

New Epoxy Resins. I. The Stability of Epoxy-Trialkoxyboroxines Triaryloxyboroxine System

C. S. CHEN,* B. J. BULKIN, and E. M. PEARCE, *Polytechnic Institute of New York, Brooklyn, New York 11201*

Synopsis

A polymer with high aromaticity and/or cyclic ring structures chain backbone usually has high heat, thermal, and flame resistance. Two diglycidyl ethers of bisphenols were prepared from 4,4'-isopropylidenediphenol (DGEBA) and 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) for evaluation. Four boroxines—trimethoxyboroxine (TMB), triethoxyboroxine (TEB), triisopropoxyboroxine (TIPB) and triphenoxyboroxine (TPB)—were used as the curing agents. DGEBA and DGEBF cured with various boroxines indicate that the trend for their respective glass transition temperature (T_g 's), degradation temperatures (T_d 's), and gel fractions are TMB-cured epoxy \approx TEB-cured epoxy < TIPB cured epoxy < TPB cured epoxy. The DGEBF system usually has a higher T_g , T_d , gel fraction, oxygen index (OI), and char yield than the related DGEBA system. DGEBF/DGEBA (80/20 mol ratio) shows a synergistic effect in regard to char formation. This effect exists not only in the copolymer system but also in blended homopolymers of the separately cured resins. A modified mechanism for the polymerization of phenyl glycidyl ether (PGE) with TMB has been proposed.

INTRODUCTION

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 foams.⁶⁻¹³ The TMB-cured epoxy resins are tough, resilient, slightly rubbery,² heat-resistant,⁶⁻⁸ and self-extinguishing.⁸ Lee and Neville¹⁴ found that TMB can be used as a primary curing agent or as a cocuring agent for epoxy resins. They describe TMB as an anhydride which provides room temperature cures in epoxy resins. The pot life of the boroxines-epoxy resin system can be extended through the use of a boroxine-amine complex,¹⁵⁻¹⁷ usually a secondary alkyl amine is used. TMB can be catalyzed by amine borane¹⁰ (e.g., $\text{Me}_3\text{N}\cdot\text{BH}_3$ or $\text{Me}_2\text{NH}\cdot\text{BH}_3$).

Christie and Medved⁴ have used TMB as a curing agent to prepare transparent epoxy castings, which are cured in a vacuum at 191°C for 4 h. The 0.25-in. (6.35-mm) thick castings have a light transmission of 88%. Parker, Fohlen, and Sawko³ prepared TMB-cured transparent epoxy panels which have a heat distortion temperatures of 110°C and are thermomechanically stable to 400°C giving high char yield and high tensile strength. Lin and Pearce⁵ have prepared colorless epoxy castings by curing epoxy with TMB for aging evaluations. They have found that the thermal decomposition energy of activation and the reaction order of cured DGEBA are 37.5 kcal/mol and 1.05, respectively. The activation energies for water diffusion into the cured resin are 19.5 kcal/mol at temperatures above T_g and 21.5 kcal/mol at temperature below T_g .

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Brown and Harshman⁸ have found that TMB-cured Epon 828 softened at 320°C. Shepherd⁹ has prepared epoxy resin foams with a high closed cell content by curing a polyepoxide at room temperature with a TMB—BF₃·MEA complex curing agent. The reaction is completed in 18 s. Lee¹¹ reports the use of TMB as an epoxy curing agent in the presence of a liquid hydrocarbon, halogenated hydrocarbon, or borate ester foaming agent to obtain rigid, hydrolytically resistant, slow-burning epoxy foams having good mechanical properties. These can be used as building-wall insulation and encapsulating materials.

Lopata and Riccitiello¹⁸ have investigated the TMB-cured bisphenol-A epoxy system by differential thermal analysis (DTA) and found that there are three exothermic peaks at approximately 390°C, 430°C, and 470°C, with the major exotherm at 430°C. They also have studied the kinetics of TMB-induced thermal polymerization of phenyl glycidyl ether by using infrared absorption spectroscopy and gel permeation chromatography to follow the course of the polymerization, and, in addition, proton and boron-11 NMR spectroscopy are used to support the kinetic model developed.¹⁹ The mechanisms that are proposed involve a fast-initiated, nonstationary, cationic polymerization with five elementary steps, including spontaneous transfer and monomer transfer steps as well as a termination reaction.

TEB, TIPB, and TPB have not been previously used as curing agents for epoxy resin. They can be used as Lewis acid catalysts for epoxy resins. Different curing agents will have different reactivities for crosslinking epoxy resins. This study was carried out for better understanding of the mechanism of the curing reaction of the boroxines curing agents and to attain a higher temperature curing of epoxy resins. In addition to TMB, TEB, TIPB, and TPB are also employed for this study.

Higher heat-resistant and thermally resistant polymers are obtained if the polymer is modified by changing the aliphatic side groups of the chain backbone to highly aromatic ring content side groups (forms cardo polymer). Factor and Orlando²⁰ have found that 1,1-dichloro-2,2-bis(4-hydroxyphenyl) ethylene (BPC) which does not contain aromatic side groups also have a very high oxygen index (56). Lin and Pearce^{5,21} report that the TMB-cured diglycidyl ether of phenolphthalein (DGEPP) has a char yield at 700°C of 47% compared to 26% for the TMB-cured diglycidyl ether of bisphenol-A (DGEBA). The oxygen index for these two materials varies in a similar manner from 43.0 to 20.5, respectively.

