

New Epoxy Compounds Derived from Substituted Maleamic Acids

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Synopsis

Eight new epoxy compounds bearing maleamic acid moieties were prepared starting from 4-(2,3-epoxypropoxy)benzaldehyde (EPB) or 2,3-epoxypropylglyoxylate monohydrate (EPG). The monomaleamic acid derived from an aromatic diamine (1,4-phenylenediamine, 4-aminophenyl ether, 4,4'-diaminodiphenylmethane or 4,4'-diaminodiphenylsulfone) reacted with EPB or EPG to afford the epoxy compounds. They were characterized by IR and ¹H-NMR spectroscopy. Their DTA traces showed that thermal polymerization started at 187–211°C. Network systems were obtained by crosslinking from the reaction of epoxy group with the maleamic carboxyl and through the olefinic bond. The TGA thermograms of crosslinked polymers showed that they were stable up to 275–295°C in N₂ or air and afforded anaerobic char yield of 47–65% at 800°C. In addition, isothermal gravimetric analysis (IGA) was used to evaluate the thermo-oxidative stability of a typical cured resin.

INTRODUCTION

Despite their relatively high cost, epoxides are now firmly established in a number of important industrial applications. They find use primarily in surface coatings and the encapsulation of electronic compounds; other applications include adhesives, castings, and laminates.

Various structurally different epoxy compounds have been synthesized.¹ The most commercial epoxy resins were prepared by the reaction of 2,2-bis(4'-hydroxyphenyl)propane (bisphenol A) and epichlorohydrin. However, other types of epoxides derived from novolac resins and various aromatic diphenols, aliphatic polyols, and polycarboxylic acids are becoming increasingly available.

In connection with our interest in development of new epoxy compounds^{2,3} with improved properties, we carried out the synthesis, characterization, and polymerization of eight new epoxides derived from substituted maleamic acids and bearing azomethine linkages. They behave as self-curing epoxy compounds because they contain maleamic acid moieties. In addition, they can be thermally crosslinked not only by means of epoxy groups, but also through the maleamic acid olefinic bond. The synthesized epoxy resins are expected to possess good heat-resistance, due to their high crosslink density and the relatively thermo-stable azomethine linkages.⁴⁻⁶

EXPERIMENTAL

Characterization Methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-

Elmer 710B spectrometer with KBr pellets. $^1\text{H-NMR}$ spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. DTA and TGA were performed on a Du Pont 990 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in N_2 atmosphere at a flow rate of $60\text{ cm}^3/\text{min}$. Dynamic TGA measurements were made at a heating rate of $20^\circ\text{C}/\text{min}$ in atmospheres of N_2 or air at a flow rate of $60\text{ cm}^3/\text{min}$. The epoxy equivalent weights (EEW) were expressed in g/mol of epoxy groups and determined by the pyridinium chloride-pyridine method.⁷

Reagents and Solvents

1,4-Phenylenediamine (Aldrich) was sublimed at about 110°C under vacuum (2–3 mm). 4,4'-Diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, and 4-aminophenyl ether (Aldrich) were purified by recrystallization from benzene, methanol, and acetonitrile, respectively. Maleic anhydride (Merck) and 4-hydroxybenzaldehyde (Aldrich) were recrystallized from acetic anhydride and distilled water, respectively. Epichlorohydrin (Aldrich) was purified by distillation. *N,N*-Dimethylformamide (DMF) (Aldrich) was dried by refluxing and fractionally distilled from calcium hydride. Benzyltrimethylammonium bromide (BTMA) and glyoxylic acid monohydrate (Aldrich) were used as supplied.

4-(2,3-Epoxypropoxy)benzaldehyde (EPB) and 2,3-epoxypropyl glyoxylate monohydrate (EPG) were used as starting materials for preparing the epoxy compounds. The synthesis and characterization of EPB and EPG has been described elsewhere.³ In brief, EPB was prepared by reacting 4-hydroxybenzaldehyde with excess of epichlorohydrin in the presence of a catalytic amount of BTMA. The reaction occurred at the boiling point of epichlorohydrin. Excess of epichlorohydrin and volatile components were subsequently removed by distillation under reduced pressure. The residue was treated with dilute sodium hydroxide and then washed with water and dried to yield EPB as a viscous undistilled liquid. An analogous procedure was used for preparing EPG from the reaction of glyoxylic acid monohydrate with epichlorohydrin in the presence of BTMA as catalyst.

