

Phosphorus-Containing Epoxy Resins: Thermal Characterization

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Received 17 January 2001; accepted 15 September 2001

ABSTRACT: Three novel aromatic phosphorylated diamines, i.e., bis *N,N'*-{3-[(3-aminophenyl)methyl phosphinoyl] phenyl} pyromellitic acid (AP), 4,4'-oxo bis *N,N'*-{3-[(3-aminophenyl)methyl phosphinoyl] phenyl}phthalamic acid (AB) and 4,4'-hexafluoroisopropylidene-bis *N,N'*-{3-[(3-aminophenyl)methyl phosphinoyl] phenyl}phthalamic acid (AF) were synthesized and characterized. These amines were prepared by solution condensation reaction of bis(3-aminophenyl)methyl phosphine oxide (BAP) with 1,2,4,5-benzenetetracarboxylic acid anhydride (P)/3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (B)/4,4'-(hexafluoroisopropylidene)diphthalic acid anhydride (F), respectively. The structural characterization of amines was done by elemental analysis, DSC, TGA, ¹H-NMR, ¹³C-NMR and FTIR. Amine equivalent weight was determined by the acetylation method. Curing of DGEBA in the presence of phosphorylated amines was studied by DSC and curing exotherm was in the temperature range of 195–267°C, whereas with conventional amine 4,4'-diamino diphenyl sulphone (D) a broad exotherm in temperature range of 180–310°C was observed. Curing of DGEBA with a mixture of phosphorylated amines and D, resulted in a decrease in characteristic curing temperatures. The effect of phosphorus content on the char residue and thermal stability of epoxy resin cured isothermally in the presence of these amines was evaluated in nitrogen atmosphere. Char residue increased significantly with an increase in the phosphorus content of epoxy network. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2235–2242, 2002

Key words: thermosets; curing of epoxy resins; differential scanning calorimetry; thermogravimetric analysis

INTRODUCTION

Epoxy resins have many attractive properties such as low shrinkage, ease of cure and processing, excellent moisture, solvent and chemical resistance, good mechanical and electrical properties and adhesive strength, and ease of modification to optimize the properties. These resins have widely been used for surface coatings, adhesives, pottings, composites and laminates, encapsulants

for semiconductors, insulating materials for electric devices, etc. Laminates based on these resins have been widely used both in electronics and aerospace industries. However, flammability of these resins is a major limitation in areas requiring high flame resistance.

Modification of epoxy backbone by utilizing monomers containing flame-retardant groups (intrinsically flame retardant) or use of flame-retardant additives has been reported in the literature for achieving the desired level of flame retardancy. For example, halogen-containing monomers such as diglycidyl ether of tetrabromo bisphenol A has been used for imparting flame retardancy to commercial laminates. Under the effects of fire or smoldering they produce very

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Contract grant sponsor: CSIR (to P.J.).

Journal of Applied Polymer Science, Vol. 84, 2235–2242 (2002)
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dense smoke and toxic decomposition products. Alternatively, high efficiency in flame retardancy of polymers can be achieved by using P-containing additives, monomers or hardeners.¹

