

에폭시 수지계 의료용 고분자 재료의 특성 연구 -Kissinger 식과 Ozawa 식에 의한 DGEBA/MDA/PGE-DMU 계의 경화특성-

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Characteristics of Medical Polymer Based on Epoxy Resin System -Cure Characteristics for DGEBA/MDA/PGE-DMU System by Kissinger and Ozawa Equations-

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Abstract The cure kinetics of diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA) system with synthesized phenyl glycidyl ether-dimethylurea (PGE-DMU) was studied by Kissinger and Ozawa equations with DSC analysis in the temperature range of 20~300°C. To investigate the reaction mechanism between epoxy group of PGE and urea group of DMU, FT-IR spectroscopy analysis was used. The epoxide group of PGE reacted with the urea group of DMU and formed a hydroxyl group which acted as a catalyst on the cure reaction of other epoxide and amine groups. The activation energy of DGEBA/MDA system without PGE-DMU was 46.5 kJ/mol and those of the system with 5 and 10 phr of PGE-DMU were 43.4 and 37.0 kJ/mol, respectively. Ozawa method also showed the same tendency.

Key words: epoxy, cure kinetics, Kissinger method, Ozawa method

1. Introduction

Epoxy resins are a major class of thermosetting polymers which are widely employed as matrices in composite materials and structural adhesives. They are amorphous and highly crosslinked polymers and this structure result in high modulus and fracture strength and shows low creep, dimensional stability, good mechanical properties and suitable chemical, environmental and electrical resistance, so that they are widely used as coating, adhesion, lamination, casting and electronic encapsulation materials with good performance.^{1~5)}

Differential scanning calorimetry (DSC) which measures the heat flow from the reacting system is a very convenient tool to study the overall cure kinetics of epoxy/amine system. It is especially more useful when detailed mechanisms have been established by other

methods such as FT-IR analysis. In such a case, the kinetic analysis of DSC data helps to determine those steps which most profoundly contribute to the overall process. It's well known that the curing mechanism of the epoxy/amine system is composed of the non-catalytic reaction and the autocatalytic reaction.^{1,2,5)} In the initial stage, noncatalytic reaction of an epoxy group with an amine group produces a hydroxyl group, which can act as a catalyst in the reaction of another epoxy group with another amine group. As curing reaction proceeds, the increasing concentration of the hydroxyl group makes the reaction rate increase vigorously.

In this study, synthesized phenyl glycidyl ether-dimethylurea (PGE-DMU) was introduced to improve the mechanical properties of epoxy/amine system and the overall cure kinetics was estimated by Kissinger and Ozawa equations. Kissinger equation^{1,2)} is

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$$-\ln\left(\frac{q}{T_p^2}\right) = \frac{E_a}{R} \times \frac{1}{T_p} - \ln\left(\frac{AR}{E_a}\right) \quad (1)$$

where, q : heating rate, T_p : a temperature where the maximum conversion rate occurs based on DSC curve, E_a : activation energy of curing, A : pre-exponential factor and R : gas constant. By using the relationship between $-\ln(q/T_p^2)$ and $1/T_p$, activation energy and pre-exponential factor could be calculated from the slope and y -intersect, respectively.

Ozawa used a liner empirical approximation given by Doyle^{3,4)}:

$$\log\beta = -0.4567 \frac{E_a}{RT} + \left(\log \frac{ZE_a}{R} - \log g(\alpha) - 2.315 \right) \quad (2)$$

Thus, at the same conversion, a plot of $\log\beta$ vs. $-1/T$ should be a straight line with a slope of $0.4567E_a/R$.

2. Experiment

2.1. Materials

The base epoxy resin was diglycidyl ether of bisphenol A (DGEBA, Epon 828) supplied by Shell Co. with an epoxide equivalent weight (EEW) of 188 g/mol, molecular weight (MW) of 385 g/mol and the viscosity of 11,000~14,000 cps at 25°C. 4,4'-methylene dianiline (MDA, Fluka Chemie AG) was a curing agent with MW of 198 g/mol. PGE-DMU as a reactive additive was synthesized by the followings; Phenyl glycidyl ether (PGE) and 1,1-dimethyl urea (DMU) were mixed at the molar ratio of 1:1 and the mixture was reacted at 130°C for 1.5h.

2.2. DSC and FT-IR Analyses

To study cure kinetics, DGEBA, MDA 30 phr (parts per one hundred of base resin) and PGE-DMU (0, 5, 10 phr) were well mixed under 80°C and the mixtures were stored at -13°C to stop the cure reaction during the storage. The samples were analyzed by DSC at the heating rates of 3, 5, 10 and 20°C/min. 3-8mg of the mixture was placed in aluminum DSC pan and dynamic DSC run was carried out on Solomat DCS-4000 instrument. Nitrogen gas was flowed at 40 ml/min to prevent the oxidation of the sample.

