

Cure Kinetics of DGEBA/MDA/GN/HQ System by DSC Analysis

J. Y. Lee, M. J. Shim*, and S. W. Kim

Dept. of Chem. Eng., Seoul City Univ., Seoul 130-743, Korea

*Dept. of Life Sci., Seoul City Univ., Seoul 130-743, Korea

(Received July 5, 1994, Accepted July 28, 1994)

DSC 분석에 의한 DGEBA/MDA/GN/HQ계의 경화반응 속도론

이재영 · 심미자* · 김상욱

서울시립대학교 화학공학과

*서울시립대학교 생명과학과

(1994년 7월 5일 접수, 1994년 7월 28일 채택)

Abstract: Cure kinetics of DGEBA(diglycidyl ether of bisphenol A)/MDA(4,4'-methylene dianiline)/GN(glutaronitrile) system with and without HQ(hydroquinone) as a catalyst was studied by Kissinger equation and Fractional life method. The activation energy of the system with HQ was somewhat lower and the pre-exponential factor of that was higher by about 30% than those of the system without HQ. As 1.25phr of HQ was added, reaction rates increased about 1.8 times.

요약: 촉매로 작용하는 HQ의 첨가에 따른 DGEBA/MDA/GN계의 경화반응 속도론 변화를 Kissinger equation과 Fractional life법에 의해 연구하였다. HQ가 첨가된 계가 첨가되지 않은 계보다 활성화 에너지는 약간 감소하였고, pre-exponential factor 값은 30% 정도 증가하였다. 그리고, HQ(1.25phr)가 첨가됨으로 인해 반응속도는 1.8배 정도 증가하였다.

1. Introduction

In the reaction of epoxy resin with diamine, it has been well established that a hydroxyl group is generated by the opening reaction of an epoxide ring with a hydrogen atom of amine, and the hydroxyl group acts as an autocatalyst so that it accelerates the reaction of epoxide group and amine group[1-6].

In this study, HQ which has two hydroxyl group was introduced to DGEBA/MDA/GN system and cure kinetics were investigated by Fractional life method[7] and Kissinger equation[8]. Fractional

life equation was used for estimation of reaction order and Kissinger equation was for activation energy and pre-exponential factor.

Fractional life equation is

$$\log(t\alpha) = \frac{\alpha^{1-n} - 1}{(n-1)k(A)_T^{n-1}} - (n-1)\log \frac{(A)_0}{(A)_T}$$

where $t\alpha$ is fractional life, which means the time required for $(A)_0$, initial concentration to fall to $\alpha(A)_0$, n is reaction order, k is rate constant and $\frac{(A)_0}{(A)_T}$ is unreacted fraction.

Kissinger equation is

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

Where q is heating rate, T_p is exothermic peak temperature, E_a and A are activation energy and pre-exponential factor, and R is gas constant.

2. Experiment

The epoxy resin (Epon 828) used in this study was DGEBA type supplied by Shell Co.. The epoxide equivalent weight was 184g/eq and

viscosity was 11,000–14,000cP at 25°C. Curing agent was MDA and reaction additive was GN. Melting point of MDA was 90°C and that of GN was 29°C. These two agents were obtained from Fluka Chemie AG. HQ as a catalyst was Hayashi Pure Chemical Ind. Ltd.. Fig. 1 shows chemical structures of DGEBA, MDA, GN and HQ.

Cure kinetics by Kissinger equation was carried out as follows. DGEBA/MDA(30phr)/GN(5phr) system with and without HQ(1.25phr) were prepared and the well-mixed sample, exactly 3mg was analyzed by DSC. Heating rates were 2, 5, 10 and 20°C/min under nitrogen atmosphere of 40ml/min.

For Fractional life method, the same sample of Kissinger equation was placed about 2~3mg in DSC pan, cured at 85, 105, 120 and 150°C in oven for required time and quenched at -3°C to stop the conversion of epoxy resin. Residual exothermic heat obtained by dynamic method and from the proportional expression of residual exothermic heat and unreacted fraction, isothermal curing curve was plotted.

