

# Characteristics of Crosslinked Resin Modified with Nitriles

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니트릴에 의해 개질된 가교구조 수지의 특성

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**초 록** 에폭시 수지를 개질하여 의료용 고분자 재료로 활용하기 위해 우선 diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA)/nitrile (MN, SN, GN) 계의 경화반응 메커니즘과 속도를 FT-IR과 DSC를 이용하여 연구하였다. DGEBA/MDA 계에 nitrile이 첨가됨으로 인해 일차아민과 니트릴기의 반응 및 수산기와 니트릴기가 반응함으로써 사슬의 길이가 확장된 그물구조가 생성되었다. 이것은 nitrile 화합물의 함량이 증가함에 따라  $T_g$ 가 감소하고, 충격강도가 증가하는 것으로부터 간접적으로 확인할 수 있었다. 일차아민과 니트릴기의 반응에 의해 DGEBA/MDA 계의 경화반응이 방해받기 때문에 니트릴 화합물의 함량이 증가함에 따라 경화반응 속도는 느려졌다.

**Abstract** The cure mechanism and cure kinetics of diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA)/nitrile(MN, SN, GN) systems were studied by FT-IR and DSC to develop new applications in the biomedical polymer fields. The network structure of the DGEBA/MDA system was changed to the chain-extended network structure by the addition of nitriles. The reactions contributed to the chain extension were the primary amine-nitrile and hydroxyl-nitrile reactions. The chain-extended network structure could be indirectly proved by the decrement of  $T_g$  and the increment of impact strength with the increasing nitrile content. The cure rate of DGEBA/MDA/nitrile system was lower than that of DGEBA/MDA system due to the disturbance of nitrile group in the reaction of primary amine and epoxide groups.

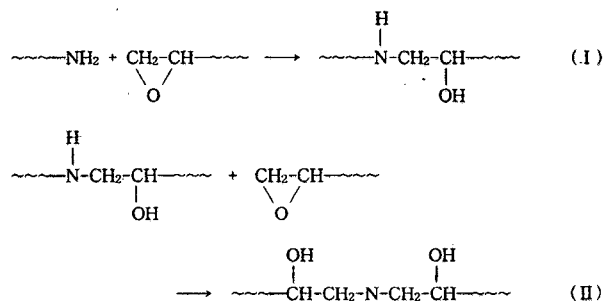
## 1. Introduction

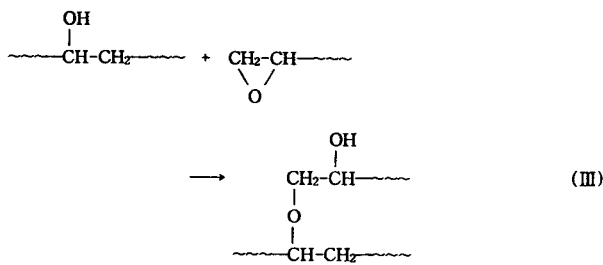
In recent, various polymers have been applied to the biomedical materials. Polyurethane is used for the catheters and blood contacting surfaces and polyformaldehyde is for the heart valve stents/orthopedics. Polyamides are applied to the membranes and sutures and thermoplastic elastomers are used for the catheters. With the more demands for the biomaterials, the more kinds of polymers should be developed and modified and they must function in a range of environments that require corrosion resistance, ultraclean manufacturing, and often surface modification to enhance biocompatibility.<sup>1~3)</sup>

Epoxy resins are used in the fields of adhesives, coatings, electrical insulators, encapsulants, structural applications, automobiles, aircrafts, etc. and many researchers have investigated to develop new epoxy resins of high performance.<sup>4~9)</sup> To improve the mechanical, thermal and electrical properties, epoxy resins or/and curing agents are modified by the following methods; (1) introduction of reactive additives, (2) incorpo-

ration of reactive liquid rubbers, and (3) mixing with different epoxy resin and curing agent. In this study, epoxy resin was modified by the first method to give them the good application for biomaterial. The reactive additives were malononitrile (MN), succinonitrile (SN) and glutaronitrile (GN).

