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Cure Kinetics of DGEBA/MDA/HQ-PGE System

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DGEBA/MDA/HQ-PGE계의 경화 반응 속도론

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Abstract: Cure kinetics of diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA) with hydroquinone-phenyl glycidyl ether(HQ-PGE) as a reactive additive, which was preliminarily synthesized, was investigated by DSC and FT-IR analyses. Kissinger equation and Arrhenius' equation were used to calculate activation energy and pre-exponential factor. When HQ-PGE was added to DGEBA/MDA system, it reduced activation energy of system. When the 5 phr of HQ-PGE was added to DGEBA/MDA system, activation energy was 7.8 kcal/mol by FT-IR analysis and 11.3 kcal/mol by DSC, in comparison with the system without HQ-PGE, activation energy decreased about 30% and 9%, respectively. According to these results, HQ-PGE, introducing agent of this system, acted as a catalyst.

요 약 : 반응성 첨가제로 HQ와 PGE를 합성시킨 HQ-PGE를 사용하여, DGEBA/MDA계의 경화반응이 일어날 때의 속도론을 DSC와 FT-IR을 이용하여 조사하였다. 그리고, Kissinger equation과 Arrhenius equation을 이용하여 활성화 에너지와 pre-exponential factor 값을 구하였다. 계의 활성화 에너지는 HQ-PGE가 첨가되었을 때 감소하였다. 합성 HQ-PGE가 5 phr 첨가되었을 때, DGEBA/MDA계의 활성화 에너지는 FT-IR로 측정하였을 때 7.8 kcal/mol, DSC로 측정하였을 때에 11.3 kcal/mol을 나타내었다. 이 값은 HQ-PGE가 첨가되지 않은 경우보다 각각 30%, 9% 감소된 값이었다. 이 결과들을 통해서 반응성 첨가제로 사용된 HQ-PGE는 본 계에서 촉매의 역할을 함을 알 수 있었다.

1. Introduction

In cure kinetics study, dynamic experiment methods were used by many investigators. These methods require some parameters such as heating rate and peak temperature. And in order to utilize them, reaction order was assumed. Therefore, these dynamic methods were investigated by DSC, TG and DTG, generally[1-4]. In other kinetic studies, the method that analysis of time to constant conversion with various cure temperatures was used by FT-IR [5-9].

To modify the epoxy resin which has handicap of brittleness, we used preliminarily synthesized HQ-PGE as reactive additive for DGEBA/MDA system. And, in order to calculate and compare activation energy and pre-exponential factor of this system, Kissinger equation was utilized by DSC[10-

14] and Arrhenius' equation was utilized by FT-IR analysis[5].

2. Experiment

We used a commercial epoxy resin DGEBA supplied by Shell Co., and introduced hardener MDA by Fluka Chemie AG. Hydroquinone-phenyl glycidyl ether(HQ-PGE) as reactive additive was preliminarily synthesized. In order to synthesize HQ-PGE, HQ and PGE were mixed with constant ratio and heated to 180℃ with constant heating rate, then reacted for 30 min. After reaction, it was kept at low temperature. HQ-PGE was added to DGEBA/MDA system at 80℃. To investigate the effect of reactive additive, contents of HQ-PGE were added from 5 phr to 20 phr. After mixing, each of them weighed 3mg, and they were placed at -17℃ to prevent continuous reaction. Using the Kissinger equation, they were heated various heating rates such as 2, 5, 10, 15, and 20℃/min by DSC.

For the FT-IR analysis, the mixture was cured in the shape of film with different temperatures and various times. Their spectra were measured by FT-IR. The time of 50% conversion of specimen was plotted with Arrhenius' equation parameter. From the results, the activation energy of reaction was calculated.

3. Results and Discussion

3. 1. DSC Analysis

DSC scans for DGEBA/MDA system with(B) and without(A) HQ-PGE at 10℃/min are shown in Fig. 1, respectively.