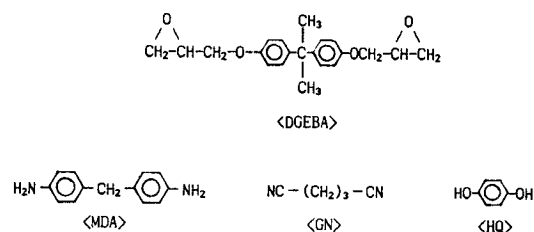


Fig. 1. Chemical structures of DGEBA, MDA, GN and HQ.

3. Results and Discussion

The relationship between residual exothermic heat and reacted fraction according to cure time at 150°C was shown in Fig. 2. With the assumption that exothermic heat during the cure was proportional to the conversion of epoxy monomer[7], residual exothermic heat could be converted to reacted fraction. Total exothermic heat was obtained from the totally uncured sample and a residual exothermic heat was from the sample cured for a time. Residual exothermic heat decreased with the increase of cure time, and consequently reacted fraction increased.

To investigate the cure kinetics of DGEBA/MDA/GN system by Fractional life method, Fig. 3 was obtained from the relationship of reacted fraction and time like in Fig. 2. Cure rate increased with increase of temperature. A time to be a reacted fraction was inversely proportional to cure rate. When reacted fraction was 0.6, relative cure rates at 105, 120 and 150°C were 2.6, 4.0 and 11.2 times, respectively, in the comparison of cure rate at 85°C.

From the curing curves in Fig. 3, $-\log \frac{(A)_0}{(A)_T}$ vs.

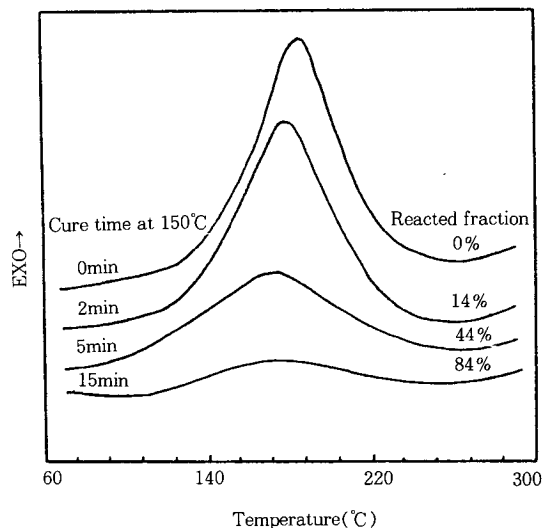


Fig. 2. Residual exothermic heat and reacted fraction for DGEBA/MDA/GN System according to cure time at 150°C by DSC.

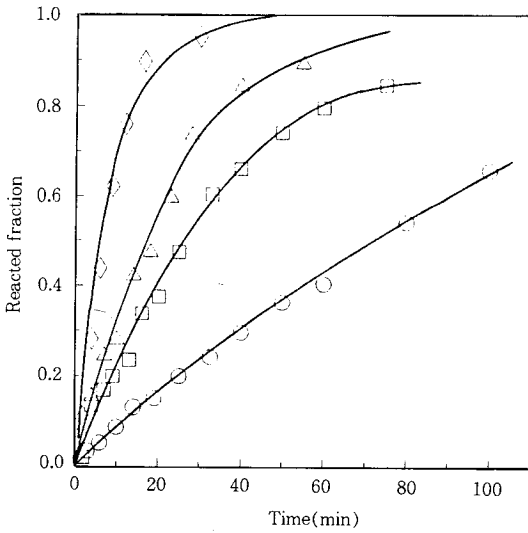


Fig. 3. Isothermal curing curves for DGEBA/MDA/GN system.

