

New Epoxy Resins. II. The Preparation, Characterization, and Curing of Epoxy Resins and Their Copolymers

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Synopsis

A polymer having high aromaticity and/or cyclic ring structures in the chain backbone usually gives high heat resistance and flame resistance. Five glycidyl ether-type epoxy resins are prepared from bisphenol A (DGEBA), 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF), 3,6-dihydroxyspiro[fluorene-9,9'-xanthane] (DGEFX), 10,10-bis(4-hydroxyphenyl)anthrone (DGEA), and 9,9,10,10-tetrakis(4-hydroxyphenyl)anthracene (TGETA) in order to study structure-thermal stability-flame resistance property relationships. In this study, trimethoxyboroxine (TMB) and diaminodiphenylsulfone (DDS) are employed as the curing agents. The char yield at 700°C under a nitrogen atmosphere and the glass transition temperature (T_g) for the uncured resins decrease according to the sequence TGETA > DGEFX > DGEA > DGEBF > DGEBA. The T_g values for these cured epoxy resins are DGEBA < DGEBF < DGEFX < DGEA. A T_g for the TGETA is not obtainable but would be expected to be the highest. The char yields at 700°C of these cured epoxy resins have the same trend as the uncured resins. DGEBF, DGEFX, DGEA, and TGETA added to the DGEBA system show increases in the char yield, T_g , and oxygen index with increasing concentration of these novel epoxy resins.

INTRODUCTION

A polymer having high aromaticity and/or cyclic ring structures in the chain backbone usually gives high heat resistance and flame resistance. Five glycidyl ether-type epoxy resins are prepared from bisphenol A (DGEBA), 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF), 3,6-dihydroxyspiro[fluorene-9,9'-xanthane] (DGEFX), 10,10-bis(4-hydroxyphenyl)anthrone (DGEA), and 9,9,10,10-tetrakis(4-hydroxyphenyl)anthracene (TGETA) in order to study structure-thermal stability-flame resistance property relationships. In this study, trimethoxyboroxine (TMB) and diaminodiphenylsulfone (DDS) are employed as the curing agents.

TMB has been used as a curing agent for epoxy resins in protective coatings, potting and encapsulation of electronic components,^{1,2} transparent epoxy panels,³⁻⁵ and epoxy forms.⁶⁻¹³ The TMB-cured epoxy resins are tough, resilient, slightly rubbery,² heat resistant,⁶⁻⁸ and self-extinguishing⁸ and have high tensile strength and a higher resistance to laser penetration than conventional transparent materials.³ They also have been reported to have exceptionally good ultraviolet stability.¹⁴

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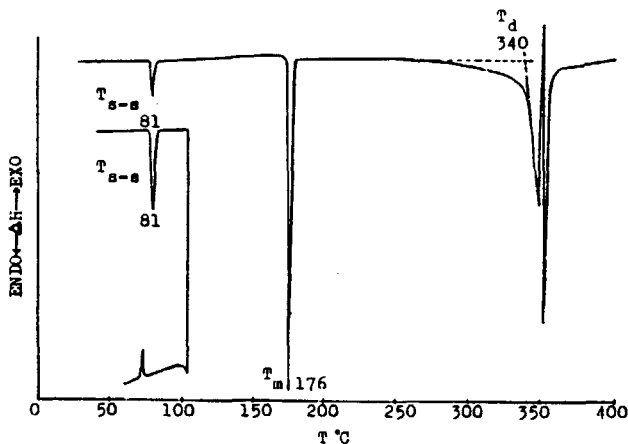


Fig. 1. DSC thermograms of diaminodiphenylsulfone (DDS). Heating rate: 10°C/min; atmosphere: N₂, 0.2 L/min.

DDS has been used as a curing agent to cure epoxy resins for reinforced plastic materials,¹⁵⁻¹⁸ molding materials,¹⁹ coatings,²⁰ adhesives,^{21,22} insulation for electric conductors,²³⁻²⁶ and foams.^{6-8,27} The DDS-cured epoxy resins have good physical and mechanical properties, heat resistance, moisture tolerance, and resistance to solvent, acid, and alkali.

Martin and Price²⁸ have investigated the effects of epoxy resin composition, curing conditions, fillers, and flame-retardant additives on the flammability and have observed that the oxygen index of DGEBA cured with various curing agents is between 19.8 to 23.8. They also have found that fillers and flame-retardant additives can increase the oxygen index to a certain level dependent on the material and the amount used.

Korshak, Solovèva, and Kamenskh²⁹ have prepared a series of epoxy resins with varying structural units. Thermoanalytical studies of the cured materials showed that the heat resistance and thermal stability of the polymers varied based on the varying structure of the elementary unit. The best thermal stability is obtained from polymers having a fluorene or anthrone group between the two phenyl groups using trimellitic anhydride and *m*-phenylenediamine as curing agents. Based upon these results, the material prepared from a diglycidyl ether of 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF), 3,6-dihydroxyspiro[fluorene-9,9'-xanthane] (DGEFX), 10,10-bis(4-hydroxyphenyl)anthrone (DGEA), or a tetraglycidyl ether of 9,9,10,10-tetrakis(4-hydroxyphenyl)anthracene (TGETA) should show higher heat resistance and thermal stability than that obtained from DGEBA.

EXPERIMENTAL

Preparation of Curing Agents

Trimethoxyboroxine (TMB) (Aldrich, 99%, bp 130°C, n_D^{20} 1.3996) was used as curing agent without any further treatment. DDS (diaminodiphenylsulfone) was obtained from Sigma Chemical Co., St. Louis, Missouri. Recrystallization from methanol gave a clear, colorless, bright crystal having a solid-to-solid transition at 81°C, a melting temperature of 176°C, and a decomposition tem-

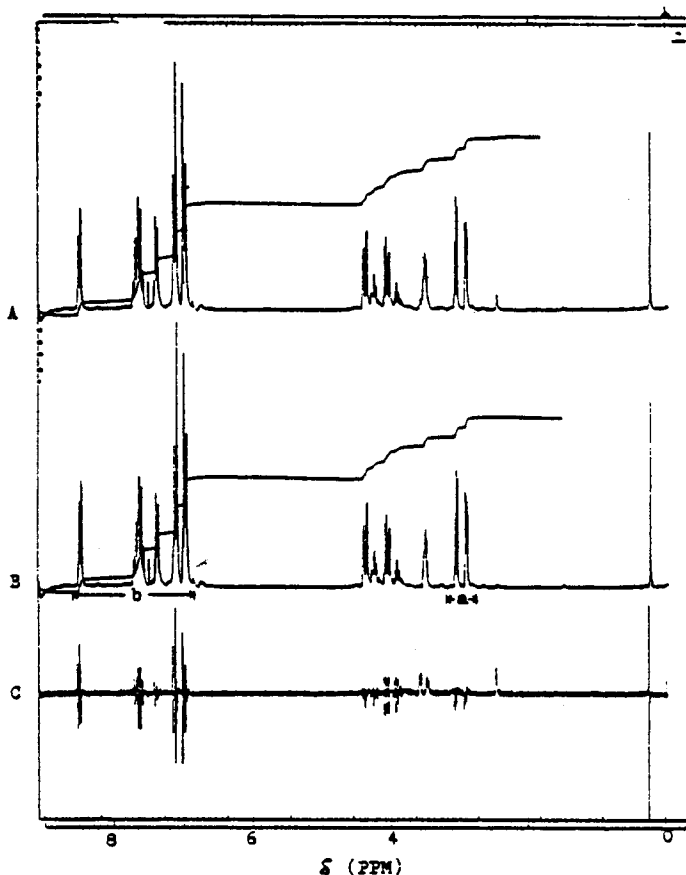


Fig. 2. 220 MHz NMR spectra of (A) DGEA, (B) DGEA + D₂O, (C) the difference of (A) and (B).

perature of 340°C as shown by differential scanning calorimeter (DSC) in Figure 1.

Preparation of Epoxy Resins and Model Compound

Preparation of Bisphenols

Bisphenol A (4,4'-isopropylidenediphenol; Aldrich analyzed grade) was recrystallized from aqueous alcohol.

