

고무에 의한 에폭시 수지의 변성에 관한 연구 : 1. CTBN의 함량이 에폭시 수지의 기계적 성질에 미치는 영향

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Rubber Modified Epoxies ; 1. Effect of CTBN Concentration on the Mechanical Properties

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요 약 : 고성능 에폭시 수지의 한 종류인 Tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)를 carboxyl-terminated 반응성 액상고무로 변성하여 고무함량 변화에 따른 기계적 성질의 변화를 연구하였다. 경화제로는 4,4'-diaminodiphenyl sulfone (DDS)를 사용하였으며, 물성의 측정에는 주사현미경, Instron, 광학현미경, Dynamic mechanical analyser(DMA)를 사용하였다. 에폭시 수지의 인장 파괴에너지는 고무함량 10phr부근에서 최대값을 나타내었으며, 이때 고무입자의 크기는 $0.25\mu\text{m}$ - $5\mu\text{m}$ 정도로 분포하고 있다.

Abstract : The mechanical properties of epoxy systems modified with a prereacted carboxyl-terminated rubber were investigated in relation to variations in incorporated rubber concentration of up to 20 parts per hundred resins(phr) at a fixed cure condition. Modified epoxy systems cured by 4,4'-diaminodiphenyl sulfone(DDS) were estimated by using scanning electron micrographs (SEM), Instron, optical micrographs, and dynamic mechanical analyser(DMA). The mechanical properties of the modified epoxy systems depend on incorporated rubber content : around 10phr of rubber the systems show maximum tensile fracture energy and the domain size of rubber particles dispersed in epoxy matrix ranges from $0.25\mu\text{m}$ to $5\mu\text{m}$.

INTRODUCTION

Incorporation of various amounts of reactive liquid rubber into epoxy resins results in enhancing fracture toughness of the cure systems. This improvement has been attributed to the in situ formation of rubbery domains of a definite size

and shape during cure. This dispersed rubber particles in continuous matrix phase apparently make the systems tougher by energy dissipation mechanism. Phase separation occurs when the rubber and epoxy become incompatible with the increase in molecular weight and rubber-rich domains precipitate in the epoxy-rich matrix.

The size and distribution of the rubbery domains, which affect end properties of the systems, are expectedly dependent on the temperature and time of cure, and the initial compatibility of liquid rubber to epoxy resins. Gillham et al.^{1,2} found in CTBN (carboxyl-terminated butadiene acrylonitrile copolymer) rubber and epoxy systems that phase separation begins well before gelation of the cure systems. Once gelation has occurred, the morphology is fixed. Therefore gel time affects final morphology of the systems. The diffusivity of rubber in epoxy matrix will decrease with increasing viscosity and the driving force for phase separation increases with increasing molecular weight during cure³. Consequently the varying extent of phase separation is attributed to the competing effects of thermodynamic compatibility and rubber transportation in a polymerizing system, in which morphological development is eventually quenched by gelation.^{4,5}

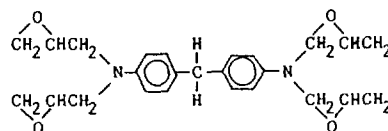
This work aims at determining an optimum CTBN content to obtain improved fracture toughness in high performance epoxy. We intent to study the effect of incorporated rubber content on the size and distribution of dispersed rubber domains, and eventually on the mechanical properties of rubber modified epoxy systems.

EXPERIMENTAL

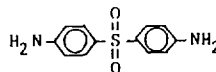
Materials

The rubber modifier employed is a reactive liquid rubber, CTBN with relatively higher acrylonitrile content manufactured by B. F. Goodrich Co. under the trade name Hycar, whose properties are given in Table 1. The epoxy systems are provided by Ciba-Geigy Co. : tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) as base resin and 4,4'-diaminodiphenyl sulfone(DDS) as hardener. Bisphenol A (BPA) is also used in the formulations to control the size and distribution of rubber domains.