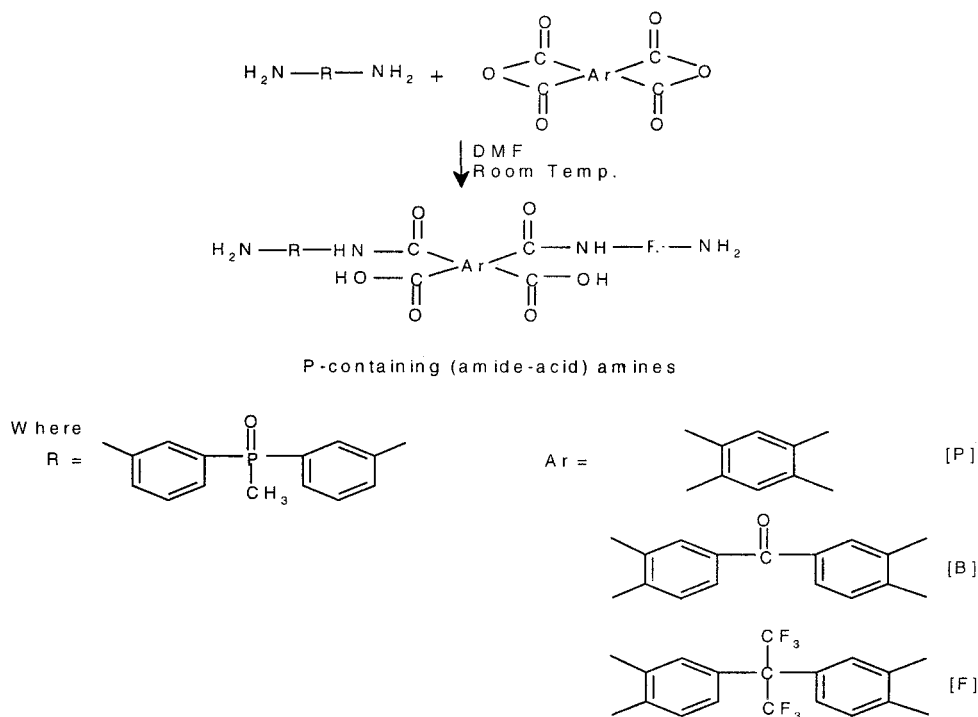
Incorporation of phosphorus and heterocyclic rings into the epoxy backbone leads to an improvement in thermal and fire resistance.² New types of epoxy resins with adequate thermal stability and high char yield have been prepared by incorporating cyclic phosphine oxide and a tetraoxirane ring in the backbone.^{3,4} Reaction of DGEBA with diallyl (or aryl) phosphate followed by curing with 4,4'-diaminodiphenyl sulfone (D) gave products with good thermal stability and flame-retardant behavior.⁵

Alternatively, phosphorus-containing amines, such as tris(3-aminophenyl) phosphine oxide, bis(3-aminophenyl)methyl phosphine oxide (BAP), bis(4-aminophenoxy)phenyl phosphine oxide and bis(3-aminophenyl)phenyl phosphine oxide, bis(3-aminophenyl) ethyl phosphine oxide, bis(3-aminophenoxy)methyl phosphine oxide, bis(3-aminophenoxy)phenyl phosphine oxide, 1,4-bis(3-aminobenzoyloxy)-2-(6-oxido-6H-dibenz [c,e][1,2]oxaphosphorin-6-yl)phenylene, etc., have been used as curing agents to impart flame retardancy to epoxy resins.⁶⁻¹⁵ Other phosphorus-containing hardeners include, novolacs, anhydrides, and acids.¹⁶⁻²¹ Ad-

vanced epoxy resins containing phosphorus have been prepared by the reaction of DGEBA with phenyl phosphite, phosphorus-containing diol bis(3-hydroxyphenyl) phenyl phosphonate, or 2-(6-oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl) 1,4-dihydroxy phenylene (ODOPB), or by the reaction of epichlorohydrin with ODOPB or BAP.²²⁻²⁸

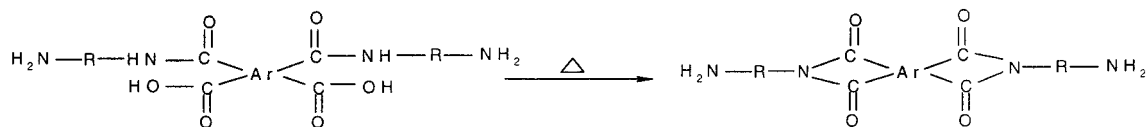
We have recently reported the curing characteristics of DGEBA using amide-amines-containing phosphine oxide group.^{29,30} Replacement of the amide group by amide acid or imides in these amines may further enhance the flame retardancy of epoxy resins. It was, therefore, considered of interest to use phosphorylated amines having amic acid linkages capable of converting into imide *in situ* for the curing of DGEBA.

In the present article curing behavior of DGEBA using diamines having phosphine oxide and amide acid linkages in the backbone is described. These novel amines, i.e., bis *N,N'*-{3-[(3-aminophenyl)methyl phosphinoyl] phenyl} pyromellitic acid (AP), 4,4'-oxo bis *N,N'*-{3-[(3-aminophenyl)methyl phosphinoyl] phenyl}phthalamic acid (AB), and 4,4'-hexafluoroisopropylidene-bis*N,N'*-{3-[(3-aminophenyl)methyl phosphinoyl] phenyl}phthalamic acid (AF) were prepared by reacting aromatic tetracarboxylic dianhydride with bis(3-aminophenyl)methyl phosphine oxide (BAP). The representative



Reaction Scheme 1

structures of these amines are depicted in Reaction Scheme 1 (AP, AB, and AF abbreviations have been used to designate these amines in the subsequent text).



EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA, Grade LY 556; epoxy equivalent 177, Hindustan Ciba Geigy Ltd.), *N,N*-dimethyl acetamide (DMAc) (CDH), *N,N*-dimethylformamide (DMF) (Merck), 4,4'-diaminodiphenyl sulfone (D) (Fluka), petroleum ether (S.D. Fine Chemicals) were used as received. Acetic anhydride (BDH) was purified by distillation and aromatic tetracarboxylic acid dianhydrides B (Aldrich), F (Hoechst Chemicals), and P (Fluka) were purified by refluxing in acetic anhydride and subsequent crystallization. Phosphorus-containing diamine BAP was prepared in the laboratory according to the procedure reported elsewhere.⁷

Synthesis of Phosphorylated Amines

Room temperature solution condensation method was used to prepare phosphorylated amines containing amide acid linkages. To a well-stirred solution of diamine BAP (2 mol) in dimethyl formamide (DMF), a solution of aromatic tetracarboxylic acid dianhydride (P/B/F) in DMF was added drop wise. After complete addition, stirring was continued for 3 h at room temperature (30–32°C). The solution was then added to ice-cold water with vigorous stirring to precipitate the phosphorylated amine. The precipitated solid was filtered, washed with water, followed by acetone and then dried in a vacuum oven.

Characterization

The amines were characterized by elemental analysis and amine equivalent weight determination. Amine equivalent was determined by acetylation with acetic anhydride in pyridine.³¹ For structural characterization IR spectra of these amines in KBr pellets were recorded using a Bio-

Amide acid groups in these phosphorylated amines may be converted to imide groups at temperatures generally used for curing of epoxy resins (~200°C) according to the following reaction scheme.

rad Digilab FTS-40 FTIR spectrometer. ¹³C- and ¹H-NMR spectra were recorded on a Bruker AC 300 spectrometer at a frequency of 300 MHz using DMSO-d₆ as solvent and tetramethyl silane as an internal standard. Thermal characterization was done by differential scanning calorimetry and thermogravimetry.

Curing Studies

A Du Pont 2100 thermal analyzer having a 910 DSC module was used to evaluate the curing behavior of DGEBA. A sample weight of 10 ± 2 mg (freshly prepared samples) and a heating rate of 10°C/min was used.

For curing studies, the samples were prepared by mixing stoichiometric amount of DGEBA and phosphorylated amines AP, AB, or AF. To study the effect of phosphorus content of diamines on the curing behavior and thermal stability of cured resins mixture of AP, AB, or AF with amine D were used. The molar ratio of phosphorylated amines and amine D was varied from 0.25 : 0.75, 0.5 : 0.5, and 0.75 : 0.25. Such amine formulations for AP : D have been designated as APD₁, APD, and AP₁D, respectively. Similarly, the designa-

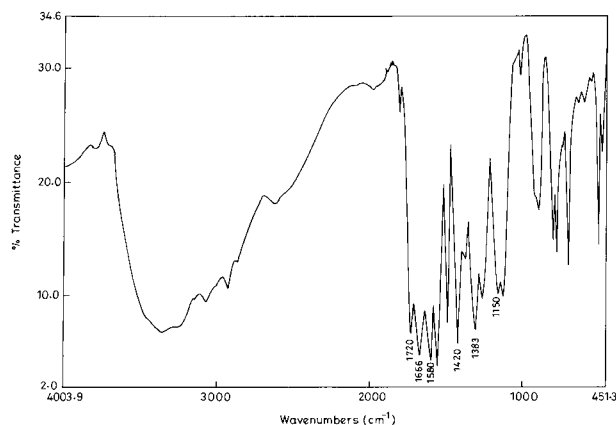


Figure 1 FTIR spectrum of amine AP.

