J. of Korean Ind. & Eng. Chemistry,
Vol.5, No.3, June 1994, 517-523

DGEBA-MDA-SN-Hydroxyl Group System and Composites -Cure Kinetics and Mechanism in DGEBA/MDA/SN/HQ System-

Mi-Ja Shim* and Sang-Wook Kim

Dept. of Chem. Eng., College of Eng., Seoul City Univ., Seoul 130-743, Korea
*Dept. of Life Sci., College of Liberal Arts and Natural Sci.,
Seoul City Univ., Seoul 130-743, Korea
(*Received February 26, 1994, Accepted April 29, 1994*)

DGEBA-MDA-SN-Hydroxyl계 복합재료의 제조 -DGEBA-MDA-SN-HQ계의 경화반응 속도론 및 메카니즘-

심 미 자* · 김 상 욱

서울시립대학교 공과대학 화학공학과
*서울시립대학교 문리과대학 생명과학과
(1994년 2월 26일 접수, 1994년 4월 29일 채택)

Abstract: The effects of cure kinetics and mechanism of DGEBA(diglycidyl ether of bisphenol A)/MDA(4, 4'-methylene dianiline) with SN(succinonitrile) and HQ(hydroquinone) as an additive and accelerator were investigated. Cure kinetics was evaluated by Kissinger equation and fractional-life method through DSC analysis. The activation energy and reaction order of DGEBA/MDA/SN system were showed independant on SN content. But in the case of HQ which has hydroxyl group as an accelerator, the activation energy and the starting cure-temperature were lower than those of DGEBA/MDA/SN system. Cure mechanism of those systems was investigated through FT-IR according to the various SN contents. The ratio was SN : HQ = 4 : 1. It has been known that the cure reactions of an epoxy-diamine system are composed of primary amine-epoxy reaction, secondary amine-epoxy reaction and epoxy-hydroxyl group reaction. But in DGEBA/MDA/SN system, primary amine-CN group reaction and CN group-hydroxyl group reaction were added to the above mentioned reactions. These reactions attributed to the long main chain and the low crosslinking density. And in DGEBA/MDA/SN/HQ system, hydroxyl group of HQ formed a transition state with epoxide group and amine group and also opened the ring of the epoxide group rapidly, then amine-epoxy reaction took place easily.

요 약: DGEBA(diglycidyl ether of bisphenol A)/MDA(4, 4'-methylene dianiline)/SN(succinonitrile)/HQ(hydroquinone)계의 경화반응 속도론 및 메카니즘을 연구하였다. SN과 HQ는 반응성 첨가제와 촉매로 도입하였다. 경화반응 속도론은 DSC 분석에 의해 Kissinger equation과 fractional-life법을 이용하여 연구하였다. DGEBA/MDA/SN 계의 활성화 에너지와 반응차수는 SN의 함량에 관계없이 거의 일정하였고, 촉매로써 HQ가 첨가됨으로 인해 활성화 에너지와 반응시작 온도가 낮아졌다. 이들 계의 반응 메카니즘을 고찰하기 위하여 SN의 함량에 따라 FT-IR을 측정하였다. 그리고, SN : HQ의 혼합비는 4 : 1이었다. Diamine으로 경화되는 에폭시 수지의 경화반응 메카니즘은 primary amine-epoxy 반응, secondary amine-epoxy 반응, epoxy-hydroxyl 반응이 일어나는 것으로 알려져 있다. DGEBA/MDA/SN/HQ 계에서는 HQ의 hydroxyl 기가 epoxy 및 amine과 결합하여 전이상태를 형성하여 epoxide ring을 빠르게 개환시켜줌으로써 amine-epoxy 반응이 쉽게 일어남을 알았다.

1. Introduction

Cure kinetics and mechanism of epoxy resins with amines and catalysts have been studied by many researchers[1~3]. It is very important to understand the kinetics and mechanism of cure, because the physical, mechanical and electrical properties of epoxy resins are strongly depend on its cure degree.

