

# Synthesis and Properties of New Tetrafunctional Epoxy Resins Containing Oxyethylene Units

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## Synopsis

Tetraglycidyl ethers of 2,2',2'',2'''[sulfonyl bis(4,1-phenylenenitrilo)]tetrakisethanol and 2,2',2'',2'''[methylene bis(4,1-phenylenenitrilo)]tetrakisethanol were synthesized and characterized. Curing reactivities of these new epoxy resins are investigated by differential scanning analysis. The mechanical, thermal, and dynamic mechanical properties of these resins cured with *p,p'*-diaminodiphenylsulfone were examined and compared to those of the conventional tetrafunctional epoxy resin (MY-720). These new epoxy resins have the advantages of being easier to handle, having higher curing reactivities, and giving cured resins with higher toughness, compared with MY-720 resin.

## INTRODUCTION

Most of epoxy resins such as bisphenol A type were prepared by the reaction of phenolic hydroxyl groups and epichlorohydrin (ECH) in the presence of excess bases (NaOH or KOH).

It has been reported<sup>1,2</sup> that a one-step epoxidation of aliphatic alcohols by ECH can be carried out smoothly using phase transfer catalysts. This is a convenient method to prepare glycidyl ethers, compared with the ordinary two-step preparation. Recently, vinyl benzyl glycidyl ether (VBGE) was prepared by reacting vinylbenzyl alcohol and ECH according to the improved method.<sup>3</sup> VBGE is an interesting monomer which contains styryl and epoxy groups and affords epoxide-containing (co)polymers by radical (co)polymerizations.<sup>3</sup> It was found that VBGE-butyl acrylate (BA) copolymer and VBGE-BA-styrene or acrylonitrile terpolymers were effective as modifiers for epoxy resins.<sup>4,5</sup>

On the other hand, the epoxidation under the phase-transfer catalyzed reaction conditions is an attractive method for the modification of structure of epoxy resins. Such an approach is shown in this paper, where new tetrafunctional epoxy resins were prepared by hydroxyethylation and epoxidation. The epoxy resins containing oxyethylene units were cured with *p,p'*-diaminodiphenylsulfone (DDS). The effect of introduction of the flexible units into epoxy resins on their curing reactivities and on the physical properties of the epoxy resins was investigated.

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## EXPERIMENTAL

### Materials

Tetrabromobisphenol A (2-hydroxyethyl) ether (Tokyo Chemical Ind. Co.) was used as received. The control epoxy resins used were the liquid bisphenol A-type epoxy resin (AER-331, Asahi Chemical Co., epoxy equivalent weight (EEW) 191) and tetraglycidyl diaminodiphenylmethane (Araldite MY-720, Ciba Geigy Co., EEW 129). DDS (Tokyo Chemical Ind. Co.) was used as a curing agent without further purification. Other reagents were used as received.

### Measurements

<sup>1</sup>H-NMR spectra were measured on a 60 or 90 MHz instrument (JEOL, JNM-90MX60 or JNX-FX90) using CCl<sub>4</sub> or CDCl<sub>3</sub> as solvents. IR spectra were obtained on Shimadzu FTIR-4000 type. High performance liquid chromatograph (HPLC) was carried out using a Shimadzu model LC6A instrument with an UV detector. The column was Zorbax ODS (4.6 mm × 25 cm). Eluents and flow rates were changed, dependent on the reaction system. Gel permeation chromatography (GPC) was performed by Shimadzu Model LC 5A Instrument with a refractometer detector. Eluent was tetrahydrofuran at a flow rate 1 mL/min. Epoxy equivalent weight (EEW) of epoxy resin was analyzed by the HCl/dioxane method.<sup>6</sup> Mechanical properties of cured resins were measured with a Shimadzu S-500 universal testing machine. Tensile strength and modulus (JIS K7113) of cured resins were determined using dumbbell specimens at a crosshead speed of 1 mm/min. Flexural strength and modulus (JIS K7203) of cured resins were obtained at a crosshead speed of 2 mm/min. Fracture toughness (ASTM E-399) was measured in a three-point bent geometry at a crosshead speed of 1 mm/min. Glass transition temperatures of cured resins were determined by differential scanning calorimetry (DSC) (Shimadzu DSC 41M type). Dynamic mechanical analysis (DMA) was performed with a DuPont DMA 982 instrument between -110 and 270°C at a heating speed of 5°C/min at variable frequency of 30 to 2 Hz.