It has been well known that the sequence of cure reactions for epoxy/amine system is as follows; (I) the reaction of epoxide group with primary amine, (II) that of epoxide group with secondary amine and (III) that of epoxide group with hydroxyl group.<sup>10~12)</sup>





A hydroxyl group generated in the reactions (I) and (II) served as a catalyst for other reactions (I) and (II). For this reason, the curing of epoxy resin with amine system is called autocatalytic reaction. These reactions happened competitively in series, so it is very difficult to interpret the cure kinetics of epoxy/amine system.

Kissinger equation was used to investigate the cure kinetics.<sup>13,14)</sup>

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

where,  $q$  is the heating rate,  $T_p$ , the temperature at which maximum peak value took place,  $E_a$ , activation energy,  $A$ , pre-exponential factor and  $R$ , gas constant. From the relationship of  $T_p$  vs.  $q$ ,  $E_a$  and  $A$  can be obtained easily.  $T_p$  and  $q$  were obtained from the data of dynamic DSC run with the assumption that the exothermic heat evolved during the cure was proportional to the extent of monomer conversion.

## 2. Experiment

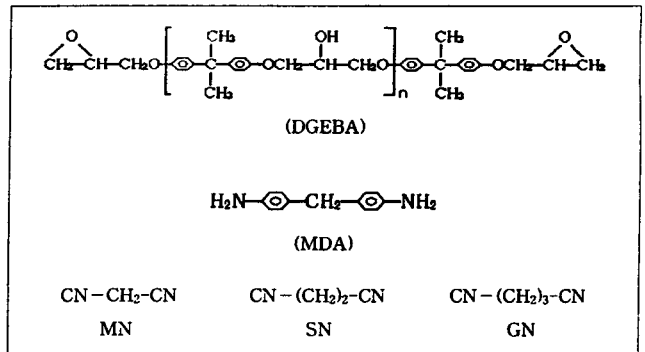
The structural formulae of diglycidyl ether of bisphenol A (DGEBA, Epon 828, Shell Co.), 4,4'-methylene dianiline (MDA), malononitrile (MN), succinonitrile (SN) and glutaronitrile (GN) were shown in Scheme 1. The MDA, MN, SN, GN were supplied by Fluka Chemie AG.

DGEBA as a base resin was cured with MDA and the nitrile compounds were used as reactive additives. Samples were prepared by mixing of DGEBA, MDA (30 phr) and nitriles. (0, 5, 10, 15 and 20 phr).

Cure mechanism was investigated by FT-IR (Shimadzu, Japan) at the range of 400~4,000  $\text{cm}^{-1}$ . Well-mixed samples were cured at 80~120°C for various time and the characteristic peaks of functional groups were traced.

To study the cure kinetics, dynamic DSC analysis was carried out at the heating rates of 2, 5, 10 and 20 °C/min under the nitrogen atmosphere of 40 ml/min.<sup>15,16)</sup>

$T_g$  was measured by DSC analysis at the heating rate



Scheme 1. The Structural Formulae of the Materials.

of 10 °C/min.

## 3. Results and Discussion

It has been well-known that *p*-phenylene group does not take part in the chemical reaction during the cure of each sample, so the peak of *p*-phenylene at 830  $\text{cm}^{-1}$  is taken as a standard within the experimental error range in order to estimate the relative intensities for other characteristic peaks. Fig.1 shows the increase and