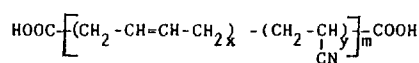
1. Tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM)



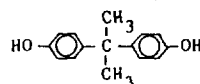
2. Diaminodiphenylsulfone (DDS)



3. Carboxyl-Terminated Butadiene-Acrylonitrile Copolymer (CTBN)



4. Bisphenol A(BPA : 4,4'-Isopropylidenediphenol)



Experimental Procedure

Prereaction of Base Resin with CTBN:

Better compatibility between epoxy base resin and rubber particle can be achieved through homogeneous reaction of epoxide ring with carboxyl group in CTBN before cure. Compatibility of TGDDM and CTBN should be enhanced through the controlled chemistry of a prereaction technique, because the systems are not compatible initially at the temperature used for cure. In the presence of triphenylphosphine (0.25 parts by weight) as catalyst the large molar excess of TGDDM (100 parts by weight) was reacted with CTBN (100 parts by weight) at 80°C for 200 minutes to get the CTBN being capped at both ends by one unit of epoxy as shown in Figure 1. Under this reaction condition it was confirmed by the

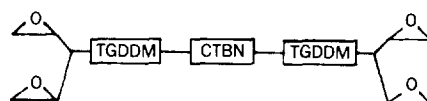


Fig. 1. TGDDM-CTBN prereacted concentrate.

titration of unreacted free carboxyl groups that almost all the charged CTBNs were converted to the epoxy endcapped form.⁶

Specimen Preparation and Measurement:

Five different resin mixtures were cured to study the morphological change and the mechanical properties of the cure systems. The incorporated rubber content was changed from zero level to 20 parts per hundred resin (phr) at an interval of 5 phr as shown in Table 2. For the viscosity control methyl ethyl ketone (MEK) was used as a diluent with the ratio of 1.5 volume of MEK to 1 weight of resin mixture. Curing was performed in a teflon-coated mold with the following cure cycle^{7,8}: 45 minutes under vacuum at 80°C, 8 minutes at 125°C, 2 hrs at 177°C and 4 hrs at 192°C. The mechanical properties of the cure systems were measured by using Instron (model 4201). Tensile specimens were machined to 120 × 10 × 3 mm. Measurement of tensile fracture energy was accomplished in the maximum cross head speed of 500 mm/min. by using Instron. Also mechanical damping ($\tan \delta$) was estimated by

DMA (Dupont model 1981) and its specimens were machined to 15.0 × 7.0 × 0.8 mm. The morphological investigation was performed by SEM (Hitachi S-510) and optical microscope (Olympus BH-2).

RESULTS AND DISCUSSION

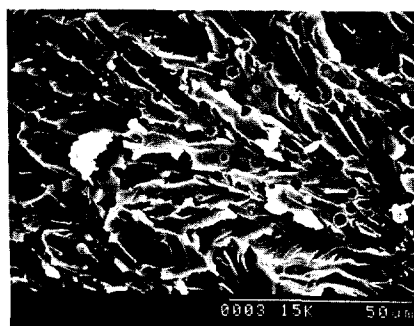
The series of rubber-modified polyfunctional epoxies cured with DDS was used to study the effect of incorporated rubber content on the mechanical properties of cure systems. An objective in this work was to get the optimum CTBN content in TGDDM at a fixed cure condition generally recommended for TGDDM/DDS systems. A preliminary experiment was executed to confirm the morphological difference of cure systems with and without BPA in initial formulation.

Table 1. Typical Properties of Hycar® CTBN.

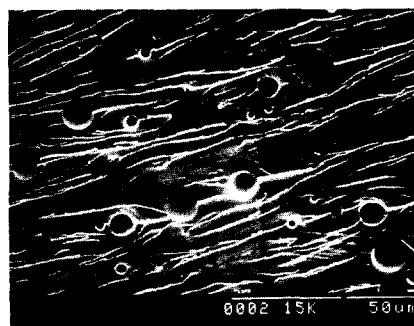
Property	1300 × 13 CTBN
Brookfield viscosity mPa · s (cP) at 27°C (79°F)	570,000
Carboxyl content %	2.4
Carboxyl content, EPHR*	0.057
Specific gravity, 25°C / 25°C (77°F / 77°F)	0.960
Percent volatiles	<2.0
Acrylonitrile content %	26
Functionality	1.8

Table 2. Formulation for TGDDM Systems.