9,9-Bis(4-hydroxyphenyl)fluorene (DGEBF) was prepared from fluorenone (Aldrich, 98%) and phenol (Aldrich, 99 + %) with a catalyst, dry hydrogen chloride, and a cocatalyst, 3-mercaptopropionic acid³⁰ (Aldrich, 99 + %). Dry hydrogen chloride was prepared by passing hydrogen chloride (Matheson, 99.0%) through concentrated H₂SO₄ for dehydration. Fluorenone (0.75 mol) was dissolved in 6 mol molten phenol, 3 mL 3-mercaptopropionic acid was added, and then dry hydrogen chloride was bubbled in for about 15 min. The system became very dark and finally changed to a viscous, clear liquid. The mixture was then purified by steam distillation to remove unreacted phenol, hydrogen chloride, and cocatalyst. After no more phenol could be collected in the distillate, the

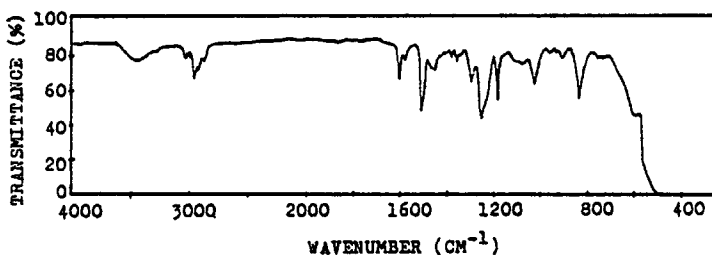


Fig. 3. Infrared spectrum of diglycidyl ether of bisphenol A (DGEBA).

product was further purified by solution in alkali, filtration to separate unreacted fluorenone, and acidification with concentrated hydrochloric acid to precipitate a white solid. The dried powder was recrystallized from anhydrous ether (Mallinckrodt analytical reagent). A transparent solvated crystal was collected from the ether solution, washed with a small amount of solvent, and then dried in a vacuum oven. A white powder with a melting point of 224°C was obtained (lit. mp 224°C,³⁰ 225–225.5°C²⁹).

3,6-Dihydroxyspiro[fluorene-9,9'-xanthane] (DGEFX) was prepared from fluorenone (Aldrich, 98%) and resorcinol (Aldrich, 98%) with dry hydrogen chloride as catalyst.¹²⁰ Fluorenone (100 g) and resorcinol (200 g) were fused together at 180–200°C, while dry hydrogen chloride was passed through the molten solution for 5 h. The reddish-brown product was poured out and cooled and then thoroughly washed with water to remove resorcinol. The bisphenol was recrystallized four times from benzene, and a glassy, yellowish crystal form which melted at 264°C and crystallized at 169°C (DSC) was obtained (lit. mp 262°C,³⁰ 232°C,³¹ and 238–239°C²⁹).

10,10-Bis(4-hydroxyphenyl)anthrone (DGEA) was prepared from anthraquinone (Aldrich, 97%) and phenol (Aldrich, 99 + %) with a catalyst, dry hydrogen chloride, and a cocatalyst, 3-mercaptopropionic acid (Aldrich, 99 + %). Anthraquinone (60 g), phenol (150 g), and 3-mercaptopropionic acid (8 g) were placed in a round-bottom flask. The mixture was heated at 65°C, and then dry hydrogen chloride was bubbled in for about 24 h. The phenol, hydrogen chloride, and cocatalyst were removed by steam distillation. This product was recrystallized from methanol as a slightly yellowish granular mass: 11.07 g (10%), mp 320–322°C (lit. mp 318–320°C³⁰ and 305–310°C^{32–37}).

Preparation of 9,9,10,10-Tetrakis(4-hydroxyphenyl)anthracene (TGETA)

10,10-Bis(*p*-anisyl)anthrone was prepared from 10,10-bis(*p*-hydroxyphenyl)anthrone and dimethyl sulfate (Aldrich, 99 + %) with sodium hydroxide as catalyst. A mixture of 7.6 g 10,10-bis(*p*-hydroxyphenyl)anthrone, 10 ml alcohol, and 100 ml 10% sodium hydroxide solution was refluxed and 30 ml dimethyl sulfate was added gradually. It was heated for 1 h and the crystalline precipitate was recrystallized from acetic acid to give a white product in 98% yield, mp 208–209°C (lit. mp 208–209°C^{33,34}).

9,9,10-Tri(*p*-anisyl)-10-hydroxyanthracene¹²⁴ was prepared from 10,10-bis(*p*-anisyl)anthrone and the Grignard reagent of *p*-iodoanisole (Aldrich, 98%). Sixteen grams 10,10-bis(*p*-anisyl)anthrone dissolved in 75 mL benzene (Aldrich, 99 + %) was added gradually to the Grignard reagent obtained from 18.9 g *p*-

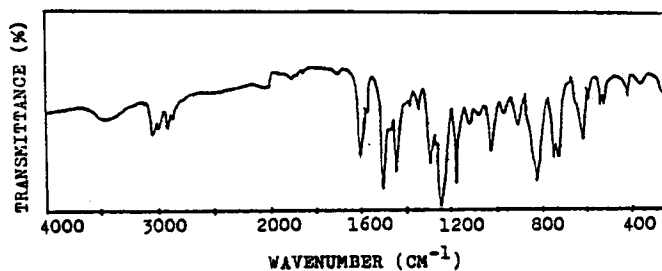


Fig. 4. Infrared spectrum of diglycidyl ether of 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF).

iodoanisole, 2.0 g magnesium, 75 mL anhydrous ether, and a small amount of ethyl iodide (Fisher reagent grade). The mixture was refluxed for 5 h and decomposed with ice and ammonium chloride; the ether-benzene layer was filtered and the solution steam distilled. The crystalline residue was recrystallized from acetic acid; it gave a yield of 19.5 g (96%), mp 228–230°C (lit. mp 226–228°C³⁴).

9,9,10-Tri(*p*-anisyl)-10-(*p*-hydroxyphenyl)anthracene was prepared from 9,9,10-tri(*p*-anisyl)-10-hydroxyanthracene and phenol with sulfuric acid (Baker reagent grade) as catalyst. A mixture of 15 g 9,9,10-tri(*p*-anisyl)-10-hydroxyanthracene, 90 g phenol, and 12 drops sulfuric acid was heated on a steam bath for 4 h, and the material was washed with hot water and recrystallized from acetic acid. The product was obtained in 98% yield, mp 315–317°C (lit. mp 310–312°C³⁴).

9,9,10,10-Tetrakis(4-hydroxyphenyl)anthracene was prepared from 9,9,10-tri(*p*-anisyl)-10-(*p*-hydroxyphenyl)anthracene and constant boiling hydrobromic acid (Alfa reagent grade, 48%). Two grams 9,9,10-tri(*p*-anisyl)-10-(*p*-hydroxyphenyl)anthracene, 20 mL 48% hydrobromic acid, and 300 mL acetic acid were refluxed for 5 h. The mixture was concentrated to a volume of about 75 ml and poured into 200 mL water. The precipitated product was recrystallized from dilute alcohol, yielded a total of 1.8 g (95%), mp 389°C by DSC measurement (lit. mp 367–374°C³⁴).

Synthesis of Glycidyl Ether-Type Epoxy Resins

The diglycidyl ethers of bisphenol A (DGEBA), 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF), and 3,6-dihydroxyspiro[fluorene-9,9'-xanthane] (DGEFX) were prepared by feeding respectively bisphenol A, 9,9-bis(4-hydroxyphenyl)fluorene, and 3,6-dihydroxyspiro[fluorene-9,9'-xanthane] and epichlorohydrin

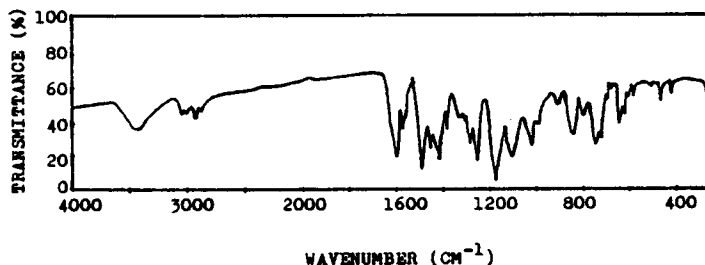


Fig. 5. Infrared spectrum of diglycidyl ether of 3,6-dihydroxyspiro[fluorene-9,9'-xanthane] (DGEFX).

