

2 관능성/4 관능성 에폭시 블렌드의 기계적 특성

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Mechanical Properties of Bifunctional/Tetrafunctional Epoxy Blends

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요 약 : Diglycidyl ether of bisphenol A(DGEBA)와 4,4'-tetraglycidyl diaminodiphenyl methane(TG-DDM)으로 구성된 에폭시 블렌드를 여섯가지 각기 다른 조성을 갖도록 배합하여 각기 다른 다섯 가지 경화조건을 이용하여 경화시켰다. 에폭시 블렌드의 경화를 위하여 당량비 만큼의 diaminodiphenyl methane(DDM)을 경화제로 첨가하였다. 에폭시 블렌드의 조성변화에 따른 유리전이 온도의 변화를 differential scanning calorimeter(DSC)를 이용하여 측정하였다. 에폭시 블렌드의 조성에 따른 밀도의 변화가 관찰되었다. 경화된 에폭시 블렌드의 인장강도 및 충격강도에 미치는 블렌드의 조성 및 경화조건변화의 영향이 관찰되었다. 충격 강도 시험에 의해 생긴 에폭시 블렌드의 파단면을 관찰하기 위하여 광학 현미경을 이용하였다.

Abstract : Epoxy/epoxy blends composed of diglycidyl ether of bisphenol A(DBGBA) and 4,4'-tetraglycidyl diaminodiphenyl methane(TGDDM) were formulated with six different blend compositions and cured under five different cure conditions. Stoichiometric amount of diaminodiphenyl methane (DDM) was used to cure the epoxy blends. Glass transition temperatures of the epoxy blends were measured using a DSC(differential scanning calorimeter). Density change with blend compositions was investigated. Effects of blend compositions and cure conditions on the tensile and impact strength of the cured epoxy/epoxy blend were investigated.

INTRODUCTION

Among several thermosetting polymers, epoxy resins are the largest segments of addition cured thermosetting polymers which are used to make structural composites in the aerospace industry. Epoxy resins have been also used as a supporting material for printed circuit boards because they have good thermal and electrical properties. The application areas of epoxy resins are wide because they are easy to handle and process and have reasonable thermal and mechanical properties. The problem with epoxy is that their upper tempera-

ture limit for structural performance is not so high and their low impact and fracture toughness.

Modification of epoxy resins has been carried out to improve the impact strength of cured epoxy parts by incorporating thermoplastic polymers,^{1~2} especially such as the low molecular weight liquid rubbers(ATBN, CTBN)^{3~5} and poly(ethylene oxide).⁶ The impact strength of an epoxy system composed of diglycidylether of bisphenol A (DGEBA) and triethylenetetramine(TETA) was considerably increased by adding the liquid rubbers(ATBN and CTBN).^{5~7} The toughness of epoxy system could be also improved by disper-

sing a lot of small rigid domains into the epoxy matrices because the microdomains dispersed in the epoxy matrices would change the fracture mechanism.⁸

In order to modify properties of thermosetting polymers, thermoset-thermoset blend systems have been also studied. For example, bismaleimide-triazine(biscyanate)(BT) type resins were developed for laminating application. Gotro et al.⁹ carried out a characterization study of a bismaleimide/biscyanate/epoxy thermoset blend for printed circuit board applications. Instead of blending bisimide resins with the epoxy resin, Scola et al.¹⁰ used an amine curing agent containing bisimide linkage in order to improve the thermal stability and mechanical properties of neat epoxy resin. They could make a superior graphite fiber reinforced composite using the bisimide amine cured epoxy resin as a composite matrix.