Polymers which are classified as "cardo" or "loop" polymers have groups which can be regarded as loops in relation to the main chain of the macromolecule.²²

The cardo polymers have high heat resistance and thermal stability. Korshak, Solovéva, and Kamenskh²³ 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 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.

On the basis of these results, the materials prepared from a diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) and cured with various different boroxines should show improvement in heat resistance, thermal resistance, and flame retardance over those obtained from the DGEBA—boroxines systems.

Crosslinking density in a network polymer has a broad effect on the various

properties of polymers such as dimensional stability and resistance to solvents and chemicals. Lin and Pearce²¹ have used tetrahydrofuran (THF) to extract the polymer that is not incorporated into the network structure (the sol fraction) and to determine the gel fraction of their polymers.

EXPERIMENTAL

Preparation of Curing Agents

TEB (triethoxyboroxine) is prepared by heating a sealed 25-mL Kontes Drying Ampoule charged with 0.0735-mol triethyl borate (Aldrich; 97%) and 0.0768-mol fused boric acid (Fisher reagent grade)²⁵ at 250°C for 24 h. TEB is then filtered to eliminate solid impurities.

TIPB (triisopropoxyboroxine) is purified by dissolving TIPB (Aldrich; tech. grade) in a large volume of diethyl ether (Mallinckrodt; Anhydrous), filtering, and evaporating the filtrate under reduced pressure.

TPB (triphenoxyboroxine) is prepared by the same method as that described by Shepherd.²⁶ For example, 0.128-mol phenol (Aldrich; 99+%), 0.041-mol trimethoxyboroxine (Aldrich; 99%), and 0.87-mol trimethyl borate (Aldrich; 99%) are charged into a round bottom flask. The mixture is heated and slowly distilled through a vigreux column until the distillate, a mixture of methanol and trimethyl borate, no longer contains methanol. The still pot residue is then subjected to a vacuum to remove the remaining trimethyl borate. The remaining solid product is triphenoxyboroxine, mp = 108–111°C (lit. mp = 75–78°C,²⁶ 98–101°C,²⁵ 96–120°C²⁷).

Preparation of Epoxy Resins and Model Compounds

Preparation of Bisphenols

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

Dry hydrogen chloride is prepared by passing hydrogen chloride (Matheson; 99.0%) through concentrated H₂SO₄ for dehydration. Fluorenone (0.75-mol) (Aldrich 98%) is dissolved in 6 mol of molten phenol, 3 mL of 3-mercaptopropionic acid is added and then dry hydrogen chloride is bubbled in for about 15 min.²⁸ The system becomes very dark and finally changes to a viscous, clear liquid. The mixture is then purified by steam distillation to remove unreacted phenol, hydrogen chloride, and cocatalyst. After no more phenol is collected in the distillate, the product is further purified by solution in alkali, filtration to separate unreacted fluorenone, and acidification with concentrated hydrogen chloride acid to precipitate a white solid. The dried powder is recrystallized from anhydrous ether (Mallinckrodt analytical reagent). A transparent crystalline product containing ether of solvatures is 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, 224°C, is obtained (lit. mp = 224°C,²⁸ 225–225.5°C²³).

*Synthesis of Glycidyl Ether Type Epoxy Resins and Model Compound-
Phenyl Glycidyl Ether*

Phenyl glycidyl ether (PGE) (Eastman Kodak Co.) is dried with BaO and fractionally distilled under reduced pressure (~60 torr). The middle fraction is collected.

The diglycidyl ethers of bisphenol-A (DGEBA) and 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) are prepared by adding bisphenol-A or 9,9-bis(4-hydroxyphenyl) fluorene and epichlorohydrin in the mole ratio of 1:10 to a heated reaction kettle containing a thermometer, mechanical stirrer, and a water cooled condenser. During a period of 2 h, 2 mol of 40% aqueous sodium hydroxide solution is added to the reaction mixture and the reaction temperature is maintained between 100°C and 110°C. The solution is filtered to separate the solid sodium chloride formed during the reaction. The salt cake is washed with additional epichlorohydrin, and the unreacted epichlorohydrin is then distilled off under a vacuum of 30 mm Hg from filtrate. After removal of epichlorohydrin is complete, the vacuum is decreased to 2 mm Hg for 30 min at 170°C.

DGEBF can be recrystallized from its acetone solution by adding absolute alcohol to this solution with vigorous agitation until this solution appears a little cloudy. This solution was allowed to stand until crystallization is complete. The white crystalline powder is collected by filtration and washed with a mixture of acetone and absolute alcohol (1:1). The dry crystalline DGEBF has melting point of 137°C.

Characterization of Epoxy Resins

Epoxy Resin Analysis

The epoxy resins prepared from the above methods were identified by NMR and IR spectroscopy. A Varian A-60 NMR Spectrometer is used for the NMR measurements and CDCl_3 (Aldrich; 99.8 atom % D, GOLD LABEL) is used as solvent. The infrared spectra are obtained on a Perkin-Elmer spectrophotometer. The glass transition temperature (T_g) and/or melting temperature (T_m) of each resin was studied by differential scanning calorimetry (a DuPont 910 Differential Scanning Calorimeter connected with a DuPont 990 Thermal Analyzer).

