# Effect of Structure of Aromatic Diamines on Curing Characteristics, Thermal Stability, and Mechanical Properties of Epoxy Resins. I

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**ABSTRACT:** The curing behavior of diglycidyl ether of bisphenol-A (DGEBA) with aromatic diamines having aryl–ether, aryl–ether–carbonyl, and aryl–ether–sulfone linkages was studied using differential scanning calorimetry (DSC). Aromatic diamines such as 1,3-bis(aminophenoxy)benzene (R), 1,4-bis(aminophenoxy)benzene (H), 2,2′-bis[4-(4-aminophenoxy)phenyl]propane (B), 4,4′-bis(4-aminophenoxy)benzophenone (P), and bis[4-(4-aminophenoxy)phenyl]sulfone (S) were synthesized and characterized in the laboratory. Curing of DGEBA was done using both stoichiometric and nonstoichiometric amounts of diamines and the reaction was monitored using DSC. The reactivity of the diamines depended on the structure. The presence of electron withdrawing groups, even though significantly apart from the reaction site, reduced the nucleophilicity. No significant change was observed in the activation energy for curing, which was around $56 \pm 2$ kJ/mol. The glass transition temperature of the epoxy network depended on the structure and was higher when diamines P and S were used in comparison to diamines R, H, and B. The cured resins were stable up to 300°C, and maximum char yield (i.e., 32% at 600°C) was obtained in DGEBA cured with diamine P. The room temperature mechanical properties only changed marginally with the structure of the diamines. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1759–1766, 1998

**Key words:** epoxy resin; aromatic diamines; thermal stability; curing characteristics; mechanical properties

## INTRODUCTION

Several approaches have been adopted in the past to control the crosslink density of an epoxy network. These include varying the epoxy resin/curing agent functional group ratio, using a difunctional epoxy prepolymer with a different average chain length, and varying the molecular size of the difunctional curing agent.

The variation in the functional group ratio of the epoxy resin/curing agent[1–4] has the problems of residual chain ends and the existence of uncrosslinked soluble fractions. Use of different average chain length of the difunctional epoxy prepolymers poses processing problems because of the higher melting temperature and viscosity of the prepolymers.[4,5] Variation in the molecular size of the curing agent is expected to provide networks with similar structures, except in the molecular weight between the crosslinks. Use of specialty curatives such as aromatic diamines has reportedly improved the performance of the epoxy resin.[6,7]

Curing of the most commonly used epoxy resin,

diglycidyl ether of bisphenol-A (DGEBA), with a variety of aromatic diamines has been extensively reported in the literature.[8-13] However, systematic studies dealing with the effect of the molecular weight of the aromatic diamines on the curing behavior, thermal stability, and mechanical properties of cured DGEBA has not been reported.

The primary objective in the present studies is to evaluate the curing behavior of DGEBA using aromatic diamines having aryl–ether {e.g. 1,3-bis-(aminophenoxy)benzene and 1,4-bis(aminophenoxy)benzene, 2,2′-bis[4-(4-aminophenoxy)phenyl]-propane}, aryl–ether–carbonyl {4,4′-bis(4-aminophenoxy)benzophenone}, and aryl–ether–sulfone {bis[4-(4-aminophenoxy)phenyl]sulfone} linkages. The thermal data of the network prepared by changing reactant equivalence ratio, mechanical properties, and thermal stability of the cured resins are also reported.

## EXPERIMENTAL

Commercially available hydroquinone, resorcinol, 4-nitrochlorobenzene (CDH), $N,N$-dimethyl acetamide (DMAc), dimethyl formamide (DMF) (all from E-Merck), 4,4′-dichlorodiphenylsulfone, 4,4′-difluorobenzophenone (Aldrich), bisphenol-A (BA) (BDH), palladium charcoal (10%) (Johnson Matthey Chemical), hydrazine hydrate 99% (IDPL), and DGEBA (grade LY556; Hindustan Ciba Geigy) were used as received. The epoxy equivalent of the resin was 176.8.

### Characterization

The $^1$H-NMR spectra were recorded in CDCl$_3$ using tetramethyl silane as an internal standard and a Jeol JNM-FX 100 FT-NMR spectrometer. The infrared spectra were recorded in KBr pellets using Digilab's Biorad FTS-40 FTIR spectrometer.

