

# Thermal Characterization of Diglycidyl Ether of Bisphenol-A/Phosphorus Containing Amines

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**ABSTRACT:** In order to improve the thermal resistance of diglycidyl ether of bisphenol-A (DGEBA), phosphorus-containing di- and tri-amines, i.e., bis (3-aminophenyl) methyl phosphine oxide (B) and tris (3-aminophenyl) phosphine oxide (T), were used as curing agents. The effect of phosphorus content on the curing characteristics and char residue of cured resins in nitrogen atmosphere was evaluated by using different molar ratios of conventional curing agent, i.e. 4, 4'-diaminodiphenyl sulfone (D) and amine B or T. Activation energy of curing, as evaluated by using the multiple heating rate method, was lowest when triamine T ( $61.0 \text{ kJmol}^{-1}$ ) was used as hardener and was highest when D ( $68.7 \text{ kJmol}^{-1}$ ) was used. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 390–395, 2001

**Key words:** phosphorus-containing amines; curing; thermal stability; epoxy resins; heat of curing

## INTRODUCTION

In order to extend the applications of epoxy resins as electronic material and in the aerospace industry, it is crucial to improve their flame and thermal resistance. Several approaches have been reported in the literature for improving the thermal and flame resistance of these resins. Aromatic bromine compounds, in conjunction with antimony oxide, have been widely used as flame retardants for epoxy resins in the past. The major problem encountered with these systems is the production of highly toxic and corrosive products during combustion.<sup>1</sup> Fire hazards and the environmental concerns of using halogen-based systems, which have been publicized by political movements, have necessitated the search for new halogen free fire retardant agents.

Organophosphorus compounds have demonstrated good ability as flame retardants.<sup>2</sup> These compounds form a carbonaceous char, thereby protecting the polymer surface from the flame action.<sup>3</sup> Beneficial interaction between flame retardants, i.e., the influence of phosphorus and nitrogen compounds, has long been recognized. Their combination leads to effects that are greater than would be expected from a linear combination of these elements alone. Flame retardants such as phosphorus-halogen mixtures, ammonium phosphate, and organophosphorus compounds have been used as additives to impart flame retardance to the epoxy resins.<sup>4–6</sup>

Another approach for improving the thermal and flame resistance is the structural modification of epoxy resins or curing agents. Incorporation of covalently bonded flame retardant groups in polymer backbone has attracted much attention because a high efficiency in flame retardation is achieved by this method.<sup>7–10</sup>

Our earlier studies with addition polyimides have shown that incorporation of phosphorus/nitrogen

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trogen in the polymer backbone improves flame resistance.<sup>11–16</sup> An improvement in thermal and fire resistance of epoxy resins by incorporation of phosphorus has also been reported in the literature.<sup>17–19</sup> Presence of cyclic phosphine oxide rings in the epoxy backbone increases char yield of epoxy resin.<sup>20–22</sup> Reaction of diglycidyl ether of bisphenol-A (DGEBA) with trialkyl or aryl phosphate followed by curing with 4, 4'-diaminodiphenyl sulfone gave products with good thermal stability and flame resistance.<sup>23</sup> It was considered of interest to use phosphorus-containing di/tri-amines as curing agents for improving the thermal stability of epoxy resins.

## EXPERIMENTAL

### Materials

DGEBA (grade LY 556; epoxy equivalent 177) was procured from Hindustan Ciba Geigy, Ltd. Chloroform, potassium hydroxide, toluene, acetic acid, hydrazine hydrate (all from Qualigens), triphenyl phosphine (Sisco Research Labs), methyl iodide (CDH), palladium charcoal (10%; CDH), concentrated HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (Merck), triphenyl phosphine oxide, petroleum ether (S. D. Fine Chemicals), and 4,4'-diaminodiphenyl sulfone (Fluka) were used as received.