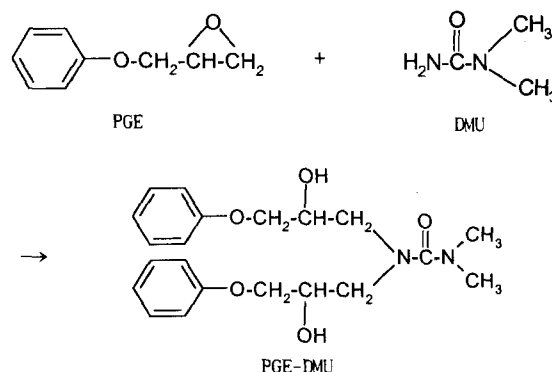
Table 1. FT-IR Characteristic Bands of PGE and Synthesized PGE-DMU

Characteristic Band (cm ⁻¹)	Assignment
916	epoxy ring
1760	carbonyl group
3188, 3364	primary amine in urea
3367	hydroxyl group

To study the cure mechanism between PGE and DMU, FT-IR analysis was carried out at a resolution of 4cm⁻¹ from 4000cm⁻¹ to 400cm⁻¹. The characteristic bands for epoxide, urea and hydroxyl groups were recorded and compared.

3. Results and Discussion

The chemical structure of the synthesized PGE-DMU was determined by FT-IR analysis. Fig. 1 shows the comparison of FT-IR spectra for PGE (a-curve) and PGE-DMU (b-curve) in the range of 4600~400cm⁻¹ and the assignments for the characteristic bands were summarized in Table 1. The reaction was nucleophilic attack on the epoxy ring by the nitrogen of DMU, which produced a hydroxyl group as shown in Scheme I. The characteristic absorption of the epoxy ring at 916cm⁻¹ was almost consumed and a new broad absorptive peak at 3368cm⁻¹ appeared after the reaction, which was the hydroxyl group band. Two sharp bands at 3188cm⁻¹ and 3364cm⁻¹ for primary amine on the DMU were not shown in spectra (b). These said that the epoxide group of PGE reacted with primary amine in DMU forming PGE-DMU with two hydroxyl groups. The structure of the PGE-DMU was estimated as follow:



Dynamic DSC curve for DGEBA/MDA system without PGE-DMU at the heating rate of 10°C/min is shown in Fig. 2. The exotherm initiated at about 90°C, the maximum exothermic peak temperature appeared at 165.2°C and exothermic reaction finished after 250°C. The exotherm is generated by the generally accepted cure reaction shown in Scheme I. The epoxy-amine cure involves four main reaction mechanisms; (1) A primary amine reacted with an epoxide group forming a secondary amine with a hydroxyl group. (2) A secondary amine reacted with other epoxide group generating a tertiary amine with another hydroxyl group. (3) The newly generated hydroxyl group plays a role of catalyst in the reactions between amine and epoxide

