,  $dQ/dt$  was also in proportion to the cure rate. With the increment of PGE-AcAm content, the reaction

Table 1. The Relationship between Heating Rates and Exothermic Peak Temperatures for DGEBA/MDA/PGE-AcAm(20 phr) System.

$q$ (°C/min)	$T_p$ (K)	$1/T_p \times 10^3$	$-\ln(q/T_p^2)$
5	415.6	2.41	10.45
10	434.9	2.30	9.85
15	450.6	2.22	9.51
20	459.9	2.17	9.27

starting temperatures and the exothermic peaks were appeared at lower temperatures, which meant that the cure reaction took place easily and the cure rate of the epoxy monomers increased by the addition of hydroxyl group in PGE-AcAm.

DSC thermograms from 30°C to 350°C for DGEBA/MDA system with 20 phr of PGE-AcAm at different heating rates were shown in Fig. 3. All thermograms showed only one exothermic peak, and with the increment of heating rate, the maximum cure rates,  $dQ/dt$  appeared at higher temperatures due to the rapid cure reaction in a short time. The exothermic heat of the thermogram was evolved from the noncatalytic epoxide-primary amine reaction, noncatalytic epoxide-secondary amine reaction, epoxide-hydroxyl reaction by which crosslinking structure was formed, catalytic epoxide-amine reaction<sup>20</sup>, however it was very difficult to get kinetic parameters for each step. Therefore, the cure kinetics were expressed by the consumption rate of epoxide monomer. To obtain kinetics parameters by Kissinger equation, the relationship between heating rates and exothermic peak temperatures were listed in Table 1 and the plot of  $-\ln(q/T_p^2)$  vs.  $1/T_p \times 10^3$  was displayed in Fig. 4. Activation energy was obtained from the slope and pre-exponential factor was from the y-intersection. The activation energy was 9.44 kcal/mol and the pre-exponential factor was  $0.31 \times 10^3 \text{ sec}^{-1}$ .

Fig. 5 showed DSC thermograms for DGEBA/MDA systems with different PGE-AcAm contents at various heating rates. All

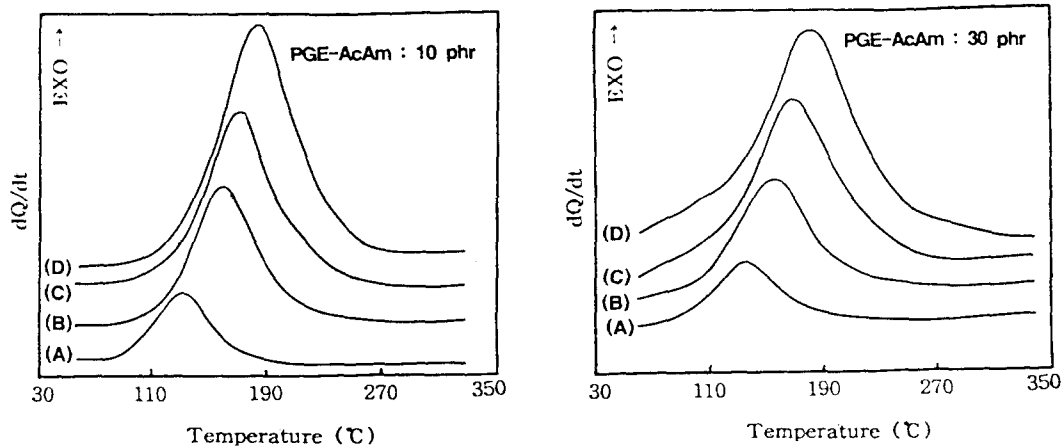


Fig. 5. DSC thermograms for DGEBA/MDA systems with different PGE-AcAm contents at various heating rates. (A)5°C/min, (B)10°C/min, (C)15°C/min and (D)20°C/min