When synthesized HQ-PGE was added to the DGEBA/MDA system, the peak temperature was lower than that of the system without HQ-PGE. Also, the initiation temperature and time showed the same tendency. Those results mean that the rate of cure reaction grows faster by synthesized HQ-PGE. It was supposed the effect of hydroxyl group,

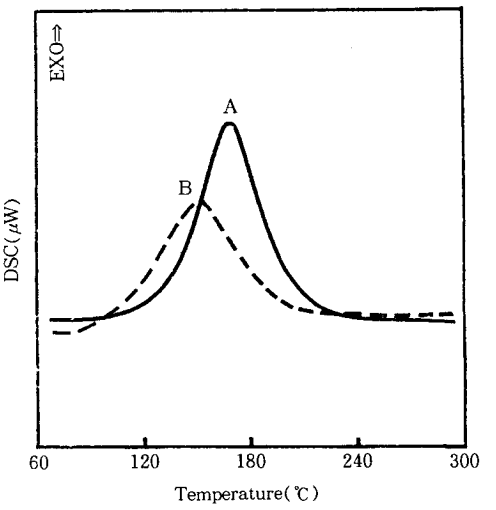

Fig. 1. DSC thermograms for DGEBA/MDA system with(B) and without(A) HQ-PGE at 10℃/min.

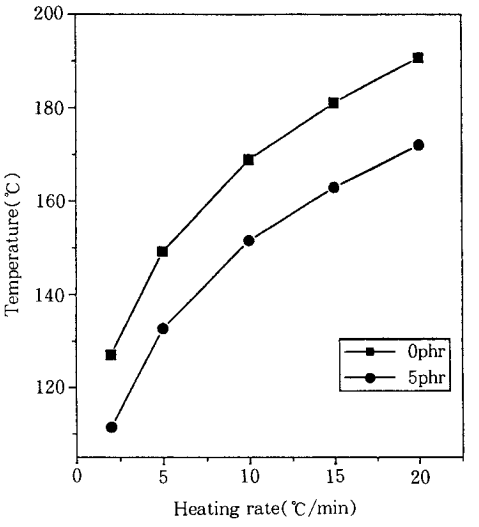

Fig. 2. Temperature at cure peak of DGEBA/MDA /HQ-PGE system with various heating rates.

which was generated by HQ and PGE, as a catalyst. In Fig. 1, we can obtain peak temperatures, so they were plotted in Fig. 2.

In order to calculate the activation energy and

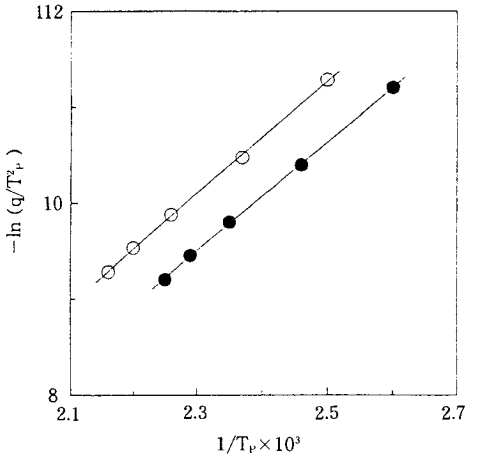

Fig. 3. Plot of $-\ln(q/T_p^2)$ vs. $1/T_p\times10^3$ for DGEBA /MDA system with HQ-PGE by Kissinger equation (○ : 0 phr, ● : 5 phr).

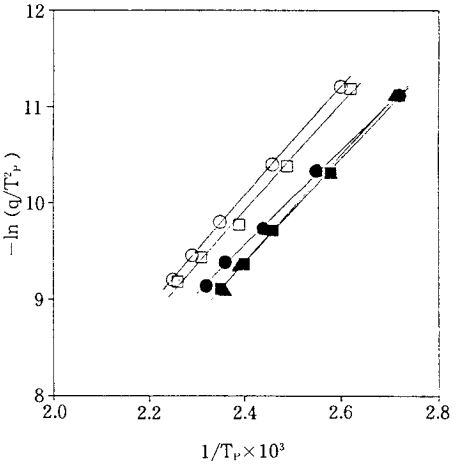

Fig. 4. Plot of $-\ln(q/T_p^2)$ vs. $1/T_p\times10^3$ for DGEBA/ MDA/HQ-PGE system with various HQ-PGE contents by Kissinger equation (○ : 5 phr, □ : 10 phr, ▲ : 15 phr, ● : 20 phr, ■ : 25 phr).