Epoxy Equivalent Weight (EEW) Determination

The ASTM D 1652-73²⁴ method is used to determine the EEW of epoxy resins. The epoxy resin, 0.2 g, is added to a 50-mL flask and then dissolved in 10 mL of 50 vol % of chlorobenzene (Aldrich analyzed grade; 99%) in chloroform. The mixture is stirred with a Teflon-coated magnetic stirring bar. Four drops of 0.1% of crystal violet (4,4',4''-methylidynetris-(*N,N*-dimethylaniline); (Eastman) solution in glacial acetic acid (J. T. Baker) is used as the indicator. The solution is titrated with 0.1*N* of hydrogen bromide in acetic acid (Eastman; 30.32% in acetic acid by titration). The hydrogen bromide solution was standardized by 0.4 g of potassium hydrogen phthalate each time before using for epoxy equivalent weight determination.

Curing Conditions for Epoxy-Boroxine Systems

TMB (Aldrich: 99%, bp = 130°C, $n_d^{20} = 1.3996$), TEB, TIPB, and TPB, 0.164 equiv, are used individually as curing agents. The curing conditions are 135°C for 3 h, 180°C for 3 h, and 218°C for 3 h.⁵ The polymerization conditions for boroxine curing agents and PGE systems are 135°C for 8 h.

The PGE, DGEBA, and DGEBF are mixed with various curing agents, respectively. Curing was carried out in a nitrogen-filled and sealed glass tube at the same conditions mentioned above.

Characterization of Cured Epoxy Resins

Dynamic Thermal Analysis

The thermal properties of various samples in this study were investigated on a DuPont 910 Differential Scanning Calorimeter (DSC) and a DuPont 990 Thermal Analyzer. The DuPont 951 Thermogravimetric Analyzer (TGA) was used with a DuPont 990 Thermal Analyzer for char residue determination. Samples having mesh sizes greater than 170 were used for DSC or TGA measurement. For DSC and TGA measurements, the nitrogen flow rate is 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 were measured by using a General Electric Model CR280KF11A Fluid Flammability Test Kit. The cured epoxy resin was made into a pellet form and placed in 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.²⁹ The oxygen index (OI) was obtained from this equation

$$OI = \frac{O_2}{O_2 + N_2} \times 100$$

where the oxygen index is 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 or N_2 is related to the volume of oxygen or nitrogen in the chamber.

Solvent Extraction of Cured Epoxy Resins

One gram of cured epoxy resin was put into a Soxhlet apparatus (Pyrex glass thimble) and extracted by tetrahydrofuran (J. T. Baker HPLC grade) for 4 days. The insoluble part is collected and dried in vacuum oven until no weight change was detected. The gel fraction is calculated as

$$\text{gel fraction} = \frac{\text{wt of insoluble material}}{\text{initial wt of material}}$$

RESULTS AND DISCUSSION

Characterization of Epoxy Resins

Structure Study on Glycidyl Ether-Type Epoxy Resins

Epoxy resins: DGEBA and DGEBF were prepared and identified by IR (Figs. 1 and 2) and NMR (Figs. 3 and 4). The infrared and NMR assignments are shown in Tables I and II.

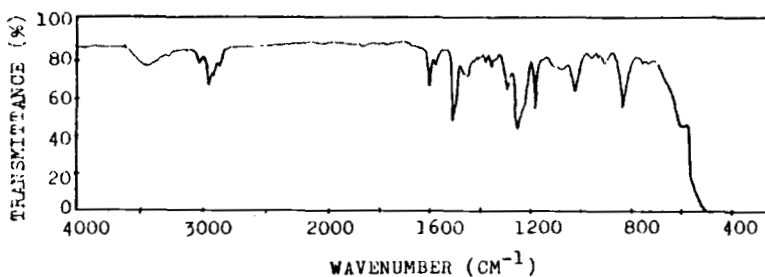


Fig. 1. Infrared spectrum of diglycidyl ether of bisphenol-A (DGEBA).

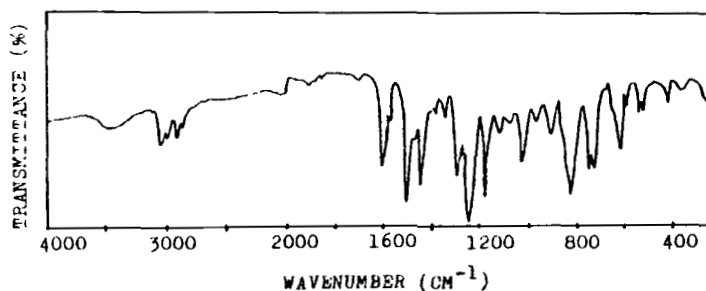


Fig. 2. Infrared spectrum of diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF).