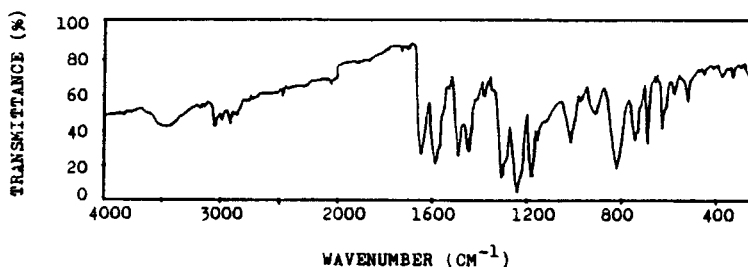


Fig. 6. Infrared spectrum of diglycidyl ether of 10,10-bis(4-hydroxyphenyl)anthrone (DGEA).

in the mole ratio of 1:10 in a heated reaction kettle containing a thermometer, a mechanical stirrer, and a water-cooled condenser. During a period of 2 h, 2 mol 40% aqueous sodium hydroxide solution was added to the reaction mixture and the reaction temperature was maintained between 100 and 110°C. The solution was filtered to separate the solid sodium chloride formed during the reaction. The salt cake was washed with additional epichlorohydrin. The unreacted epichlorohydrin was then distilled off under a vacuum of 30 torr from filtrate. After no additional epichlorohydrin could be removed under this pressure, the vacuum was decreased to 2 torr for 30 min at 170°C.

The diglycidyl ethers of 10,10-bis(4-hydroxyphenyl)anthrone (DGEA) and tetraglycidyl ether of 9,9,10,10-tetrakis(4-hydroxyphenyl)anthracene (TGETA) were prepared by the same procedures as above, except that the initial reactant feed ratio of the bis- or tetraphenols to epichlorohydrin was 1:20.

DGEBF and DGEA could be recrystallized from their acetone solutions by adding poor solvent (e.g., absolute alcohol) into these solutions with vigorous agitation until these solutions appeared a little cloudy. These solutions then stood until complete precipitation occurred. The white crystalline powders were collected by filtration and washed with a mixture of acetone and absolute alcohol (1:1). The crystalline DGEBF and DGEA had melting points of 137 and 163°C, respectively.

Characterization of Epoxy Resins

Epoxy Resin Analysis

The epoxy resins prepared from the above methods were identified by NMR and IR spectroscopy. Varian A-60 and 220 NMR spectrometers were used for the NMR measurements, and CDCl_3 (Aldrich, 99.8 atom % D, GOLD LABEL) were used as solvent. The infrared spectra were obtained on a Perkin-Elmer

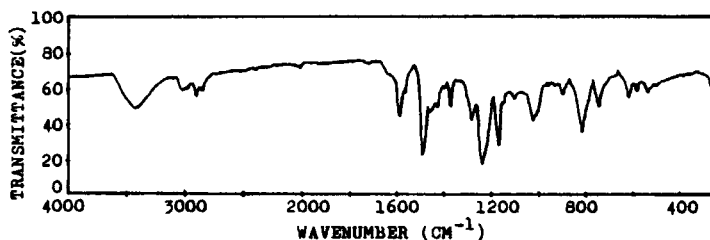


Fig. 7. Infrared spectrum of tetraglycidyl ether of 9,9,10,10-tetrakis(4-hydroxyphenyl)anthracene (TGETA).

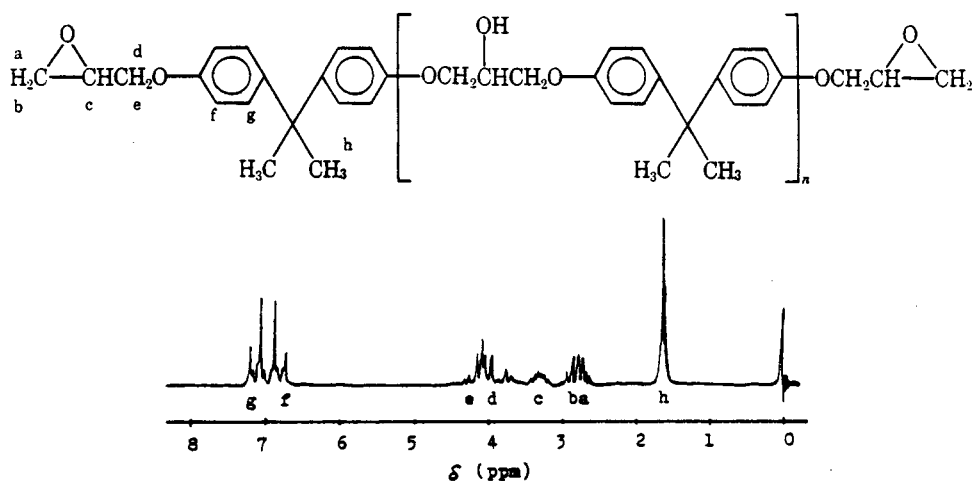


Fig. 8. ¹H 60-MHz NMR spectrum of diglycidyl ether of bisphenol A (DGEBA).

spectrophotometer. The glass transition temperature (T_g) and/or melting temperature (T_m) of each resin was studied by differential scanning calorimetry (du Pont 910 Differential Scanning Calorimeter connected with du Pont 990 Thermal Analyzer).

Epoxy Equivalent Weight (EEW) Determination

The ASTM D 1652-73³⁸ method or 220 MHz proton NMR was used to determine the EEW of epoxy resins. Epoxy resin, 0.2 g, was added to a 50-mL flask and then dissolved in 10 ml 50 vol % chlorobenzene (Aldrich analyzed grade, 99%)

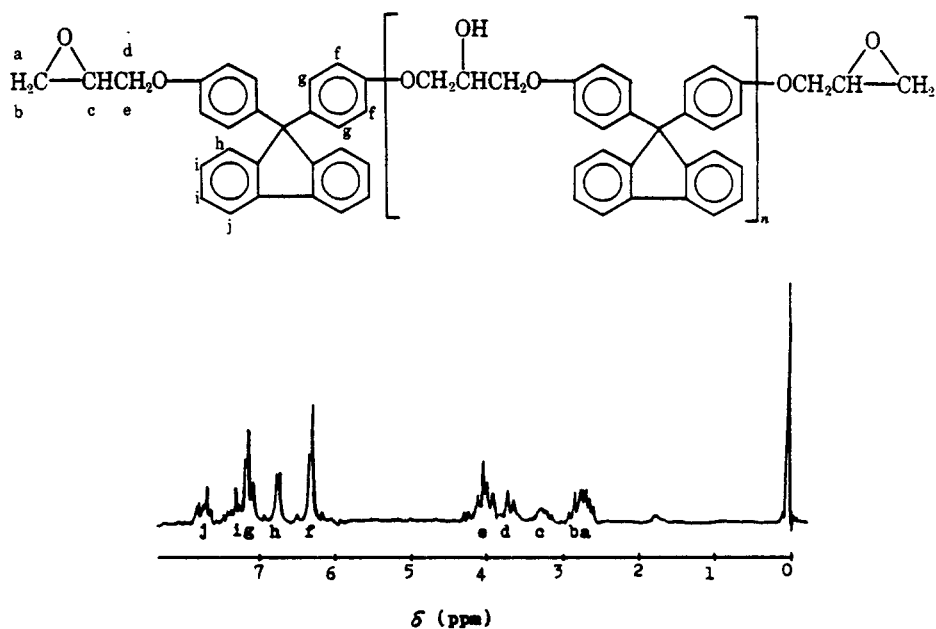


Fig. 9. ¹H 60-MHz NMR spectrum of diglycidyl ether of 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF).

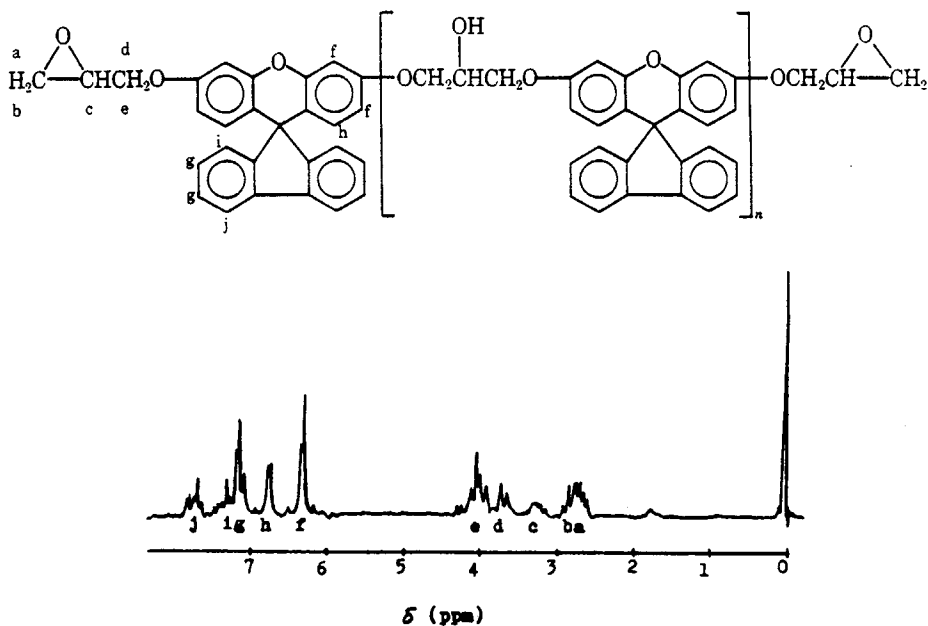


Fig. 10. ^1H 60-MHz NMR spectrum of diglycidyl ether of 3,6-dihydroxyspiro[fluorene-9,9'-Xanthane] (DGEFX).