Preparation of Epoxy Compounds 1a–1d and 2a–2d

Epoxy Compounds 1a and 2a

A flask equipped with a dropping funnel and a N_2 inlet was charged with a solution of 1,4-phenylenediamine (1.3409 g, 12.4 mmol) in DMF (10 mL). Maleic anhydride (1.2159 g, 12.4 mmol), dissolved in DMF (10 mL), was added dropwise to the stirred solution at ambient temperature under N_2 . An exothermic reaction was observed. Stirring of the mixture at ambient temperature was continued in a stream of N_2 for 2 h. The monomaleamic acid thus prepared was mixed with EPB (2.2094 g, 12.4 mmol) at room temperature. A slightly exothermic reaction was observed and the mixture was stirred at 50°C in a stream of N_2 for 10 h. About two-thirds of the solvent, as well as volatile components, were subsequently removed by distillation under reduced pressure. The residue was poured into ice-water and the solid obtained was filtered off,

washed with water, and dried into a vacuum oven at about 60°C to afford epoxy compound 1a as a red solid (3.54 g, yield 78%, melting temperature 128–135°C).

The same procedure was used to prepare epoxy compound 2a. The monomaleamic acid prepared from the reaction of 1,4-phenylenediamine (1.5031 g, 13.9 mmol) with maleic anhydride (1.3630 g, 13.9 mmol) in DMF (20 mL) reacted with EPG (2.0586 g, 13.9 mmol) to afford epoxy compound 2a as a light red solid (3.14 g, yield 71%).

Epoxy Compounds 1b and 2b

The monomaleamic acid obtained from the reaction of 4-aminophenyl ether (3.6443 g, 18.2 mmol) with maleic anhydride (1.7846 g, 18.2 mmol) in DMF (35 mL) reacted similarly with EPB (3.2429 g, 18.2 mmol) to afford epoxy compound 1b as a brown solid (7.60 g, yield 91%, melting temperature 125–134°C).

The monomaleamic acid prepared from the reaction of 4-aminophenyl ether (4.6656 g, 23.3 mmol) with maleic anhydride (2.2848 g, 23.3 mmol) in DMF (30 mL) reacted similarly with EPG (3.4507 g, 23.3 mmol) to afford epoxy compound 2b as a light brown solid (7.84 g, yield 82%).

Epoxy Compounds 1c and 2c

The reaction of 4,4'-diaminodiphenylmethane (3.7870 g, 19.1 mmol) with maleic anhydride (1.8729 g, 19.1 mmol) in DMF (35 mL) afforded the monomaleamic acid, which reacted similarly with EPB (3.4032 g, 19.1 mmol) to give epoxy compound 1c as a yellow solid (7.76 g, yield 89%, melting temperature 103–111°C).

The monomaleamic acid prepared from the reaction of 4,4'-diaminodiphenylmethane (5.2938 g, 26.7 mmol) with maleic anhydride (2.6182 g, 26.7 mmol) in DMF (40 mL) reacted similarly with EPG (3.9543 g, 26.7 mmol) to afford epoxy compound 2c as a light brown solid (8.18 g, yield 75%, melting temperature 179–185°C).

Epoxy Compounds 1d and 2d

The reaction of 4,4'-diaminodiphenylsulfone (3.7991 g, 15.3 mmol) with maleic anhydride (1.5003 g, 15.3 mmol) in DMF (35 mL) afforded the monomaleamic acid, which reacted similarly with EPB (2.7262 g, 15.3 mmol) to give epoxy compound 1d as a yellow solid (5.59 g, yield 72%, melting temperature 93–104°C).

The monomaleamic acid prepared from the reaction of 4,4'-diaminodiphenylsulfone (5.1152 g, 20.6 mmol) with maleic anhydride (2.02200 g, 20.6 mmol) in DMF (40 mL) reacted similarly with EPG (3.0509 g, 20.6 mmol) to afford epoxy compound 2d as a pale yellow solid (6.91 g, yield 73%, melting temperature 132–145°C).