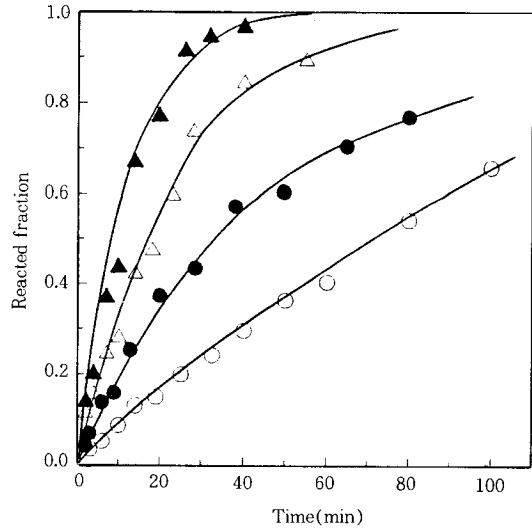


Fig. 5. Isothermal curing curves for DGEBA/MDA/GN system with and without HQ. GN(○) and GN/HQ(●) at 85°C ; GN(□) and GN/HQ(■) at 150°C.

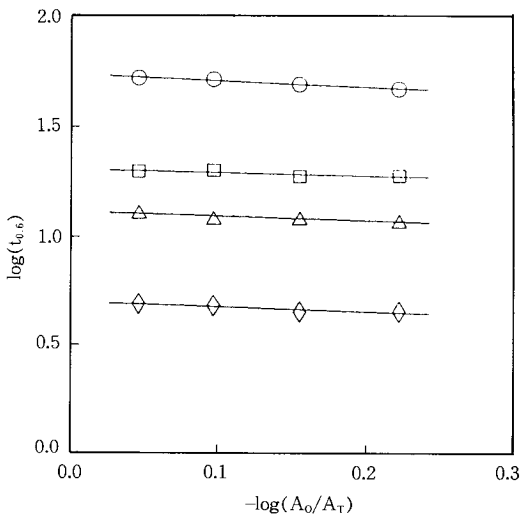


Fig. 4. Computation of reaction orders for DGEBA/MDA/GN system by Fractional life equation. (○) 85°C, (□) 105°C, (△) 120°C and (◇) 150°C.

$\log(t_{0.6})$ by Fractional life equation was shown in Fig. 4. Reaction orders were obtained from slopes, $-(n-1)$ and shown in Table 1. The values varied between 0.70~0.83.

Fig. 5 compared isothermal curing curves for

Table 1. Reaction Orders for DGEBA/MDA/GN System with and without HQ

System Temperature(°C)	DGEBA/MDA/GN	DGEBA/MDA/GN/HQ
85	0.70	0.92
105	0.83	0.89
120	0.79	0.77
150	0.77	0.90

DGEBA/DMA/GN system with those for DGEBA/MDA/GN/HQ system. As Shown in Fig. 3, cure rate for DGEBA/MDA/GN/HQ system increased with increase in cure temperature. In comparison of cure rates of two systems, that of the system with HQ was 1.8 times as fast as that of the system without HQ. Shechter et al.[6] suggested the role of hydroxyl group as a catalyst. He also found out that water, isopropanol and phenol which have hydroxyl group acted 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[6,

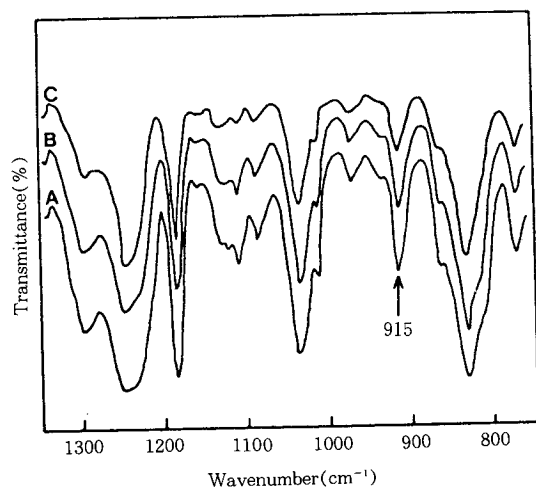


Fig. 6. FT-IR spectra of DGEBA/MDA/GN system with and without HQ. (A) DGEBA/MDA/GN system uncured, (B) DGEBA/MDA/GN system cured at 120°C for 15min, (C) DGEBA/MDA/GN/HQ system cured at 120°C for 15min.