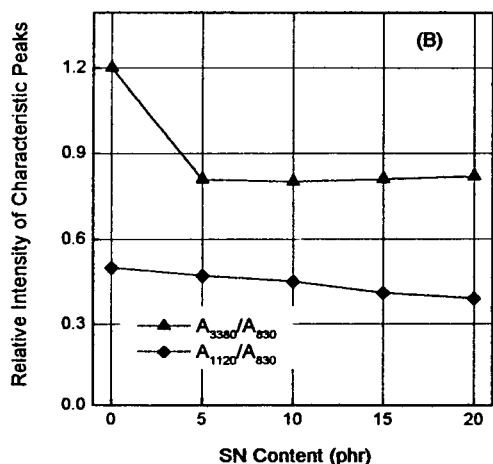
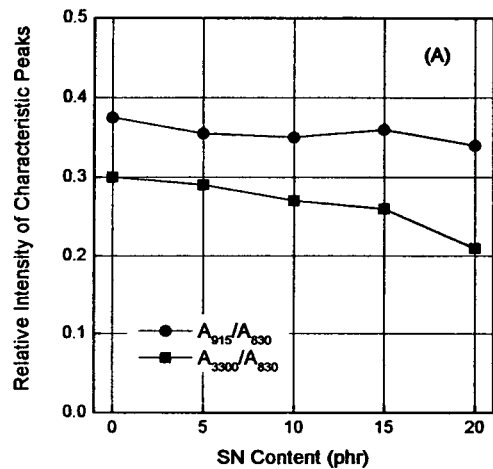
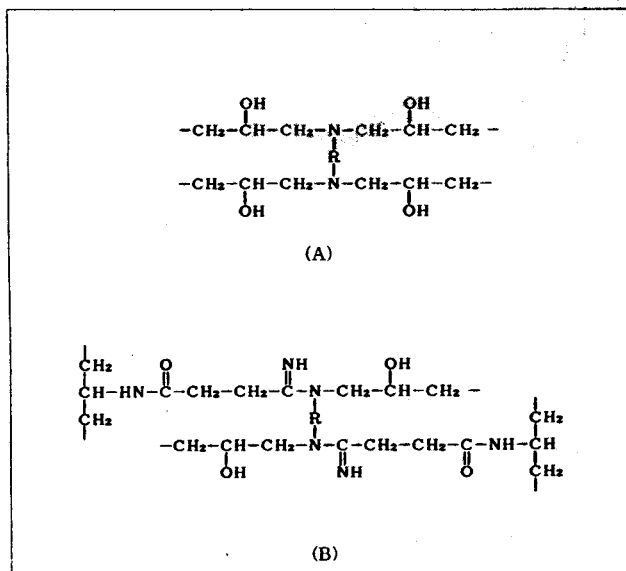


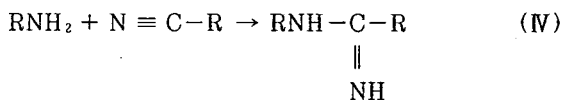
Fig. 1. FT-IR spectra for the DGEBA/MDA/SN system (A) cured at 80°C for 30 min and (B) cured at 110°C for 1 hr



Scheme 2. The network structure of the DGEBA/MDA system (A) and the chain-extended network structure (B) by the addition of SN.

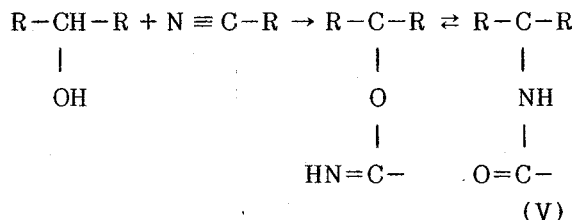
decrease of the FT-IR characteristic peaks for the functional groups participated in cure reaction. Fig. 1 (A) is for the little cured samples in the initial stage which are cured at 80°C for 30 min and Fig. 1 (B) is for the almost cured samples in the final stage which are cured at 110°C for 1 hr.