### Preparation of Diamines/Triamines

Bis (3-aminophenyl) methyl phosphine oxide (B) and tris (3-aminophenyl) phosphine oxide (T) were prepared by nitration of diphenyl methyl phosphine oxide or triphenyl phosphine oxide and subsequent reduction using Pd/C (10%) and hydrazine hydrate according to the procedure reported in the literature.<sup>11</sup>

Diphenyl methyl phosphine oxide was synthesized by reacting triphenyl phosphine (39.3 g, 0.15 mol) with methyl iodide (10 mL) using a mixture of chloroform (130 mL) and petroleum ether (200 mL) as solvent. The mixture was stirred overnight. The precipitated white solid was filtered, washed with ether, and dried under vacuum. The dried solid (61 g) was refluxed in a mixture of water (300 mL) and 40% KOH (75 mL) for 2 h, and the benzene that evolved was collected using a Dean Stark apparatus. The reaction mixture was cooled to room temperature and washed with 100 mL toluene (five to six times) using a separating funnel. All the toluene ex-

tracts were collected and dried overnight over anhydrous MgSO<sub>4</sub>. The solvent was distilled under vacuum (yield = 80%, m.pt. = 110–113°C).

Diphenyl methyl phosphine oxide was nitrated using 75 mL of conc. H<sub>2</sub>SO<sub>4</sub> and 75 mL of conc. HNO<sub>3</sub> at 0°C. The nitrating mixture, on cooling, was added to a solution of diphenyl methyl phosphine oxide (22 g) in conc. H<sub>2</sub>SO<sub>4</sub> (85 mL) at low temperature over a period of 2 h, maintaining the temperature below 10°C. The ice bath was then removed and stirring continued for ≈2 h. The reaction mixture was poured slowly, while stirring, into 500 mL of a mixture of water and ice, to give a gummy yellow solid. The solid was filtered and washed with water until washings were neutral. The product was recrystallized from (2:1) ethanol:acetic acid (yield = 75%, m.pt. = 202°C).

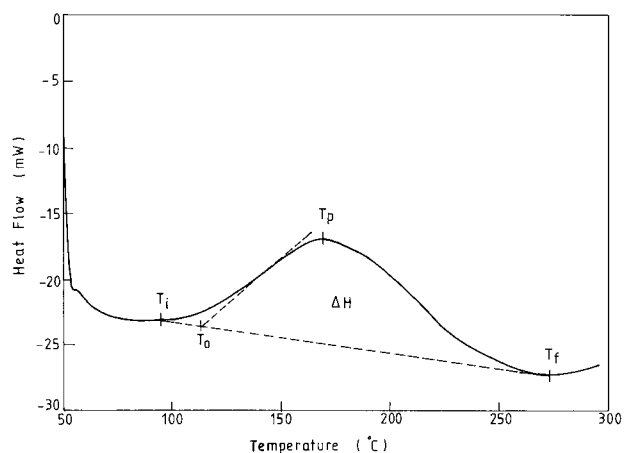
Ethanol solution of dinitro compound (10% w/v) was reduced catalytically using Pd/C and hydrazine hydrate. The reaction was exothermic, hence the contents were cooled in the initial stages. After nearly all the solid dissolved, the clear solution was gently refluxed for 2 h with stirring. The hot solution was filtered and concentrated by removing ethanol under reduced pressure. On cooling, white crystals of diamine B were obtained (yield = 60%, m.pt. = 157°C).

A similar procedure for nitration, followed by reduction, was adopted to prepare T starting from triphenyl phosphine oxide (yield = 65%, m.pt. = 258–260°C).

### Curing Studies

Curing behavior of DGEBA was investigated using stoichiometric amounts of amines. The curing was monitored by recording DSC traces in static air atmosphere using a DuPont 2100 thermal analyzer with a 910 DSC module. A sample weight of 10 ± 2 mg (freshly prepared samples) and a heating rate of 10°C min<sup>-1</sup> was used.

For curing studies the fresh samples were prepared by dissolving a known amount of amine in ethanol and adding it to DGEBA. This was done to facilitate uniform mixing of amines in DGEBA. Ethanol was then removed by vacuum stripping. The epoxy resins containing stoichiometric amounts of amines B, T, or D have been designated as BE, TE, or DE, respectively. Curing behavior of DGEBA was also investigated using stoichiometric amounts of mixed amines, i.e., B:D and T:D. The molar ratio of these amines (B/T:D) varied from 0.25:0.75, 0.5:0.5, and 0.75:0.25. These samples have been designated BDE1/



**Figure 1** DSC scan of DGEBA/triamine T at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in static air atmosphere.