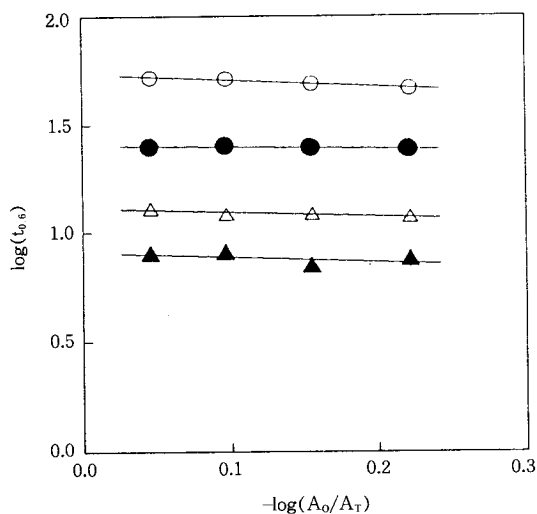


Fig. 7. Computation of reaction orders for DGEBA/MDA/GN system with and without HQ by Fractional life equation. GN(○) and GN/HQ(●) at 85°C ; GN(□) and GN/HQ(■) at 150°C.

9]. Therefore epoxide ring opened rapidly and easily

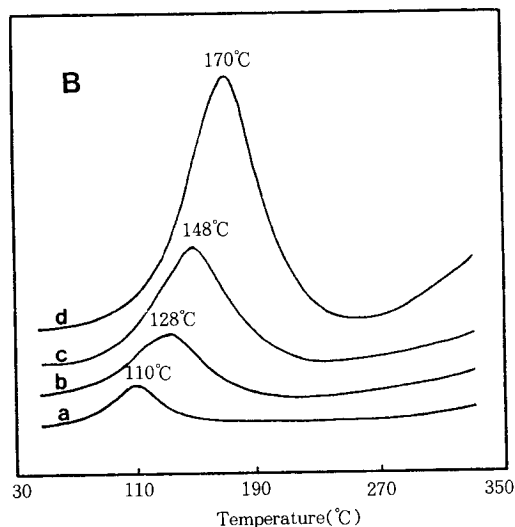
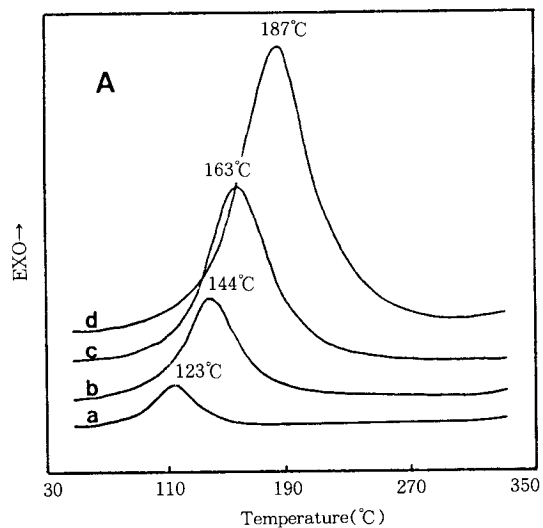


Fig. 8. DSC scans for DGEBA/MDA/GN system with(B) and without(A) HQ at different heating rates. (a) 2°C/min, (b) 5°C/min, (c) 10°C/min and (d) 20°C/min.

and cure rate increased. The role of hydroxyl group in HQ was also confirmed by FT-IR spectra. As shown in Fig. 6, epoxide band at 915cm⁻¹ was more consumed by addition of HQ.