in chloroform. The mixture was stirred with a Teflon-coated magnetic stirring bar. Four drops of 0.1% crystal violet [4,4',4''-methylidynetris(*N,N*-dimethylaniline), Eastman] solution in glacial acetic acid (J.T. Baker) was used as the indicator. The solution was titrated with 0.1 *N* hydrogen bromide in acetic acid (Eastman, 30.32% in acetic acid by titration). The hydrogen bromide solution was standardized by 0.4 g potassium hydrogen phthalate each time before using it for epoxy equivalent weight determination. The EEW of DGEA was determined by 220 MHz NMR. This resin was dissolved in CDCl_3 using one small drop of D_2O (Aldrich, 100.0 atom % D, GOLD LABEL) to exchange the hydroxyl proton, and TMS (tetramethylsilane, Aldrich, 99.9+% NMR grade) was used as the internal reference (Fig. 2). The n value could be calculated through the known values of I_b (the intensity of the aromatic proton resonance) and I_a (the terminal methylene proton of the oxirane ring) by

$$n = \frac{I_b - 4I_a}{16} \quad (1)$$

When n was determined, EEW could be easily obtained.

Curing Processes in the Epoxy-Variou s Curing Agent System

The curing cycle for the boroxine curing system was 135°C for 3 h, 180°C for 3 h, and 218°C for 3 h.^{5,39} For DDS, the cycle was 5 h at 125°C and an additional 4 h at 200°C.

The DGEBA, DGEBF, DGEFX, DGEA, or TGETA was mixed with the curing agent. The two-component epoxy systems were prepared by blending DGEBF, DGEFX, DGEA, or TGETA with Epon 828 (DGEBA) at 130°C, then mixed with these various curing agents. The curing was carried out in a nitrogen-filled and sealed glass tube at the same conditions mentioned above.

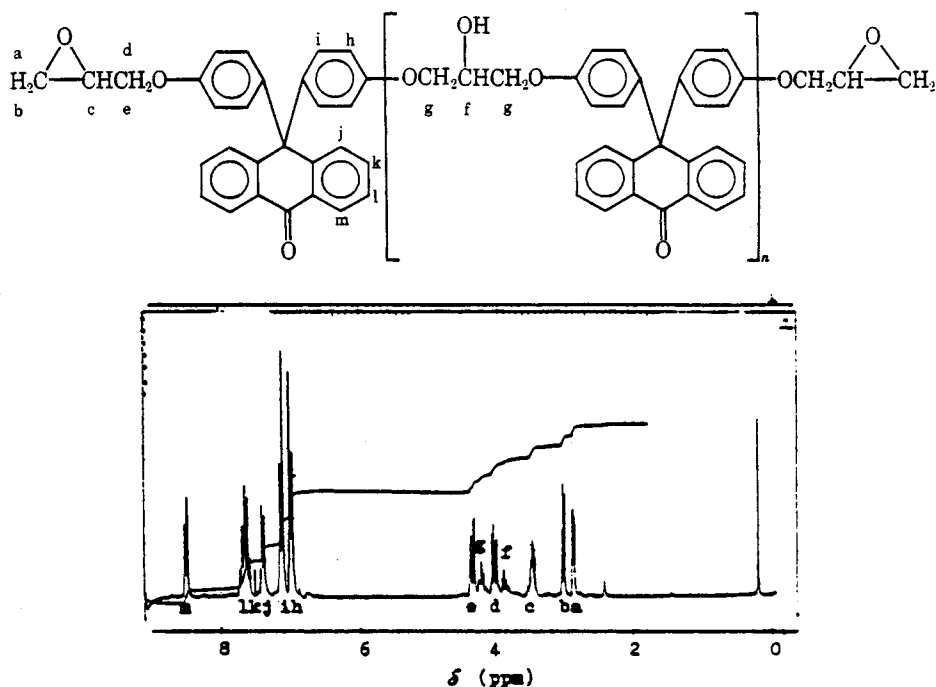


Fig. 11. 220-MHz Proton NMR spectra of DGEA.

Characterization of Cured Epoxy Resins

Dynamic Thermal Analysis

The thermal properties of various samples in this study were investigated on a du Pont 910 Differential Scanning Calorimeter (DSC) connected with a du Pont 990 Thermal Analyzer for DSC thermograms. The du Pont 951 Thermogravimetric Analyzer (TGA) was connected with a du Pont 990 Thermal Analyzer for char residue and/or the activation energy of thermal decomposition determination. Samples having mesh numbers greater than 170 were used for DSC or TGA measurement. For DSC and TGA measurements, the nitrogen flow rate was 0.2 and 0.3 L/min, respectively, with a heating rate of 10°C/min.

Oxygen Index Measurement

The oxygen index of the various samples in this study was measured by using the General Electric model CR 280 KF 11 A Fluid Flammability Test Kit. The cured epoxy resin was made into a pellet form and placed a sample cup mounted on the cup holder in the flame chamber, and a mixture of oxygen and nitrogen was passed upward through the chimney at a flow rate of 3–5 cm/s. The test followed the manual procedure.⁴⁰ The oxygen index (OI) was obtained from the equation

$$OI = \frac{[O_2]}{[O_2] + [N_2]} \times 100 \quad (2)$$

where the oxygen index was the concentration of oxygen (percent by volume in the gas mixture in the combustion chamber) which will just support burning, but not support burning at the next lower concentration of oxygen; $[O_2]$ and $[N_2]$

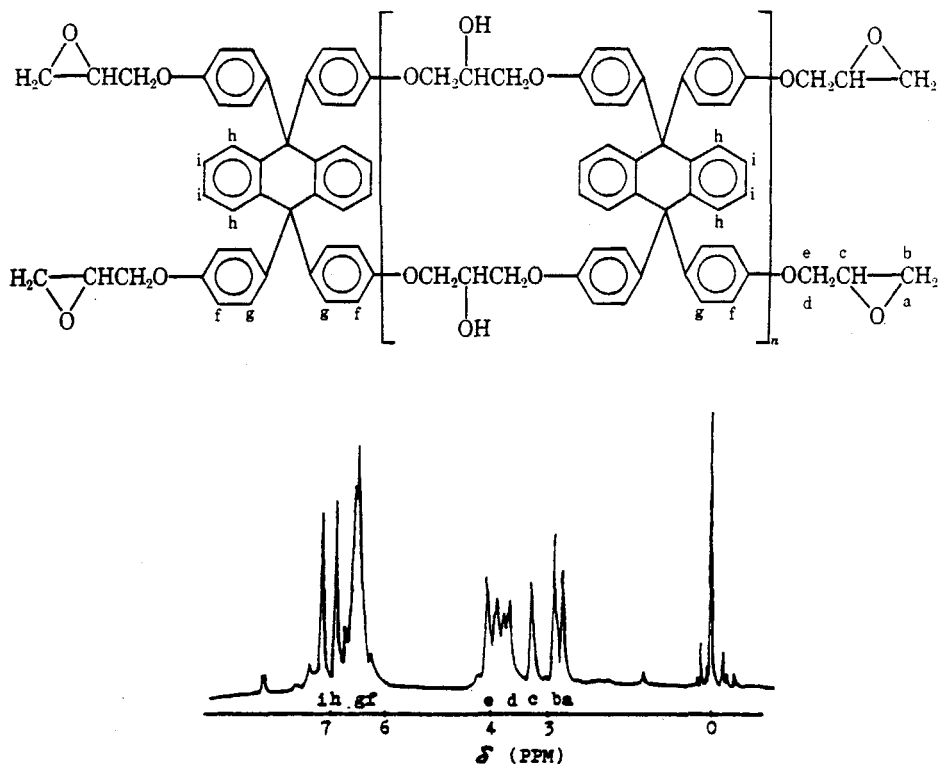


Fig. 12. 220-MHz NMR spectrum of tetraglycidyl ether of 9,9,10,10-tetrakis(4-hydroxyphenyl)anthracene (TGETA).

were related to the respective volumes of oxygen and nitrogen in the chamber.