### Preparation of Diamines

The diamines R, H, and B were prepared by reacting aromatic dihydroxy compounds with 4-nitrochlorobenzene in the presence of anhydrous K$_2$CO$_3$. The dinitro compounds thus obtained

were reduced by using hydrazine hydrate and Pd/C (Scheme 1).

The synthesis of diamine R was carried out by dissolving resorcinol (20.0 g, 0.18 mol) in DMF (150 mL) in a three-necked flask equipped with a reflux condenser (with a guard tube) and a nitrogen inlet. Powdered anhydrous K$_2$CO$_3$ (50.0 g) was added and the mixture was stirred for 2 h in an N$_2$ atmosphere. A solution of 4-nitrochlorobenzene (55.0 g, 0.36 mol) in DMF (100 mL) was slowly added through a dropping funnel. The reaction mixture was stirred for 6 h at 100°C in the N$_2$ atmosphere, cooled, and then added to 1% aqueous NaOH ($\approx$ 500 mL). The precipitated 1,3-bis(nitrophenoxy)benzene (NR) was collected by filtration, washed, dried, and recrystallized from benzene [melting point (mp) 108–110°C, yield 78%].

NR (25.0 g, 0.071 mol) was dissolved in 150 mL methanol : DMAc (2 : 1 ratio) solution in a 500-mL three-necked flask equipped with a reflux condenser and a dropping funnel. Pd/C (0.8 g) was added and the mixture was warmed to 50°C. Hydrazine hydrate (22 mL, 0.43 mol) was added dropwise over a 45-min period with constant stirring. The contents were refluxed for 2 h, cooled, and filtered to remove the catalyst. The diamine was recovered by precipitation in water, dried, and recrystallized from ethanol (mp 116–118°C, yield 76%). $^1$H-NMR (CDCl$_3$): $\delta$, 3.2 ($s$, 4H, NH$_2$), 6.5–7.3 ($m$, 12H, aromatic).

A similar procedure was adopted to prepare diamine H (from hydroquinone) (mp 174–176°C, yield 75%). $^1$H-NMR (CDCl$_3$): $\delta$, 3.2 ($s$, 4H, NH$_2$), 6.4–7.2 ($m$, 12H, aromatic). The mp of the intermediate dinitro compound was 234–237°C (yield 66%).

Diamine B [mp 129–131°C, yield 72%; $^1$H-NMR (CDCl$_3$): $\delta$, 1.6 ($s$, 6H, CH$_3$), 3.2 ($s$, 4H, NH$_2$), 6.6–7.3 ($m$, 16H, aromatic)] was prepared using BA as the starting material. The intermediate dinitro compound had a melting point of 120–122°C (yield 78%).

Diamines P and S were prepared by condensation of sodium 4-aminophenate with dihaloaromatic compounds (Scheme 2).

Diamine P was synthesized by reacting 4-aminophenol (23 g, 0.211 mol) in 225 mL DMAc : toluene (2 : 1 v/v) with a slurry of NaOH (8.0 g, 0.2 mol) in water (5.0 mL) in a three-necked flask equipped with a Dean and Stark trap. The water was removed by azeotropic distillation, and toluene was removed by heating to 140°C. Then the temperature was reduced to 100°C and 4,4′-
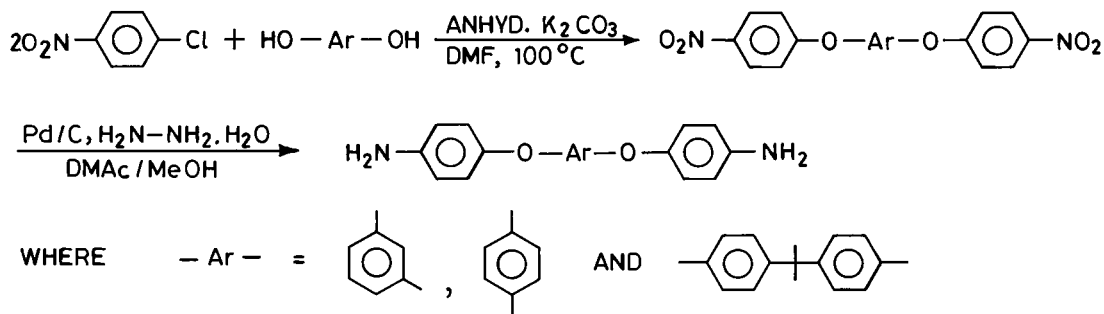
**Scheme 1**    Preparation of diamines R, H and B.