The thermal stability of epoxy resin would be improved by introducing higher temperature performance resins such as polyimide and cyanate resin. Woo et al.¹¹ reported that the co-cured structure of epoxy(TGDDM+DDS)-bismaleimide(diphenylmethane BMI(60 wt%) + tolylene BMI(40 wt%)) thermoset blend was a homogeneous intercrosslinked network. According to their results, the thermal stability(glass transition temperature) of epoxy resin increased linearly with BMI composition. Cure kinetics and chemorheological study for the epoxy(DGEBA)-cyanate(4,4-diphenyl methane dicyanate) blends formulated to enhance thermal stability and electrical properties of epoxy resin were studied by Chen.¹²

The impact and tensile properties of epoxy(TGDDM)/epoxy(DGEBA) blends cured under five different cure conditions were investigated in this study. The effects of blend compositions on the mechanical properties of cured epoxy/epoxy blends were also investigated. Optical microscopy was also used to study the fracture surfaces of the blends.

EXPERIMENTAL

Materials. Epoxy resins and amine curing agent used in this study were DGEBA(YD 128 from Kudo Chem. Co.), TGDDM(MY 720 from Ciba-Geigy) and DDM(4,4'-Diaminodiphenyl methane from Tokyo Chem.). Epoxide equivalent weight of the DGEBA and TGDDM were 185~190 and 120~135 g/eq respectively. The density of DGEBA and TGDDM were 1.16 and 1.21 g/cm³(both at 25°C) respectively. Active amine hydrogen equivalent weight of the DDM was 49.5 g/eq. H. The stoichiometric amount of DDM was introduced for all the blend formulations. The weight compositions of DGEBA/TGDDM blends were 100/0, 80/20, 60/40, 20/80 and 0/100 respectively. The molecular structures of materials employed in this study are shown in Fig. 1.

Preparation of Molded Parts for Mechanical Tests. A silicon rubber spacer(200×190×3 mm) was used as a mold to produce cured DGEBA/TGDDM blend parts. Mold release agent was applied on the resin contacting surfaces of bottom and top steel mold plates for each casting operation. The blend mixture was formulated by mixing the two epoxy resins(DGEBA and TGDDM) at 90°C and then dissolving the curing agent(DDM). The reactant mixture was degassed in a vacuum oven before pouring it into the mold. The following five different curing conditions were used to produce specimens for the mechanical tests.

- 1) 120°C for 6 hrs
- 2) 120°C for 3 hrs and 150°C for 3 hrs
- 3) 150°C for 6 hrs
- 4) 120°C for 3 hrs, 150°C for 2 hrs and 175°C for 1 hr
- 5) 175°C for 4 hrs

Differential Scanning Calorimetry. A DuPont DSC 910 supported by a DuPont thermal analyzer (TA) was used in order to measure glass transition temperatures of the cured epoxy/epoxy blends. Small cured blend parts with about 10~15 mg were sampled from the casted epoxy/epoxy blend parts, and placed in the DSC cell where nitrogen

Mechanical Properties of Bifunctional/Tetrafunctional Epoxy Blends

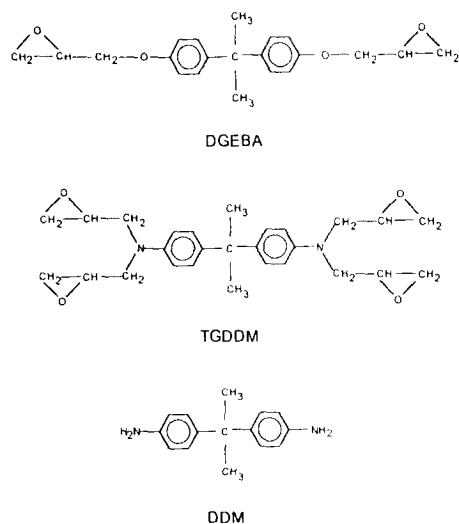


Fig. 1. Chemical structures of epoxy resins and curing agent.

gas flew continually. The heating rate used was 10 °C/min. The scanning range was from 25 to 350°C.

Density Measurement. In order to measure densities of the epoxy/epoxy blends, the ASTM D 792-66 was employed. The specimens with void free surface were prepared for the density measurements. The sizes of specimens were smaller than 1 cm³. At least five specimens were prepared for each experimental condition to obtain reasonable density data from the measurements.