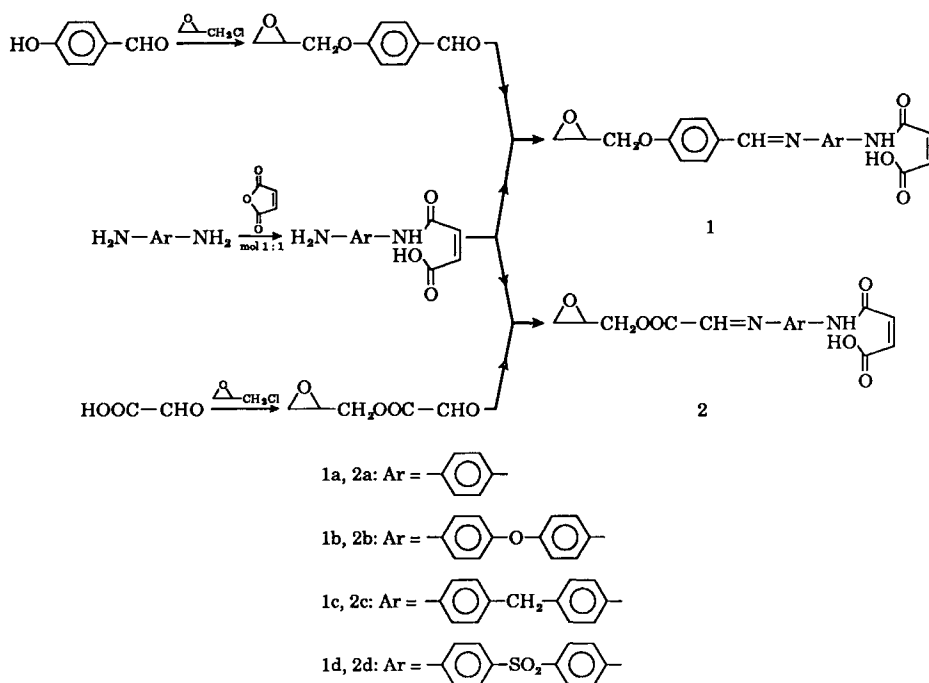
General Procedure for Curing of Epoxy Compounds

The epoxy compound isolated was heated in a shallow dish placed into a circulated air oven at 230°C for 15 h to afford a crosslinked polymer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Epoxy Compounds

The new epoxy compounds bearing azomethine linkages were prepared according to the reaction sequences outlined in Scheme 1:



Scheme 1

More particularly, the monomaleamic acid derived from an aromatic diamine (1,4-phenylenediamine, 4-aminophenyl ether, 4,4'-diaminodiphenylmethane or 4,4'-diaminodiphenylsulfone) reacted with EPB or EPG to afford the epoxy compounds. EPB and EPG were prepared from the reaction of 4-hydroxybenzaldehyde or glyoxylic acid monohydrate, respectively, with epichlorohydrin in the presence of BTMA as catalyst.³ The monomaleamic acid derived from an aromatic diamine was prepared almost exclusively by adding portion-wise maleic anhydride to a stirred solution of equimolar amount of diamine in DMF.^{8,9} The solution of monomaleamic acid in DMF thus prepared was mixed with an equimolar amount of EPB or EPG to yield the epoxy compounds. DMF was used as reaction medium due to the limited solubility of the monomaleamic acid. At this stage, the epoxy group of EPB or EPG might react with the free amino group of the substituted monomaleamic acid. However, this undesirable reaction did not occur to a detectable extent, because the amino group reacted with the formyl group of EPB or EPG. Note that the preparation of several self-curing epoxy compounds has been based on this selective reaction.^{3,10} In the present case, the preparation of epoxy compounds, as well as their isolation and drying, was performed under the possible most mild conditions possible, to preclude or minimize their polymerization.

All epoxy compounds, except 2a and 2b, showed a broad and unclear melting temperature. In the case of epoxides 2a and 2b, a melting temperature was not distinguished. Upon gradual heating, the synthesized epoxides are crosslinked from the reaction of the epoxy group with the maleamic carboxyl and through the maleamic olefinic bond. The formation of crossbonds should be responsible for this behavior.