Materials	phr
Prereaction mixture (TGDDM 50 wt % CTBN 50 wt %)	10, 20, 30, 40
TGDDM	95, 90, 85, 80
BPA	24
DDS	44



a) 1000×(5phr Hycar 1300×13)



b) 1000×(5phr Hycar 1300×13)

Fig. 2. Scanning electron micrographs of rubber modified epoxy (TGDDM-DDS) with 24phr BPA (a) and without BPA(b).

The inclusion of a diphenol results in toughness synergism through having the dispersed rubber particles to form bimodal distribution.

Difference can be observed in dispersed rubber phase and also in the fracture surface of the

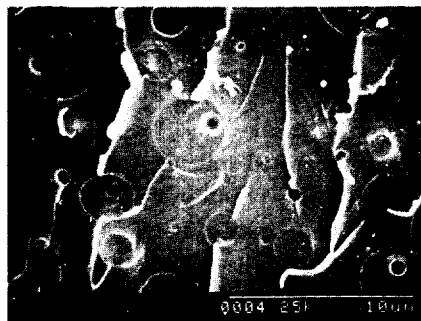
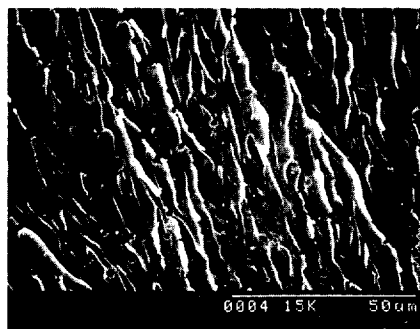


Fig. 3. Scanning electron micrograph of rubber modified epoxy (TGDDM-DDS) with 24phr BPA. Magnification : 5000 \times .

cure systems with and without BPA as shown in Fig.2. The system with BPA has a rougher fracture surface and the smaller domain size of dispersed rubber particles in comparison with that without BPA. Moreover the system with BPA shows that dispersed rubber particles should have better adhesion to the epoxy matrices : more craze formation around the cavities, out of which rubber has been torn, is observed. Photograph of the same surface as in Fig.2(b) is shown in Fig.3 at higher magnification. It indicates that size of rubber particles has substantially bimodal character, which can be attributed to the toughness synergism demonstrated by Riew et al.,⁸ and Sultan and McGarry⁹ : smaller particles with the diameter of 0.25 μm to 0.35 μm and large particles with the diameter of 2 μm to 5 μm .

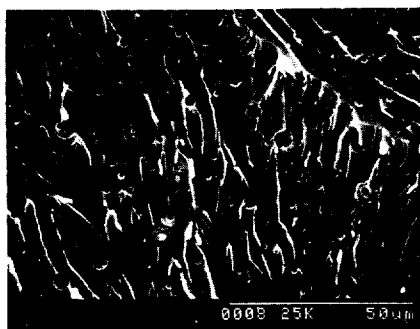
Fig.4 (a)-(d) represent SEMs of rubber modified



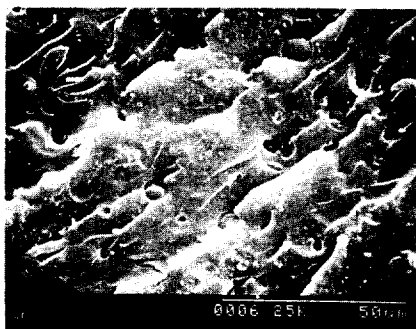
(a) 1000 \times



(c) 1000 \times



(b) 1000 \times



(d) 1000 \times

Fig. 4. Scanning electron micrographs of rubber modified epoxy (TGDDM-DDS) with 5phr(a), 10phr (b), 15phr(c) 20phr(d) Hycar 1300 \times 13.