Impact Strength Measurement. The Tinius Olsel Model 66 Izod Impact Tester was used for measurement. The impact strength measuring experiment was carried out according to the ASTM D 256-73 Method A. Five specimens were prepared for each experimental condition to obtain reasonable impact test data. Each impact strength value was taken by averaging the five experimental values. The dimensions of specimens were 63.6 mm long, 12.7 mm wide and 3 mm thick. A notch of 2.5 mm depth was placed at the center of each specimen.

Tensile Strength Measurement. Tensile properties of the epoxy/epoxy blends were measured by Instron Model 1125 Tensile Tester. ASTM D

638-76 was employed to measure the tensile properties of the epoxy/epoxy blends. Dimensions of specimens were 165 mm long, 13 cm wide, 3 mm thick. The gage length was 50 mm. A crosshead speed was 1 mm/min. Five specimens were prepared for each experimental condition for accuracy of the measurement. Each tensile strength value for each condition was obtained by averaging the five experimental values.

RESULTS AND DISCUSSION

Glass Transition Temperature of the Epoxy/Epoxy Blends. Glass transition temperatures of the cured epoxy/epoxy blends were measured using the DSC with a heating rate of 10°C/min. Fig. 2 shows the glass transition temperatures of epoxy/epoxy blends, cured under the cure condition (5), as a function of blend composition. The glass transition temperature of pure DGEBA and TGDDM cured under the cure condition (5) were 148°C and 181°C respectively. The reactivity of DGEBA to the aromatic amine curing agent, DDM is usually higher than that of TGDDM because the mobility of DGEBA is higher because of its low molecular weight (M_n = about 380) comparing to TGDDM (M_n = about 530). In general, TGDDM needs high temperature to activate the curing reaction through epoxide ring opening because it has high bulk viscosity. The glass transition temperature of the blends were higher, especially over about 40 wt% TGDDM contents, than the T_g value calculated using an idealized simple linear addition rule (line connecting T_g of DGEBA and T_g of TGDDM). This positive deviation from ideality was considered to be caused by the fact that the cured structure of the epoxy/epoxy blends would be different with typical nonreactive thermoplastic blends because both epoxy resin were reactive.

Usually a random copolymer of two monomers with different T_g 's has a glass transition which lies somewhere in between the T_g 's of the respective homopolymers.¹³ If this glass transition is studied as a function of comonomer concentration, in ideal

situation very simple relations between the T_g 's of the homopolymers and those of the copolymers are observed as like Fox equation¹⁴ indicating negative deviation.

In order to establish analytical relations between T_g and structural features of amorphous networks and to allow prediction of T_g with changes in chemistry, a model for a polymer network was developed by Chomppf.¹⁵ In this model the network polymer is treated as a ter-polymer of branch points, chain segments and chain ends, each of which contributes a different amount of free volume to the total system. The cured structure of the epoxy/epoxy blends would contain DGEBA-DDM and TGDDM-DDM linkage mainly. The DGEBA-DGEBA, TGDDM-TGDDM and DGEBA-TGDDM linkages could be produced by an autocatalytic reaction of hydroxyl group produced through the epoxide ring opening reaction. The reactivity of TGDDM to DDM might be increased by blending DGEBA because the mobility of TGDDM would be increased slightly. Owing to these reasons, the crosslinking density of the epoxy/epoxy blends would be higher than the weight average value calculated using a simple linear contribution of each epoxy resin. The positive deviation of T_g data shown in Fig. 2 was considered to be caused by the more complicated network structure resulted from the complex reaction mechanism of the epoxy/epoxy blends.

