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EFFECT OF PHOSPHORUS CONTENT ON THERMAL BEHAVIOUR OF DIGLYCIDYL ETHER OF BISPHENOL-A/PHOSPHORUS CONTAINING AMINES[*]

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Abstract

Curing of diglycidyl ether of bisphenol-A (DGEBA) with phosphorus containing amide amines i.e. bis[3(3'-aminobenzamido phenyl)]methyl phosphine oxide (MB), bis[3(4'-aminobenzamido phenyl)]methyl phosphine oxide (PB), tris[3(3'-aminobenzamido phenyl)] phosphine oxide (MT) and tris[3(4'-aminobenzamido phenyl)] phosphine oxide (PT) and conventionally used curing agent 4,4'-diaminodiphenyl sulfone (D) was studied by DSC. The amines MB, PB, MT and PT were synthesised in the laboratory and were characterized by determining elemental composition, melting point, and amine equivalent. Structural characterization was done by ^{1}H-NMR and FTIR. The onset temperature of curing depended on the nucleophilicity of the amines and was in the order $MT \approx MB < PT < PB < D$. The exothermic peak temperatures were in the order $D > PB > PT > MT \approx MB$. The char residue of cured epoxy resin was significantly higher when phosphorus was incorporated in the cured network. Using mixed amine formulations based on amine D and P-containing amines and the molar ratio of these amines could easily control the curing characteristics. A linear relationship between char yield and P-content was observed in such formulations.

Keywords: curing and char yield, diglycidyl ether of bisphenol-A (DGEBA), phosphorus containing amide-amines, thermal behaviour

Introduction

Several approaches have been reported for improving the flame and thermal resistance of epoxy polymers for extending their application as electronic material and in aerospace industry. In the commercially available diglycidyl ether of bisphenol-A, the presence of glycidyl units enhances the processability but reduces the thermal and flame resistance. Flame resistant epoxy resins containing flame-retardants such as aluminium oxide trihydrate, halogenated compounds (generally used in combination with antimony oxide), phosphorus, phosphorus-nitrogen and phosphorus-halogen

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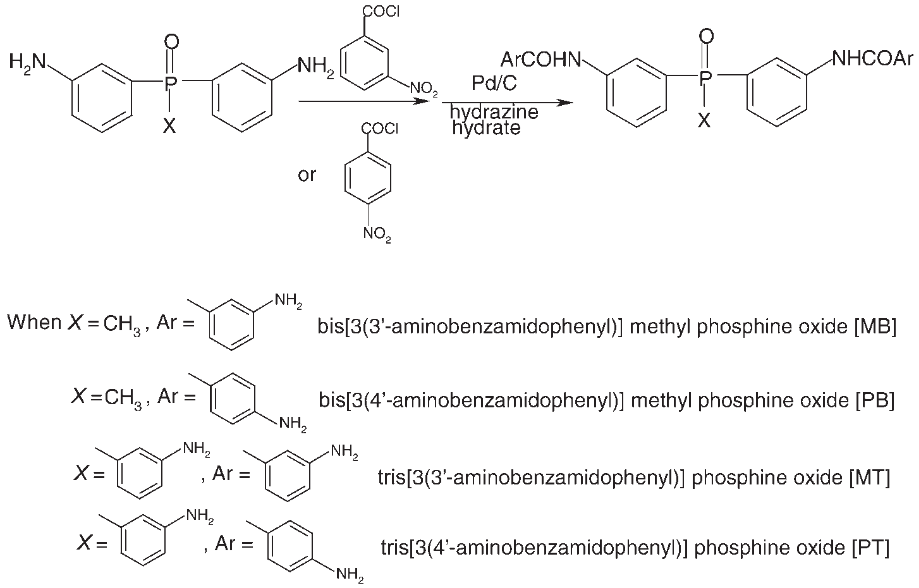
compounds have been reported in literature [1]. The major problem encountered with halogen compounds is the production of highly toxic and corrosive products during combustion [2]. Phosphorus-nitrogen synergism to improve the thermal and flame resistance is well reported in literature. This is probably due to the formation of P–N bonded intermediates [3, 4]. The incorporation of phosphorus and heterocyclic rings into epoxy polymer leads to the improvement in thermal and fire resistance [5–9]. Phosphorus containing amines such as tris(3-aminophenyl) phosphine oxide, bis(3-aminophenyl)methyl phosphine oxide, bis(4-aminophenoxy)phenyl phosphine oxide and bis(3-aminophenyl)phenyl phosphine oxide etc. when used as curing agents yielded cured epoxy network with better flame retardant properties than conventionally used curing agent [10–15].