In the initial stage of the cure reaction in DGEBA/MDA system without SN, the primary amine is reacted with epoxide group by the following mechanism (I) of the introduction section. This means that the intensities of the characteristic peaks for primary amine at 3300 cm<sup>-1</sup> and epoxide group at 915 cm<sup>-1</sup> should decrease. However, in the case of DGEBA/MDA system with SN, the intensity of primary amine decreased, but that of epoxide group was almost constant. It was due to the following reaction between primary amine and nitrile.<sup>13)</sup>



In the final stage of the cure reaction in DGEBA/MDA system without SN, the hydroxyl group is reacted with epoxide group to form ether linkage by the following mechanism (III) of the introduction section. This means that the intensity of the characteristic peak for hydroxyl group at 3380 cm<sup>-1</sup> should decrease in the final stage and that for ether linkage at 1120 cm<sup>-1</sup> should increase. However, the intensity of ether linkage decreased with the increasing SN content and it was

due to the reaction of hydroxyl and nitrile groups. This reaction was expressed as follows.<sup>13)</sup>



From the results of the mechanism (IV) and (V), the network structure of the DGEBA/MDA system [Scheme 2(A)] was changed to chain-extended network structure [Scheme 2(B)] by the addition of SN. These mechanisms were also applied to the system with other nitriles.

The chain-extended network structure could be indirectly proved by the decrement of T<sub>g</sub> and the increment of impact strength with the increasing nitrile content as shown in Fig. 2 and 3.

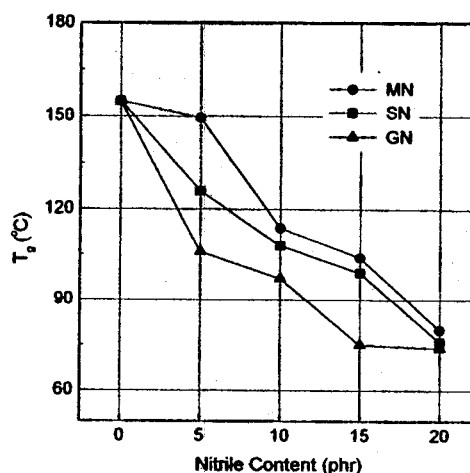


Fig. 2. Decrement of T<sub>g</sub> with the increment of nitrile content.

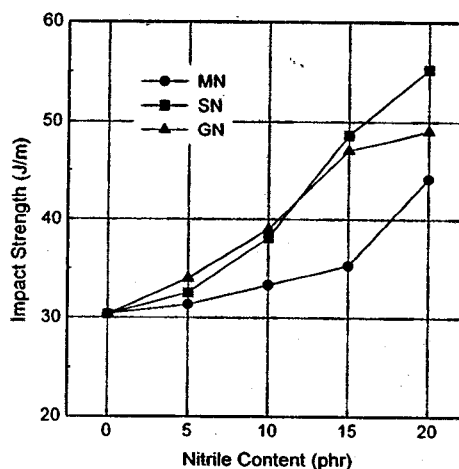


Fig. 3. Increment of impact strength with the increment of nitrile content.

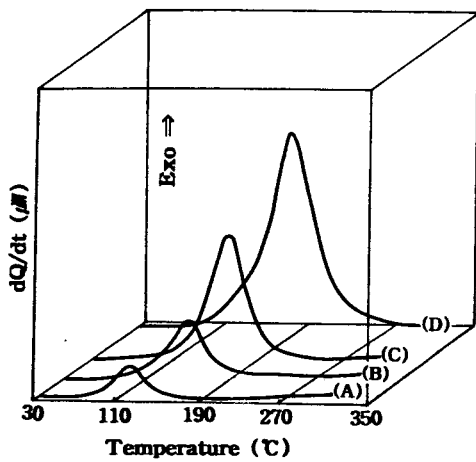


Fig. 4. DSC curves for DGEBA/MDA system at the different heating rates heating rates; (A) 2 $^{\circ}C/min$ , (B) 5 $^{\circ}C/min$ , (C) 10 $^{\circ}C/min$  and (D) 20 $^{\circ}C/min$ .