TDE1, BDE2/TDE2, and BDE3/TDE3, respectively.

Activation energy for the curing reaction of DGEBA with stoichiometric amounts of B, T, D, or B/T:D (0.5:0.5) was determined using the multiple heating rate method ( $5, 10, 15, 20^{\circ}\text{C min}^{-1}$ ). The assumption made in this method is that the peak maximum represents a point of constant conversion for each heating rate, and the temperature dependence of the reaction rate constant obeys the Arrhenius equation.

### Thermal Stability

Thermal stability of epoxy resins, cured isothermally for 1 h (at  $190^{\circ}\text{C}$  when D was used as the curing agent and at  $150^{\circ}\text{C}$  in B, T, or B/T:D systems) was evaluated by using a DuPont 2100 thermal analyzer with a 951 TG module. A sample weight of  $10 \pm 2$  mg, a heating rate of  $10^{\circ}\text{C min}^{-1}$ , and a nitrogen atmosphere (flow rate  $60 \text{ cm}^3/\text{min}$ ) were used for recording TG/DTG traces.

## RESULTS AND DISCUSSION

### Curing Studies

The curing of epoxy resin depends on the structure of the amine and its stoichiometry. The effect of these parameters was evaluated in the present work. A typical DSC scan showing curing of DGEBA with T is shown in Figure 1. The exothermic transition associated with curing was characterized by determining

$T_i$  = kick-off temperature, where the curing starts.

$T_o$  = temperature of onset of exotherm obtained by extrapolating the steepest portion of the exotherm to the base line.

$T_p$  = temperature of peak position of exotherm.

$T_f$  = temperature of the end of the exotherm. This was taken as the temperature where the exotherm levels with the base line in the final stage of cure.

$\Delta H$  = heat of curing reaction, obtained from the area under the exothermic transition.

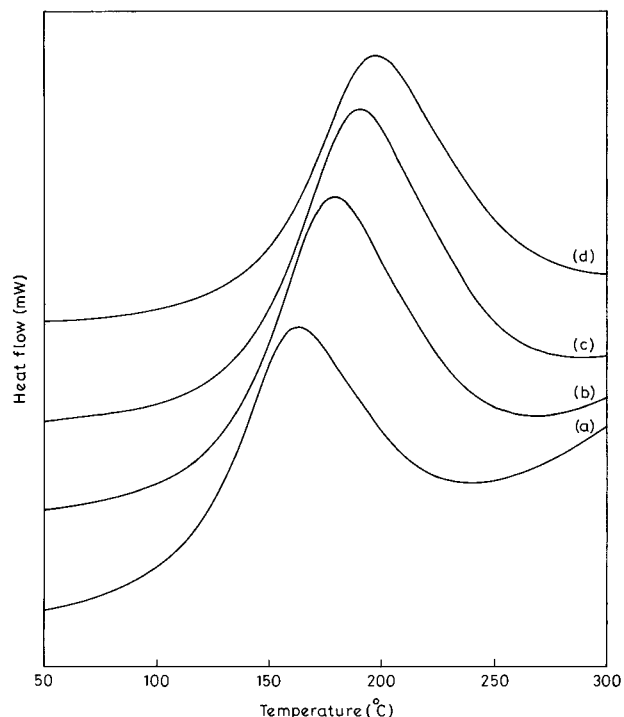
The results of the DSC scans are summarized in Table I. Reaction of an amine with an oxirane ring is a nucleophilic addition and the presence of an electron withdrawing group is expected to reduce the nucleophilicity of amine. This is obvious from the  $T_i$  value, which was highest in the case of D having sulfone as electron withdrawing group. On the basis of  $T_o$  and  $T_p$  values, it is concluded that triamine T is more reactive than B, as  $T_o$  and  $T_p$  are higher in the case of B, followed by diamine D.