Epoxy compounds were characterized by IR and $^1\text{H-NMR}$ spectroscopy. The IR and $^1\text{H-NMR}$ spectral data are listed in Table I. Figure 1 presents typical IR spectra of epoxy compounds 1c and 2c as well as of polymer 1c'. The epoxy group could be identified by the absorption bands around 1260, 1160, and 840 cm^{-1} . A broadening of the carbonyl absorption was observed in some cases due to a partial overlapping of the carboxylic, amide, and ester carbonyl. More particularly, compounds 1a–1d showed absorptions at about 1720 (carboxylic $\text{C}=\text{O}$) and 1670 cm^{-1} (amide $\text{C}=\text{O}$). Compounds 2a–2d exhibited absorptions near 1710 (carboxylic and ester $\text{C}=\text{O}$) and 1670 cm^{-1} (amide $\text{C}=\text{O}$). All compounds showed a broad and strong absorption around 3600–2800 cm^{-1} associated with the carboxylic OH and amide NH stretching vibrations. Finally, the absorption band at about 1620 cm^{-1} was assigned to the azomethine and the maleamic acid olefinic bond.

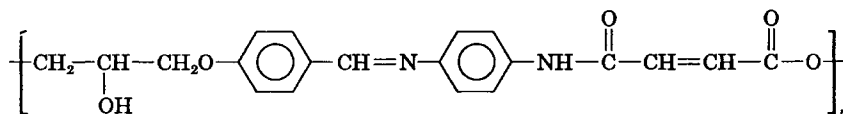
The $^1\text{H-NMR}$ spectra of epoxy compounds showed a broad singlet at about 10.50 δ assigned to carboxylic proton which was exchangeable to D_2O . The broad multiplet around 8.50 δ was attributed to $\text{CH}=\text{N}$ and NHCO protons. The maleamic olefinic protons resonated near 6.10 δ . Finally, the epoxy group was identified by the multiplets at about 3.80, 3.20, and 2.50 δ .

The epoxy equivalent weights (EEW) of all compounds were determined by the pyridinium chloride–pyridine method⁷ and are listed in Table I.

Crosslinking of Epoxy Compounds and Thermal Stabilities of Cured Resins

The epoxy compounds were crosslinked by heating at 230°C for 15 h. Throughout the text, the cured resins obtained from epoxy compounds 1a–1d and 2a–2d are referred to by the notations 1a'–1d' and 2a'–2d', respectively.

The synthesized epoxy compounds behave as self-curing epoxy compounds because they contain free maleamic acid segments. Hence, they can be thermally polymerized by reacting the epoxy group with the maleamic acid moiety. Compound 1a, as an example, initially affords the following polymer structure:



The pendent hydroxy groups react subsequently with other epoxy groups to yield ether crossbonds. Further thermal crosslinking can be achieved through the olefinic bond and probably through the azomethine bond.¹¹ Thus, the completely cured epoxy resins have a highly crosslinked structure, and therefore are somewhat brittle. However, the high crosslink density of these resins renders them more heat-resistant.

TABLE I
Epoxy Equivalent Weights as well as IR and ¹H-NMR Spectral Data of Epoxy Compounds