### Preparation of Epoxy Resins

#### *Hydroxyethylation*

2,2',2'',2'''[Methylene bis(4,1-phenylenenitrilo)]tetrakisethanol (MPTE) was prepared from the reaction of diethanolaniline and formaldehyde using hydrogen chloride as catalyst according to the method of Petrov and Talkovsky.<sup>7</sup> Yield 90%, mp 112–120°C (lit.<sup>7</sup>: yield 91%, mp 114–115°C).

2,2',2'',2'''[Sulfonyl bis(4,1-phenylenenitrilo)]tetrakisethanol (SPTE) was prepared as follows: A 2-L four-necked flask was charged with *p,p'*-dichlorodiphenylsulfone 57.4 g (0.2 mol) and diethanolamine 210.3 g (2.0 mol). The flask was purged with N<sub>2</sub> and an N<sub>2</sub> atmosphere was maintained throughout the reaction (190–200°C for 4 days). After the reaction was over, the resulting hydrogen chloride was removed by washing with aqueous sodium carbonate solution, and the residual diethanolamine was evaporated *in vacuo* at 130–140°C. The crude product was separated as a white solid by adding water, filtered, dried *in vacuo*, and obtained as a milky white crystal (yield 81%, mp

164–177°C). Pure SPTE was obtained as a yellow crystal by recrystallization from ethanol. Yield 65%, mp 176–178°C (lit.<sup>8</sup>: yield 45–55%, mp 177–178°C).

It is noteworthy that this procedure is different from that of the literature,<sup>8</sup> where two-step reactions were carried out using diaminodiphenyl sulfone as a starting material.

### Epoxidation

Epoxidation was carried out under the phase-transfer catalyzed reaction conditions according to the modified method of the previous paper.<sup>4</sup> A typical procedure was briefly described.

A four-necked flask was charged with ECH 270.1 g (2.92 mol), 50% aqueous sodium hydroxide solution [NaOH 240 g (6.0 mol)] and tetrabutylammonium hydrogensulfate 6.8 g (0.02 mol). SPTE 42.5 g (0.1 mol) solution [dimethyl sulfoxide 80 g + ECH 100 g (1.08 mol)] was added below 20°C under vigorous stirring over a period of 1 h. The reaction mixtures were kept below 20°C for additional 5 h with stirring. After the reaction was over, the reaction mixture was poured into ice water and extracted several times with benzene. The benzene solution was neutralized by washing with aqueous NaCl-saturated solution, dried over anhydrous magnesium sulfate, and the solvent was evaporated. The crude product was dried *in vacuo* at 60°C. A yellow, viscous liquid was obtained in a yield of 96% (Table I).

It must be noted that ECH is used as reactant and solvent in the general procedure for the phase-transfer catalyzed epoxidation, but a mixture of ECH and dimethyl sulfoxide was used for SPTE and MPTE because of their poor solubility in ECH.

TABLE I  
Preparation and Characterization of Epoxy Resins

Abbreviation	Structure	Yield (%)	mp (°C)	EEW <sup>a</sup>		Note
				Obsd	Calcd	
DDM		81	—	163	150	Orange liquid
DDS		97	—	180	162	Viscous yellow liquid
BA		99	—	236	214	Orange liquid
TBBA		67 (95) <sup>b</sup>	86–90	381	372	White crystalline

<sup>a</sup> Epoxy equivalent weight.

<sup>b</sup> Crude yield (95% purity).