D is generally used as a hardener for curing of epoxies. Incorporation of a phosphorus-containing amine along with D is expected to affect the curing behavior and thermal stability of the cured network. Therefore, mixed amines (B+D, T+D) were used for curing of DGEBA.

Addition of 0.25 mole fraction of B or T to D decreased  $T_i$  significantly.  $T_o$  and  $T_p$  also showed a decrease on addition of B/T to D.  $\Delta H$  increased with increasing amounts of B/T as a curing agent. These studies clearly indicate that curing of epoxy resin can be controlled and tailored by using a mixture of amines as hardener.

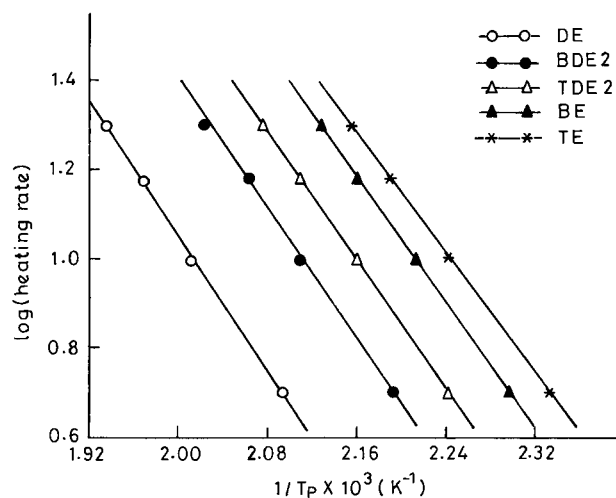
**Table I** Results of DSC Scans of DGEBA in the Presence of Stoichiometric Amounts of Amines

Sample Designation	$T_i$ ( $^{\circ}\text{C}$ )	$T_o$ ( $^{\circ}\text{C}$ )	$T_p$ ( $^{\circ}\text{C}$ )	$T_f$ ( $^{\circ}\text{C}$ )	$\Delta H$ (J/g)
DE	165	184	224	310	173
BE	97	128	179	275	320
TE	96	115	173	264	298
BDE1	150	167	214	272	219
BDE2	135	150	201	269	291
BDE3	127	140	189	268	328
TDE1	117	144	207	279	190
TDE2	112	121	188	271	220
TDE3	90	115	180	269	233



**Figure 2** Effect of heating rate on curing exotherm of DGEBA/diamine B. (a)  $5^{\circ}\text{C min}^{-1}$  (b)  $10^{\circ}\text{C min}^{-1}$  (c)  $15^{\circ}\text{C min}^{-1}$  (d)  $20^{\circ}\text{C min}^{-1}$ .

Curing of DGEBA with amines B, D, or T was also studied by using heating rates of 5, 10, 15, and  $20^{\circ}\text{C min}^{-1}$ . Figure 2 shows the typical DSC scans at different heating rates for the curing of DGEBA with stoichiometric amounts of amine B, i.e., sample BE. Similar traces were obtained by



**Figure 3** Evaluation of activation energy for the curing of DGEBA with various amines.

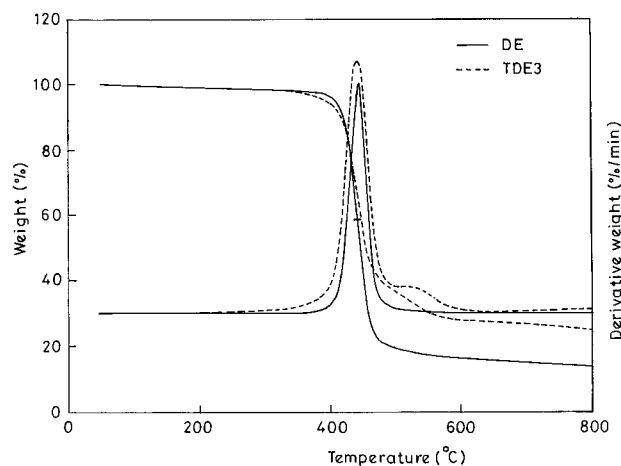
**Table II** Activation Energy of Curing of DGEBA with Stoichiometric Amounts of Amines

Sample Designation	Activation Energy ( $\text{kJ mol}^{-1}$ )
DE	68.7
BE	64.1
TE	61.0
BDE2	66.7
TDE2	66.2

using triamine T or diamine D or a mixture of the two. From these traces, exotherm peak position  $T_p$  was noted and a plot of  $T_p$  versus  $\log \Phi$  (i.e., heating rate) was obtained using regression analysis (Fig. 3.). Activation energy determined from these plots was found to vary from 61.0 to 68.7  $\text{kJ mol}^{-1}$  (Table II). Activation energy of the mixed components (BDE2 and TDE2) was found to be an average of the pure components (B/T and D).