Compound	EEW ^{a,b} (g/mol)	IR wave number (cm ⁻¹)	¹ H-NMR Chemical shifts (δ in ppm) ^c
1a	397 (366.4)	1262, 1180, 844 (ether); 1731, 1687 (C=O); 3640-2500 (OH and NH); 1618 (C=N and C=C); 1508 (aromatic)	10.55 (bs, 1H, COOH); 8.52 (bm, 1H, CH=N and 1H, NHCO); 7.78-7.20 (m, 8H, aromatic); 6.10 (m, 2H, olefinic); 3.80 (m, 2H, CH ₂ OPh); 3.27 (m, 1H, CHCH ₂ O); 2.80 (m, 2H, epoxy CH ₂)
1b	491 (458.5)	1260, 1175, 850 (ether); 1718, 1670 (C=O); 3600-2800 (OH and NH); 1619 (C=N and C=C); 1505 (aromatic)	10.60 (bs, 1H, COOH); 8.32 (bm, 1H, CH=N and 1H, NHCO); 7.82-6.83 (m, 12H, aromatic); 6.20 (m, 2H, olefinic); 3.87 (m, 2H, CH ₂ OPh); 3.50 (m, 1H, CHCH ₂ O); 2.52 (m, 2H, epoxy CH ₂)
1c	497 (456.5)	1238, 1163, 820 (ether); 1710, 1660 (C=O); 3560-2850 (OH and NH); 1593 (C=N and C=C); 1503 (aromatic)	10.57 (bs, 1H, COOH); 8.43 (bm, 1H, CH=N and 1H, NHCO); 7.90-6.78 (m, 12H, aromatic); 6.12 (m, 2H, olefinic); 3.97 (m, 2H, CH ₂ OPh); 3.66-3.50 (m, 2H, PhCH ₂ Ph and 1H, CHCH ₂ O); 2.63 (m, 2H, epoxy CH ₂)
1d	550 (507.4)	1260, 1140, 828 (ether); 1717, 1676 (C=O); 3560-2850 (OH and NH); 1594 (C=N and C=C); 1507 (aromatic)	10.63 (bs, 1H, COOH); 8.50 (bm, 1H, CH=N and 1H, NHCO); 8.20-6.57 (m, 12H, aromatic); 6.31 (m, 2H, olefinic); 3.73 (m, 2H, CH ₂ OPh); 3.25 (m, 1H, CHCH ₂ O); 2.67 (m, 2H, epoxy CH ₂)
2a	351 (318.3)	1270, 1185, 843 (ether); 1734, 1650 (C=O); 3600-2680 (OH and NH); 1622 (C=N and C=C); 1504 (aromatic)	10.48 (bs, 1H, COOH); 8.47 (bm, 1H, CH=N and 1H, NHCO); 7.75-7.25 (m, 4H, aromatic); 6.13 (m, 2H, olefinic); 3.55 (m, 2H, COOCH ₂); 3.07 (m, 1H, CHCH ₂ O); 2.46 (m, 2H, epoxy CH ₂)
2b	448 (410.4)	1220, 1162, 838 (ether); 1705, 1675 (C=O); 3660-2800 (OH and NH); 1608 (C=N and C=C); 1503 (aromatic)	10.54 (bs, 1H, COOH); 8.36 (bm, 1H, CH=N and 1H, NHCO); 7.86-6.76 (m, 8H, aromatic); 6.17 (m, 2H, olefinic); 3.50 (m, 2H, COOCH ₂); 3.10 (m, 1H, CHCH ₂ O); 2.57 (m, 2H, epoxy CH ₂)
2c	452 (408.4)	1250, 1180, 843 (ether); 1707, 1677 (C=O); 3610-2740 (OH and NH); 1613 (C=N and C=C); 1510 (aromatic)	10.46 (bs, 1H, COOH); 8.38 (bm, 1H, CH=N and 1H, NHCO); 7.48-6.50 (m, 8H, aromatic); 6.14 (m, 2H, olefinic); 3.70-3.53 (m, 2H, COOCH ₂ and 2H, PhCH ₂ Ph); 3.13 (m, 1H, CHCH ₂ O); 2.51 (m, 2H, epoxy CH ₂)
2d	495 (459.3)	1263, 1153, 839 (ether); 1730, 1640 (C=O); 3650-2850 (OH and NH); 1605 (C=N and C=C); 1507 (aromatic)	10.58 (bs, 1H, COOH); 8.54 (bm, 1H, CH=N and 1H, NHCO); 8.26-6.63 (m, 8H, aromatic); 6.15 (m, 2H, olefinic); 3.53 (m, 2H, COOCH ₂); 3.20 (m, 1H, CHCH ₂ O); 2.56 (m, 2H, epoxy CH ₂)

^a Epoxy equivalent weights in g/mol of epoxy groups.

^b Numbers in parentheses indicate the calculated values.

^c In DMSO-d₆ solution (bm = broad multiplet; bs = broad singlet; m = multiplet).