## Curing Procedure

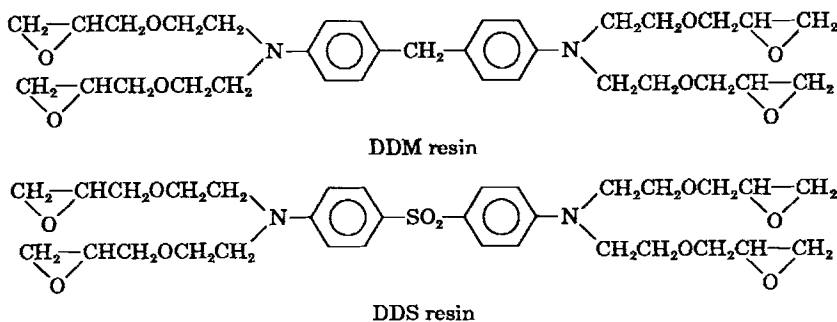
A mixture of the epoxy resin and DDS was heated at 120°C to homogenize and degas, and poured into a silicon mold preheated at 100°C. The curing conditions were at 120°C for 1 h followed by at 180°C for 5 h. The curing agent, DDS, was used stoichiometrically to the epoxy content.

## RESULTS AND DISCUSSION

## Preparation of Epoxy Resins

Epoxy resins were prepared from polyhydric alcohols using tetrabutylammonium hydrogensulfate as the phase-transfer catalyst except for tetrabromobisphenol A bis(2-hydroxyethyl) ether, where tetrabutylammonium bromide was used because of difficult separation of the organic phase from the reaction mixture (emulsion formation) in the presence of the former catalyst. The structure of the epoxy resins is shown in Scheme 1. Table I shows some characteristic properties of the epoxy resins prepared.

Tetraglycidyl ethers of both MPTE and SPTE are novel epoxy resins, which are abbreviated as DDM and DDS resins, respectively. Figure 1 shows IR spectra of the new tetrafunctional epoxy resins. Epoxy group absorptions were observed at 904 and 903  $\text{cm}^{-1}$  in IR spectra of DDM and DDS resins, respectively. The epoxy groups show the signals in the region of ca. 2.5–3.2 ppm in the  $^1\text{H-NMR}$  spectra of the epoxy resins (Fig. 2). GPC patterns of both DDM and DDS resins in Figure 3 are similar to that in the commercial tetrafunctional epoxy resin, MY-720. The presence of lower elution time peak (higher-molecular-weight) products suggests that the further reaction of the resulting epoxy group and the residual hydroxy groups proceeds even slightly. In practice, the EEW values of the new tetrafunctional epoxy resins became a little larger than the calcd ones. It is well known that MY-720 epoxy resin contains 15–20% less epoxy group than the pure tetraglycidyl ethers of *p,p'*-diaminodiphenylmethane.<sup>9</sup> DDM resin is a liquid one with low viscosity and easy to handle, compared with MY-720.



Scheme 1. Structure of new epoxy resins.

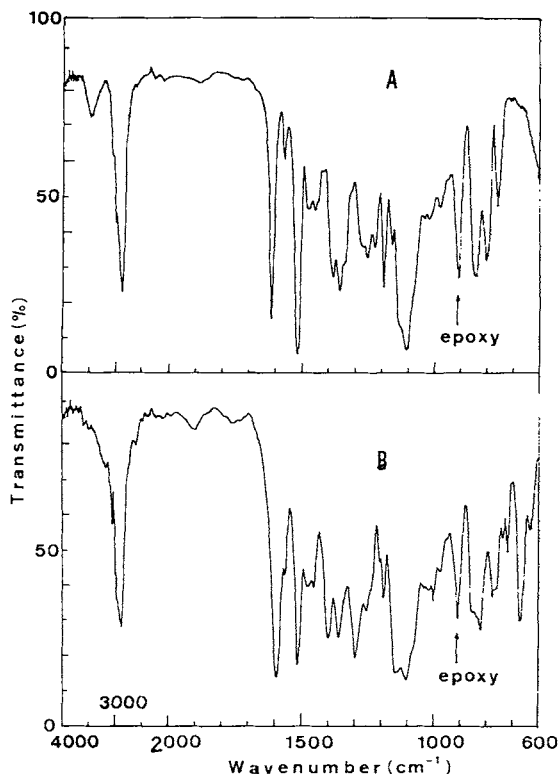


Fig. 1. IR spectra of new epoxy resins: (A) DDM resin; (B) DDS resin.