Table I Results of CHN Analysis and Amine Equivalent of Phosphorylated Amines

Amine	% Carbon	% Hydrogen	% Nitrogen	Amine Equivalent
AP	58.5 (60.8)	4.0 (4.5)	6.8 (7.8)	347 (355)
AB	60.2 (63.4)	4.1 (4.4)	5.9 (6.8)	398 (407)
AF	55.4 (57.7)	3.5 (3.8)	5.5 (6.0)	459 (468)

Figures in parenthesis indicate the calculated values.

tion used for AB : D and AF : D were ABD₁, ABD, AB₁D, and AFD₁, AFD, and AF₁D, respectively.

The exothermic transition associated with curing was characterised by determining the following parameters: T_o is the temperature of onset of exotherm, T_p is the temperature of peak position of exotherm, T_f is the temperature of end of the exotherm, ΔH is the heat of curing reaction. T_o and T_f were obtained by extrapolation.

To determine the activation energy for curing reaction of DGEBA with stoichiometric amounts of amines AP, AB, and AF, the multiple heating rate method (5, 10, 15, 20°C min⁻¹) of Ozawa³² was used. 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. To calculate activation energy of curing, the log of heating rate was plotted against $1/T_p$.

Thermal Stability

Isothermal curing of DGEBA containing stoichiometric amounts of phosphorus-containing amines or mixture of amines was done by heating at 150°C (1 h) and 220°C (3 h). Thermal stability of the cured resin in nitrogen atmosphere (flow rate 60 cm³/min) was evaluated using a Dupont 2100 thermal analyser having a 951 TG module. A sample weight of 10 ± 2 mg, heating rate of 20°C/min was used.

RESULTS AND DISCUSSION

Characterization of Phosphorylated Amines

The phosphorylated amines were obtained in ≈90% yield. The color ranged from white to yellow. These amines were insoluble in low boiling solvents such as acetone, methyl ethyl ketone, chloroform, methanol, and ethanol, but were soluble in amide solvents, i.e., DMF and DMAc. Table I shows the results of CHN analysis and amine equivalent of

these phosphorylated amines. The observed values agreed well with the assigned structure of the amines. The phosphorus content in amine AP was highest (4.36%) and lowest in AF (3.31%).

In the IR spectrum, absorption bands at 1720 and 1660 cm⁻¹ indicative of amide acid linkage were present (Fig. 1). In the ¹H-NMR spectrum, the methyl protons attached to phosphorus appeared at 1.93 ppm, a broad signal centred at $\delta = 11.4$ ppm due to amide acid protons, i.e., —COOH was also present (Fig. 2). The proton resonance signal due to —NH₂ protons could not be distinguished from the DMSO-d₆ protons, which were observed at $\delta = 3.7$ ppm. A complex pattern was obtained in the aromatic region (6.7–8.3 ppm), corresponding with the number of protons present in the amines. The structure of the phosphorylated amines was thus confirmed by ¹H-NMR. In ¹³C-NMR a multiplet centred at $\delta = 167$ ppm shows the presence of —CO (amide $\delta = 166.3$ ppm and —COOH $\delta = 167.2$ ppm) (Fig. 3).

In the DSC scan of these amines, no sharp endotherm indicative of melting was observed. A broad endotherm was observed below 100°C, and may be due to removal of the adsorbed water. A second broad endotherm was observed in the tem-

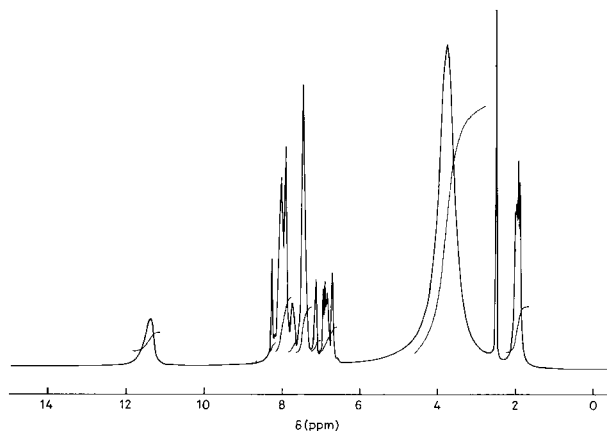


Figure 2 ¹H-NMR spectrum of amine AP.