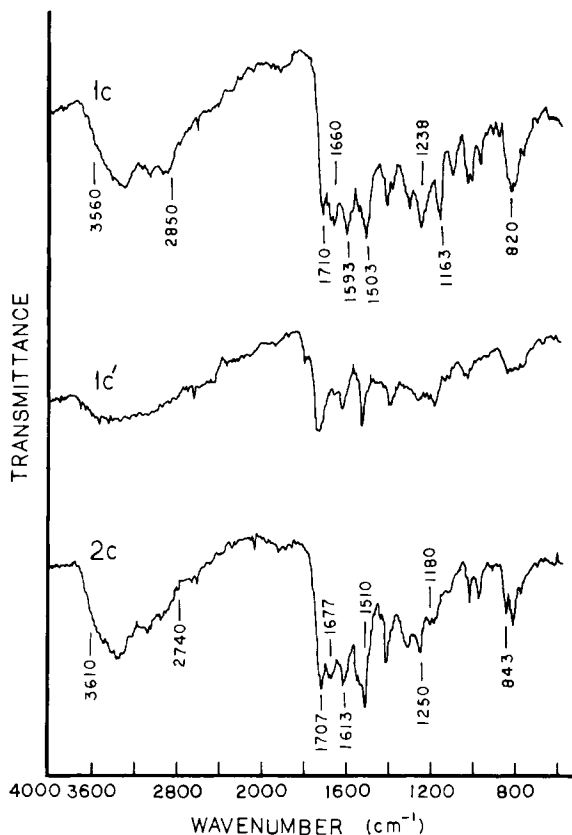


Fig. 1. IR spectra of epoxy compounds 1c and 2c as well as of cured resin 1c'.

An attempt was made to elucidate the structure of cured resins by means of IR spectroscopy. Note that the cured resins were insoluble, even in polar aprotic solvents, and, therefore, interpretable ¹H-NMR spectra could not be obtained. Figure 1 shows the IR spectrum of resin 1c'. Upon comparing the IR spectra of 1c and 1c', it can be seen that the latter showed a broadening. The relative intensity of the absorption bands at 3560–2850 cm⁻¹ (OH and NH stretching) as well as at 1593 cm⁻¹ (C=N and C=C) was significantly reduced in the spectrum of 1c'. This behavior confirms the elimination of the carboxy group, as well as that of the olefinic and azomethine bonds attained after complete curing. In addition, the absorptions at 1238, 1163, and 820 cm⁻¹ associated with the epoxy group were also reduced remarkably in 1c'. The formation of ether crossbonds during curing does not allow a complete disappearance of the absorptions assigned to the ether structure.

Thermal crosslinking of epoxy compounds was investigated by DTA in N₂. Figures 2 and 3 show typical DTA traces of epoxy compounds 1a–1d before and after curing, respectively. The uncured samples showed exotherms started at 187–211°C; these were attributed to the thermally induced crosslinking reactions because the respective cured samples did not exhibit an exotherm in this temperature region. The onset temperatures (*T*₀) for polymerization were

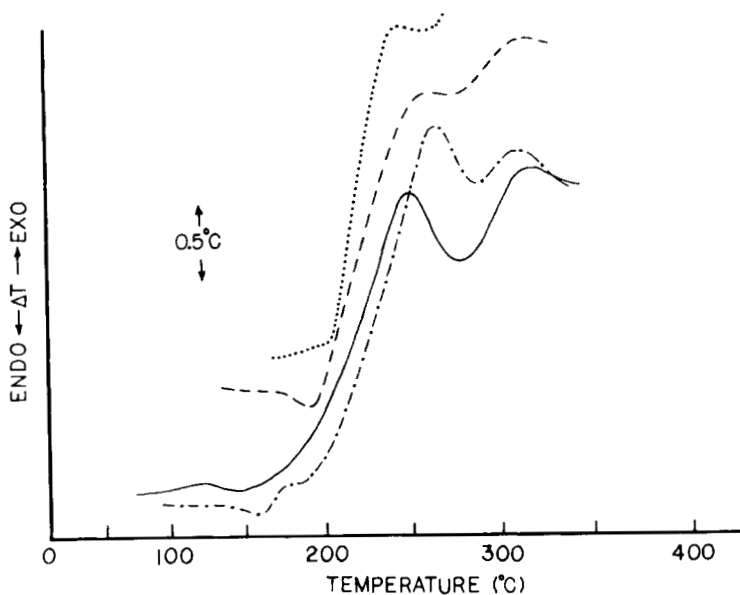


Fig. 2. DTA traces of epoxy compounds 1a (—), 1b (---), 1c (--), and 1d (···) in N_2 .