The curing reaction of epoxy resin is highly exothermic. Calorimetric techniques such as DSC[4~8] have been used to study cure kinetics with the assumption that the exothermic heat during the cure is proportional to the extent of monomer conversion[9~10]. Kissinger equation[5] through DSC is a dynamic run and it could be expressed;

$$-\ln(q/T_P^2) = E_a/RT_P - \ln(AR/E_a)$$

where, q : heating rate(℃/min), T_p : exothermal peak temperature(K), E_a : activation energy(cal/mol), A : pre-exponential factor, R : gas constant. Accurate activation energy and pre-exponential factor were calculated from the relationship between exothermal peak temperatures and heating rates.

Fractional-life equation[2] is

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

where, t_α: fractional-life, n : reaction order, k : rate constant, $(A)_0/(A)_T$: unreacted fraction. From the isothermal run, the reaction order can be calculated.

The cure mechanism of epoxy resin with amine has consisted of three reactions : (Ⅰ) primary amine-epoxide group(PA-E) reaction, (Ⅱ) secondary amine-epoxide group(SA-E) reaction and (Ⅲ) epoxide group-hydroxyl group(E-OH) reaction. And, hydroxyl group generated during reaction or added previously has acted as a catalyst[11~15].

In this work, the effects of SN and HQ as an additive and an accelerator on cure kinetics and mechanism of DGEBA/MDA/SN system and DGEBA/MDA/SN/HQ system were studied.

2. Experimental

2. 1. Materials

The epoxy resin of DGEBA type was Epon 828 (E. W.=184g/eq, 11,000~14,000 cP at 25℃) supplied by Shell Co.. The curing agent was MDA(4, 4′-methylene dianiline, m. p.=90℃). SN(succinonitrile, m. p.=57℃) was used as an additive and HQ (hydroquinone, m. p.=172℃) as an accelerator. MDA and SN, and HQ were supplied by Fluka Chemie. AG, and Hayashi Pure Chemical Ind. Ltd., respectively.

2. 2. Preparation of Samples

DGEBA/MDA/SN systems were prepared by mixing of DGEBA, MDA(30phr, which was larger than stoichiometric ratio, 26phr for more complete reaction), and SN of various contents. In DGEBA/MDA/SN/HQ systems, the ratio of SN : HQ was 4 : 1.

2. 3. Methods

Cure kinetics was investigated by Dynamic method (Kissinger equation) and fractional-life method. Dynamic run procedure was as follows : the well mixed sample(3.0mg) was placed in DSC container and DSC analysis was performed at heating rates of 2, 5, 10 and 20℃/min under nitrogen atmosphere of 40ml/min.

Fractional-life method was carried out as follows : the well mixed sample(2~3mg) was placed in DSC container, cured at 85, 95, 105, 120, 130 and 150℃ for required time, and quenched at -3℃ to stop the reaction instantly. The unreacted fraction was determined by dynamic run and isothermal curing curve of unreacted fraction vs. time was shown in Fig. 3.

Cure mechanisms were investigated by FT-IR spectrometry according to the various SN contents.

3. Results and Discussion

3. 1. Kinetics

DSC scans for DGEBA/MDA/SN and DGEBA/MDA/SN/HQ at various heating rates was shown in Fig. 1, respectively. In DGEBA/MDA/SN system, exothermic was appeared about 80℃ and temperatures of exothermal peak shifted to the right with raising of heating rates. In DGEBA/MDA/SN/HQ system, exothermic appeared at 55℃ and temperatures of exothermal peak had same tendency, but lowered 16℃ than DGEBA/MDA/SN system casued the role of hydroxyl group of HQ as a catalyst. Hydroxyl group forms a transition state with epoxide and amine group, and opened the epoxide ring easily and rapidly. Therefore, epoxide-amine reaction can take place at lower temperature. The mechanism for the transition state will be shown in detail later.

Table 1 was obtained from the relationship between exothermal peak temperatures and heating rates. Activation energy and pre-exponential factor could be calculated through relationship between $-\ln(1/T_P^2)$ and $1/T_P$ of Kissinger equation and shown in Fig. 2. Activation energy for DGEBA/MDA/SN was 11.48 kcal/mol and that for DGEBA/MDA/SN/HQ was 10.91 kcal/mol, the latter was a little smaller than the former. The same tendency of the other SN contents was shown in Table 2. When 5phr of HQ was added to DGEBA/MDA/SN (5phr), the activation energy decreases about 20%. It could be also explained by the role of hydroxyl group of HQ as previously stated.