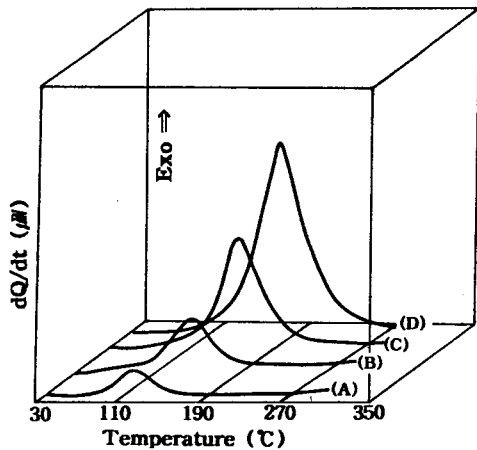


Fig. 5. DSC curves for DGEBA/MDA system with 5 phr of SN heating rates; (A) 2 $^{\circ}C/min$ , (B) 5 $^{\circ}C/min$ , (C) 10 $^{\circ}C/min$  and (D) 20 $^{\circ}C/min$ .

Fig. 4 shows the DSC curves for DGEBA/MDA system from 30 $^{\circ}C$  to 350 $^{\circ}C$  at four different heating rates. Each cure curve shows only one exothermic peak regardless of the heating rate and the temperature,  $T_p$ , at which the maximum peak value appears increases with increasing heating rate. Fig.5 shows the DSC curves for DGEBA/MDA system with 5 phr of SN at 2, 5, 10 and 20  $^{\circ}C/min$ . These curves also show only one exothermic peak regardless of the heating rate and  $T_p$  value increases with increasing heating rate. The only one  $T_p$  meant that the cure mechanisms (I ~ III) for DGEBA/MDA system and the mechanisms (I ~ V) for the system with nitriles took place competitively and serially in one stage.

To get the activation energies and the pre-exponential factors for two systems, the heating rate,  $q$  vs. the temperature,  $T_p$  was plotted in Fig. 6.  $T_p$  values of DGEBA/MDA/SN system were higher about 4 $^{\circ}C$  than those of DGEBA/MDA system without SN. This was

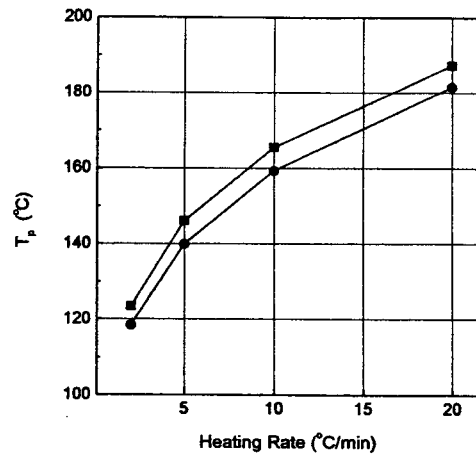


Fig. 6.  $T_p$  values at the different heating rates for DGEBA/MDA system with(■) and without(●) SN (5 phr).

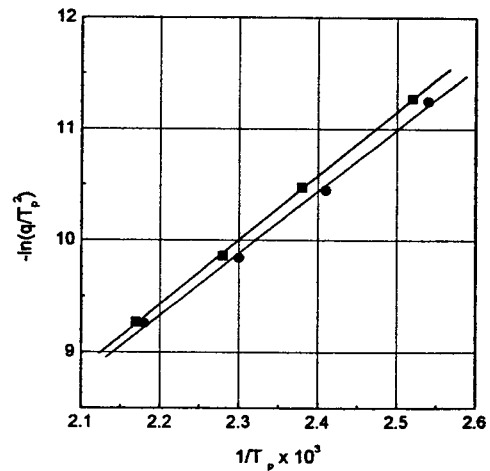


Fig. 7. Kissinger plots for DGEBA/MDA system with(■) and without(●) SN (5 phr).

due to the disturbance of the cure reaction by SN.  $1/T_p$  and  $-\ln(q/T_p^2)$  were obtained from Fig. 6 and listed in Table 1. The Kissinger plots were illustrated in Fig. 7 and the linear equations were as follows.

$$-\ln(q/T_p^2) = 5.535 \times 10^3 \cdot 1/T_p - 2.849$$

for DGEBA/MDA system

$$-\ln(q/T_p^2) = 5.747 \times 10^3 \cdot 1/T_p - 3.218$$

for DGEBA/MDA/SN system

The activation energy could be calculated from the slope and the pre-exponential factor from the intersection. The activation energy and pre-exponential factor for DGEBA/MDA system were 46.02 kJ/mol and  $1.59 \times 10^3 \text{ sec}^{-1}$ , and those values for DGEBA/MDA/SN system were 47.78 kJ/mol and  $2.39 \times 10^3 \text{ sec}^{-1}$ .