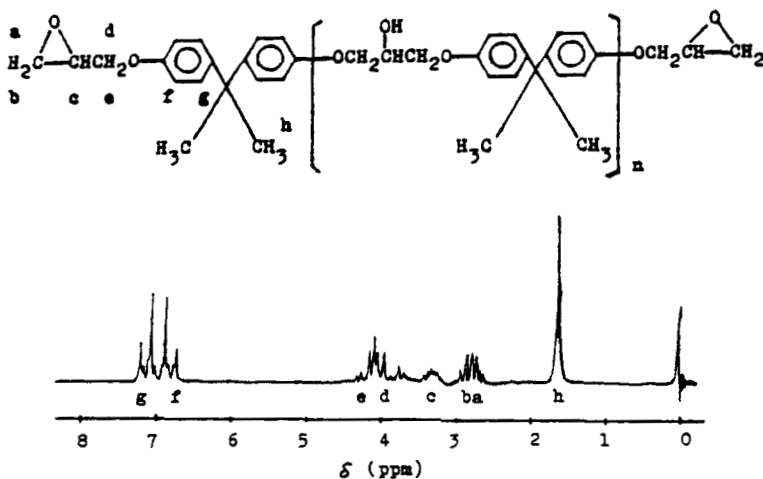


Fig. 3. ^1H 60 MHz NMR spectrum of diglycidyl ether of bisphenol-A (DGEBA).

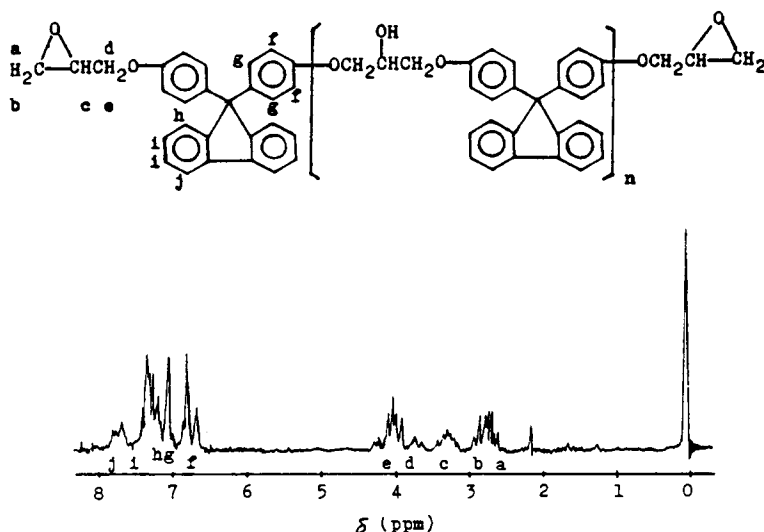


Fig. 4. ^1H 60 MHz NMR spectrum of diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF).

Properties of Epoxy Resins Derived from Bisphenols




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

DGEBF is a white crystalline solid which has a melting temperature of 137°C (lit. mp = 132°C ⁵). After the molten monomer is quenched, only a softening temperature at 38°C (lit. = 30°C ,⁵ 70°C ²¹) can be observed. DGEBF has a higher glass transition temperature and char yield than DGEBA.

Curing Reaction Studies with Various Curing Agent Systems

The properties of the cured epoxy resins are varied by the compositions of the systems, the structures of the epoxy resins, the curing agents, the curing conditions, and the curing cycles. A reaction mechanism for the polymerization of phenyl glycidyl ether initiated by trimethoxyboroxine (TMB) has been proposed by Lopata and Riccitiello.¹⁹ It involves a fast-initiated nonstationary cationic polymerization with five elementary steps, including spontaneous and monomer transfer as well as a termination reaction. However, these experiments were carried out in aluminum sample cups (open system) cured in an oven, and do not detect any gas product formation. This mechanism cannot explain the rigid foam formation of TMB-cured Bakelite ERL 3794¹⁴ and TMB cured vinylcyclohexene dioxide.³⁰ When TMB, TEB, TIPB, and TPB have been polymerized with PGE in a nitrogen-filled and sealed 25-mL dry ampoule (curing agent 0.164 equiv/epoxy equiv) for 8.5 h at 135°C , then opened and evacuated under vacuum system, the weight loss indicates volatile byproduct formation. These byproducts probably are CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, *i*- $\text{C}_3\text{H}_7\text{OH}$, and $\text{C}_6\text{H}_5\text{OH}$, and indicate that at least 1.78%, 1.89%, 1.92%, and 5.16%, respectively, are volatile byproducts which form in the TMB, TEB, TIPB, and TPB systems. The 220 MHz proton NMR spectra (Fig. 5) of the cured systems also show resonance at 4.59 ppm and

TABLE I
 Infrared Transmittance Assignments for the Epoxy Resins

Wave no. (cm ⁻¹)	DGEBA	DGEBF	Functional group	Vibration mode
3438 3420	x	x	} R—OH	$\nu(\text{O—H})$
3040 3030 2992	x	x x	} arylene	$\nu(\text{C—H})$
2952	x		} methyl	$\nu(\text{C—H})$
2912 2908 2862 2859	x	x x	} methylene	$\nu(\text{C—H})$
1599 1598 1578 1576	x	x x	} phenylene	quadrant stretching
1501 1495	x	x	} 	semicircle stretching
1440		x	} 	
1240 1235	x	x	} Ar—O—R	$\nu(\text{C—O—C})$
1180 1175	x	x	} Ar—H	in plane C—H deformation
906	x	x	} 	ring deformation
828 816	x	x	} <i>p</i> -phenylene	in-phase out of plane hydrogen wagging
742 728		x x	} <i>o</i> -phenylene	in-phase out of plane hydrogen wagging

resonance between 1.11 and 1.20 ppm, and these bands can be assigned to the protons attached to a carbon-carbon double bond and the protons on the methyl group of the ethyl and isopropyl groups, respectively. These may indicate either monomer transfer¹⁹ with PGE or proton abstraction with alkoxide anion and subsequent termination by the respective alkoxide anion. The NMR spectra