Diglycidyl ethers of hydroxyethylated bisphenol A (abbreviated as BA resin) and tetrabromobisphenol A (abbreviated as TBBA resin) were also prepared by the different way from the conventional one and characterized as shown in Table I. This one-step way for epoxidation is comparable or more effective in comparison with the conventional two-step way on the basis of simpler handling and obtaining higher purity and yield of epoxy resins.

### Mechanical and Thermal Properties of Cured Epoxy Resins

Table II shows the mechanical properties of epoxy resins cured with DDS. MY-720 resin was cured under two kinds of curing conditions on the basis of results of the following DSC. The first trace of DSC for MY-720 resin cured under the usual curing conditions (120°C/1 h + 180°C/5 h) showed an exothermic peak which disappeared in the second run (Fig. 4). The exothermic peak in the first run may be due to the post-cure of the epoxy group. Then, the harder conditions (150°C/4 h + 200°C/7 h) was examined for the curing of MY-720 resin, but the DSC curve also showed a exothermic peak (Fig. 4). The curing of tetraglycidyl ether of *p,p'*-diaminodiphenylmethane was investigated in detail by DSC and FTIR,<sup>9</sup> which shows that it was difficult to obtain the fully cured system because of network steric restriction. There is, in fact, little difference between the mechanical properties of two kinds of cured MY-720 resins (Table II).

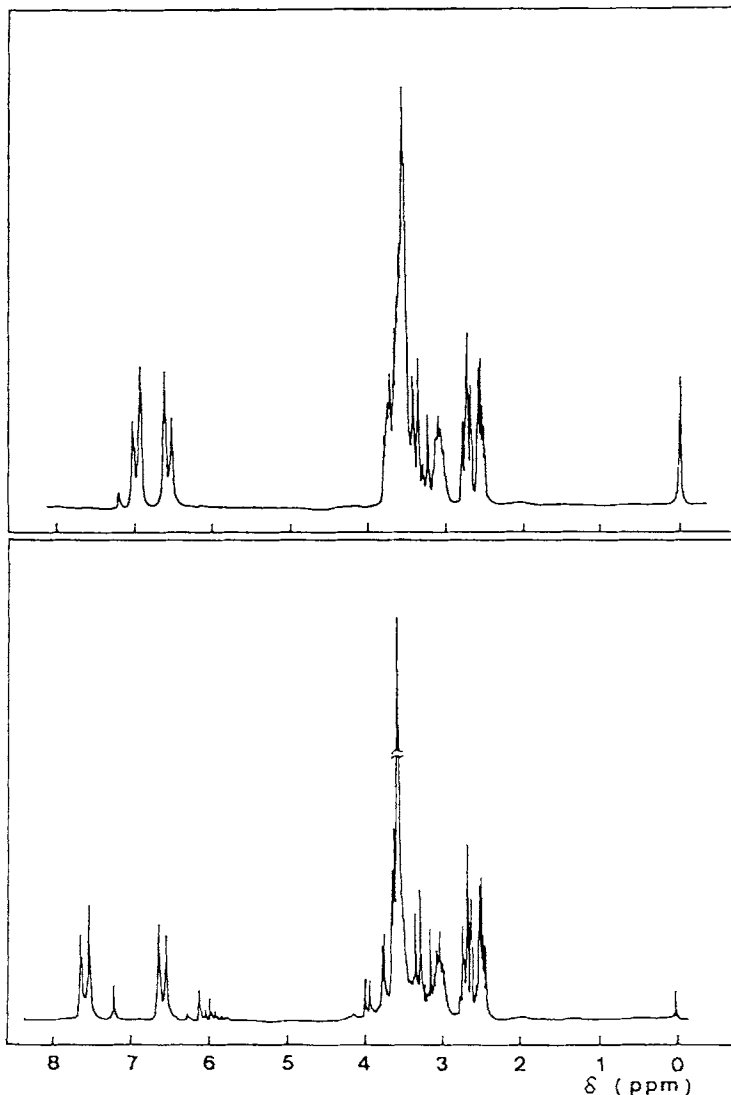


Fig. 2.  $^1\text{H-NMR}$  spectra of new epoxy resins: (A) DDM resin (upper); (B) DDS resin (bottom); solvent,  $\text{CDCl}_3$ ; internal standard, TMS.