pre-exponential factor, heating rate and peak temperature were utilized by Kissinger equation. The equation is described below.

$$-\ln\left(\frac{q}{T_p^2}\right)=\frac{Ea}{RT_p}-\ln\left(\frac{AR}{Ea}\right) \quad (1)$$

where q : heating rate (K/min)
T_p : peak temperature (K)
Ea : activation energy (cal/mol)
A : pre-exponential factor
R : gas constant

Kissinger equation, which makes use of dynamic run, has merit that it is easy to calculate for parameters and can easily obtain activation energy as well as pre-exponential factor[10, 15]. From this equation, a plot of parameters was obtained. The plot of parameters of DGEBA/MDA system without(A) and with(B) 5 phr of HQ-PGE was shown in Fig. 3. And to prove the effect of contents of HQ -PGE, the plot of parameters was shown in Fig. 4, when various contents of HQ-PGE was added.

The activation energy and pre-exponential factor of these system were calculated from slope and Y intercept of linear graph in Fig. 3 and 4. For instance, when 5 phr of HQ-PGE was added to DGEBA/MDA system, the activation energy decreased about 9% than without HQ-PGE.

The values of peak temperature with different times and heating rates are listed in Table 1. And the activation energy and pre-exponential factor calculated from the relations of the data by Kissinger equation are also listed in Table 2. As shown in Table 2, the value of activation energy decreased with increasing of contents of HQ-PGE. However, pre-exponential factor has no relation to contents of HQ-PGE.

3.2. FT-IR Analysis

In the FT-IR study of the cure characteristics of the epoxy resin system with different cure conditions, it is necessary to analyze the change of the specific peak of some functional groups, in this system, especially epoxide, ether, and hydroxyl group. Because changes of these functional group mean measure of the extent of cure reaction, so we can confirm degree of cure.

To investigate the peak intensity of the epoxide group, we referred to the *p*-phenylene(830 cm^{-1})

Table 1. Temperature at Peak with Different Heating Rate and HQ-PGE Contents

HQ-PGE Contents / Heating Rates	0 phr	5 phr	10 phr	15 phr	20 phr
2℃/min	127.1	111.5	108.1	95.8	94.7
5℃/min	149.2	132.7	128.3	114.5	118.5
10℃/min	169.0	151.6	145.1	134.2	137.1
15℃/min	181.0	163.0	158.9	145.2	148.6
20℃/min	190.6	172.1	168.4	150.9	157.6

Table 2. Activation Energy and Pre-exponential Factor for the DGEBA/MDA System with Various HQ-PGE Contents

HQ-PGE Contents(phr)	Ea (kcal/mol)	A(s^{-1})
0	11.99	4.45×10^3
5	11.32	3.51×10^3
10	11.09	3.03×10^3
15	11.07	5.03×10^3
20	9.81	0.82×10^3

peak which gave the constant intensity value as inert during cure reaction of epoxy resin, so it is used as an internal standard. The peak intensity of absorbance at 915cm^{-1} is divided by the absorbance at 830cm^{-1}. The calculated value of the relative epoxide peak intensity was depicted a type of reacted fraction. When DGEBA/MDA/HQ-PGE(5 phr) system cures with various times and different temperatures, the reacted fraction of the epoxide group (915cm^{-1}) is shown in Fig. 5.

As shown in Fig. 5, as reaction temperature increased, the time which reaches to 50% conversion decreased. From this figure, we can obtain parameters by Arrhenius' equation. When some species A, react with assumption that reaction order is n, reaction rate is below.

