

Cure Mechanism of DGEBA/MDA/SN System

Mi-Ja Shim* and Sang-Wook Kim

*Dept. of Chemical Engineering, * Division of Liberal Arts, Seoul City University, Seoul 130-743, Korea*

Abstract : To modify the toughness of epoxy for matrix, succinonitrile(SN) was introduced to diglycidyl ether of bisphenol-A (DGEBA)/methylene dianiline(MDA) system. Cure reaction mechanism of the DGEBA/MDA/SN system was studied through Fourier transform infrared(FT-IR) spectrometry. As a result, the reaction of nitrile group of SN with secondary amine and with hydroxyl group prevented the reaction of hydroxyl groups with epoxide group from crosslinking. Nitrile groups produced amide group by reacting with hydroxyl groups and made a lowered crosslink density in chain networks.

1. Introduction

The reaction of epoxy with curing agent makes three dimensional network.^{1,2)} The epoxy is applied in various fields because it can react with many compounds in variety. Such diverse applications are aircraft component, automotive component, boats, building products, etc.^{3,4)} However, generally the epoxy cured has a fault: brittleness of high crosslink density causes a resin matrix to get bent and break in composite materials. To solve such problems many scientists have studied^{5~8)} and improved physical properties using many methods.^{4~11)} Previous studies generally were included adding a copolymer or modified hardners.

This study deals with the effect of reactive additives on cure mechanism and on the toughness of a epoxy matrix.

2. EXPERIMENTAL

2.1. Material

The bisphenol-A based epoxy resin (DGEBA), Epon 828 supplied by Shell Co. was used for epoxy system. The resin had epoxy equivalent weight of 184g/eq. The viscosity ranged 11,000-14,000 cps at the room temperature. The curing agent of aromatic diamine, 4,4'-methylene dianiline(MDA) was

supplied by Fluka Chemie AG. Succinonitrile (SN) supplied by Fluka Chemie AG was used as the reactive additive in this epoxy system.

2.2. Preparation of samples and methods for measurement

The exothermal behavior of cure was investigated through the dynamic run method¹²⁾ which analyzed the effect of the heating rate on the temperature at maximum reaction rate by Differential Scanning Calorimetry(DSC).

DGEBA, 30 parts per hundred parts of resin (phr) of MDA more than stoichiometry ratio (26phr) for more complete reaction and SN were mixed up at 80°C and cured for 1hr in the film type for FT-IR spectrometry according to SN content.

3. RESULTS AND DISCUSSION

It was reported in the DGEBA/MDA system that active hydrogen of amino groups caused to cleave epoxide groups producing hydroxyl groups and hydroxyl groups reacted with another epoxide groups resulting in the ether crosslinking. It was known that the reaction of secondary amine with another epoxide groups mainly produced tertiary amines to catalyze further reactions in high temperature of about 200°C²⁾ Beside these three reactions, two reactions in the DGEBA/MDA system with SN can be considered : (1) the reaction of nitrile

groups of SN with secondary amine which may or may not react with epoxide groups and (2) the reaction of nitrile groups with hydroxyl groups.

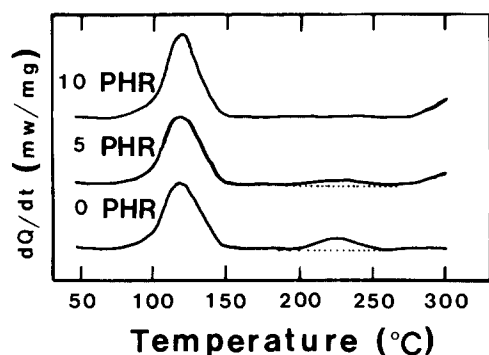
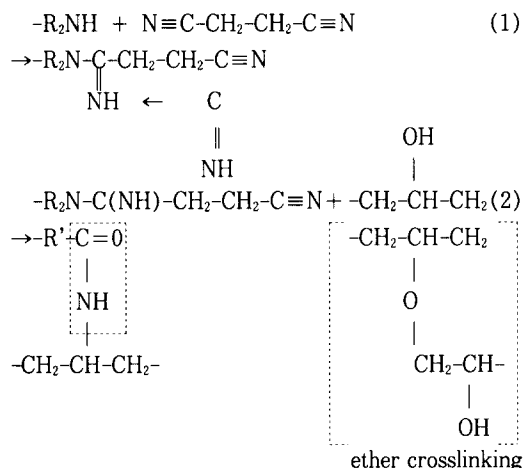


Fig. 1. DSC scans of DGEBA/MDA system with SN and without SN by 2°C/min.