Fig. 7 is obtained from isothermal curing curves in Fig. 5. Reaction orders could be calculated by Fractional life equation and shown in Table 1. They

Table 2. Activation Energy and Pre-exponential Factor for DGEBA/MDA/GN System with and without HQ

Contents(phr)		Activation energy(kcal/mol)	Pre-exponential factor(sec ⁻¹)
GN	HQ		
5	0	11.25	2.00 × 10 ³
5	1.25	11.08	2.78 × 10 ³
5	5	10.16	2.60 × 10 ³

varied between 0.77 and 0.92, which were about the same value for DGEBA/MDA/GN system. The observed variation of reaction orders with temperature could be due to complex reaction of epoxy resin. Some common reaction pathways proposed by previous workers were amine group-epoxide group reaction, catalytic reaction of hydroxyl group, ether linkage of epoxide group-hydroxyl group, amine group-nitrile group reaction, hydroxyl group-nitrile group reaction, etc.[10, 11]. These reactions might make certain different contributions to the total reaction. If cure temperature changed, reaction pathways would change, and so reaction orders might vary.

DSC scans for DGEBA/MDA/GN system with (B) and without(A) HQ at different heating rates are shown in Fig. 8, respectively. With the addition of HQ, exothermic peak temperature lowered about 16°C. From the relationship of heating rates g and exothermic peak temperatures, T_p by Kissinger equation, activation energy and pre-exponential factor could be calculated, and these values were listed in Table 2. Activation energy of DGEBA/MDA/GN/HQ system was a little smaller than that of DGEBA/MDA/GN system. To prove the effect of HQ, 5phr of HQ was added and its activation energy and pre-exponential factor were also listed in Table 2. In this case, activation energy decreased about 9.7%. Lower exothermal peak temperature and activation energy were explained by the formation of termolecular transition state.

4. Conclusion

From these results, the following conclusions

could be drawn.

1. As HQ introduced to DGEBA/MDA/GN system, reaction rate increased about 1.8 times.
2. With addition of HQ(5phr), activation energy decreased about 9.7% and pre-exponential factor showed a 30% increase.
3. And exothermic peak temperature lowered about 16°C. From these results, it is thought that HQ acted as a catalyst and opened the epoxide ring rapidly and easily.
4. The reaction orders for DGEBA/MDA/GN system was 0.70-0.83, and those for DGEBA/MDA/GN/HQ system varied 0.77~0.92.

Acknowledgement

This work was financially supported by Sun Kyong group.

References

1. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci.*, A-1, **8**, 1357(1970).
2. C. C. Riccardi, H. E. Adabbo, and R. J. J. Williams, *J. Appl. Polym. Sci.*, **29**, 2481(1984).
3. M. R. Keenan, *ibid.*, **33**, 1725(1987).
4. P. Peyser and W. D. Bascom, *ibid.*, **21**, 2359 (1977).
5. L. Shechter, J. Wynstra, and R. P. Kurkijy, *Ind. Eng. Chem.*, **48**, 94(1956).
6. C. S. Cherm and G. W. Poehlein, *Polym. Eng. and Sci.*, **27**, 789(1987).
7. S. N. Lee and W. B. Yuo, *ibid.*, **27**, 1317(1987).
8. R. B. Prime, "Thermal Characterization of Polymeric Materials", Ch. 5, E. A. Turi, Academic

- Press, New York(1982).
9. K. Kishore, M. Joseph, V. Dharumaraj, and M. N. Vijayshree, *J. Appl. Polym. Sci.*, **31**, 2829(1986).
 10. T. F. Saunder, M. F. Levy, and J. F. Serino, *J. Polym. Sci.*, A-1, **5**, 1609(1967).
 11. S. W. Cho, M. J. Shim, and S. W. Kim, "Computer Aided Innovation of New Materials II", 1439, North Holland(1993).