difluorobenzophenone (19.6 g, 0.09 mol) was added in parts. The reaction mix was stirred at 120°C for 6 h under an $N_2$ atmosphere, cooled, and added to water. The precipitates were collected by filtration, dried, and recrystallized from ethanol (mp 156–158°C, yield 58%). A similar procedure was adopted to prepare diamine S (mp 193–195°C, yield 84%).

In the IR spectrum of the above diamines, a characteristic absorption band due to the $NH_2$ stretch was observed at 3500–3300 cm$^{-1}$, N—H in-plane bending at 1660–1600 cm$^{-1}$, C—N stretching at 1255 ± 5 and 1210 cm$^{-1}$. The asymmetric stretching vibrations (1270–1260 cm$^{-1}$) due to the C—O—C group present in the diamines overlapped with the C—N stretching vibrations of the amino group. The absorption band due to C—O—C symmetric stretching was observed around 1020 cm$^{-1}$. The IR spectrum of P showed a strong absorption band at 1647 cm$^{-1}$ due to the stretching vibration of the carbonyl (—CO—) group. Strong absorption bands at 1312 and 1165 cm$^{-1}$, which are attributed to asymmetric and symmetric stretching vibrations of the sulfone group (—$SO_2$—), were observed in the IR spectrum of S.

## Thermal Characterization

### *Curing of Epoxy Resins*

The samples were prepared by mixing a known amount of diamines and DGEBA using a small amount of acetone as the diluent to facilitate mixing. Acetone was later removed by vacuum stripping.

The curing behavior of DGEBA with diamines was monitored by differential scanning calorimetry (DSC) in the temperature range of 50–300°C using a Du Pont 9900 Thermal Analyzer with a 910 DSC module. A sample weight of 10 ± 2 mg and heating rate of 10°C/min was used.

To determine the activation energy for the curing reaction of epoxy resin with aromatic diamines, dynamic DSC scans of resins having stoichiometric amounts of diamines at four different heating rates (i.e., 5, 10, 15, and 20°C/min) were recorded.

The thermal behavior of DGEBA cured with stoichiometric amount of diamines was also evaluated. The glass transition temperatures ($T_g$) of the cured resin were determined by DSC studies. These studies were carried out in static air at a
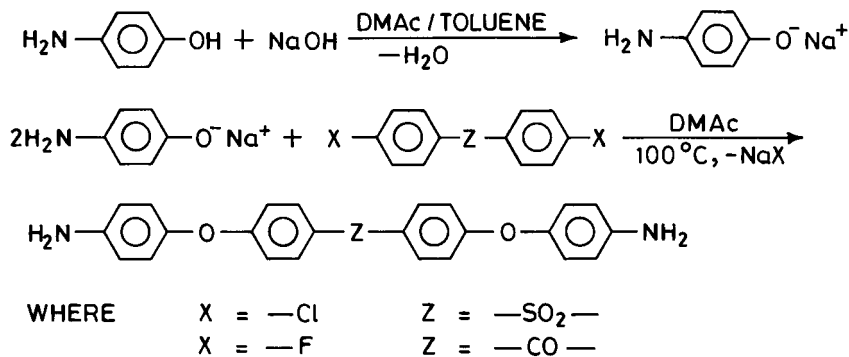


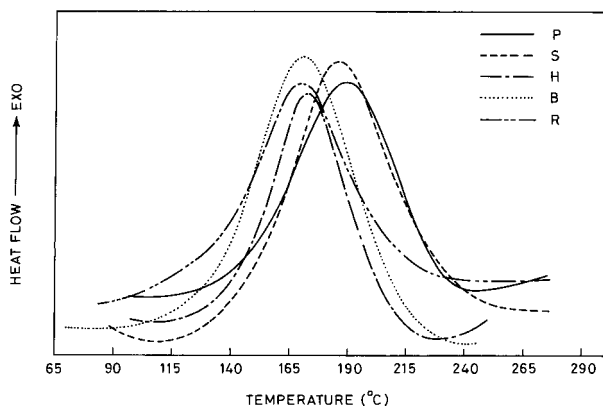**Scheme 2**    Preparation of diamines P and S.