Density of the Epoxy/Epoxy Blends. Density data of the epoxy/epoxy blends cured under the cure condition (5) were measured using the ASTM D 792-66, and shown in Fig. 3 as a function of blend compositions. The specimens for the density measurements were smaller than 1 cm^3 , and their surfaces were void free. The density of each specimen was calculated by the following equation.

$$\rho(\text{density}) = \frac{W_d + W_s}{W_d} \times 0.9975 (\text{g/cm}^3)$$

W_d : weight of dried specimen at 23°C

W_s : weight measured in the distilled water at 23°C

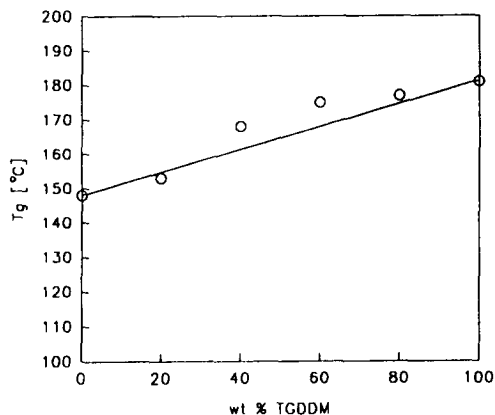


Fig. 2. Glass transition temperature of the epoxy/epoxy blend as a function of blend composition. cure condition (5).

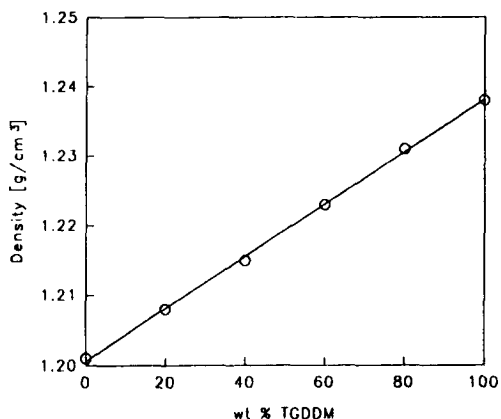


Fig. 3. Density of the epoxy/epoxy blend with TGDDM contents. cure condition (5).

The density of the epoxy/epoxy blend was almost linearly proportional to TGDDM contents as shown in Fig. 3, and each density data lay on the straight line connecting the density value of pure DGEBA and pure TGDDM.

Tensile Properties of the Epoxy/Epoxy Blends. Tensile modulus data of the epoxy/epoxy blends cured under the cure condition (5) were shown in Fig. 4 as a function of TGDDM composition. The tensile modulus of DGEBA was 4.25 kgf/mm^2 and that of pure TGDDM 5.56 kgf/mm^2 . The tensile modulus increased linearly with TGDDM contents.

The stiffness of the epoxy/epoxy blend increased as the contents of TGDDM was increased because TGDDM was stiffer than DGEBA.

The tensile strength data of the epoxy/epoxy blend cured under the cure condition (5) shown in Fig. 5 indicate a different trend compared to the tensile modulus data shown in Fig. 4. The tensile strength (maximum load at breaking point) of pure DGEBA ($3.23 \times 10^2 \text{ kgf/mm}^2$) was higher than that of pure TGDDM ($2.7 \times 10^2 \text{ kgf/mm}^2$). Even though the pure DGEBA resin was more flexible, it had higher tensile strength because its strain rate at breaking point was higher. The tensile strength of the epoxy/epoxy blend indicated maximum value at about 60 wt% TGDDM contents. It was considered that this result was caused by the intercrosslinking between DGEBA and TGDDM produced through the autocatalytic reaction between epoxide ring and hydroxyl group from the epoxide ring opening reaction.

Fig. 6 shows the tensile strength data of pure DGEBA cured under the five different cure conditions. The highest tensile strength for pure DGEBA resin was observed from the sample cured under the cure condition (1). This result indicated indirectly that the crosslinking density was lowest and the ductility was highest for this curing condition. The chemical conversion for the epoxide ring would increase as the curing temperature was inc-

reased if the curing time period was same. The chemical conversion of pure DGEBA resin cured under the cure condition (5) would be highest among the five different samples.

Impact Strength of the Epoxy/Epoxy Blends.