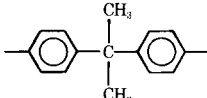
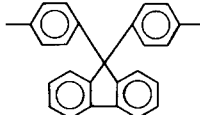
TABLE II
 NMR Band Assignments for Various Epoxy Resins

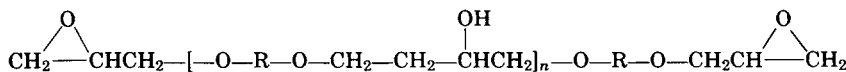
DGEBA		DGEBF	
peak	δ (ppm)	peak	δ (ppm)
g	7.23-6.97	j	7.77-7.53
f	6.95-6.66	i,h	7.51-7.18
e,d	4.30-3.49	g,f	7.18-6.58
c	3.47-3.13	e,d	4.24-3.54
b,a	2.97-2.59	c	3.44-2.96
h	1.72-1.47	b,a	2.94-2.52

probably indicates that alkene formation is 3.5%, 7.7%, 8.5%, and 7.5% for TMB, TEB, TIPB, and TPB with the PGE system. The mechanism proposed by Lopata and Riccitiello¹⁹ can be modified by one more possible termination step showing the formation of methanol (Fig. 6).

The DSC thermograms of TMB, TEB, TIPB, and TPB after mixing with DGEBA or DGEBF (curing agent 0.164 equiv/epoxy equiv) are shown in Figures 7 and 8. From these studies, the curing onset temperature for DGEBA is higher than that for DGEBF. The reason for this is that the DGEBA is already partially cured to a B stage after mixing with the curing agent, whereas the DGEBF is still relatively unreacted.

 TABLE III
 Properties of Epoxy Resins Prepared from Epichlorohydrin and Bisphenols

Type of resin	DGEBA	DGEBF
R		
Color	pale yellow	white
Epoxy equiv wt	189.3 (177.2)	254
\bar{n}	0.13 (0.05)	0.11
T_g (°C)	-24	38
T_m (°C)	—	137
Char yield N_2 ^{700°C}	2.4	21.4


 TABLE IV
 Characterization of TMB-, TEB-, TIPB-, and TPB-cured DGEBA

Epoxy resin Curing agent	DGEBA			
	TMB	TEB	TIPB	TPB
Equiv ratio of curing agent/epoxy resin	0.164	0.164	0.164	0.164
T_g (°C)	83	81	92	106
T_d (°C)	368	370	378	398
Gel fraction	71.1%	68.1%	73.4%	75.8%
O I _(pellet)	22.8	22.6	22.6	22.2
Char yield N_2 ^{700°C}	33.0%	32.8%	32.8%	30.8%

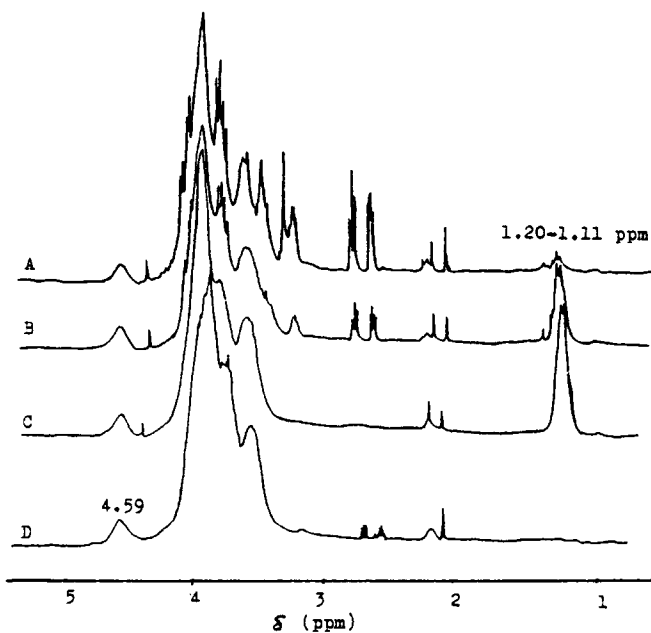


Fig. 5. ^1H 220 MHz NMR spectra of TMB (A)-, TEB (B)-, TIPB (C)-, and TPB (D)-cured PGE (cured at 135°C for 8.5 h in nitrogen-gas-filled and Sealed dry ampoules; these samples evacuated before sampling). (Curing agent: 0.164 equiv/epoxy equiv.)