**Figure 1**   DSC scans of DGEBA having stoichiometric amounts of different diamines at a heating rate of 10°C/min.

heating rate of 5°C/min using $7 \pm 1$ mg of powdered sample in each experiment.

### *Thermal Stability*

The thermal stability of cured epoxy resin was determined by using a Du Pont 9900 Thermal Analyzer with a 951 thermogravimetric (TG) module. The measurements were carried out in an $N_2$ atmosphere (flow rate 60 mL/min) at a heating rate of 10°C/min, and a sample weight of $10 \pm 1$ mg was used in each experiment.

### Mechanical Properties

Dogbone-shaped tensile test specimens were prepared using a silicone rubber mold with eight dumbbell-shaped ($0.3 \times 0.15 \times 2.6$ cm$^3$) cavities. A mixture of DGEBA and a stoichiometric amount of diamine was poured in these cavities and isothermal curing was carried out at 100°C for 4 h followed by postcuring in an oven at 150°C for 2 h. After cooling the samples were taken out and finishing was done using fine sandpaper.

To determine the room temperature mechanical properties of the cured resins, an Instron IX Automated Material Testing System 1.09 with a gauge length of 2.6 cm and crosshead speed of 3 mm/min was used. An average of five specimens were tested for each formulation.

## RESULTS AND DISCUSSION

The curing of DGEBA depends upon the structure of the diamine, the stoichiometry of the functional groups, and the thermal history. The effect of these parameters is discussed in the following text.

### Effect of Structure of Diamine on Curing Exotherm

The DSC scans of DGEBA having a stoichiometric amount of different diamines at a heating rate of 10°C/min are shown in Figure 1. The DSC scans were characterized by determining the temperature of the deviation from the baseline ($T_i$), the extrapolated onset temperature of curing ($T_o$), the exotherm peak position ($T_p$), the temperature of completion of the exotherm ($T_f$), and the heat of curing ($\Delta H$). The results are summarized in Table I.

The onset temperature of the exotherm depended upon the reactivity of the diamine. The values of $T_i$ and $T_o$ showed the following trend:

$$B < R < H < P \approx S$$

The reactivity of diamines P and S was found to be lowest. These diamines contain electron withdrawing carbonyl ($-CO-$) and sulfone ($-SO_2-$) groups that may be responsible for the reduced reactivity. However, the sulfone and carbonyl groups are far away from the reaction site (i.e., $NH_2$ group) and they still influenced the nucleophilicity of the amino group.

A higher reactivity was observed with *meta* linkage containing diamine (R) than the corresponding *para* linkage containing diamine (H). The flexibilizing effect of meta linkage may be responsible for this difference in reactivity. A similar trend in the reactivity of the diamines containing meta linkages, $-CH_2-$, and $-SO_2-$ groups was observed by Patel et al.[14] and Dine Hart and Wright.[15] Therefore, the presence of electron withdrawing groups and the flexibility of the diamines seems to be the controlling factors for the reactivity of the diamines.

**Table I   Results of DSC Scans of DGEBA/Diamines (Stoichiometric Amount) at Heating Rate of 10°C/min**

| Sample | $T_i$ (°C) | $T_o$ (°C) | $T_p$ (°C) | $T_f$ (°C) | $\Delta H$ (J/g) |
|--------|-----------|-----------|-----------|-----------|-------------------|
| R | 96 | 133 | 170 | 250 | 315 |
| H | 114 | 138 | 171 | 239 | 369 |
| B | 86 | 128 | 170 | 247 | 270 |
| P | 121 | 147 | 186 | 257 | 304 |
| S | 114 | 149 | 189 | 273 | 279 |

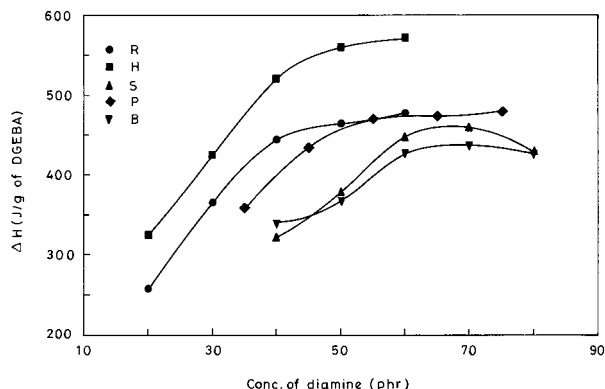**Figure 2** $\Delta H$ per unit weight of epoxy resin versus concentrations of diamines.