Solvent Extraction of Cured Epoxy Resins

One gram cured epoxy resin was put into a Soxhlet apparatus (Pyrex glass thimble) and extracted with tetrahydrofuran (J. T. Baker HPLC grade) for four days. The insoluble part was collected and dried under vacuum oven until no weight change was detected. The gel fraction was calculated as

$$\text{gel fraction} = \frac{\text{weight of insoluble material}}{\text{initial weight of material}} \quad (3)$$

RESULTS AND DISCUSSION

Characterization of Epoxy Resins

Structure Study on Glycidyl Ether-Type Epoxy Resins

The epoxy resins DGEBA, DGEBF, DGEFX, DGEA, and TGETA are identified by IR (Figures 3-7) and NMR (Figs. 8-12). The IR and NMR assignments are shown in Tables I and II. Conjugation with two phenyl groups lowers the frequency of the C=O group stretching of DGEA to 1648 cm^{-1} . The delocalization of the π electrons of the carbonyl group reduces the double bond character

of the C=O bond, causing absorption at lower frequencies than is normally found in aliphatic ketones. Because of the additional deshielding effect of the carbonyl group, the ortho protons of the DGEA are shifted slightly further downfield ($\delta \sim 8.27$) than the other ring protons.

Properties of Epoxy Resins Derived from Bisphenols and Tetraphenol

The epoxy resins in this study are prepared by reacting epichlorohydrin with bisphenols or tetraphenol. The properties of these epoxy resins are summarized in Table III.

TABLE I
Infrared Transmittance Assignments for the Five Epoxy Resins

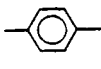
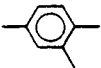
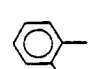
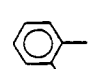

Wave no. (cm^{-1})	DGEBA	DGEBF	DGEFX	DGEA	TGETA	Functional group	Vibration mode
3470				x		R—OH	$\nu(\text{O—H})$
3438		x					
3420	x				x		
3410			x			Arylene	$\nu(\text{C—H})$
3048				x			
3046			x				
3040	x				x		
3030		x					
2992		x					
2988			x			Methyl	$\nu(\text{C—H})$
2986					x		
2982				x		Methylene	$\nu(\text{C—H})$
2952	x						
2912	x		x				
2910				x	x		
2908		x				Ketone	$\nu(\text{C=O})$
2862		x					
2860			x	x		Phenylene	Quadrant stretching
2859	x				x		
1648				x			
1600			x			Phenylene	Quadrant stretching
1599	x						
1598		x					
1592					x		
1586				x		Semicircle stretching	
1578	x						
1576		x					
1564			x				
1501	x						
1495		x				Semicircle stretching	
1494					x		
1490				x		Semicircle stretching	
1486			x				
1461					x		
1442			x	x		Semicircle stretching	
1440		x					
1436					x		

TABLE I. (Continued from previous page.)

Wave no. (cm^{-1})	DGEBA	DGEBF	DGEFX	DGEA	TGETA	Functional group	Vibration mode
1250			x			Ar—O—R	$\nu(\text{C—O—C})$
1240	x			x	x		
1235		x					
1180	x					Ar—H	In-plane C—H deformation
1178				x			
1175		x	x				
1172					x		Ring deformation
906	x	x		x	x		
904			x				
836			x			p-phenylene	In-phase out-of-plane hydrogen wagging
828	x						
820				x			
818					x		
816		x				o-phenylene	In-phase out-of-plane hydrogen wagging
746					x		
742		x					
740			x	x			
728		x					

DGEBF, DGEFX, and DGEA have been prepared by Korshak et al., and when cured with trimellitic anhydride or *m*-phenylenediamine, they gave very good heat resistance and high thermal stability.⁴¹ DGEBF was a white crystal having a melting temperature of 137°C (lit. mp 132°C⁵). After the molten monomer is quenched, only a softening temperature at 38°C (lit. 30°C,⁵ 70°C⁴¹) can be observed. The white crystalline DGEA has a melting temperature of 163°C, and showed only a softening temperature at 48°C if the molten DGEA was quenched.

The order of the glass transition temperatures was TGETA > DGEFX > DGEA > DGEBF > DGEBA (Table III). The increase in glass transition temperature going from DGEBA to TGETA appeared to correspond to an increase in side chain stiffness due to the larger side chain and lower degree of free conformational rotation. The order of char yield at 700°C and nitrogen atmosphere was also TGETA > DGEFX > DGEA > DGEBF > DGEBA (Table III and Fig. 13). The increase of char yield from DGEBA to TGETA corresponded to the ease and degree of aromatization and cyclization of these resins.

Curing Reaction Studies with Various Curing Agent Systems

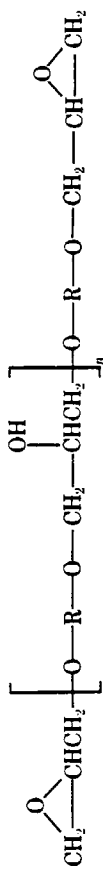
The DSC thermograms of DDS after mixing with DGEBA, DGEBF, DGEFX, DGEA, and TGETA (curing agent 1.2276 equiv/epoxy equiv) are shown in Figure 14. The curing onset, extrapolated onset, and maximum exothermic temperature are summarized in Table IV. It was difficult to distinguish differences in reactivity for the DDS curing systems with DGEBA, DGEBF, DGEFX, DGEA, and TGETA.

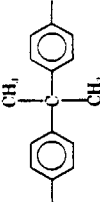
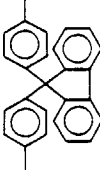

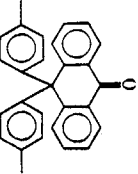
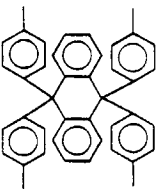
There was an interesting small endotherm at 80°C in the DSC thermograms for the DDS curing systems. May et al.⁴² have explained a similar observation

TABLE II
NMR Band Assignments for Various Epoxy Resins

DGEBA		DGEBF		DGEFX		DGEA		TGETA	
Peak	δ , ppm	Peak	δ , ppm	Peak	δ , ppm	Peak	δ , ppm	Peak	δ , ppm
g	7.23-6.97	j	7.77-7.53	j	7.82-7.61	m	8.27-8.21	i	7.20-7.10
f	6.95-6.66	i, h	7.51-7.18	i	7.41-7.23	l, k	7.49-7.32	h	6.92-6.78
e, d	4.30-3.49	g, f	7.18-6.58	g	7.23-7.00	j	7.17-7.11	g, f	6.70-6.30
c	3.47-3.13	e, d	4.24-3.54	h	6.80-6.69	i	6.91-6.80	e, d	4.18-3.70
b, a	2.97-2.59	c	3.44-2.96	f	6.39-6.23	h	6.78-6.70	c	3.40-3.30
h	1.72-1.47	b, a	2.94-2.52	e, d	4.24-3.50	e	4.19-4.12	b, a	2.94-2.71
				c	3.50-3.00	g	4.09-3.97		
				b, a	2.98-2.58	d	3.89-3.76		
						f	3.71-3.65		
						c	3.34-3.22		
						b	2.86-2.81		
						a	2.72-2.65		

TABLE III
 Properties of Epoxy Resins Prepared from Epichlorohydrin and Bisphenols or Tetraphenol



	DGEBA	DGEBF	DGEFX	DGEA	TGETA
R					
Color	Pale yellow	White	Yellowish brown	White	White
Epoxy equivalent weight	189.3 (177.2)	254	415.7	343.3	204.2
\bar{n}	0.13 (0.05)	0.11	0.87	0.45	0.07
T_g , °C	-24	38	58	48	143
T_m , °C	—	137	—	163	—
Char yield at 700°C, N ₂ , %	2.4	21.4	41.9	32.2	49.6

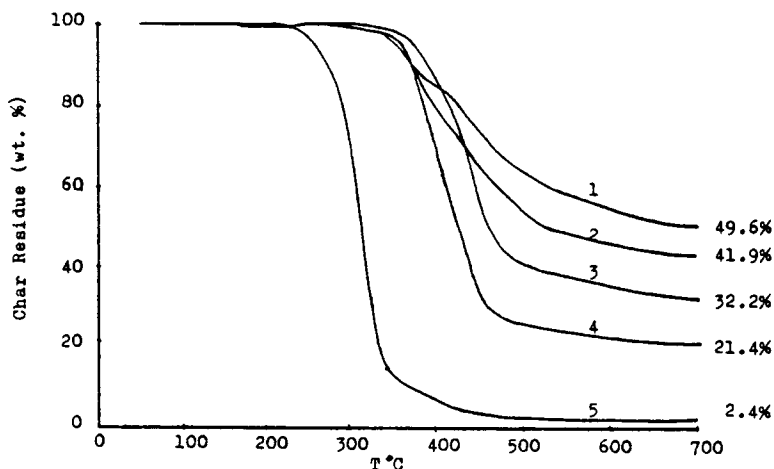


Fig. 13. TGA of various uncured epoxy resins: (1) TGETA; (2) DGEFX; (3) DGEA; (4) DGEBF, (5) DGEBA. Heating rate: 10°C/min; atmosphere: N₂, 0.3 L/min.