Characterization of Cured Epoxy Systems with Various Curing Agent Systems

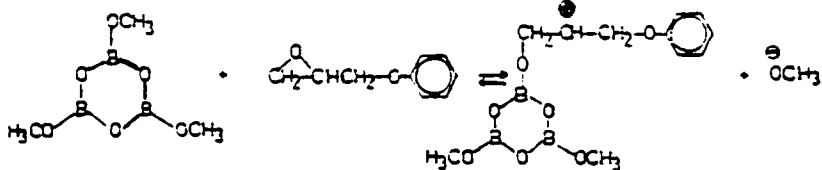
The epoxy equivalent weights (EEW) of DGEBA and DGEBF are 177.2 and 254 g/equiv, respectively.

The glass transition temperature (T_g), degradation temperature (T_d) (obtained by extrapolated TGA thermogram), gel fraction, oxygen index (OI), and char yield (700°C , N_2) of the TMB-, TEB-, TIPB-, and TPB- (0.164 equiv/epoxy equiv)-cured DGEBA and DGEBF are summarized (Tables IV and V). For the cured epoxy resins, the T_g may be affected by crosslinking density (related to gel fraction) and the molecular structure. The TMB-cured DGEBA compared with TEB-cured DGEBA appear to have similar crosslinking densities based on their T_g 's. Thus, the relative T_g values are TMB-cured DGEBA \approx TEB-cured DGEBA < TIPB-cured DGEBA < TPB-cured DGEBA. The T_d 's and

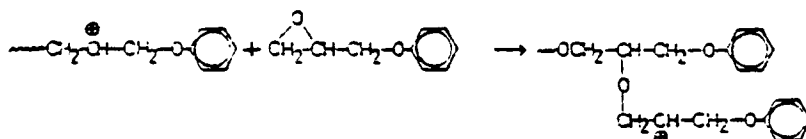
TABLE V
Characterization of TMB-, TEB-, TIPB-, and TPB-cured DGEBA

Epoxy resin Curing agent	DGEBF			
	TMB	TEB	TIPB	TPB
Equiv ratio of curing agent/epoxy resin	0.164	0.164	0.164	0.164
T_g ($^\circ\text{C}$)	111	109	120	123
T_d ($^\circ\text{C}$)	402	406	412	422
Gel fraction	71.2%	69.6%	83.9%	84.2%
O I _(pellet)	29.0	29.1	29.1	29.8
Char yield $_{\text{N}_2}^{700^\circ\text{C}}$	40.1%	40.6%	40.9%	43.1%

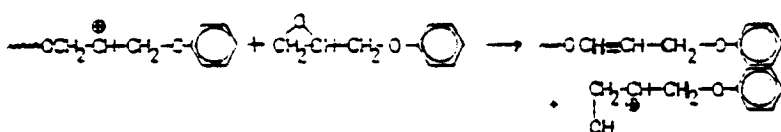
1. INITIATION



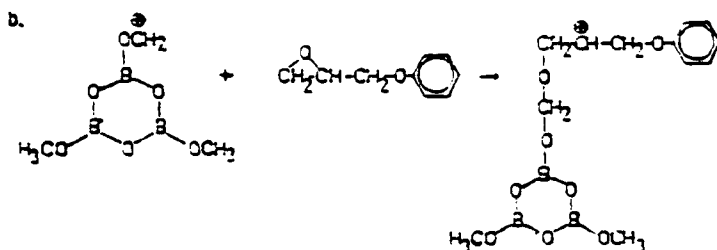
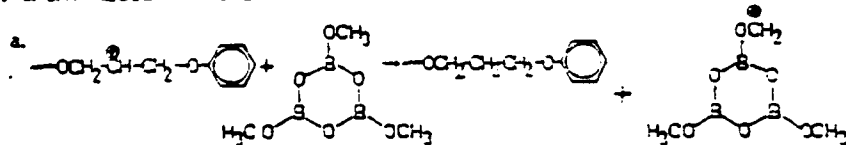
2. PROPAGATION



3. MONOMER TRANSFER



4. SPONTANEOUS TRANSFER



5. TERMINATION

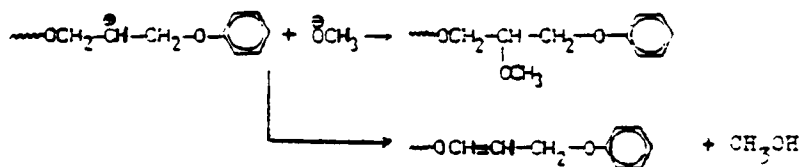


Fig. 6. Proposed mechanism for the polymerization reaction of trimethoxyboroxine and phenyl glycidyl ether.

the gel fractions show a similar trend. In addition, the TMB-, TEB-, TIPB-, and TPB-cured DGEBF's show similar results. Usually the DGEBF system has a higher T_g , T_d , gel fraction, OI, and char yield than the DGEBA system. Lin²¹ reported that the char yield of TMB-cured DGEBF is 42.3% compared to a 26% char yield for the TMB-cured DGEBA, whereas the char yield of the TMB cured epoxy mixture of DGEBA (77.1 mol %) and DGEBF (22.9 mol %) is 39.2%.