The exothermic peak positions were comparable when diamines R, H, and B ($\approx$ 152 $\pm$ 1°C) were used. However, higher values were observed with diamines P and S (169 and 189°C). The heat of curing was highest in H and was lowest in B.

### Effect of Functional Group Nonequivalence on Curing Behavior

To investigate the effect of the nonequivalence of the functional groups on curing behavior, different concentrations of diamines ranging from 20 to 80 phr were used. The $T_i$ and $T_o$ depended on the reactivity of the diamine; hence, it remained unchanged with the concentration of diamine. The exothermic peak position either remained the same or decreased marginally ($\approx$ 10°C) with an increase in amine concentration. The major difference was found in the heat of polymerization. The extent of cure is expected to increase with amine concentration until the stoichiometric ratio is reached. The observed increase in $\Delta H$ values can thus be explained easily. The molecular weights of the diamines were different; therefore, to assess the extent of cure, $\Delta H$ per unit weight of epoxy resin was calculated. These results are shown in Figure 2. The following order of $\Delta H$ per unit weight of epoxy resin was observed:

$$H > R \approx P > B \approx S$$

The molecular weight of diamines B and S were the highest. Therefore, higher concentrations of diamines are needed to cure a unit weight of epoxy resin. The diffusion of the amino group to the epoxy site may be hindered by a higher molecular weight of diamine, and this can explain the lower values observed in B and S.

### Activation Energy of Curing Reaction

The dynamic DSC scans at four different heating rates of DGEBA/B (stoichiometric amount) are given in Figure 3. The $T_i$, $T_o$, $T_p$, and $T_f$ shifted to higher temperatures while there was a decrease in heat of polymerization ($\Delta H$) with increasing scan rate. Similar curves were also obtained for other epoxy/amine systems (Table II).

A relationship between activation energy ($E_a$), the heating rate ($\phi$), and the peak exotherm temperature ($T_p$) based on the work of Ozawa[16] was used to calculate $E_a$.

$$E_a = R\Delta \log \phi / 0.4567\Delta(1/T_p)$$

The activation energy of the curing reaction of various epoxy/amine systems determined from regression plots using the above equation are listed in Table II. No significant change in the activation energy of the curing reaction of the epoxy/amine systems was observed ($\approx$ 56 $\pm$ 2 kJ/mol). $E_a$ was marginally lower for more reactive diamines (R, H and B) as compared to other diamines.

### Effect of Structure of Diamines on $T_g$ of Cured Resin

The $T_g$ values of cured DGEBA with stoichiometric amounts of diamines were determined using DSC studies (Table II). A typical curve obtained for P cured DGEBA is shown in Figure 4. The $T_g$ was recorded as the midpoint temperature be-
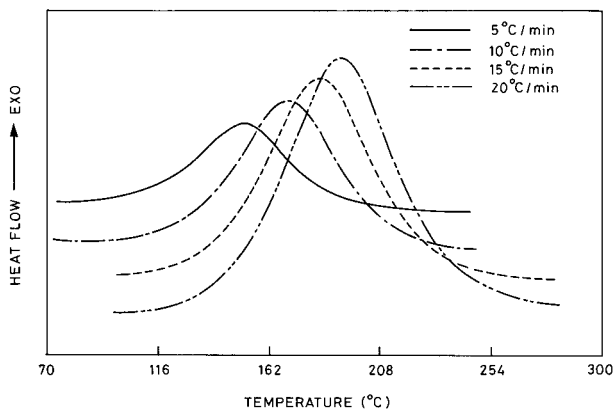