In our efforts to quantify the effect of phosphorus content in epoxy network on thermal stability we synthesized phosphorus containing aromatic amide-amines. These amines were prepared by reacting bis(3-aminophenyl)methyl phosphine oxide (B)/tris(3-aminophenyl)phosphine oxide (T) with 3/4-nitrobenzoyl chloride followed by the reduction of the corresponding nitro compound (Scheme 1).



(Figures in square brackets indicate the letter designation of various amines)

Scheme 1 Reaction sequence describing preparation of P-containing amide-amines

In order to study the effect of P-content on the thermal behaviour of epoxy resin, phosphorus containing amines were partially replaced by conventionally used 4,4'-diaminodiphenyl sulfone (D) as a curing agent. The molar ratios of phosphorus containing amines and amine D were varied as 0.25:0.75, 0.5:0.5 and 0.75:0.25. These mixed amines have been designated by writing subscript 1, 2, 3 respectively to the letter designation of phosphorus containing amines. For example, PB:D in the molar ratios of 0.25:0.75, 0.5:0.5 and 0.75:0.25 has been designated as PB_1, PB_2 and PB_3 respectively. Similarly MT_1, MT_2 and MT_3 indicate the molar ratios of MT:D as 0.25:0.75, 0.5:0.5 and 0.75:0.25 respectively.

Experimental

Materials

Diglycidyl ether of bisphenol-A (DGEBA, Grade LY 556; epoxy equivalent 177, Hindustan Ciba Geigy Ltd.), N,N-dimethyl acetamide (DMAc) (CDH), palladium charcoal (10%) (CDH), 4,4'-diaminodiphenyl sulfone (D) (Fluka), hydrazine hydrate and acetic acid (Qualigens), *m*-nitrobenzoyl chloride (Fluka), *p*-nitrobenzoyl chloride (Merck) were used as received. Phosphorus containing amines B and T were prepared according to the procedure reported elsewhere [16].

Synthesis of amide-amines

The phosphorus containing amide-amines MB, PB, MT and PT were prepared by reacting *m*-/*p*-nitrobenzoyl chloride with B or T followed by reduction using Pd/C (10%) and hydrazine hydrate. Stoichiometric amount of *m*-/*p*-nitrobenzoyl chloride was added to a well-stirred solution of amine B or T in dry N, N-dimethyl acetamide. The solution was vigorously stirred and the temperature gradually raised to100°C for 1 h. The nitro compound was isolated by precipitation in ice-cold water and subsequent filtration. The product was washed with dil. $NaHCO_3$ and distilled water and then dried at 60–70°C in a vacuum oven.

The dried nitro compound, ethanol and Pd/C (10%) were placed in a three-necked flask and hydrazine hydrate was added dropwise with stirring. The reaction was exothermic and hence cooling was necessary in initial stages. Once the exothermic reaction subsided, the mixture was gently refluxed for 2 h. Pd/C was then filtered off and amide-amines were precipitated in ice-cold water. Precipitated amines were then filtered off and dried under reduced pressure at room temperature. These amines were purified by recrystallisation from ethanol.

Characterization

Amide-amines were characterized by elemental analysis, melting point (by DSC) and amine equivalent [17] determination. Structural characterization was done by FTIR using a Biorad Digilab FTS-40 FTIR spectrometer.

^{1}H-NMR spectra were recorded on a Bruker AC 300 spectrometer at a frequency of 300 MHz using DMSO-d_6 as solvent and tetramethyl silane (TMS) as an internal standard.

Curing studies

A DuPont 2100 thermal analyzer having a 910 DSC module was used to evaluate the curing behaviour of DGEBA. For curing studies, the samples were prepared by mixing stoichiometric amount of DGEBA with the amide-amines or conventionally used curing agent 4,4'-diaminodiphenyl sulfone (D) or a mixture of D with phosphorus containing amines. A sample mass of 10±2 mg and a heating rate of 10°C min^{-1} was used.

The exothermic transition associated with curing was characterised by determining T_i (kick-off temperature of curing), T_o (temperature of onset of exotherm), T_p (temperature of peak position of exotherm), T_f (temperature of the end of the exotherm) and ΔH (heat of curing reaction).

In order to determine the activation energy for the curing reaction of DGEBA with stoichiometric amounts of amide-amines (i.e. MB, PB, MT and PT) multiple heating rate method (5, 10, 15, 20°C min^{-1}) of Ozawa [18] 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 Arrhenius equation. In order to calculate activation energy of curing, log of heating rate was plotted *vs.* $1/T_p$.