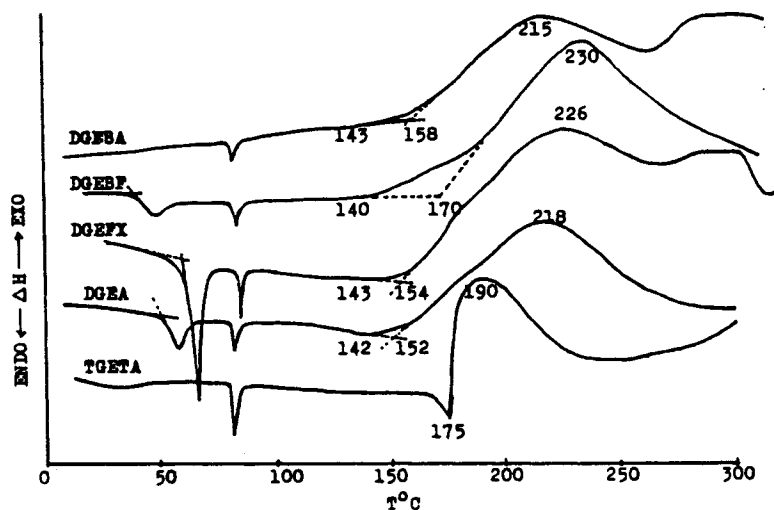


Fig. 14. DSC thermograms of DDS after mixing with DGEBA, DGEBF, DGEFX, DGEA, and TGETA. Curing agent: 1.2276 equiv/epoxy equiv; heating rate: 10°C/min; atmosphere: N₂, 0.2 L/min.

as the vaporization of a small amount of solvent left in the epoxy formulation. DSC thermograms of DDS (Fig. 1) have shown that this endotherm was mainly due to a solid-solid phase transition. Other endotherms are probably due to such effects as short-range orientation.

TABLE IV
Summary of DSC Thermograms of DDS Mixtures with DGEBA, DGEBF, DGEFX, DGEA, and TGETA^a

	DGEBA	DGEBF	DGEFX	DGEA	TGETA
Curing onset, °C	143	140	143	142	—
Extrapolated onset, °C	158	170	154	152	175
Maximum exothermic temperature, °C	215	230	226	218	190

^a Curing agent 1.2276 equiv/epoxy equiv.

TABLE V
Char Yield and T_g of DDS (1.2276 Equiv/Epoxy Equiv) Cured Epoxy Resin Comixtures^a

	A	B	C	D	E	F
Char yield at 700°C, N ₂ , %	14.8	25.6	32.3	40.2	42.2	40.6
T_g , °C	73	75	87	93	120	138

^a Epon 828 and DGEFX ((A) 0%, (B) 20%, (C) 40%, (D) 60%, (E) 80%, and (F) 100%). Curing conditions: 125°C for 5 h and 200°C for 4 h.

Characterization of Cured Epoxy Systems with Various Curing Agent Systems

The T_g values and char yields of the DDS (1.2276 equiv/epoxy equiv) cured epoxy resin comixtures of Epon 828 and DGEFX increase as more DGEFX is added (Table V). DGEFX shows a synergistic effect with DGEBA in regard to char formation (Fig. 15). The oxygen index may also have had a relationship with the char yield for this system (Fig. 16). The degradation exotherms are related to their compositions (Fig. 17).

The T_g values and char yields of the DDS cured epoxy resin comixtures of Epon 828 and DGEA increase with increasing DGEA content (Table VI). The relationship between T_g and the mole fraction of DGEA for the comixtures of DGEA and Epon 828 cured by DDS indicated that DGEA increases the T_g of DGEBA in a nonlinear synergistic manner (Fig. 18). A linear relationship between oxygen index and char yield was found (Fig. 19).

The T_g values and char yields of the TMB (0.164 equiv/epoxy equiv) cured epoxy resin comixtures of Epon 828 and DGEA indicated that DGEA increases the glass transition temperature and the char yield of the DGEBA system (Table VII). A linear relationship between oxygen index and char yield was indicated (Fig. 20).

DDS (1.2276 equiv/epoxy equiv) cured epoxy resin comixtures of Epon 828 and TGETA at various compositions indicated that char yields were increasing

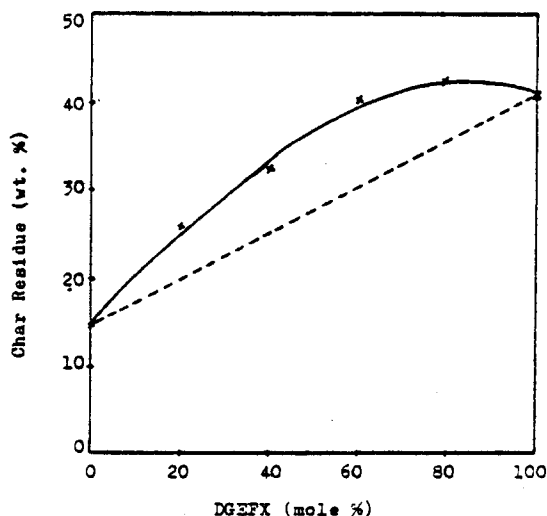


Fig. 15. Char residue at 700°C as function of mole fraction of DGEFX in the copolymer of DGEFX and Epon 828. Curing agent: DDS, 1.2276 equiv/epoxy equiv; curing conditions: 125°C for 5 h and 200°C for 4 h.

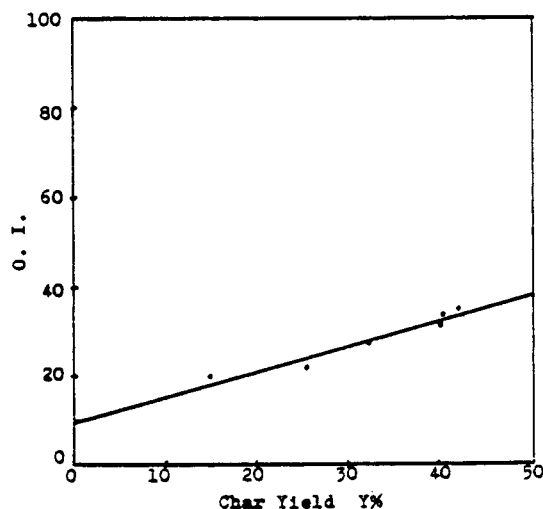


Fig. 16. Oxygen index vs. char yield at 700°C of the copolymer of DDS-cured DGEFX and Epon 828. Curing agent: DDS, 1.2276 equiv/epoxy equiv; curing conditions: 125°C for 5 h and 200°C for 4 h.

from 14.8 to 40.9% (Fig. 21). A linear relationship with OI and char yield was obtained for this system (Fig. 22). The same epoxy compositions using a different curing agent (TMB, 0.164 equiv/epoxy equiv) and curing cycle were investigated by TGA (Fig. 23), which showed that their char yields were increasing from 28.9 to 52.1% with increasing amounts of TGETA. The synergistic char formation effect in this system occurred at high concentrations of TGETA (Fig. 24). Again, there may have been a linear relationship between OI and char yield for this study (Fig. 25 and Table VIII).