Impact strength data of epoxy/epoxy blends cured under the cure condition (5) were shown in Fig. 7 as a function of blend composition. The impact strength of the epoxy/epoxy blend decreased with TGDDM contents. The impact strength of pure DGEBA ($2.53 \text{ kgf} \cdot \text{cm/cm}$) was slightly higher than that of pure TGDDM ($2.0 \text{ kgf} \cdot \text{cm/cm}$). DGEBA resin is more ductile compared to TG-

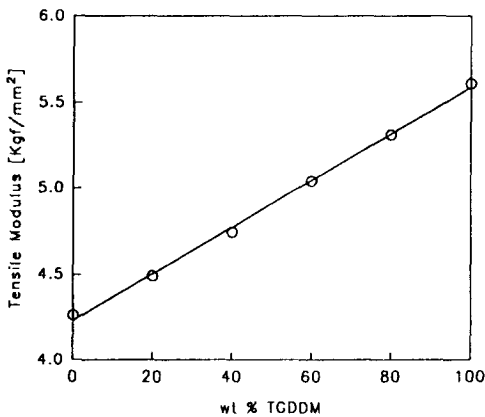


Fig. 4. Effect of blend composition on the tensile modulus of the blend. cure condition (5).

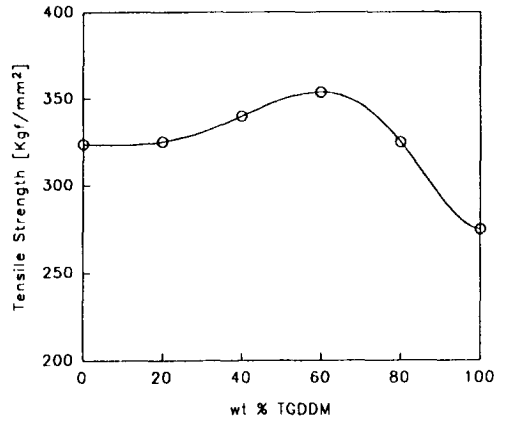


Fig. 5. Effect of blend composition on the tensile strength of the blend. cure condition (5).

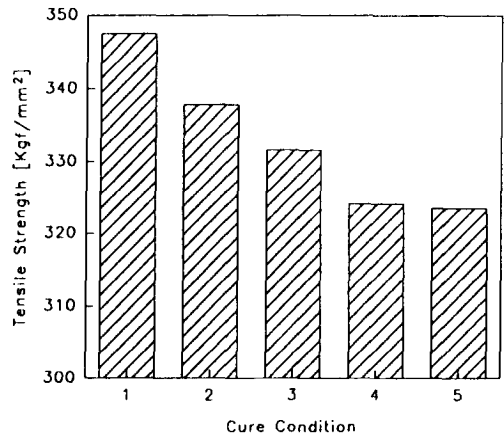


Fig. 6. Effect of cure conditions on the tensile strength of pure DGEBA.

DDM resin because crosslinking density of DGEBA resin is lower than that of TGDDM resin.

Fig. 8 shows the impact strength data of the epoxy/epoxy blend, containing 20 wt% of TGDDM, cured under the five different cure conditions. The impact strength of the blend was affected largely by cure conditions. The impact strength of the blend cured under the cure condition (1) was highest. From this result, it was considered that the crosslinking density was lowest and the flexibility highest for the sample cured under the cure condition (1).

Optical micrographs for the fracture surfaces of

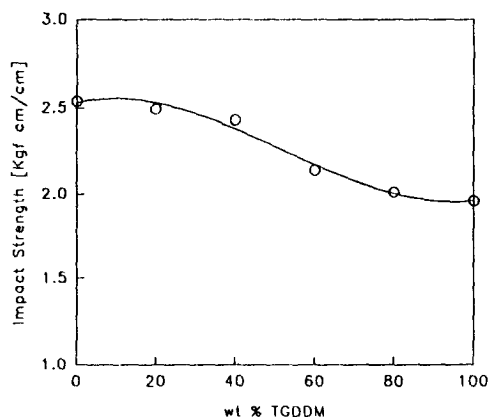


Fig. 7. Effect of blend composition on the impact strength of the blend, cure condition (5).