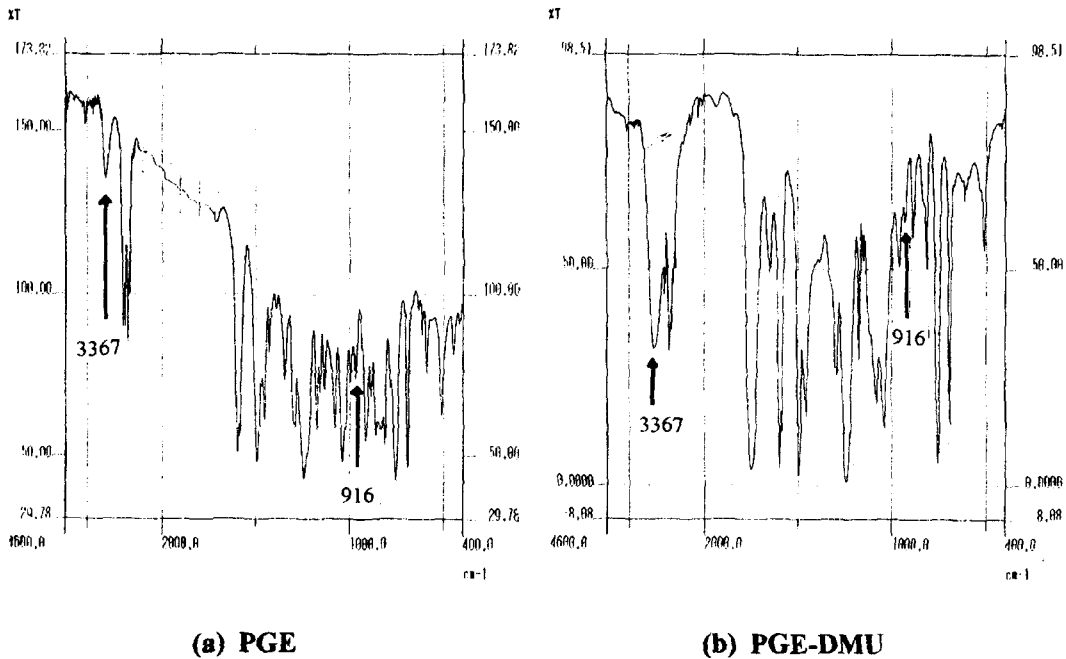


Fig. 1. FT-IR spectra of (a) PGE and (b) PGE-DMU.

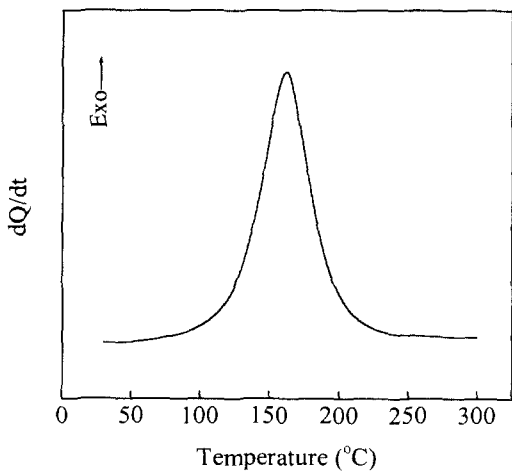
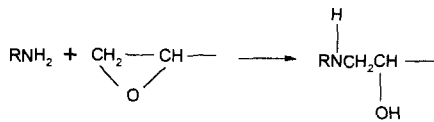
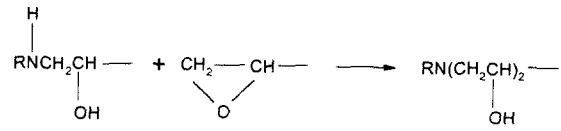


Fig. 2. DSC curve for DGEBA/MDA without PGE-DMU at 10 °C/min.

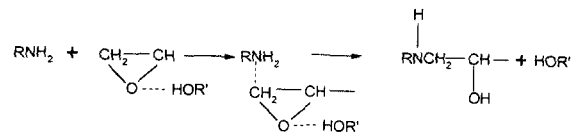
groups and make the cure rate accelerated by the formation of termolecular transition state, so the cure reaction is called autocatalytic reaction. (4) The hydroxyl group reacted with epoxide group and formed ether linkage with a hydroxyl group.



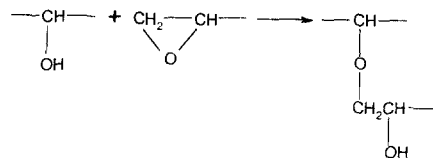
(1) Primary amine-Epoxide reaction



(2) Secondary amine-Epoxide reaction



(3) Autocatalytic Reaction



(4) Ether Linkage Formation

Scheme I. Cure mechanisms in diamine-epoxy system

Dynamic DSC curves from 20 °C to 300 °C for DGEBA/MDA system with 5 phr of PGE-DMU at the heating rates of 3, 5, 10 and 20 °C/min were shown in Fig. 3. The exothermic peak temperature at 10 °C/min appeared around 80 °C and the maximum peak temperature was shown at 178.0 °C. The peak temperature and the reaction starting temperature were appeared at lower points than those for the DGEBA/MDA system without PGE-DMU system. This meant that the cure reaction took place easily and the cure rate of the

Table 2. The Relationship between Heating Rates and Exothermic Peak Temperatures for DGEBA/MDA/PGE-DMU (5phr) System.

q (°C/min)	T _p (K)	1/T _p × 10 ³	-ln(q/T _p ²)	E _a (kJ/mol)	A (sec ⁻¹)
3	395.0	2.53	10.86	43.4	4.39 × 10 ³
5	409.4	2.44	10.42		
10	430.7	2.32	9.83		
20	451.0	2.22	9.23		

Table 3. Activation Energy from Ozawa Equation of DGEBA/MDA/PGE-DMU (5phr) System.