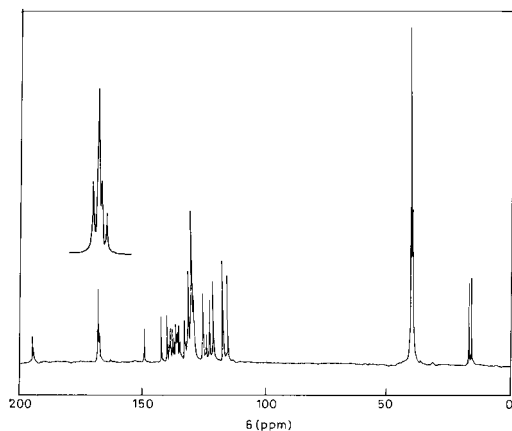


Figure 3 ^{13}C -NMR spectrum of amine AB.

perature range of 160–250°C, and may be due to loss of residual solvent (DMF) or thermal cyclization of amide acid to imide (Fig. 4). Such thermal imidization reactions in this temperature range have been reported in the literature.³³ This was further confirmed by TG analysis of amine AP, where a weight loss of around 6% was observed in temperature range of 130–270°C. The calculated loss of water from amine AP is 5.1%, which correlates well with weight loss observed in this region. Similar results were obtained in case of other amines. It is, thus, obvious that the amide acid group converts to imide when these amines are heated above 150°C.

Curing Studies

To evaluate the effect of structure of amines on curing behavior of DGEBA, studies were carried out using a stoichiometric ratio of DGEBA and amines (i.e., for D, AP, AB, and AF, the amount of amines used correspond to 35, 100, 115, and 132 phr, respectively).

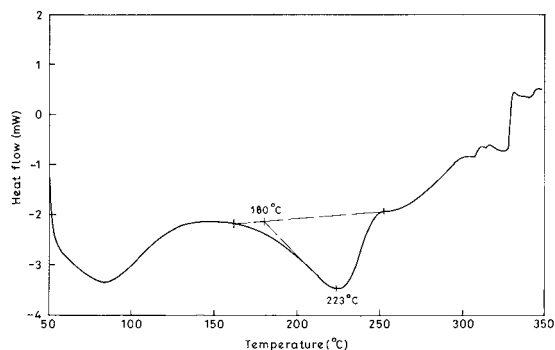


Figure 4 DSC scan of amine AB.

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

Amine Designation	D	AP	AB	AF
T_o (°C)	180	207	195	201
T_p (°C)	224	220	208	226
T_f (°C)	310	242	231	267
ΔH (J/g)	454	153	155	136
Activation Energy (kJ mol ⁻¹)	69	128	79	99

A broad exotherm was observed when DGEBA was cured with amine D (180–310°C), whereas in phosphorylated amines the curing exotherm was relatively sharp and narrower, and was in the temperature range of 195–267°C. The heat of curing (J/g) was higher when amine D was used as the curing agent. The characteristic curing temperatures are summarized in Table II (Fig. 5).

The curing of epoxy resin proceeds by the nucleophilic attack of amine on the oxirane carbon. A stronger nucleophile can initiate the curing process at a lower temperature. Therefore, onset temperature of exotherm (T_o) may be used as a criterion for evaluating the relative reactivity of various amines. The lowest T_o was observed with amine D (180°C), and the highest with AP (207°C). The observed order of T_o values was AP > AF > AB > D. Thus, amine D, despite having a strong electron withdrawing sulphone group, was apparently more reactive than phosphorylated amines. However, one has to consider the endothermic cyclodehydration reaction of phosphorylated amines, which was observed in the temper-

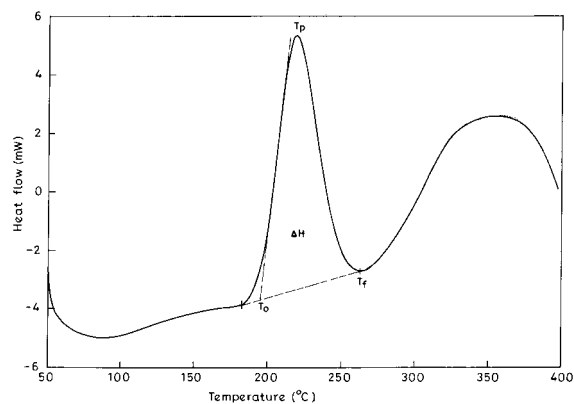


Figure 5 DSC scan of DGEBA in the presence of stoichiometric amount of amine AF.