Isothermal curing curves of DGEBA/MDA/SN system for the fractional-life method was illustrated in Fig. 3. The isothermal temperature range of 85~150℃ was not safficient to complete the reaction in short time, but low to detect. As shown in Fig. 3, degree of conversion at a time was proportional to cure rate and also increased with the increase of cure temperature. Cure rates for 105℃, 120℃ and 150℃ at 60% conversion are 2.4times, 6.0times and 7.6times, respectively, in comparison of that for 85℃.

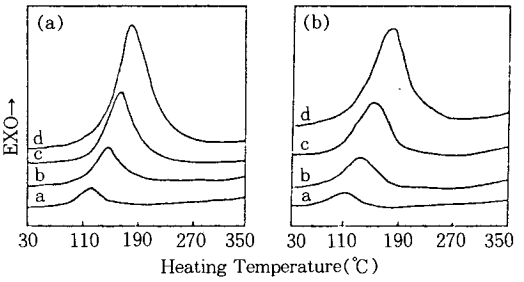


Fig. 1. DSC scans for DGEBA/MDA/SN (MDA=30phr, SN=5phr) system with(B) and without (A) HQ(1.25phr) at various heating rates : (a) 2℃/min, (b) 5℃/min, (c) 10℃/min and (d) 20℃/min.

Table 1. Data Obtained from Fig. 1 to Use Kissinger Equation

system	Heating rate, q(℃/min)	Temp. at peak, T_P(℃)	$1/T_P\times10^3$	$-\ln(q/T_p^2)$
DGEBA/MDA/SN	2	123.1	2.52	11.27
	5	146.0	2.38	10.46
	10	165.4	2.28	9.86
	20	186.2	2.17	9.26
DGEBA/MDA/SN/HQ	2	109.6	2.61	11.20
	5	128.4	2.49	10.38
	10	148.9	2.37	9.79
	20	171.5	2.25	9.20

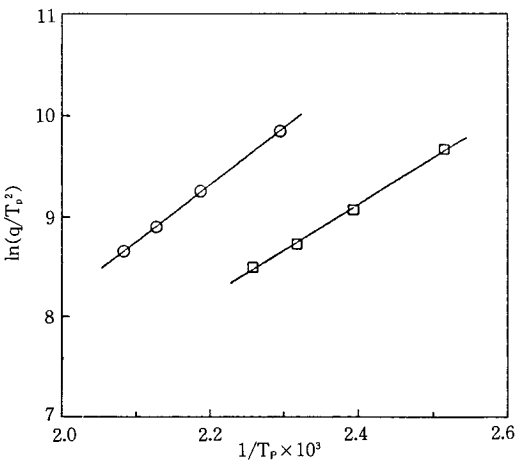


Fig. 2. Plots of $-\ln(q/T_P^2)$ vs. $(1/T_P)\times10^3$ by Kissinger equation for DGEBA/MDA/SN(5phr) with(□) and without(○) HQ(1.25phr).

Table 2. Kinetic Parameters for DGEBA/MDA/SN System with and without HQ

Contents (phr)		E_a(kcal/mol)	A(sec^{-1})
SN	HQ		
5	0	11.48	5.24×10^3
5	1.25	10.91	4.46×10^3
5	5	9.10	4.52×10^3
10	0	11.39	2.34×103
10	2.5	10.73	4.14×103
15	0	12.03	4.77×10^3
15	3.75	11.18	17.62×10^3