The DSC trace of cured DDM resin did not show an exothermic peak. This indicates that DDM resin is more reactive than MY-720 resin. The epoxy groups in DDM resin are linked via flexible oxyethylene unit to the phenylene ring, as shown in Scheme 1: the less extent of network steric restriction for the epoxy group will lead to an increase in the curing reactivity.

Cured DDM resin has a comparable mechanical strength to cured MY-720 resin. The former resin has the advantage of having larger fracture toughness,  $K_{IC}$  than the latter (Table II). The drawback is a lower glass transition temperature ( $T_g$ ) of the former. The  $T_g$  value of cured MY-720 resin could not be obtained by DSC (Fig. 4) owing to the exothermic peak. The approximate  $T_g$  value is  $215^\circ\text{C}$  from the second run of DSC trace (Fig. 4). The  $T_g$  can be also obtained from the  $\tan \delta$  maximum by the dynamic mechanical analysis. The

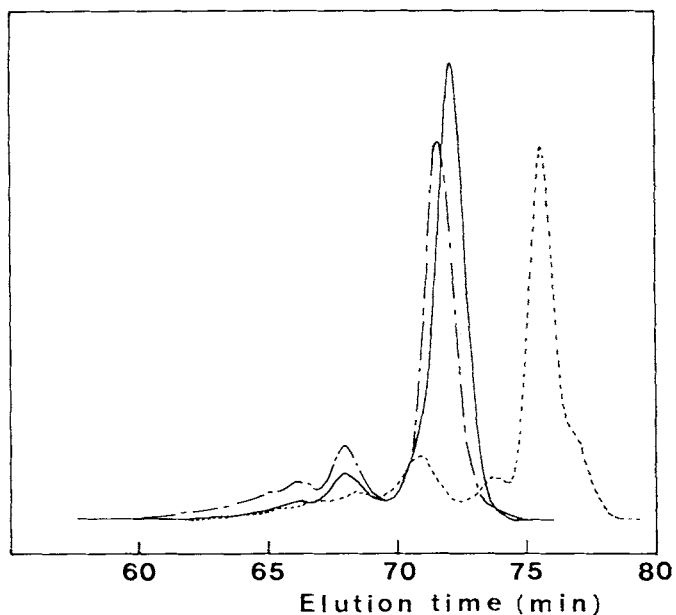


Fig. 3. GPC profiles of tetrafunctional epoxy resins: (—) DDM resin; (---) DDS resin; (- - -) MY-720 resin; eluent, THF at 1 mL/min of flow rate.

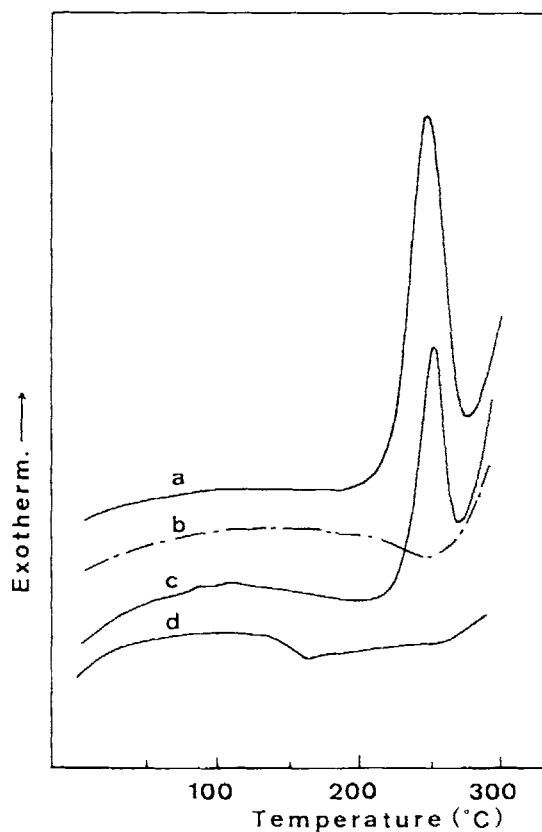


Fig. 4. DSC traces of cured resins; heating rate,  $10^{\circ}\text{C}/\text{min}$ : (a) the first run for MY-720 resin (13.1 mg) cured at  $120^{\circ}\text{C}/1\text{ h} + 180^{\circ}\text{C}/5\text{ h}$ ; (b) the second run for cured MY-720 resin; (c) MY-720 resin (15.3 mg) cured at  $150^{\circ}\text{C}/4\text{ h} + 200^{\circ}\text{C}/7\text{ h}$ ; (d) cured DDM resin.