$$-\frac{dC_A}{dt}=kC^n_A \tag{2}$$

$$-\frac{dC_A}{C^n_A}=kdt \tag{3}$$

By integration and arrangement

$$C_{A0}^{1-n}[(1-x)^{1-n}-1]=k(n-1)t \tag{4}$$

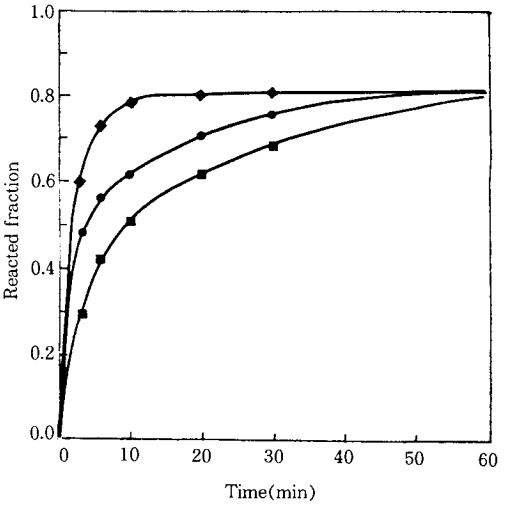

Fig. 5. Plot of reacted fraction of epoxide group (915cm^{-1}) with various cure times (■ : 110 ℃, ● : 140℃, ◆ : 170℃).

where x : conversion of A.

Assume Arrhenius' equation and rearrange,

$$C_{A0}^{1-n}[(1-x)^{1-n}-1]=k'e^{-Ea/RT}(n-1)t \tag{5}$$

$$t=\frac{C_{A0}^{1-n}[(1-x)^{1-n}-1]}{k'(n-1)e^{-Ea/RT}}$$

$$=A\,e^{Ea/RT} \tag{6}$$

where, $A=\frac{C_{A0}^{1-n}[(1-x)^{1-n}-1]}{k'(n-1)}=\text{const}$

Ea : activation energy

R : gas constant

T : temperature

Thus, in case of half conversion of A, eq. (6) transforms into below

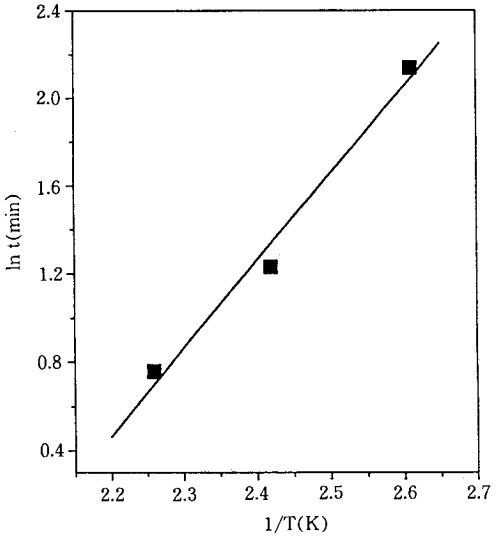

Fig. 6. Arrhenius plot of time to reach 50% conversion vs. time for the FT-IR results.

$$t_{1/2} = A \exp\left(\frac{Ea}{RT}\right) \quad (7)$$

where $t_{1/2}$: a time to be half conversion

The plot of ln time(min) vs. 1/T(K) was shown in Fig. 6. In this plot, we can calculate the activation energy from the slope, 7.8 kcal/mol. In comparison with the activation energy by DSC, the value of FT-IR is smaller than that of DSC. It seems that the FT-IR is more sensitive for the cure reaction process than DSC. Therefore, it resulted in the difference of value between FT-IR analysis and DSC method. However, both of them suggested useful information.

4. Conclusion

1. When HQ and PGE reacted with each other, they generated hydroxyl group.

2. The initiation temperature and peak temperature of reaction with 5 phr of HQ-PGE are lower than those of the case without HQ-PGE. When the contents of HQ-PGE increased, initiation temperature and peak temperature of the system showed the same behavior, as well.

3. When 5 phr of HQ-PGE was added, activation energy decreased about 9% than without HQ-PGE by DSC analysis and as the contents of HQ-PGE increased, activation energy decreased. However, the pre-exponential factor has no relation with the contents of HQ-PGE.

4. In case of FT-IR analysis, when 5 phr of HQ-PGE was added, activation energy was reduced about 30% than without additive. It seems that the FT-IR is more sensitive for the cure reaction process than DSC.

5. In conclusion, we can consider HQ-PGE introduced to DGEBA/MDA system as a catalyst.

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