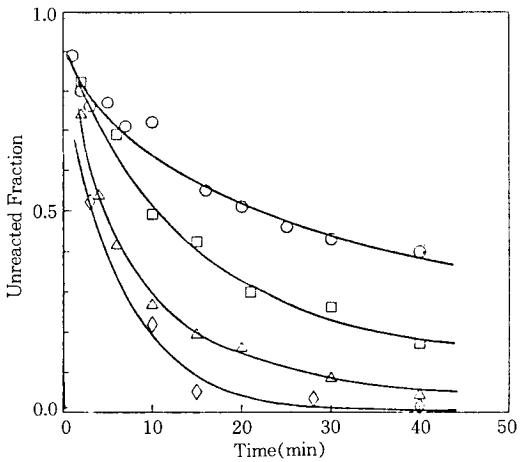


Fig. 3. Isothermal curing curves for DGEBA/MDA/SN(5phr) : (○)85℃, (□)105℃, (△)120℃ and (◇)150℃.

Table 3. Reaction Orders for DGEBA/MDA/SN (5phr) with and without HQ(1.25phr) Systems at Various Temperatures

System / Temp.(℃)	DGEBA/MDA/SN	DGEBA/MDA/SN/HQ
85	1.41	1.45
105	1.41	1.22
120	1.48	1.35
150	1.50	1.24

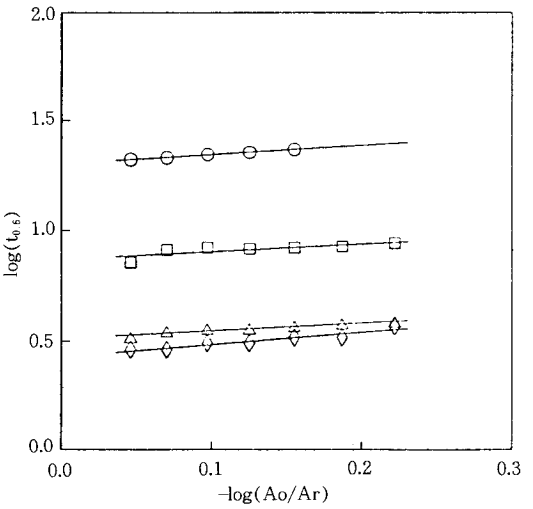


Fig. 4. Computation of reaction orders based on Fig. 3 by using fractional-life method equation : (○) 85℃, (□) 105℃, (△) 120℃ and (◇) 150℃.

Fig. 4 shows plots of log $t_{0.6}$ vs. log$\{(A)_0/(A)_T\}$ for DGEBA/MDA/SN system at various isothermal conditions and reaction orders could be obtained from the slopes [slope=-(n-1)]. The reaction orders not included in Fig. 4 were shown in Table 3. The values varied between 1.41 and 1.50 in our temperature range. Generally, reaction order is constant independent of reaction temperature. But, in this system, various reaction orders was found. The cure reaction pathways of epoxy system are mainly composed of PA-E reaction, SA-E reaction and E-OH reaction. In addition, PA-CN group reaction, amine / hydroxyl group complex formation, CN group-hydroxyl group reaction, etc. took place at the same time with the main reaction. Because above pathways acted different contributions to the total reaction at different temperatures individually, reaction orders might be various. The reaction orders which were obtained at DGEBA/MDA/SN/HQ system at various temperature were illustrated in Table 3. They varied between 1.24 and 1.45.

3. 2. Mechanism

Fig. 5 shows the FT-IR spectra of DGEBA/MDA/SN system cured for different time at 80℃, at which appearence of exothermal peak was found. In

sepctrum A, primary amine gave two sharp absorption peaks in the region of 3500~3300cm^{-1} and epoxide group gave at 915cm^{-1}. As cure reaction was proceeded, these peaks decrease and new absorption peaks occured at 1120cm^{-1} due to ether linkage and 3650~3200cm^{-1} corresponded to the overlap of secondary amine and hydroxyl group. So, the reaction (1), (2) and (3) observed in PGE (phenyl glycidyl ether) model[16] compound also occured in the system.