determined from the DTA traces and are as follows: 1a: 187°C; 2a: 196°C; 1b: 191°C; 2b: 202°C; 1c: 193°C; 2c: 198°C; 1d: 203°C; 2d: 211°C. It can be seen that all epoxy compounds showed comparable T_0 values and that they exhibited, therefore, almost the same polymerization reactivity. Hence, the chemical

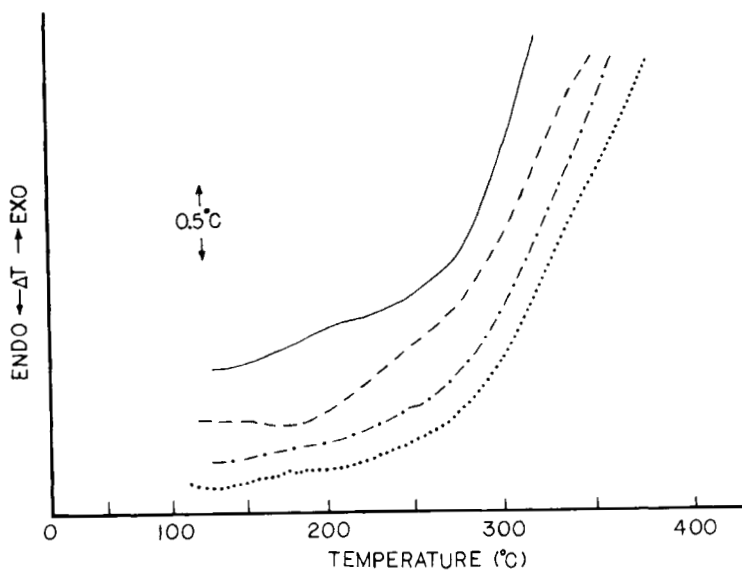


Fig. 3. DTA traces of cured resins 1a' (—), 1b' (---), 1c' (--), and 1d' (···) in N_2 .

structure of the aromatic diamine utilized for preparing the monomaleamic acid did not have remarkable influence on the polymerization reactivity of epoxy compounds. However, on comparing the epoxides **a–d** with both of the glycidyl ethers **1** and glycidyl esters **2**, it is seen that epoxide **d** showed a somewhat higher T_0 and consequently lower reactivity. The lower basicity of 4,4'-diaminodiphenylsulfone utilized for preparing the monomaleamic acid of epoxide **d** was probably responsible for this behavior. Finally, the glycidyl ethers **1** showed slightly higher reactivity than did the respective glycidyl esters **2**.

The thermal stabilities of cured resins were evaluated by dynamic TGA in N_2 and air atmospheres. Figure 4 shows typical TGA traces of polymers **1b'**, **2b'**, **1c'**, and **2c'** in N_2 and air atmospheres. Table II gives some of the TGA data, particularly, the initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}), the temperature of complete pyrolysis (TCP) both in N_2 and air as well as the anaerobic char yield (Y_c) at $800^\circ C$, and the temperatures at which the polymers showed a weight loss of 30 and 60% in air. Upon gradual heating, the polymers did not show a weight loss up to $275\text{--}295^\circ C$ in N_2 or air. They afforded an anaerobic char yield of 47–65% at $800^\circ C$. The relative thermal stabilities of polymers could be judged on the basis of IDT values. Polymers **1'** derived from glycidyl ethers were slightly more heat-resistant than the respective polymers **2'** obtained from glycidyl esters. The ether structure has proved more thermostable than ester one for epoxy resins.² In the present case, the more aromatic structure of EPB (compared to EPG) contributed to the higher heat-resistance of polymers **2'**. Thermal stabilities of polymers **a–d** did not differ significantly. This supports the conclusion that chemical structures of aromatic diamines utilized for the preparation of monomaleamic acid did not affect remarkably thermal stabilities of cured resins. Degradation of polymers was not influenced greatly by the presence of oxygen, because the IDT in air was slightly lower than that in N_2 .