### Thermal Stability

TG/DTG traces of isothermally cured epoxy resins were recorded in  $\text{N}_2$  atmosphere (Fig. 4.). The initial decomposition temperature (IDT), temperature of maximum rate of weight loss ( $T_{\text{max}}$ ) and final decomposition temperature ( $T_2$ ) were noted from TG traces. In those cases where two step decomposition was observed, these temperatures were noted for both of the steps (Table III). Cured resins were stable up to  $350^{\circ}\text{C}$  and started decomposing above this temperature. The relative ther-



**Figure 4** TG/DTG traces of cured DE and TDE3 samples in nitrogen atmosphere at a heating rate of  $20^{\circ}\text{C min}^{-1}$ .

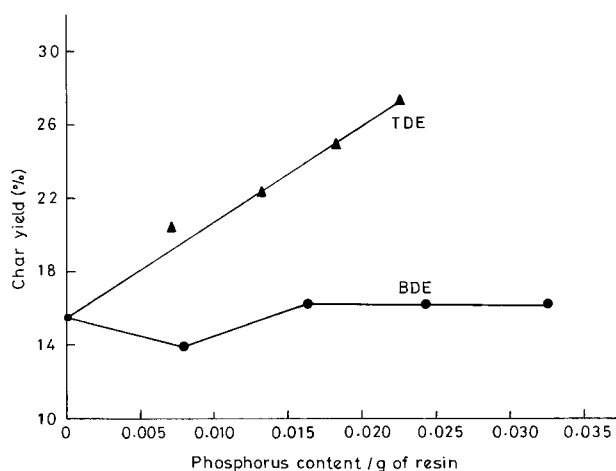
**Table III Thermal Behavior of DGEBA Cured with Stoichiometric Amounts of Amines (Heating Rate = 20°C min<sup>-1</sup>, Nitrogen Atmosphere)**

Sample Designation	IDT (°C)	T <sub>max</sub> (°C)	T <sub>2</sub> (°C)	% Wt. Loss (°C)	% Char Yield at 800°C
DE	366	442	510	84.5	15.5
BDE1	361	445	524	86	14
BDE2	352	445	528	83.6	16.4
BDE3	348	440	533	83.6	16.4
BE	343	442	537	83.6	16.4
TDE1	343	444	533	79.8	20.2
TDE2	343	444	521	76.1	22.2
	521	552	578	1.7	
TDE3	346	444	501	67	24.9
	501	524	588	8.1	
TE	353	440	489	62.2	27.4
	489	523	588	10.4	

mal stability of the cured resins was compared by determining percent char yield at 800°C. Increase in phosphorus content/g of resin resulted in an increase in the char yield when T + D were used, whereas no such effect was observed when B + D were used. Figure 5 shows the effect of phosphorus content/g of resin on char yield. Single step decomposition was observed in the BE, DE, and BDE samples, whereas a two step decomposition was observed in the TE and TDE samples. The weight loss in the second step decreased with increasing molar ratio of D in the TDE samples.

## CONCLUSIONS

The significant conclusion of this study is that incorporation of phosphorus alone is not enough



**Figure 5** Effect of phosphorus content on char yield in nitrogen atmosphere at 800°C.

for improving the anaerobic char yield of cured DGEBA. The structure of the network plays a significant role in the formation of char. The phosphorus content of BDE resins was higher than the TDE resins, but the char residue was unaffected in the former. On the other hand, in TDE resins, 76% improvement in char residue was observed by increasing the phosphorus content/g of resin from 0.0 to 0.0224.

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