epoxy systems with various CTBN content. The fracture surfaces show that core and sphere are clearly contrasted in the rubber particles. The mechanism for the formation of the rubber particles may be predicted as follows¹⁰: 1) The rubber molecule is capped by epoxy monomer on both side, as shown in Fig.1, because the molar equivalence of TGDDM to CTBN is much higher than stoichiometry. 2) The epoxy endcapped CTBN arranges itself in the epoxy matrix, so that the rubbery part is aligned toward the inside and the epoxy part toward outside. As long as chains are growing, these arrangements are only local. 3) When the system becomes denser (i.e., as branches and cross-links start to form), these local arrangements form "droplet". 4) The droplets have a higher concentration of rubber in the center: this rubber is apparently the core as shown in the SEMs. The sphere itself is bonded chemically to the matrix, but it is different from the matrix in the rubber concentration. The sphere may be mainly attributed to the strain energy absorption during the fracture test.¹¹

Morphology of fracture surface in Fig.4(a), (b) shows that the crack is stopped or detoured when it meets the rubber particle. It is also shown that shear bands bring about the strain yield and so strain energy is absorbed or dissipated.¹²

Fig.4(c), (d) represent the pictures of fracture surface with the CTBN content of 15 phr and 20phr. In Fig.4(c) it is shown that the number of the rubber particles is much increased in comparison with the CTBN content of 5phr(a) and 10phr (b), but the size and the shape are about the same. Fig.4(d) shows that the size and the number of dispersed rubber particles are much different from the previous three fracture surfaces. Such difference in morphologies offers the much lower mechanical properties to be observed in Fig.5 and Fig. 6.

A plot of tensile strength versus incorporated CTBN content is given in Fig.5. Tensile strength has a maximum value around 10phr rubber content and decreases with the increasing CTBN content

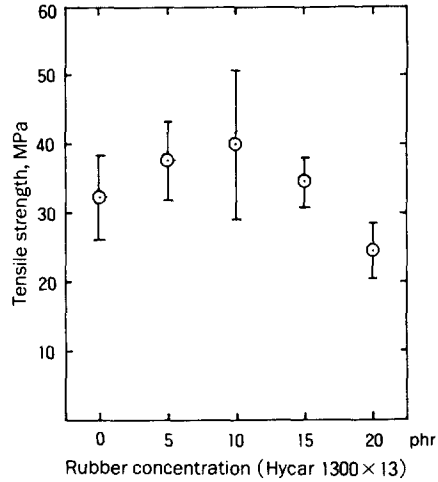


Fig. 5. Effect of CTBN concentration in TGDDM-DDS on tensile strength.

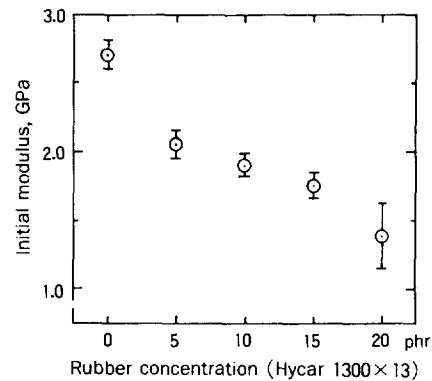


Fig. 6. Effect of CTBN concentration in TGDDM-DDS on initial tensile modulus.

beyond 10phr. It is also observed that tensile strength of the modified epoxy systems with 20phr rubber content is lower than that of unmodified epoxy, which may be caused by large-sized aggregated rubber particles acting as defect during the tensile test.

Fig.6 and Fig.7 show initial tensile modulus and elongation versus incorporated CTBN content respectively. These results should come from the plasticizing effect of the dissolved CTBN in the epoxy systems. Tensile fracture energy for the

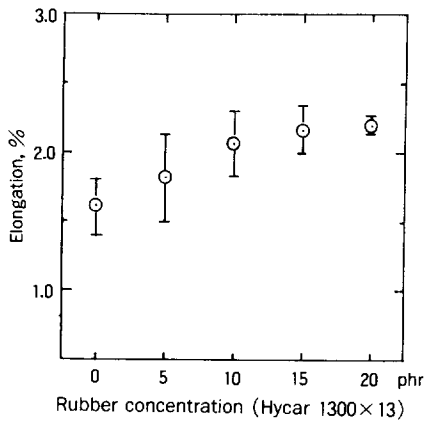


Fig. 7. Effect of CTBN concentration in TGDDM-DDS on elongation.