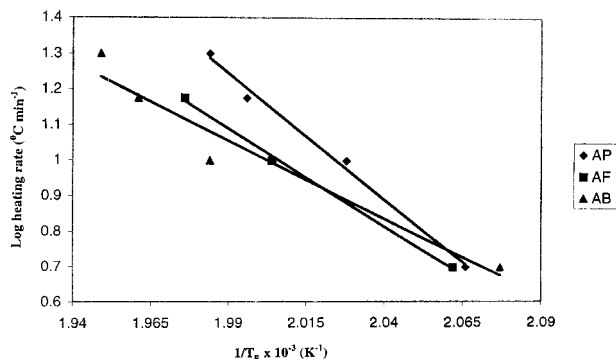


Figure 6 Evaluation of activation energy for the curing of DGEBA with P-containing amide acid amines.

ature range of 160–250°C. It is quite likely that curing (exotherm) and cyclodehydration reaction overlap, resulting thereby in an apparent increase in T_o . Heat of curing of DGEBA was also significantly less with phosphorylated amines.

Therefore, for comparison of reactivity of various amines it would be better to use the magnitude of exothermic peak temperature T_p . The exothermic peak temperature, T_p , in amines AP, AF, and D, was comparable (i.e., $223 \pm 3^\circ\text{C}$). However, for AB, T_p was 208°C , which is 15°C lower than the other amines. These results thus indicate that AB was more reactive as a nucleophile than AP, AF, or D.

The activation energy of curing of DGEBA with these amines was in the order $\text{AP} > \text{AF} > \text{AB} > \text{D}$ (Table II) (Fig. 6).

When mixed amines were used for curing of DGEBA, the characteristic curing temperatures depended on the molar ratios of the diamines (Table III). An increase in phosphorylated amine

Table III Results of DSC Scans of DGEBA in the Presence of Mixed Phosphorylated Amines and Amine D

Amine Designation	T_o (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
APD ₁	189	219	300	318
APD	199	220	275	246
AP ₁ D	205	223	258	214
ABD ₁	172	211	281	262
ABD	183	208	261	252
AB ₁ D	192	207	245	218
AFD ₁	176	219	291	260
AFD	178	204	265	238
AF ₁ D	181	220	268	178

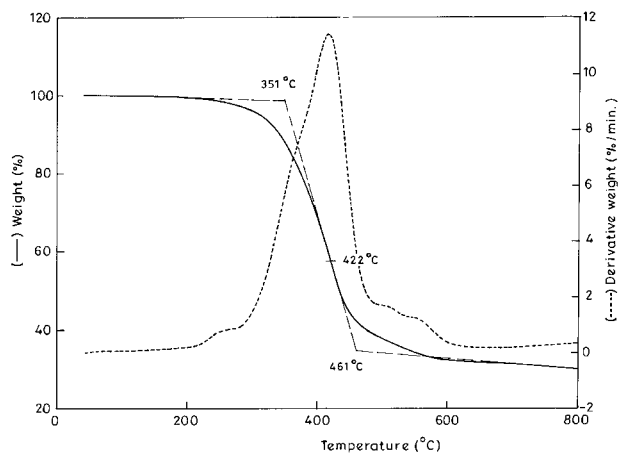


Figure 7 TG/DTG trace of DGEBA cured isothermally with amine AP.

increased T_o values from 189 to 205°C in APD, 172 to 192°C in ABD, and 176 to 181°C in AFD. The ΔH values decreased with increase in phosphorylated amine concentration, while T_p value was affected only marginally.

Thermal Stability

TG/DTG traces of isothermally cured epoxy resins were recorded in N_2 atmosphere (Fig. 7). The extrapolated initial decomposition temperature (T_{ei}), temperature of maximum rate of mass loss (T_{max}) and extrapolated final decomposition temperature (T_{ef}) were noted from TG traces. The relative thermal stability of the cured resins was compared by determining % char yield at 800°C .