$$RNH_2 + C(O)CR' \longrightarrow RNHC(OH)CR' \quad (1)$$

$$RNHC(OH)CR' + C(O)CR' \longrightarrow RN(C(OH)CR')_2 \quad (2)$$

$$CR'(OH)CR' + C(O)CR' \longrightarrow CR'(OH)CR'(OC(OH)CR') \quad (3)$$

Fig. 6 showed the FT-IR spectra of DGEBA/MDA system with various SN contents at 170℃ for 1hr. As SN content increased, unreacted epoxide group has remained and intensity of ether linkage band decreased. Moreover, the band of =C=N- at 1650cm^{-1} increased. This tendency indicated that nitrile group of SN reacted with primary amine as shown in reaction (4) [16] so the ether linkage in reaction (3) has been disturbed.

$$RNH_2 + N\equiv C-CH_2- \longrightarrow RNH-C(=NH)-CH_2- \quad (4)$$

$$-CR'(OH)- + N\equiv C-CH_2- \rightarrow -CR'(O-)- \rightleftarrows -CR'(NH-)- \quad (5)$$
$$NH=C-CH_2- \qquad O=CH_2-$$

The reaction of nitrile and hydroxyl group could made imino group(-C(=NH)-O-) or amide group (-C(=O)-NH-) in reaction (5) [16]. As shown in Fig. 6 the absorption band of =C=O at 1750cm^{-1} increased because more amide group was produced than imino group.

Effect of HQ as a catalyst was shown in Fig. 7. Epoxide group of (B) is consumed more than that

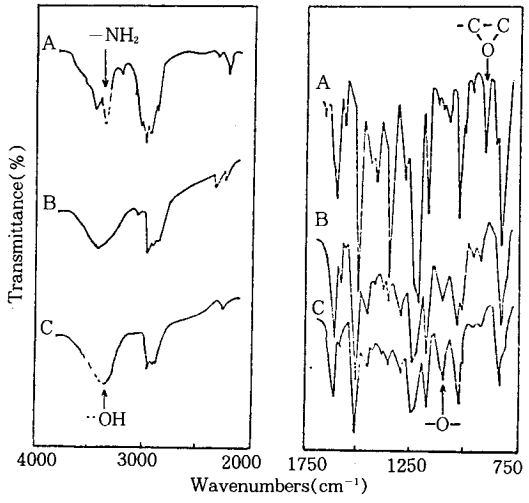


Fig. 5. FT-IR spectra of DGEBA/MDA/SN(15phr) system : (A) uncured, (B) cured at 80℃ for 1hr, (C) cured at 80℃ for 2hr.

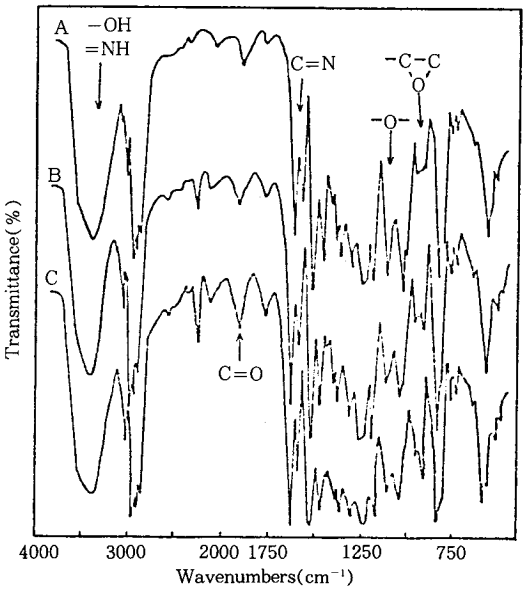


Fig. 6. FT-IR spectra of DGEBA/MDA/SN system cured at 170℃ for 1hr SN : (A) 0phr, (B) 10phr, (C) 15phr.