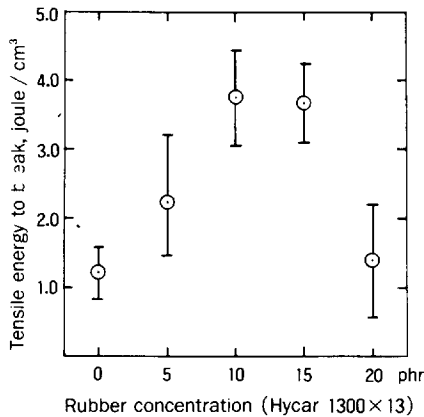


Fig. 8. Effect of CTBN concentration in TGDDM-DDS on tensile energy to break (cross head speed : 500mm / min.).

various modified epoxy systems is given in Fig. 8. These data are obtained in the tensile impact test carried out at the cross head speed of 500mm / min.. It is noted that the tendency of this result is similar to that of tensile strength (Fig.5). It seems, however, that the sharp drop in tensile fracture energy for 20phr is due to the formation of large-sized aggregated rubber particles. Optical microscope was used for confirming the aggregation phenomena of rubber particles in higher concentration. Fig. 9 shows two optical micrographs taken for cure systems with the CTBN content

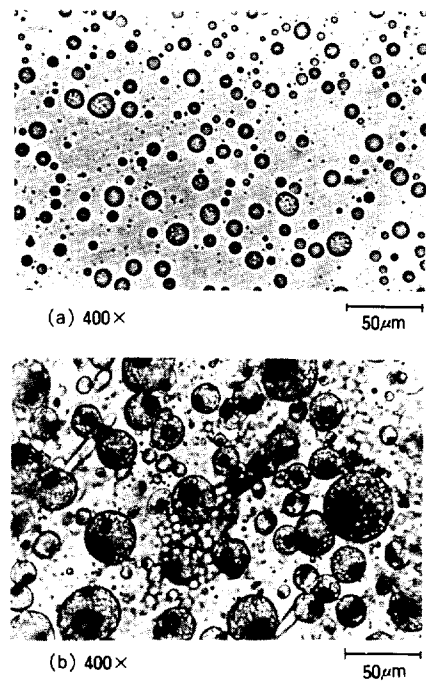


Fig. 9. Optical micrographs of rubber modified epoxy (TGDDM-DDS) with 15phr(a), 20phr(b) Hycar 1300×13.

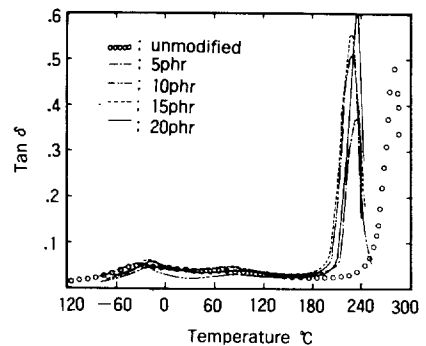


Fig. 10. DMA damping spectra for unmodified & modified epoxy resin

of 15phr and 20phr. As the systems were cured between two pressed parallel glass plates to get proper samples for optical microscope, the size of dispersed rubber particles are not consistent with that of the previous SEMs(Fig.4(c) and (d)). Aggregated rubber particles, however, can be shown in case of the rubber content of 20phr.

Fig.10 represents the mechanical damping described as $\tan \delta$ with the variation of incorporated CTBN content. The peak temperature is shifted to the lower temperature due to the plasticizing effect of dissolved rubber in epoxy systems as expected.^{13,14} It is shown, however, in Fig. 10 that the peak for the systems with 20phr rubber content is shifted inversely to the higher temperature, which would be the result of lower dissolved rubber content in continuous epoxy phases due to the intensive aggregation of rubber phases.

CONCLUSION

1. It is observed that to obtain maximum toughness in CTBN-modified epoxy the optimum content of CTBN is around 10phr. At this CTBN content tensile strength shows also the maximum.
2. It is confirmed that the CTBN particles form bimodal distribution at this experimental condition, the larger particle size ranging from $2\mu\text{m}$ to $5\mu\text{m}$ and the smaller one from $0.25\mu\text{m}$ to $0.35\mu\text{m}$.

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