**Figure 3** Dynamic DSC scans of DGEBA/B (stoichiometric amount) at four different heating rates.

**Table II   Results of DSC Scans of DGEBA/Diamines (Stoichiometric Amount) at Different Heating Rates and Glass Transition Temperature ($T_g$) of Cured Resins**

| Sample | $\phi$ (°C/min) | $T_i$ (°C) | $T_o$ (°C) | $T_p$ (°C) | $T_f$ (°C) | $\Delta H$ (J/g) | $E_a$ (kJ/mol) | $T_g$ of Cured Resin (°C) |
|---|---|---|---|---|---|---|---|---|
| R | 5  | 84  | 118 | 152 | 225 | 329 |    |     |
|   | 15 | 102 | 142 | 184 | 271 | 311 | 54 | 141 |
|   | 20 | 109 | 148 | 192 | 275 | 303 |    |     |
| H | 5  | 111 | 126 | 154 | 211 | 381 |    |     |
|   | 15 | 133 | 145 | 182 | 272 | 406 | 54 | 146 |
|   | 20 | 137 | 158 | 191 | 280 | 402 |    |     |
| B | 5  | 83  | 113 | 152 | 227 | 286 |    |     |
|   | 15 | 104 | 139 | 183 | 274 | 262 | 54 | 142 |
|   | 20 | 107 | 146 | 192 | 284 | 256 |    |     |
| P | 5  | 94  | 134 | 169 | 230 | 346 |    |     |
|   | 15 | 127 | 157 | 198 | 269 | 302 | 58 | 157 |
|   | 20 | 128 | 168 | 209 | 282 | 286 |    |     |
| S | 5  | 107 | 132 | 189 | 230 | 304 |    |     |
|   | 15 | 113 | 155 | 199 | 292 | 288 | 59 | 157 |
|   | 20 | 114 | 165 | 209 | 302 | 279 |    |     |

tween the extrapolated onset and endset temperatures.

The higher structural symmetry of H as compared to R results in the formation of a more regular and rigid crosslinked polymer network. Thus, a higher $T_g$ was observed in the case of H. A lower $T_g$ was observed with B as compared to P and S as a result of flexibility imparted by the aliphatic isopropylidene linkage to the crosslinked network. It was observed that the epoxy network consisting of P and S had higher $T_g$ compared to that of R and H, in spite of the fact that the former had lower crosslink density than the latter. This

may result from the rigidity imparted by the carbonyl ($-CO-$) and sulfone ($-SO_2$) groups to the crosslinked network.

## Thermal Stability

The thermal stability of epoxy resin samples cured with a stoichiometric amount of diamines was determined by recording TG/derivative TG (DTG) traces in an $N_2$ atmosphere. The TG traces obtained for various epoxy/amine systems were almost identical and showed a single step decomposition. A typical TG/DTG trace obtained for DGEBA cured with diamine P is shown in Figure 5. The relative thermal stability of various resins
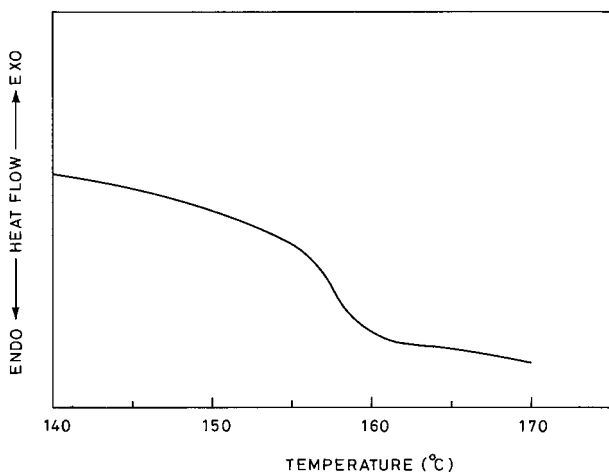