Figure 1 shows the thermograms of the DGEBA/MDA system and the DGEBA/MDA/SN system (5 and 10phr of SN). In the DGEBA/MDA system, the first cure exothermic peak was appeared in the range of 80°C and 150°C, and the second cure exothermic peak was appeared in the range of 200°C and 250°C. In contrast, for the DGEBA/MDA/SN system the first peak is almost the same as in the DGEBA/MDA system but the second exothermic peak was disappeared. It is observed that SN prevents the reaction of secondary amine with epoxide groups from crosslinking

to increase the crosslink density at near 200°C.

As can be seen from Figure 2 and Figure 3, A_{830} (absorbance of p-phenylene at 830 cm^{-1}) was constant for every samples within a experimental error range.¹³⁾ Thus the peak at 830 cm^{-1} was taken as an internal standard for relative intensity. The relative intensity, A_{3300} (absorbance of NH₂ stretching)/ A_{830} decreases but A_{915} (absorbance of epoxide)/ A_{830} is almost constant in the FT-IR spectra of uncured samples with increasing SN.

As the reactivity of nitrile groups was confirmed previously,^{12,14,15)} It can be considered that nitrile groups of SN react with secondary amine in eq.(1)

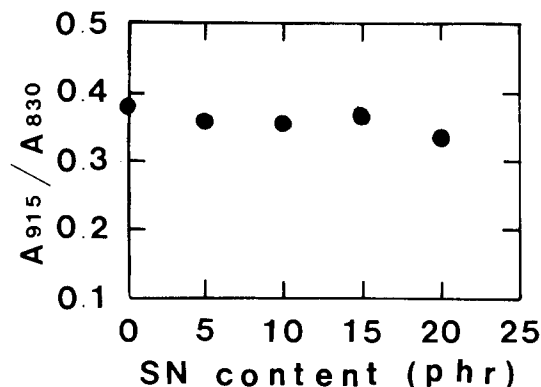


Fig. 2. The relative intensity of epoxide and primary amine for the DGEBA/MDA system with SN.

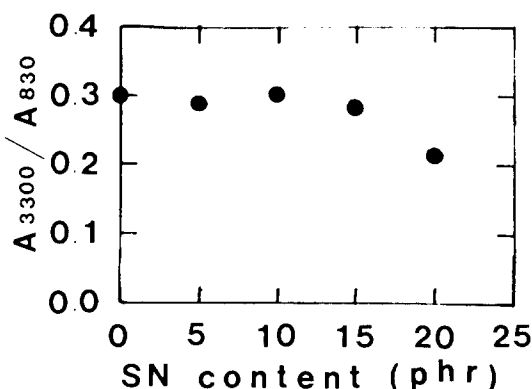


Fig. 3. The relative intensity of epoxide and primary amine for the DGEBA/MDA system without SN.

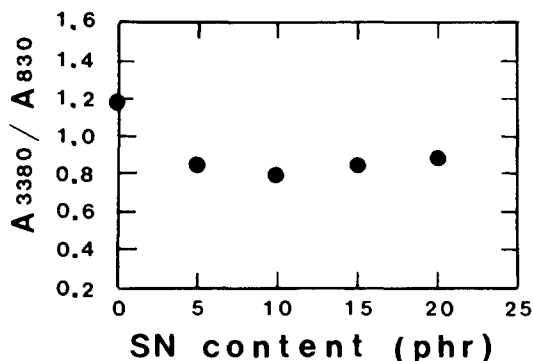


Fig. 4. The relative intensity of the hydroxyl and the aliphatic ether for the DGEBA/MDA system with SN.