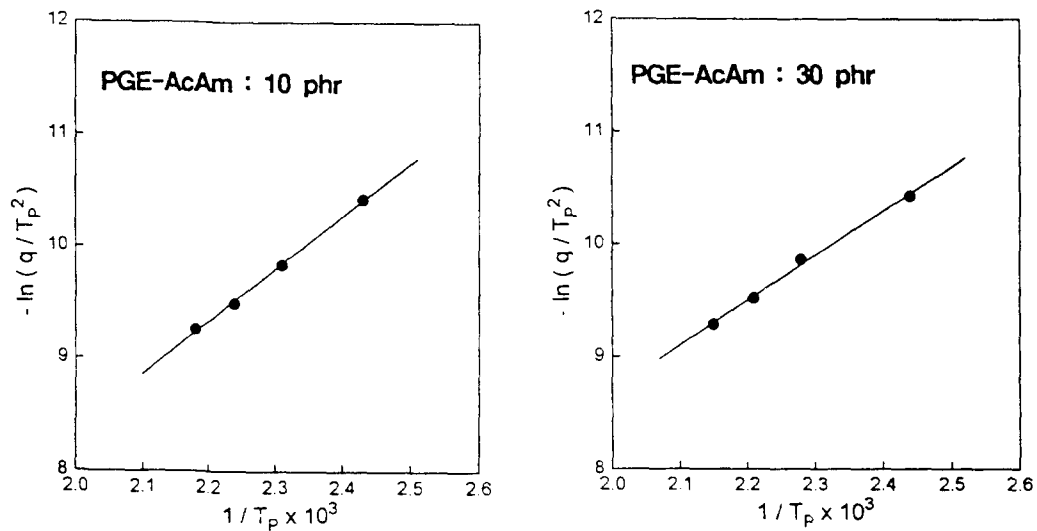


Fig. 6. Kissinger equation for DGEBA/MDA systems with different PGE-AcAm contents.

thermograms also showed only one exothermic peak, and with the increment of heating rate, the maximum cure rates,  $dQ/dt$  appeared at higher temperatures. The exothermic peak temperatures of the system with 30 phr of PGE-AcAm were lower about 5°C than those of the system with 10 phr of PGE-AcAm and this implied the acceleration effect of hydroxyl groups in PGE-AcAm. To get kinetic parameters by Kissinger equation, straight lines were plotted in Fig.6, and activation energy and pre-exponential factor were listed in Table 2. For

the DGEBA/MDA system, kinetic parameters were also listed in Table 2. As shown in this Table, the activation energy decreased with the increment of PGE-AcAm content, and the value of 0 phr of PGE-AcAm was 11.11 kcal/mol and that of 30 phr of PGE-AcAm was 7.91 kcal/mol, which was decreased about 40%. To plot the conversion,  $\alpha$  vs. time,  $t$  at 80°C from these data, the rate constant  $k$  was calculated and reaction order was assumed to be  $n=2$ , which was the general value for epoxy system, and the plots were shown in

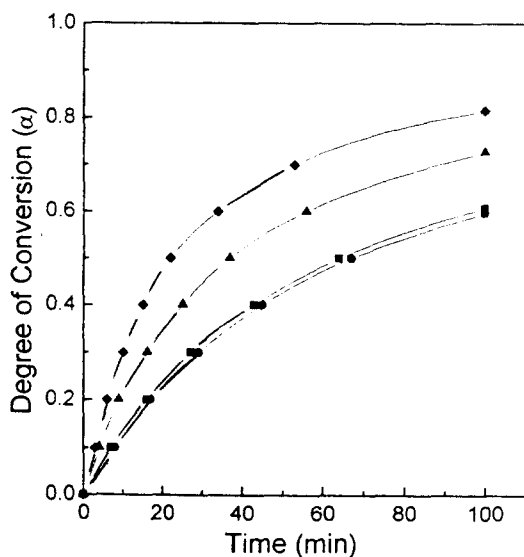


Fig. 7. Plot of degree of conversion ( $\alpha$ ) vs. time at 80°C for DGEBA/MDA system with various contents of PGE-AcAm. PGE-AcAm : (●) 0 phr, (■) 10 phr, (▲) 20 phr and (◆) 30 phr

Table 2. Kinetic Parameters for DGEBA/MDA/PGE-AcAm Systems.

PGE-AcAm (phr)	Ea (kcal/mol)	A(sec <sup>-1</sup> )
0	11.11	$1.86 \times 10^3$
10	9.61	$0.23 \times 10^3$
20	9.44	$0.31 \times 10^3$
30	7.91	$0.58 \times 10^2$

Fig. 7. As the content of PGE-AcAm increased, the cure rate increased and the acceleration effect of hydroxyl group in PGE-AcAm compound was confirmed.

#### 4. Conclusion

From these results, the following conclusions were obtained.

1) In FT-IR analysis, the band of amine group in AcAm, and the band of epoxide group in PGE decreased and that of hydroxyl group appeared. Therefore, it was found that an epoxide group was reacted with an amine group and formed a hydroxyl group. By chemical titration, 84% of epoxide group was con-

verted.

2) With the increment of PGE-AcAm, exothermic peak temperature was appeared at lower point and activation energy decreased. The activation energy of DGEBA/MDA system was 11.11 kcal/mol and that of the system added with 30 phr of PGE-AcAm was 7.91 kcal/mol.

3) The acceleration effect of hydroxyl group in PGE-AcAm was confirmed by plotting of cure of degree vs. time. As the content of PGE-AcAm was added, the cure rate increased.

#### Acknowledgement

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