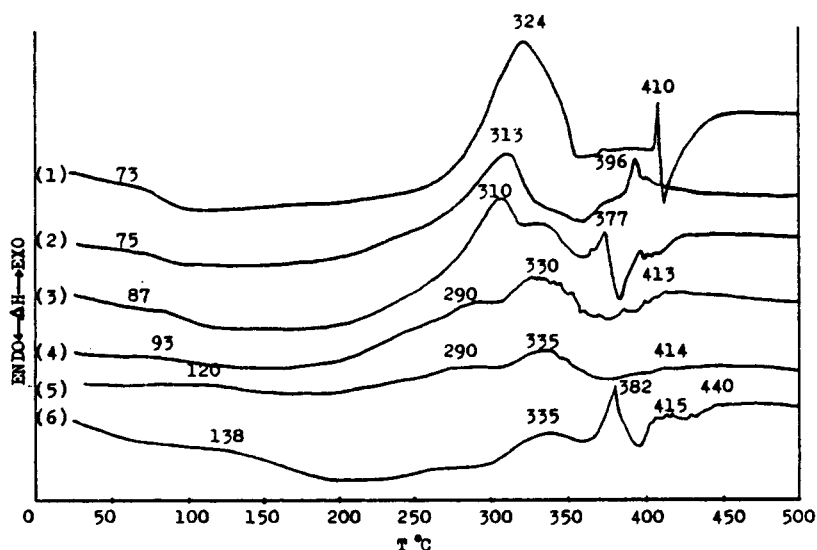


Fig. 17. DSC thermograms of DDS-cured epoxy copolymer. Epon 828 and DGEFX (1) 0%, (2) 20%, (3) 40%, (4) 60%, (5) 80%, and (6) 100%; curing agent: 1.2276 equiv/epoxy equiv; curing conditions: 125°C for 5 h and 200°C for 4 h; heating rate: 10°C/min; atmosphere: N₂, 0.2 L/min.

TABLE VI
Char Yield and T_g of DDS (1.2276 Equiv/Epoxy Equiv) Cured Epoxy Resin Comixtures^a

	A	B	C	D	E	F
Char yield at 700°C, N ₂ , %	14.8	24.3	22.9	29.0	33.4	33.5
T_g , °C	73	100	113	115	128	140

^a Epon 828 and DGEA (A) 0%, (B) 20%, (C) 40%, (D) 60%, (E) 80%, and (F) 100%. Curing conditions: 125°C for 5 h and 200°C for 4 h.

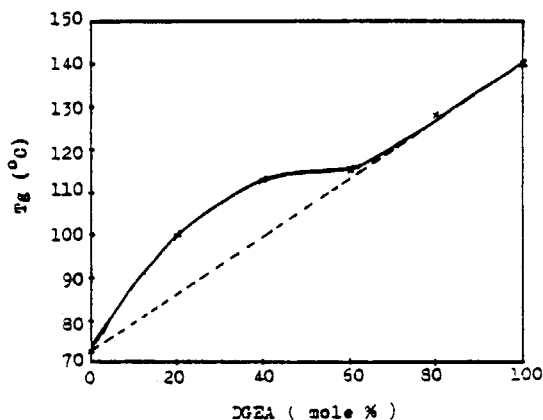


Fig. 18. T_g as function of mole fraction of DGEA in the copolymer of DGEA and Epon 828. Curing agent: DDS, 1.2276 equiv/epoxy equiv; curing conditions: 125°C for 5 h 200°C for 4 h.

The T_g values, char yields, and gel fractions for DDS (1.2276 equiv/epoxy equiv) or TMB (0.164 equiv/epoxy equiv) cured DGEBA, DGEBF, DGEFX, DGEA, and TGETA are summarized in Tables IX and X. Their T_g values had

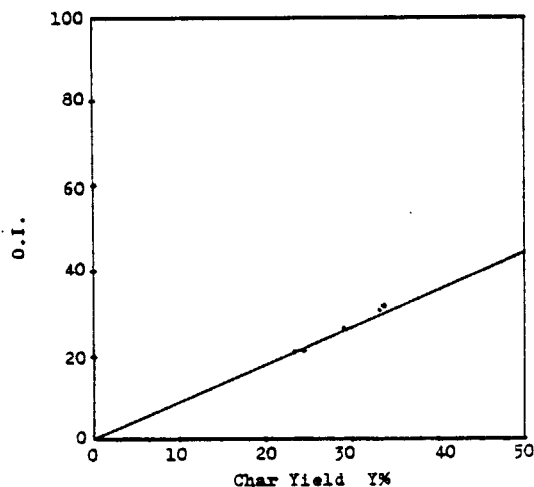


Fig. 19. Oxygen index vs. char yield at 700°C of the copolymer of DDS-cured DGEFX and Epon 828. Curing agent: DDS, 1.2276 equiv/epoxy equiv; curing conditions: 125°C for 5 h and 200°C for 4 h.

TABLE VII
Char Yield and T_g of TMB (0.164 Equiv/Epoxy Equiv) Cured Epoxy Resin Comixtures^a

	A	B	C	D	E	F
Char yield at 700°C, N ₂ , %	28.9	36.4	39.0	41.1	49.6	48.1
T_g , °C	60	64	98	103	149	162

^a Epon 828 and DGEA (A) 0%, (B) 20%, (C) 40%, (D) 60%, (E) 80%, and (F) 100%. Curing conditions: 135°C for 3 h, 180°C for 3 h, and 218°C for 3 h.

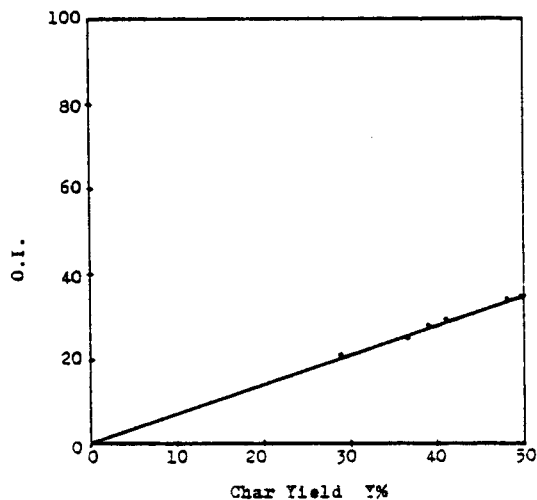


Fig. 20. Oxygen index vs. char yield at 700°C of the copolymer of DDS-cured DGEFX and Epon 828. Curing agent: DDS, 1.2276 equiv/epoxy equiv; curing conditions: 135°C for 3 h, 180°C for 3 h, and 218°C for another 3 h.

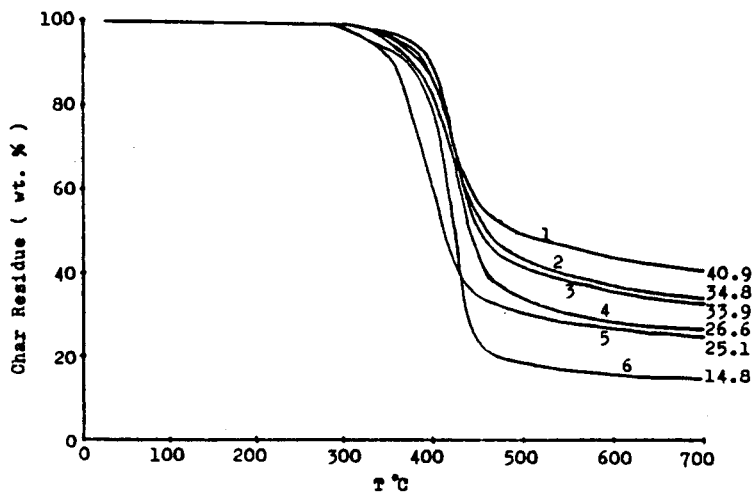


Fig. 21. TGA for various compositions of TGETA with Epon 828. Curing agent: DDS, 1.2276 equiv/epoxy equiv; curing conditions: 125°C for 5 h and 200°C for 4 h; heating rate: 10°C/min; atmosphere: N₂, 0.3 L/min; Epon 828 (mol %): (1) 0, (2) 20, (3) 40, (4) 60, (5) 80, (6) 100.

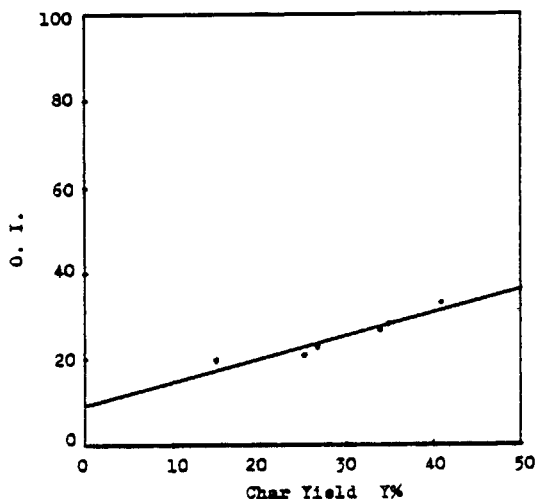


Fig. 22. Oxygen index vs. char yield at 700°C of the copolymer of DDS-cured DGEFX and Epon 828. Curing agent: DDS, 1.2276 equiv/epoxy equiv; curing conditions: 125°C for 5 h and 200°C for 4 h.

the trend DGEBA < DGEBF < DGEFX < DGEA, whether they are cured with DDS or TMB. A T_g for TGETA was not obtainable but would be expected to be the highest. The following relationship held for char residue: DGEBA < DGE BX < DGEFX < DGEA < TGETA. The amounts of gel formed for the DDS-cured epoxy resins were DGEBA > DGEBF \geq DGEA > TGETA > DGEFX, but for the TMB cured epoxy resins they were TGETA \geq DGEA > DGEBF = DGEBA > DGEFX.