**Figure 4**   DSC scan of DGEBA cured by a stoichiometric amount of diamine P.
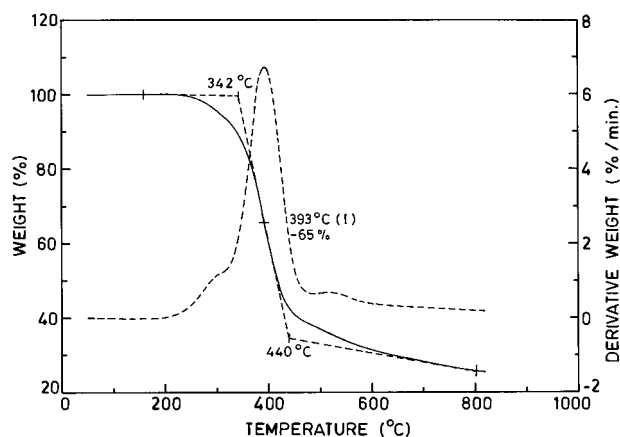


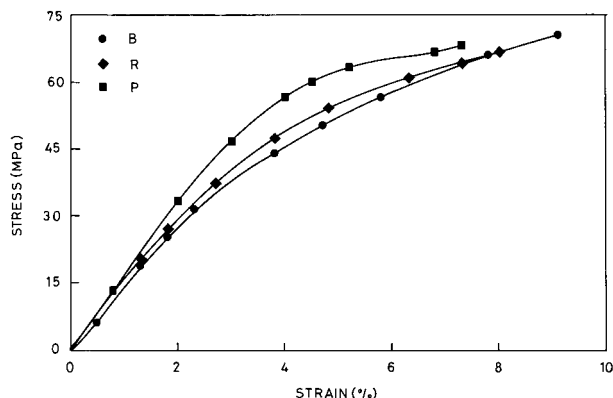**Figure 5**   TG/DTG trace of DGEBA cured with a stoichiometric amount of diamine P.

**Table III   Results of TG Studies of DGEBA/Diamines (Stoichiometric Amount)**

| Sample | $T_1$ (°C) | $T_{max}$ (°C) | $T_2$ (°C) | Char at 600°C (%) |
|--------|-----------|----------------|-----------|-------------------|
| R | 359 | 389 | 417 | 17 |
| H | 353 | 383 | 413 | 23 |
| B | 359 | 399 | 453 | 24 |
| P | 342 | 393 | 440 | 32 |
| S | 359 | 393 | 445 | 26 |
| E | 353 | 376 | 403 | 24 |



**Figure 6** Stress versus strain diagrams of DGEBA cured with a stoichiometric amount of diamines R, B, and P.

was assessed by determining the initial decomposition temperature ($T_1$), the temperature of the maximum rate of weight loss ($T_{max}$), the final decomposition temperature ($T_2$), and the percent char residue left at 600°C. $T_1$ and $T_2$ were obtained by extrapolation. The results are summarized in Table III. All the samples were stable up to 300°C, and a significant weight loss occurred only beyond this temperature. The highest char yield was obtained for DGEBA cured with diamine P. This may have been due to the reaction of the carbonyl group with the unreacted amino groups present in the polymer network at elevated temperatures.

### Room Temperature Mechanical Properties

The typical stress versus strain diagrams obtained for DGEBA cured with stoichiometric amounts of R, B, and P are shown in Figure 6 and the results are listed in Table IV. The room temperature mechanical properties were not significantly affected by a change in the structure of the diamines. The molecular structure of the

cured epoxy network remained frozen below $T_g$; thus, changes in the crosslink density of the network were not expected to bring significant changes in room temperature mechanical properties. These changes might become significant at elevated temperatures.

### CONCLUSION

The curing of epoxy resin by aromatic diamines containing aryl-ether, aryl-ether-carbonyl, and aryl-ether-sulfone linkages was influenced by the structure of the diamine. The presence of electron withdrawing groups reduced the nucleophilicity of the diamines, thereby decreasing their reaction with DGEBA. The $T_g$ of the cured resin depended on the structure of the epoxy network. However, the room temperature mechanical properties were unaffected by the structure of the epoxy network.

**Table IV   Room Temperature Mechanical Properties of DGEBA Cured with Diamines (Stoichiometric Amount)**

| Sample | Strain at Peak (%) | Stress at Peak (MPa) | Strain at Break (%) | Stress at Break (MPa) | Young's Modulus (MPa) |
|--------|--------------------|----------------------|---------------------|-----------------------|------------------------|
| R | 8.0 | 67.0 | 8.0 | 67.0 | 1609 |
| H | 6.3 | 60.7 | 6.3 | 60.7 | 1606 |
| B | 9.1 | 70.7 | 9.1 | 70.1 | 1630 |
| P | 7.2 | 68.4 | 7.3 | 68.4 | 1778 |
| S | 7.8 | 72.9 | 7.9 | 72.7 | 1728 |
| E | 8.4 | 72.7 | 8.4 | 72.6 | 1777 |

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