TABLE II  
 Physical Properties of Cured Epoxy Resin<sup>a</sup>

	DDM	DDS	MY-720	MY-720 <sup>b</sup>	BA	TBBA	AER-331
Tensile strength (kgf/mm <sup>2</sup> )	8.89 ± 0.68	9.35 ± 1.25	9.73 ± 0.68	9.44 ± 0.43	8.07 ± 0.13	9.16 ± 0.24	9.08 ± 1.03
Tensile modulus (kgf/mm <sup>2</sup> )	190 ± 5	207 ± 5	217 ± 10	237 ± 6	155 ± 7	177 ± 6	154 ± 4
Elongation (%)	7.3 ± 1.4	6.7 ± 1.4	5.4 ± 0.6	5.3 ± 0.4	9.6 ± 0.5	8.7 ± 0.6	8.1 ± 1.5
<i>n</i> <sup>c</sup>	6	5	4	5	6	4	7
Flexural strength (kgf/mm <sup>2</sup> )	15.2 ± 1.3	19.2 ± 0.7	17.3 ± 2.7	15.1 ± 2.1	15.7 ± 0.6	17.8 ± 0.8	16.0 ± 1.0
Flexural modulus (kgf/mm <sup>2</sup> )	414 ± 20	455 ± 6	500 ± 13	542 ± 20	373 ± 18	441 ± 12	356 ± 7
<i>n</i> <sup>c</sup>	7	5	5	5	10	7	7
<i>K<sub>1c</sub></i> (MN/m <sup>3/2</sup> )	0.86 ± 0.06	0.74 ± 0.04	0.69 ± 0.01	0.72 ± 0.04	0.78 ± 0.08	0.70 ± 0.05	0.62 ± 0.08
<i>n</i> <sup>c</sup>	6	6	4	4	8	8	6
<i>T<sub>g</sub></i> <sup>d</sup> (°C)	142	188	—	—	87	118	187
<i>T<sub>max</sub></i> <sup>e</sup> (°C)	179	208	> 265	> 265	103	139	205

<sup>a</sup> Curing conditions, 120°C/1 h + and 180°C/5 h. The ±x values show standard deviations.

<sup>b</sup> Curing conditions, 150°C/4 h + and 200°C/7 h.

<sup>c</sup> Number of specimens.

<sup>d</sup> Obtained from DSC.

<sup>e</sup> Obtained from DMA.



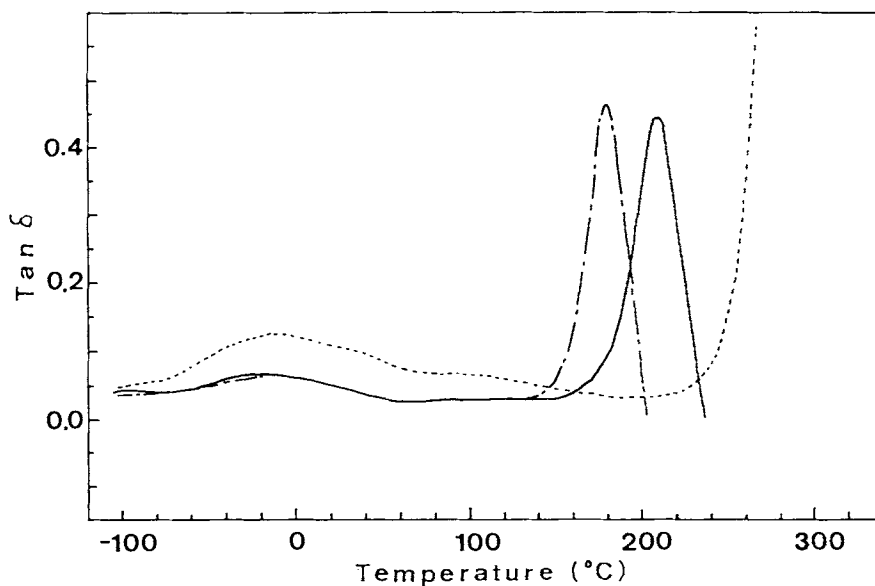


Fig. 5. Temperature dependence of  $\tan \delta$  for cured resins: (---) DDM resin; (—) DDS resin; (-·-·), MY-720 resin cured at 150°C/4 h + 200°C/7 h.