Fig. 8 shows the DSC curves for DGEBA/MDA systems with MN, SN and GN at the heating rate of 10  $^{\circ}C/min$ .  $T_p$  value of DGEBA/MDA system appeared at a higher temperature than those of the system with ni-

Table 1. The Relationship of  $1/T_p \times 10^3$  vs.  $-\ln(q/T_p^2)$ .

System	$1/T_p \times 10^3$	$-\ln(q/T_p^2)$
DGEBA/MDA	2.54	11.25
	2.41	10.45
	2.30	9.84
	2.18	9.26
DGEBA/MDA/SN	2.52	11.27
	2.38	10.47
	2.28	9.86
	2.17	9.27

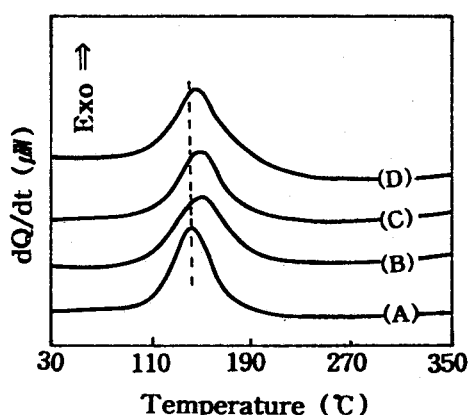


Fig. 8. DSC curves for DGEBA/MDA system with 5 phr of nitriles at 10°C/min, (A) DGEBA/MDA, (B) DGEBA/MDA/MN, (C) DGEBA/MDA/SN and (D) DGEBA/MDA/GN

Table 2. Activation Energies and Pre-exponential Factors for DGEBA/MDA System with Various Contents of Nitriles.

System	Nitrile Content (phr)	Activation Energy (kJ/mol)	Pre-exponential factor (sec <sup>-1</sup> )
DGEBA/MDA	0	46.02	$1.59 \times 10^3$
DGEBA/MDA/MN	5	47.65	$2.95 \times 10^3$
	10	48.74	$2.72 \times 10^3$
	15	49.74	$3.27 \times 10^3$
DGEBA/MDA/SN	5	47.78	$2.39 \times 10^3$
	10	48.69	$2.34 \times 10^3$
	15	50.37	$4.77 \times 10^3$
DGEBA/MDA/GN	5	47.40	$2.00 \times 10^3$
	10	48.74	$3.17 \times 10^3$
	15	49.74	$4.20 \times 10^3$

trile compounds.

Activation energies and pre-exponential factors for the DGEBA/MDA system with various contents of nitriles were also calculated by the Kissinger equation and these values were listed in Table 2. The activation energy increased with the introduction of nitrile compounds.

The results of the increasing  $T_p$  value and activation energy with the incorporation of nitrile compounds implied that the cure reaction of DGEBA/MDA/nitrile

system was more difficult and needed more energy than that of DGEBA/MDA system. It was due to the disturbance of nitrile group in the reaction of primary amine and epoxide groups.

#### 4. Conclusions

The network structure of the DGEBA/MDA system was changed to the chain-extended network structure of DGEBA/MDA/nitrile systems by the reactions of primary amine-nitrile groups and hydroxyl-nitrile groups. The chain-extended network structure could be indirectly proved by the decrement of  $T_g$  and the increment of impact strength with the increasing nitrile content. The cure rate of DGEBA/MDA/nitrile system was lower than that of DGEBA/MDA system due to the disturbance of nitrile group in the reaction of primary amine and epoxide groups.

#### Acknowledgement

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