In the TG traces of isothermally cured DGEBA with various amines a major mass loss of 43–80% was observed in the temperature range of 330 – 460°C (Table IV). A minor mass loss ($11 \pm 3\%$) was also observed above this temperature. About 3–6% mass loss was observed in the temperature range of 207 – 278°C in case of DGEBA cured with phosphorylated amines, while no such mass loss was observed in amine D. The first stage of mass loss may be due to the decomposition of the phosphine oxide group.³⁴ In DGEBA cured with phosphorylated amines, T_{max} (corresponding to the temperature of maximum rate of mass loss) was in the order $\text{AB} < \text{AF} < \text{AP}$. The char yield of cured DGEBA at 800°C was in the order $\text{AF} \approx \text{AB} > \text{AP}$. Phosphorus rich char was first formed in the decomposition of the phosphorus containing epoxy resin. This char is relatively thermally stable, thus protecting the resin from oxidation and resulting in higher char yields compared to non-

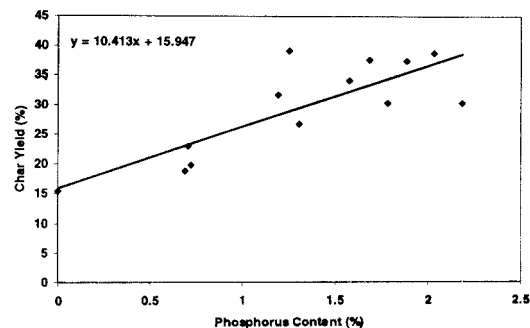
Table IV Thermal Behavior of Isothermally Cured DGEBA with Various Amines (Heating Rate 20°C/Min)

Amine Designation	Decomposition Temperature (°C)			Wt loss (%)	Char Yield at 800°C (%)
	T_{ei}	T_{max}	T_{ef}		
D	424	442	461	84.5	15.5
AP	207	243	270	3.1	30.45
	351	422	450	55.92	
	493	534	573	10.53	
AB	217	247	278	4.9	38.9
	331	367	411	47.1	
	517	548	577	9.1	
AF	226	245	265	5.6	37.6
	343	389	427	43.4	
	487	552	597	13.4	

phosphorylated resin. Increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and decrease the thermal conductivity of the burning materials, and restricts the flammability of the materials.³⁵

Table V Thermal Behavior of Isothermally Cured DGEBA with Mixed Amines AP/AB/AF and D (Heating Rate 20°C/Min)

Amine Formulation	Decomposition Temperature (°C)			Wt loss (%)	Char Yield at 800°C (%)
	T_{ei}	T_{max}	T_{ef}		
APD ₁	385	424	457	80.15	19.85
APD	373	424	456	73.24	26.76
AP ₁ D	351	421	454	61.00	30.45
	495	550	573	8.55	
ABD ₁	400	428	457	77.0	23.0
	352	404	447	51.03	
ABD	529	569	609	9.71	39.26
	209	243	273	2.25	
	335	400	457	52.63	
AB ₁ D	522	559	593	7.32	37.8
	390	427	449	70.84	
	500	536	577	10.22	
AFD ₁	366	418	446	57.36	18.94
	518	564	607	10.81	
	345	395	435	53.78	
AF ₁ D	523	557	609	11.92	34.30

**Figure 8** Plot showing the effect of phosphorus content on the char yield of DGEBA.

The results of thermal decomposition of DGEBA cured with mixed amines are summarized in Table V. Addition of amine D reduced the char yield of the cured resins. A single step decomposition was observed when DGEBA was cured with nonphosphorylated amine D. However, on addition of phosphorylated amines, i.e., in mixed amine formulations, a multistep (two- to three-step) decomposition was observed. A plot of the char yield vs. phosphorus content for DGEBA cured with phosphorylated diamines or mixed amines (Fig. 8) shows a linear dependence obeying the expression

$$\text{char yield (\%)} = 15.95 + 10.4 P (\%)$$

A comparison of phosphorylated amide acid amines and phosphorylated amide amines³⁰ show that the char yields of cured DGEBA were much higher when the former amines were used.

CONCLUSIONS

Introduction of phosphine oxide groups in amine hardeners for epoxy resins leads to a decrease in onset temperature of degradation but increases the char yield of cured resins significantly. By controlling the phosphorus content in the hardener it is possible to regulate thermal behavior of epoxy resin.

The financial assistance provided by CSIR to one of the authors (P. Jain) is gratefully acknowledged.

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