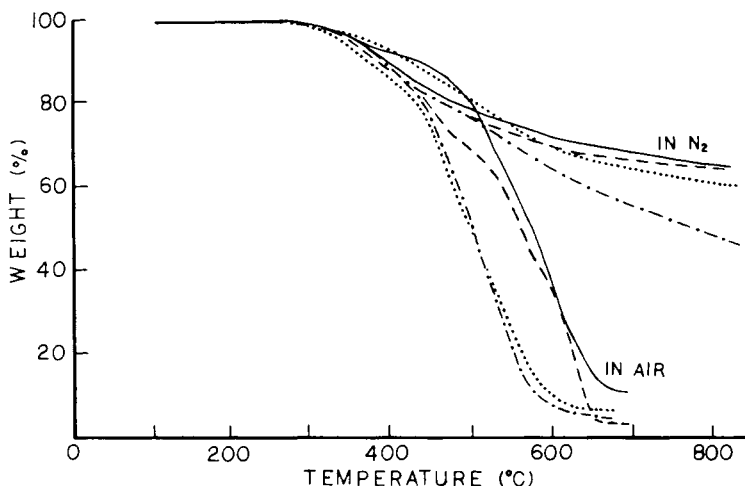


Fig. 4. TGA thermograms of cured resins **1b'** (—), **2b'** (---), **1c'** (- -), and **2c'** (···) in N_2 and air.

TABLE II
Thermal Stabilities of Cured Resins

Polymer	In N ₂					In air				Temp in °C for weight loss	
	IDT ^a (°C)	PDT ^b (°C)	PDT _{max} ^c (°C)	TCP ^d (°C)	Y _c (800°C) ^e (%)	IDT (°C)	PDT (°C)	PDT _{max} (°C)	TCP (°C)		
										30%	60%
1a'	283	329	400	503	62	276	321	355, 582	609	508	563
1b'	291	329	404	521	65	286	321	370, 589	630	527	591
1c'	294	325	400	527	65	291	325	367, 625	646	495	584
1d'	295	351	452	478	45	285	355	404, 567	641	518	576
2a'	278	336	422	517	59	275	329	400, 578	633	489	571
2b'	283	336	441	521	49	279	321	377, 519	572	464	517
2c'	278	350	444	617	61	275	311	363, 498	586	460	519
2d'	291	367	400	469	47	291	336	381, 537	630	498	561

^a Initial decomposition temperature.

^b Polymer decomposition temperature.

^c Maximum polymer decomposition temperature.

^d Temperature of complete pyrolysis.

^e Char yield at 800°C.

Figure 5 presents the isothermal gravimetric analysis (IGA) traces of polymer 1b' in static air at 260, 280, 300, 320, and 340°C. After 20 h of isothermal aging at these temperatures, polymer 1b' showed a weight loss of 14.3, 24.3, 39.0, 54.3, and 78.0%, respectively.

CONCLUSIONS

1. New glycidyl ethers or esters were obtained by reacting EPB or EPG with the monomaleamic acid derived from an aromatic diamine.

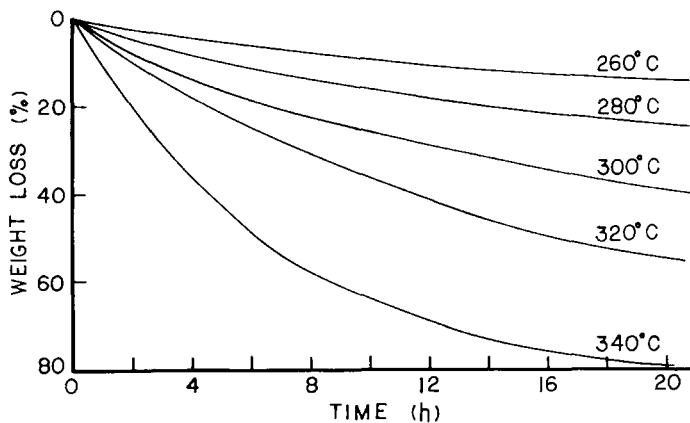


Fig. 5. IGA traces of cured resin 1b' in static air at 260, 280, 300, 320, and 340°C.

2. Upon gradual heating, the epoxy compounds were self-crosslinked from the reaction of epoxy group with the maleamic carboxyl and through the olefinic bond.
3. Chemical structures of aromatic diamines utilized for preparing the monomaleamic acids did not influence greatly the onset temperature (T_0) for polymerization as well as the thermal stabilities of cured resins.
4. Thermal polymerization of epoxy compounds started at 187–211°C. The cured resins did not show a weight loss up to 275–295°C in N_2 or air and afforded anaerobic char yield of 47–65% at 800°C.

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