DMA result of cured MY-720 resin did not show the  $\tan \delta$  maximum in the temperature region of 100–265°C. Then its  $T_g$  is believed to be beyond 265°C as shown in Figure 5. Cured DDS resin has comparable mechanical properties to MY-720 resin except for  $T_g$ .

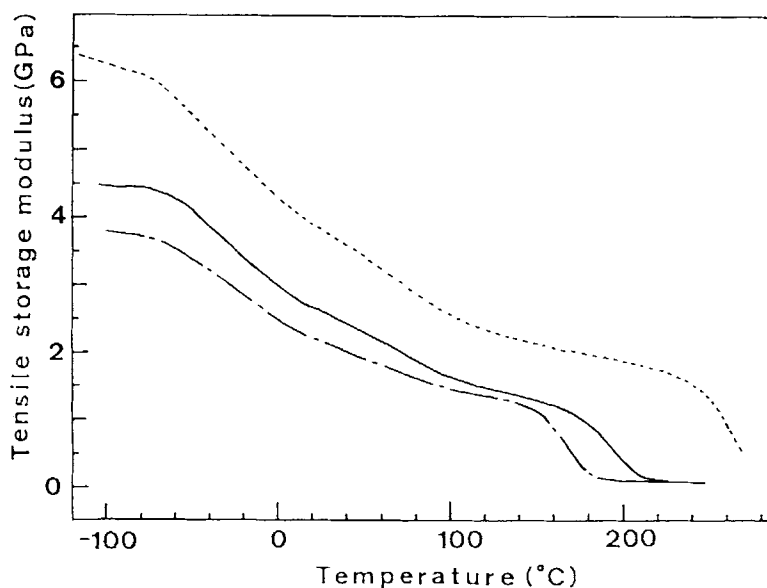


Fig. 6. Temperature dependence of tensile storage moduli for cured resins: (---) DDM resin; (—) DDS resin; (-·-·) MY-720 resin cured at 150°C/4 h + 200°C/7 h.

The mechanical properties of cured BA resin are not so good as those of commercial AER 331 epoxy resin perhaps owing to introducing flexible oxyethylene unit except for the  $K_{IC}$  value, in which BA resin is superior to AER 331 resin. Cured TBBA resin has a unflammable structure owing to bromine atoms and a comparable or better mechanical properties to AER 331 resin except for  $T_g$ .

### Dynamic Mechanical Analysis of the Cured Resins

Figures 5 and 6 show DMA results for the cured tetrafunctional epoxy resins. The peak position of the  $\alpha$ -relaxation in the  $\tan \delta$  curves for cured MY-720 resin did not show the peak maximum, but the  $\tan \delta$  curve indicates that the peak maximum may appear beyond a slight higher temperature than 265°C (Fig. 5). The  $\alpha$ -relaxation temperature in the  $\tan \delta$  curve for DDS resin was higher than that for DDM resin. This shows that the higher polarity of the sulfone group increases an attracting force between polymer chains. Storage moduli for the cured new tetrafunctional epoxy resins were lower than that for cured MY-720 resin in the temperature range of -110-265°C owing to introducing flexible oxyethylene units (Fig. 6). In spite of incompleteness of curing, cured MY-720 resin forms the network with higher crosslink density. Cured DDS resin has higher storage modulus than that for cured DDM resin, which corresponds to the structural difference (sulfonyl and methylene groups).

In conclusion, the new tetrafunctional epoxy resins, DDM and DDS resins, have the advantage of easier handling, having higher curing reactivities and giving cured resins with higher toughness, compared with the conventional epoxy resin. The drawback is a decrease in the glass transition temperature of the cured resin.

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