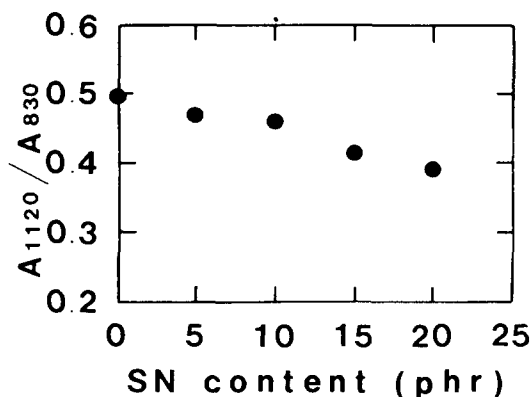


Fig. 5. The relative intensity of the hydroxyl and the aliphatic ether for the DGEBA/MDA system without SN.

selectively to extend a molecular length.

The FT-IR spectra of the samples cured at 110°C show that the reactive intensity (Fig.4, Fig.5) of A_{3380} (absorbance of OH stretch)/ A_{830} and A_{1120} (absorbance of aliphatic ether)/ A_{830} are decreased with increasing SN. It is observed that consumption of hydroxyl groups is not due to reacting with nitrile groups of SN as shown in eq.(2). Since A_{1120} resulted from the reaction of hydroxyl groups with epoxide groups, ether crosslinkage decreases with SN ratios.

In this meaning, it is considered that the addition of SN makes a chain bond length

longer and crosslink density lower. As reported previously, the reactions of epoxy resin with MDA take place at first in the DGEBA/MDA/SN system. It can be deduced that (1) the reaction of nitrile groups with secondary amine makes a chain bond length longer and (2) the reaction of nitrile groups with hydroxyl groups produce amide group among the molecular chains resulting in a decrease of the crosslink density.

4. CONCLUSION

In order to improve the toughness of the epoxy, SN is added to the DGEBA/MDA system. The cure reaction mechanism of the DGEBA/MDA/SN system was following three reactions, namely, the reaction of the primary amine of MDA with epoxide group, secondary amine with another epoxide groups, and the hydroxyl groups with another epoxide groups. In addition, nitrile groups of SN reacted with secondary amine groups and with hydroxyl groups. Consequently nitrile groups of SN made a bond length longer between chains in crosslinking networks and reduced the crosslink density. Thus, we can expect to improve the toughness of epoxy with SN for matrix.¹⁶⁾

Acknowledgement

This work was supported by the Sun Kyong Group

REFERENCES

1. R.S. Bauer(ed.), Epoxy Resin Chemistry I, American Chemical Society (1979)
2. H. Lee and K. Neville(eds.), Handbook of Epoxy Resins, America, New York(1967)
3. L.T. Manzione, J.K. Gillham and C.A. McPherson, J.Appl. Polym. Sci., **26**, 889 (1981)
4. L.C. Chan, H.N. Nae and J.K. Gillham, J. Appl. Polym. Sci., **29**, 3307 (1981)
5. Carrillo, Newell, Brown and Phelan(eds.), Material pathway to the future, America,

- California(1988)
6. D.L. Hunston, Tech. Rev., **6**, 176 (1984)
 7. M.R. Piggott and B.J. Harris, J. Mater. Sci., **15**, 2523 (1980)
 8. M. Woo and M.R. Piggott, J. Comp. Tech. Res., **9**, 101 (1987)
 9. S.N. Lee and W.B. Yuo, Polym. Eng. Sic., **27**, 17 (1987)
 10. R.E. Smith and C.H. Smith, J. Appl. Polym. Sci., **31**, 929 (1986)
 11. M. Ito, H. Hata and K. Kamagata, J. Appl. Polym. Sci., **33**, 1843 (1987)
 12. T.F. Saunder, M.F. Levy and J.F. Serino, J. Polym. Sci., **A-15**, 1609 (1967)
 13. S.C. Lin, B.J. Bulkin and E.M. Pearce, J. Polym. Sci., **17**, 3121 (1979)
 14. G.D. Diana, E.S. Zalay and R.A. Cutler, J. Org. Chem., **30**, 298 (1965)
 15. Yu. I. Mushkin and A.I. Finkel'shein, Zh. Org. Khim., **1**, 721 (1965)
 16. S.W. Cho, M.J. Shim and S.W. Kim, J. Korean Mater. Res., **2**, 191 (1992)