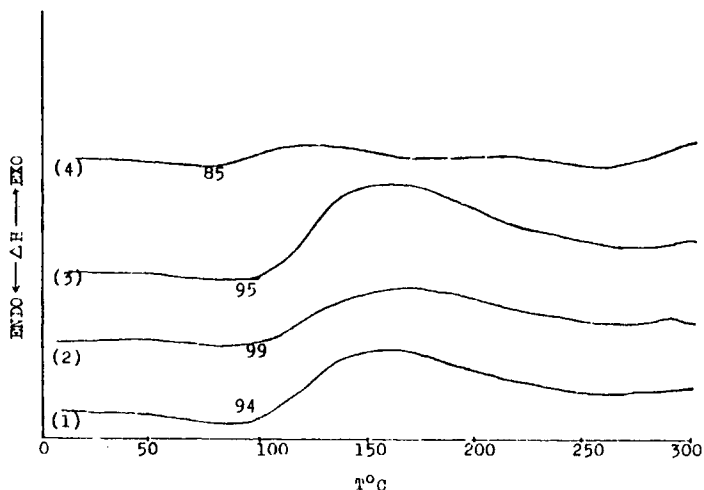


Fig. 7. DSC thermograms for DGEBA after mixing with (1) TMB, (2) TEB, (3) TIPB, and (4) TPB. Heating rate: 10 °C/min; ATM: N₂, 0.2 LPM.

This indicates a synergistic char formation effect for DGEBA and DGEBF mixtures. Even a blend of TMB-cured DGEBA (80 mol %) and TMB-cured DGEBF (20 mol %) has a char yield of 36.0% which is higher than a calculated value of 33.5% based on a linear relationship (Fig. 9). Visual observation of these chars indicates that the char of TMB-cured DGEBF is expanded, while the char of TMB-cured DGEBA or the blended epoxy resin is diminished in volume. Previous studies on polycarbonates based on bisphenol-A and 2,2-bis(4-hydroxyphenyl)-1,1-dichloroethylene in either polymer blends or copolymers have been reported to have the same oxygen index.²⁰

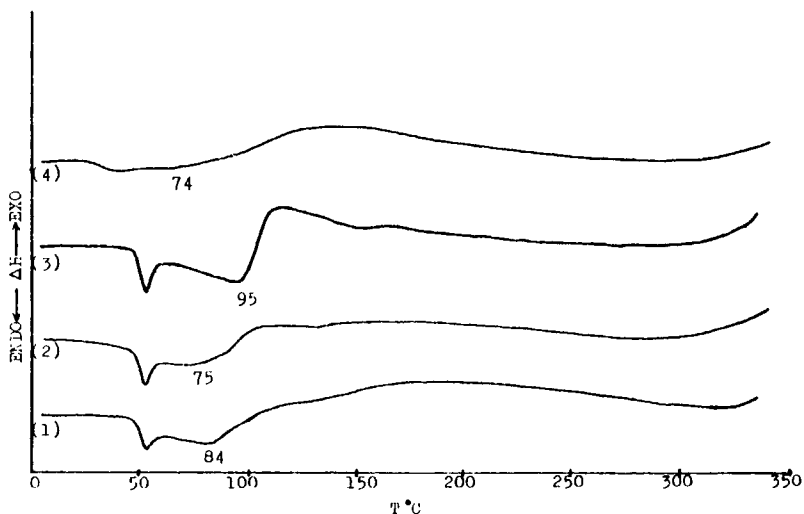


Fig. 8. DSC thermograms for DGEBF after mixing with (1) TMB, (2) TEB, (3) TIPB, and (4) TPB. Heating rate: 10 °C/min; ATM: N₂, 0.2 LPM.

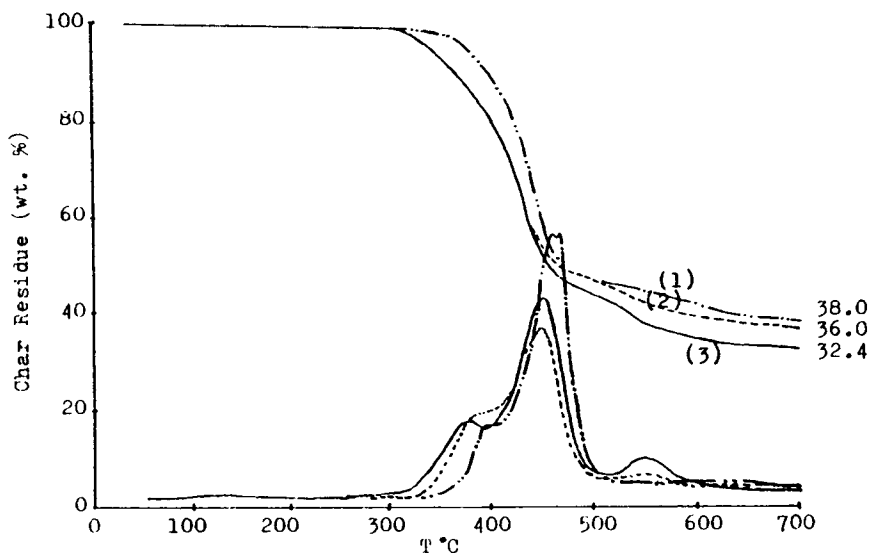


Fig. 9. TGA for (1) TMB-cured DGEBF, (2) TMB-cured DGEBF (20 mol %) blended with TMB-cured DGEBA (80 mol %), and (3) TMB-cured DGEBA. Curing agent: TMB, 0.164 equiv/epoxy equiv. Heating rate: 10°C/min; ATM: N₂, 0.3 LPM.