Conversion	Activation Energy(kJ/mol)
0.3	60.4
0.4	63.9
0.5	60.0
0.6	63.9

epoxy monomer increased by the addition of PGE-DMU due to the catalytic role of hydroxyl group in PGE-DMU. As the heating rate increased, the maximum cure rates, dQ/dt appeared at higher temperature due to the rapid cure reaction in a short time. The cure reaction of the system consists of many mechanisms as shown in Scheme I, however it is very difficult to get kinetic parameters for each step. Therefore, the cure kinetics are expressed by the consumption rate of epoxy monomer.

To obtain kinetic parameters by Kissinger equation, the relationship between heating rates and exothermic peak temperatures were listed in Table 2. The plot of $-\ln(q/T_p^2)$ vs. $1/T_p \times 10^3$ was displayed in Fig. 4. The activation energy and pre-exponential factor were obtained from the slope and the y-intersection, respectively and they were also listed in Table 2. The activation energy of DGEBA/MDA system with 5 phr

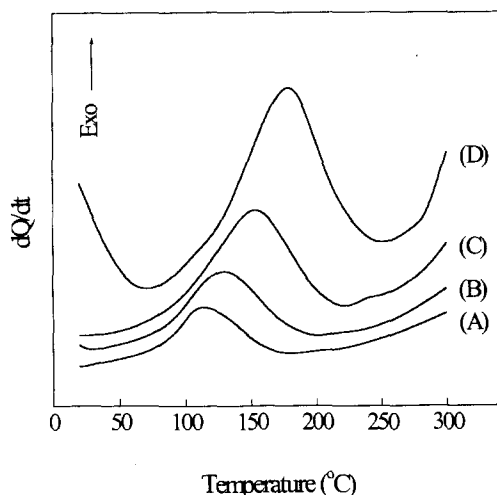


Fig. 3. DSC curves for DGEBA/MDA/PGE-DMU(5 phr) system at various heating rates. (A) 3°C/min, (B) 5°C/min, (C) 10°C/min and (D) 20°C/min

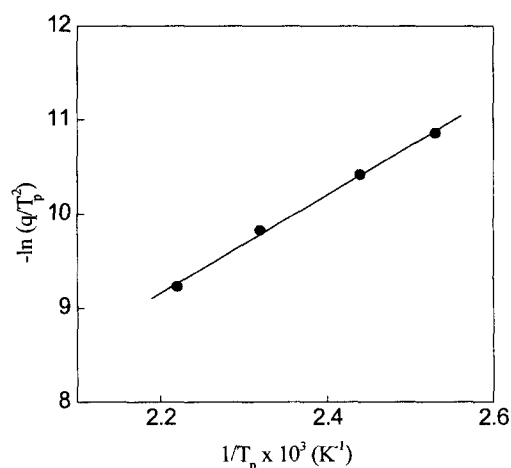


Fig. 4. Kissinger plot for DGEBA/MDA/PGE-DMU(5 phr) system.

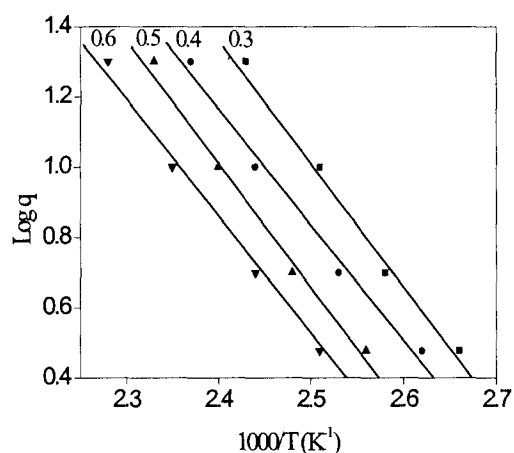


Fig. 5. Ozawa plot for DGEBA/MDA/PGE-DMU(5phr) system at different conversions.

of PGE-DMU was 43.4 kJ/mol and pre-exponential factor was $4.39 \times 10^3 \text{ s}^{-1}$.

Fig. 5 showed Ozawa relationships between Log (q) and 1/T derived from the Fig. 3 and activation energy at different conversion is calculated from the slope of each straight line and it is listed in Table 3. The average value is 62.0 kJ/mol, which is some higher than that from Kissinger equation.