This study has supported the concept that the higher aromaticity or cyclic structure content of these epoxy resins gave higher char residues and glass transition temperatures. The relationship between gel fraction and the structure of these epoxy resins is still unclear.

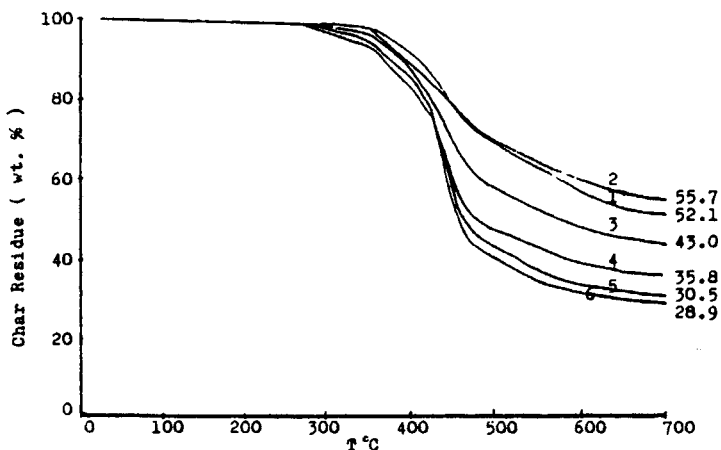


Fig. 23. TGA for various compositions of TGETA with Epon 828. Curing agent: TMB, 0.164 equiv/epoxy equiv; curing conditions: 135°C for 3 h, 180°C for 3 h, and 218°C for 3 h; heating rate: 10°C/min; atmosphere: N₂, 0.3 L/min; Epon 828 (mol %): (1) 0, (2) 20, (3) 40, (4) 60, (5) 80, (6) 100.

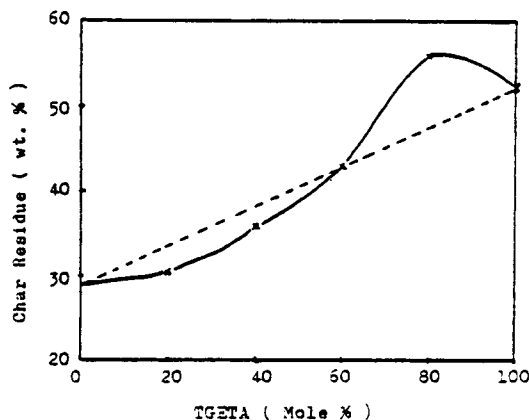


Fig. 24. Char residue at 700°C as function of mole fraction of TGETA in the copolymer of TGETA and Epon 828. Curing agent: TMB, 0.164 equiv/epoxy equiv; curing conditions: 135°C for 3 h, 180°C for 3 h, and 218°C for another 3 h.

CONCLUSIONS

Five epoxy resins—DGEBA, DGEBF, DGEFX, DGEA and TGETA—were prepared from epichlorohydrin and bisphenol A, 9,9-bis(4-hydroxyphenyl)fluorene, 3,6-dihydroxyspiro[fluorene-9,9'-xanthane], 10,10-bis(4-hydroxyphenyl)anthrone, and 9,9,10,10-tetrakis(4-hydroxyphenyl)anthracene, respectively. The feed mole ratios of epichlorohydrin to bisphenols or tetraphenol were 10:1 for DGEBA, DGEBF, and DGEFX and 20:1 for DGEA and TGETA. DGEBF and DGEA were solids having melting points of 137 and 163°C, respectively. The glass transition temperatures for uncured DGEBA, DGEBF, DGEA, DGEFX, and TGETA were -24, 38, 48, 58, and 143°C, respectively. The glass transition temperatures have corresponded to an increase of aromatic ring

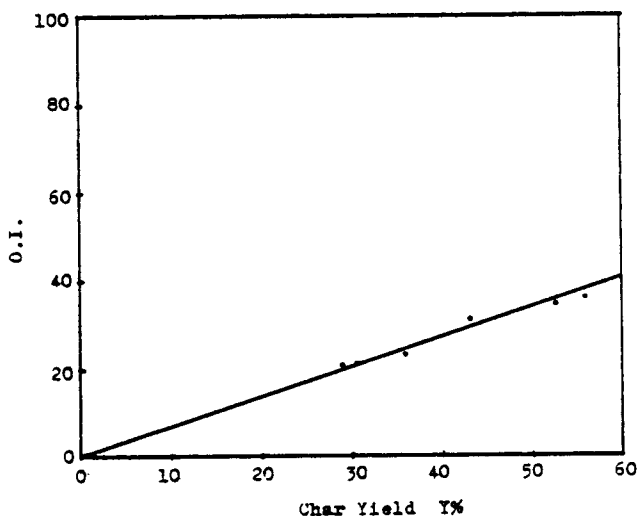


Fig. 25. Char residue at 700°C as function of mole fraction of TGETA in the copolymer of TGETA and Epon 828. Curing agent: TMB, 0.164 equiv/epoxy equiv; curing conditions: 135°C for 3 h, 180°C for 3 h, and 218°C for 3 h.

TABLE VIII
Char Yield and OI of TMB (0.164 Equiv/Epoxy Equiv) Cured Epoxy Resin Comixtures^a

	A	B	C	D	E	F
Char yield at 700°C, N ₂ , %	28.9	30.5	35.8	43.0	55.7	52.1
OI	20.4	21.0	23.2	31.0	36.0	34.5

^a Epon 828 and TGETA (A) 0%, (B) 20%, (C) 40%, (D) 60%, (E) 80% and (F) 100%. Curing conditions: 135°C for 3 h, 180°C for 3 h, and 218°C for 3 h.

TABLE IX
Characterization of DDS (1.2276 Equiv/Epoxy Equiv) Cured Epoxy Resins^a

	DGEBA	DGEBF	DGEFX	DGEA	TGETA
<i>T_g</i> , °C	73	125	138	140	
Char yield at 700°C, N ₂ , %	14.8	26.0	40.6	33.5	40.9
Gel fraction, %	91.2	87.6	47.0	87.1	81.6

^a Curing conditions: 125°C for 5 h and 200°C for 4 h.

TABLE X
Characterization of TMB (0.164 Equiv/Epoxy Equiv) Cured Epoxy Resins^a

	DGEBA	DGEBF	DGEFX	DGEA	TGETA
<i>T_g</i> , °C	83	111	127	162	
Char yield at 700°C, N ₂ , %	33.3	40.1	50.2	48.1	52.1
Gel fraction, %	71.1	71.2	0.4	83.5	84.1

^a Curing Conditions: 135°C for 3 h, 180°C for 3 h, and 218°C for 3 h.

content in the chain backbone. The order of char yield at 700°C under a nitrogen atmosphere for the uncured resins was TGETA > DGEFX > DGEA > DGEBF > DGEBA. Their char yields were 49.6, 41.9, 32.2, 21.4, and 2.4%, respectively. The increase in char yield from DGEBA to TGETA also has corresponded to their degree of aromaticity of the presence of cyclic ring structures in these resins.

DGEBF, DGEFX, DGEA, and TGETA added to the DGEBA system increases the char yield, *T_g*, and oxygen index with increasing concentration. DGEFX showed a synergistic effect with DGEBA in regard to char formation for the DDS curing system. TGETA and DGEA also have shown similar effects with DGEBA for the TMB curing system. In addition, DGEA has increased the *T_g* of DGEBA in a nonlinear synergistic manner in the DDS curing system. The oxygen index appeared to have a linear relationship with char yield. The *T_g* values have shown the relationship DGEBA < DGEBF < DGEFX < DGEA, whether they were cured with DDS or TMB. A *T_g* for TGETA was not obtainable but would be expected to be the highest. The following relationship has held for char residue: DGEBA < DGEBF < DGEA < DGEFX < TGETA. The amount of gel formed for the DDS- or TMB-cured epoxy resins did not show a clear relationship between gel fraction and the structure of these epoxy resins. This study supports the concept that the higher aromaticity or cyclic structure content of these epoxy resins gave higher char residues and glass transition temperatures.

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