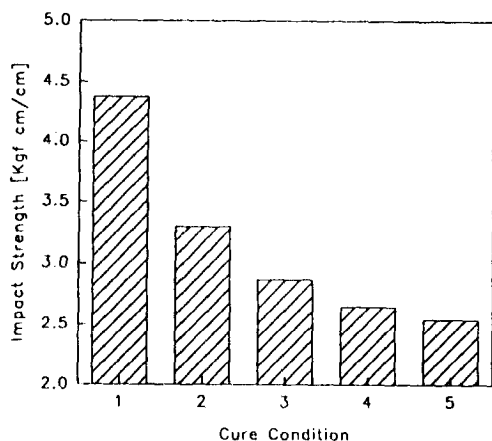
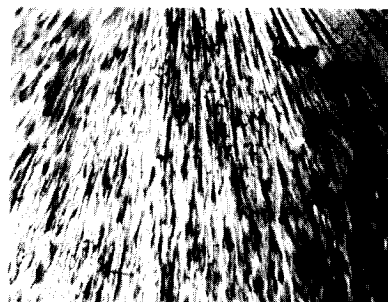


Fig. 8. Effect of cure conditions on the impact strength of the blend containing 20 wt% of TGDDM.

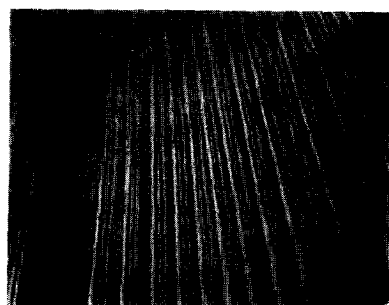
the epoxy/epoxy blend containing 20 wt% of TGDDM are shown in Fig. 9 for three different cure conditions(cure condition (1), (3) and (5)). The patterns of fracture surfaces of the blends could describe well the results of impact strength data shown in Fig. 8. Comparing the fracture surface for the blend cured under cure condition (1)(Fig. 9 (a)) with the fracture surface for the blend cured



(a)



(b)



(c)

Fig. 9. Optical micrographs for fracture surfaces of the blend containing 20 wt% of TGDDM($\times 400$). (a) cure condition (1), (b) cure condition (3), (c) cure condition (5).

under cure condition (5) (Fig. 9(c)), it was shown that the blend cured under the cure condition (1) was more ductile than the blend cured under the cure condition (5). Fig. 9(a) shows a lot of fine cracks on the fracture surface. But Fig. 9(c) shows that the fracture surface was resulted from only a few large cracks. This was resulted from the difference in crosslinking density between the blends cured under the various cure conditions. The crosslinking density of the blend would be affected by cure condition, which affected directly chemical conversion of the blend system. The higher the chemical conversion, the higher the crosslinking density of the epoxy/epoxy blend. It is noticeable that impact strength of thermosetting polymer decreases with crosslinking density but hardness (modulus) increases with crosslinking density. In order to control mechanical properties of epoxy resin the amount of crosslinking agent can be changed.

CONCLUSIONS

The epoxy/epoxy blend composed of bifunctional and tetrafunctional epoxy monomers were cured under the five different cure conditions. The glass transition temperatures of the blends were increased with TGDDM contents, and indicated positive deviation from the weight average value calculated from the glass transition temperature of pure DGEBA and TGDDM. Density of the epoxy blend increased linearly with TGDDM contents. The tensile and impact strength of the blend was affected largely by cure conditions and blend compositions. The tensile modulus of the blends were linearly increased with TGDDM contents. The impact strength of the blends were decreased with TGDDM contents. The tensile strength of the blends indicated maximum value at 60 wt% TGDDM contents. Optical micrographs for fracture surfaces could describe well the impact test result.

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