Fig. 6 shows dynamic DSC curves for DGEBA/MDA system with 10 phr of PGE-DMU at the heating rates of 3, 5, 10 and 20°C/min. The shape of the curves is similar to that of 5 phr, but the reaction initiation tem-

Table 4. The Relationships between Heating Rates and Exothermic Peak Temperatures for DGEBA/MDA/PGE-DMU (10phr) System.

q(°C/min)	T(K)	1/T _p × 10 ³	-ln(q/T _p ²)	E _a (kJ/mol)	A (sec ⁻¹)
3	387.9	2.58	10.82	37.0	2.05 × 10 ³
5	405.5	2.47	10.40		
10	428.1	2.34	9.82		
20	450.3	2.22	9.22		

Table 5. Activation Energy from Ozawa Equation of DGEBA/MDA/PGE-DMU (10phr) System

Conversion	Activation Energy(kJ/mol)
0.3	45.9
0.4	47.2
0.5	45.3
0.6	46.4

perature and the maximum exothermic peak temperature appears at lower temperature. This means that cure reaction was accelerated by the catalytic role of hydroxyl group in PGE-DMU, as shown in Scheme I. The relationships between heating rates and exothermic peak temperatures were listed in Table 4 and the plot of -ln(q/T_p²) vs. 1/T_p × 10³ was displayed in Fig. 7. Activation energy is 37.0 kJ/mol and pre-exponential factor is 2.05 × 10³, which are lower than those of the system with 5 phr of PGE-DMU due to the hydroxyl group acted as a catalyst.

Fig. 8 showed Ozawa plots and activation energies at different conversions are obtained and listed in Table 5. The activation energies are lower than those of the system with 5phr of PGE-DMU. The average value for 10 phr of PGE-DMU is 46.2 kJ/mol, which is some higher than that from Kissinger equation.

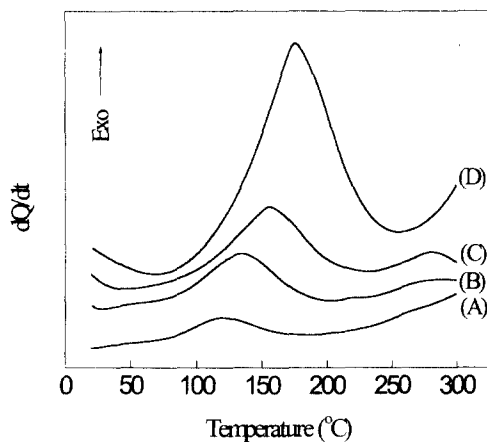


Fig. 6. DSC curves for DGEBA/MDA/PGE-DMU(10 phr) system at various heating rates. (A) 3°C/min, (B) 5°C/min, (C) 10°C/min and (D) 20°C/min

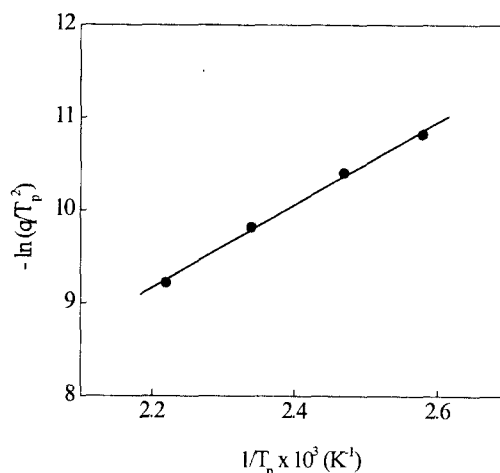


Fig. 7. Kissinger plot for DGEBA/MDA/PGE-DMU(10 phr) system.

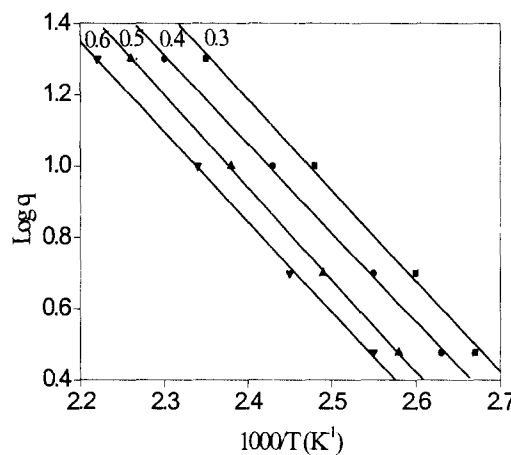


Fig. 8. Ozawa plot for DGEBA/MDA/PGE-DMU(10 phr) system at different conversions.

4. Conclusion

In FT-IR analysis, it was found that epoxide group of PGE reacted with urea group generating PGE-DMU having hydroxyl group. As the content of synthesized PGE-DMU increased, cure reaction initiation temperature and exothermic peak temperature appeared at lower point and activation energy decreased. These meant that cure reaction was accelerated by the catalytic role of hydroxyl group in PGE-DMU. In Kissinger equation, the activation energy fo DGEBA/MDA system was 43.3 and 37.0 kJ/mol, respectively. Ozawa

method also showed the decreasing activation energy with increasing PGE-DMU content.

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