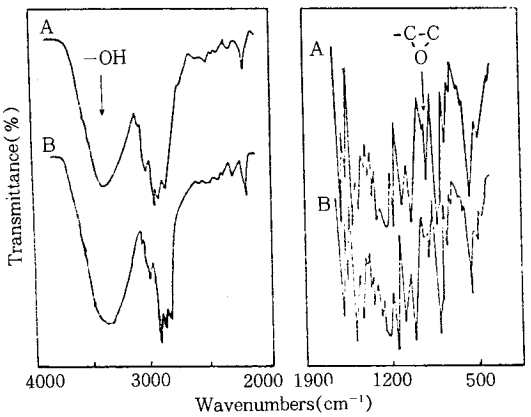
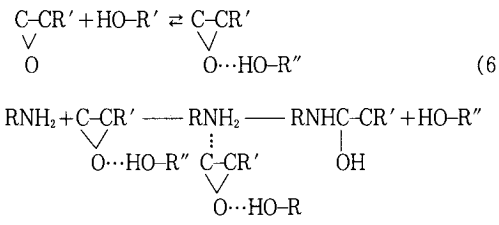


Fig. 7. FT-IR spectra of DGEBA/MDA/SN(15phr) system with(B) or without(A) HQ(3.75phr) cured at 80℃ for 1hr.

of (A), but hydroxyl group of (B) is produced more than that of (A). This proves that the added hydroxyl group of HQ contributes to the consumption of epoxide group. Chapman and Parker[15] proposed the mechanism of hydroxyl group as a catalyst. Hydroxyl group of HQ formed a transition state with epoxide group and opened the ring of the epoxide group(reaction (6)) rapidly, lead to easy amino-epoxy reaction.



(6)

4. Conclusion

The activation energy and starting cure-temperature of DGEBA/MDA/SN/HQ system was lower than those of DGEBA/MDA/SN. The activation energy of DGEBA/MDA/SN was about 11.6kcal/mol and starting cure-temperature was 80℃. Those values are almost constant independent of the SN contents. For DGEBA/MDA/SN system with HQ as a catalyst, the activation energy is 10.9kcal/mol and starting cure-temperature is about 55℃. So, HQ can be used as an accelerator. Reaction orders of DGEBA/MDA/SN system vary between 1.41~1.50, and those of DGEBA/MDA/SN/HQ system vary between 1.24~1.45.

Cure mechanism of DGEBA/MDA/SN system are mainly composed of PA-E reaction, SA-E reaction, ether linkage. And, PA-CN group reaction and CN group-hydroxyl group reaction take place, making the main chain length longer and crosslinking density lower. For the DGEBA/MDA/SN/HQ system, a transition state of hydroxyl group as a catalyst occurs besides the reactions of DGEBA/MDA/SN system.

Acknowledgement

This work was supported by the Korean Ministry of Education Research Fund for Advanced Materials in 1993.

References

1. D. L. Hunston, *Tech. Rev.*, **6**, 176 (1984).
2. S. N. Lee and W. B. Yuo, *Polym. Eng. Sci.*, **27**, 1317 (1987).
3. P. Peyser and W. D. Bascom, *J. Appl. Polym. Sci.*, **21**, 2359 (1977).
4. A. Sabra, J. P. Pascault, and G. Seytre, *ibid.*, **32**, 5147 (1986).
5. R. B. Prime, Thermal Characterization of Polymeric Mateials, E. A. Turi, ed., Academic Press, Chap. 5., New York, (1982).
6. J. V. Duffy, E. Hui, and B. Hattmann, *J. Appl. Polym. Sci.*, **33**, 2959 (1987).
7. M. R. Keenan, *ibid.*, **33**, 1725 (1987).
8. C. C. Riccardi, H. E. Adabbo, and R. R., *J. Williams, ibid.*, **29**, 2481 (1984).
9. H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).
10. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci.*, A-1, **8**, 2839 (1970).
11. S. W. Cho, M. J. Shim, and S. W. Kim, Comput-

er Aided Innovation of New Materials II, 1439, North-Holland (1993).
12. G. D. Diana, E. S. Zalay, and R. A. Cutler, *J. Org. Chem.*, **30**, 298 (1965).
13. U. M. Bokare and K. S. Gandhi, *J. Polym. Sci.*, **18**, 857 (1980).
14. C. S. Chern and G. W. Poehlein, *Polym. Eng. Sci.*, **27**, 788 (1987).
15. N. B. Chapmann and R. E. Parker, *J. Chem. Sci.*, **2**, 1925 (1959).
16. T. F. Saunder, M. F. Levy, and J. F. Serino, *J. Polym. Sci.*, A-1, **5**, 1609 (1967).