CONCLUSION

The glass transition temperatures for uncured DGEBA and DGEBF are -24°C and 38°C, respectively. The glass transition temperatures correspond to an increase of aromatic ring content in the chain backbone. The order of char yield at 700°C under a nitrogen atmosphere for the uncured resins is DGEBF > DGEBA. Their char yields are 21.4% and 2.4%, respectively. The increase of char yield from DGEBA to DGEBF also corresponds to the higher degree of aromaticity in the DGEBF.

Lopata and Riccitiello have proposed a mechanism for the polymerization of PGE with TMB. This mechanism does not account for the formation of small amounts of methanol. Our studies show that CH₃OH, C₂H₇OH, and C₆H₅OH appear to be volatile byproducts from the reaction of PGE and TMB, TEB, and TIPB and TPB, respectively. Therefore, we have proposed an additional termination step to account for the formation of the respective hydroxyl compounds.

DGEBA and DGEBF cured with various boroxines indicate that the trend for their respective T_g 's, T_d 's and gel fractions are TMB cured epoxy \approx TEB cured epoxy < TIPB cured epoxy < TPB cured epoxy. The DGEBF system usually has a higher T_g , T_d , gel fraction, OI, and char yield than the related DGEBA system. DGEBF/DGEBA (80/20 mole ratio) shows a synergistic effect in regard to char formation. This effect exists not only in the copolymer system but also in blended homopolymers of the separately cured resins.

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References

1. H. Brunner and M. J. Waghorn, Brit. Pat. 910,899 (1962); *Chem. Abst.* **58**, 3564g (1963).
2. J. W. Shepherd, U.S. Pat. 3,259,591 (1966); *Chem. Abstr.*, **65**, 9131d (1966).
3. J. A. Parker, G. M. Fohlem, and P. M. Sawko, "Development of Transparent Composites and Their Thermal Responses," paper presented at Conference on Transparent Aircraft Enclosures, Las Vegas, Nevada, Feb. 5-8, 1971.
4. H. Christie and T. Medved, "High Temperature Resistant Transparent Plastics," Report No. AD-261-098 (1961).
5. S. C. Lin, Ph.D., thesis, Department of Chemistry, Polytechnic Institute of New York, 1978.
6. H. H. Chen and A. C. Nixon, *Am. Chem. Soc., Div. Org. Coating, Plastics Chem., Preprints*, **23**(1), 221 (1963).
7. H. H. Chen and A. C. Nixon, *SPE Trans.*, **5**(2), 90 (1965).
8. L. E. Brown and J. B. Harshman, AEC Accession No. 35935, Report No. MLM-CF-64-8-1 (1964).
9. J. W. Shepherd, U.S. Pat. 3,310,507 (1967); *Chem. Abstr.*, **67**, 22590c (1967).
10. A. J. Krol, U.S. Pat. 3,355,306 (1967); *Chem. Abstr.*, **68**, 13740v (1968).
11. H. L. Lee, U.S. Pat. 3,378,504 (1968); *Chem. Abstr.*, **69**, 3482u (1968).
12. M. S. Matta, Report No. MLM-1440, U.S. Atomic Energy Commission, Washington, D.C. (1967).
13. L. E. Brown and J. D. Nutter, Report No. MLM-1641 U.S. Atomic Energy Commission, Washington, D.C. (1969).
14. H. Lee and K. Neville, *SPE J.*, **16**, 315 (1960).
15. D. T. Haworth and G. F. Pollnow, *Ind. Eng. Chem. Prod. Res. Dev.*, **1**, 185 (1962).
16. A. B. Burg, *J. Am. Chem. Soc.*, **62**, 2228 (1940).
17. H. R. Snyder, J. A. Kuck, and J. R. Johnson, *J. Am. Chem. Soc.*, **80**, 3611 (1958).
18. E. S. Lopata and S. R. Riccitiello, *J. Appl. Polym. Sci.*, **19**, 1127 (1975).
19. E. S. Lopata and S. R. Riccitiello, *J. Appl. Polym. Sci.*, **21**, 91 (1977).
20. A. Factor and C. M. Orlando, *J. Polym. Sci., A-1*, **18**, 579 (1980).
21. S. C. Lin and E. M. Pearce, *J. Polym. Sci., A-1*, **17**, 3059 (1979).
22. S. V. Vinogradova and Ya. S. Vygodskii, *Russ. Chem. Rev.*, **42**(7), 551 (1973).
23. V. V. Korshak, L. K. Soloveva, and I. V. Kamenskh *Vysokomol. Soyed.*, **13**, 150 (1977).
24. ASTM D 1652-73, Standard Method of Test for Epoxy Content of Epoxy Resins, *ASTM*, **28**, 341 (1975).
25. M. F. Lappert, *J. Chem. Soc.*, 2790 (1958).
26. J. W. Shepherd, U.S. Pat. 3,093,675 (1963).
27. United States Borax and Chemical Corporation, Brit. Pat. 868,289 (1961).
28. P. W. Morgan, *Macromolecules*, **3**, 536 (1970).
29. General Electric Model CR 280KF11A Fluid Flammability Test Kit, Test Procedure Manual, 4541 K 25-001c.
30. L. W. Hartzel et al., Quick-Curing Foam Systems, MLM-1397 (1968).

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