Thermogravimetric analysis

Isothermal curing of DGEBA containing stoichiometric amounts of amines of varying P-content was done by heating at 150°C (1 h). Thermal stability of the cured resin in nitrogen atmosphere (flow rate 60 $\text{cm}^3\ \text{min}^{-1}$) was evaluated using a DuPont 2100 thermal analyser having a 951 TG module. A sample mass of 10±2 mg and a heating rate of 20°C min^{-1} was used.

Results and discussion

Characterization of amines

The amines were obtained in ~70% yield. The colour ranged from white to light yellow. These amines were insoluble in solvents such as acetone, methyl ethyl ketone, and chloroform, but were soluble in methanol, ethanol, DMF and DMAc. Table 1 shows the results of CHN analysis and amine equivalent of these phosphorus containing amines. Calculated values of elemental analysis and amine equivalent weight agreed well with the experimentally determined values.

Table 1 Results of CHN analysis and amine equivalent of amide-amines

Amine	Carbon/%	Hydrogen/%	Nitrogen/%	Amine equivalent
MB	65.27 (66.94)	5.04 (5.16)	11.11 (11.57)	475 (484)
PB	65.42 (66.94)	5.13 (5.16)	11.42 (11.57)	479 (484)
MT	67.58 (68.82)	4.73 (4.85)	12.18 (12.35)	674 (680)
PT	67.92 (68.82)	4.98 (4.85)	12.01 (12.35)	669 (680)

(Figures in parenthesis indicate the calculated values)

In the DSC scans of amide-amines MB and PB melting endotherm with a peak temperature at 162 and 166°C respectively was observed while no melting endotherm was observed in amines MT or PT.

In the IR spectra of these amines the absorption bands at ~1640 cm^{-1} due to carbonyl group and doublet at ~3200–3350 cm^{-1} due to $–NH_2$ and –NH group were observed besides the characteristic absorptions due to phosphine oxide or aromatic and methyl groups (Fig. 1a).

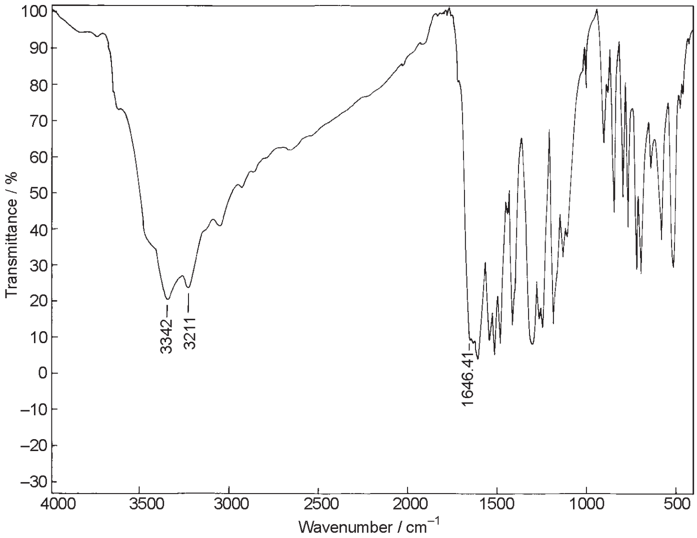


Fig. 1a FTIR spectrum of tris[3(4'-aminobenzamido phenyl)] phosphine oxide (PT)

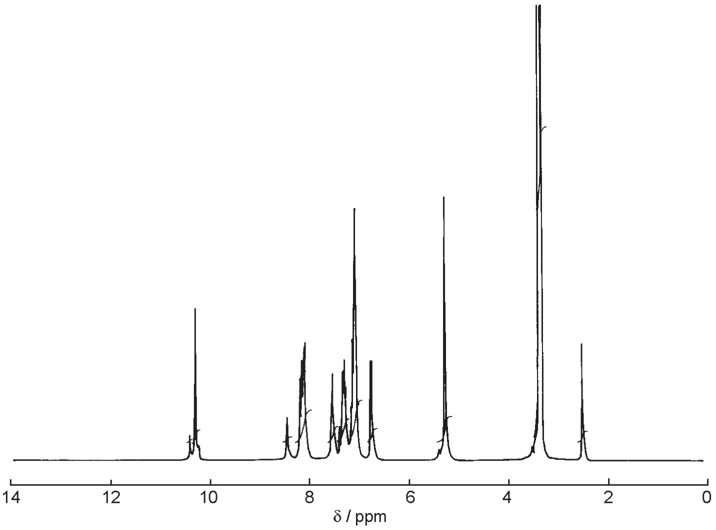


Fig. 1b ^{1}H-NMR spectrum of tris[3(3'-aminobenzamido phenyl)] phosphine oxide (MT)

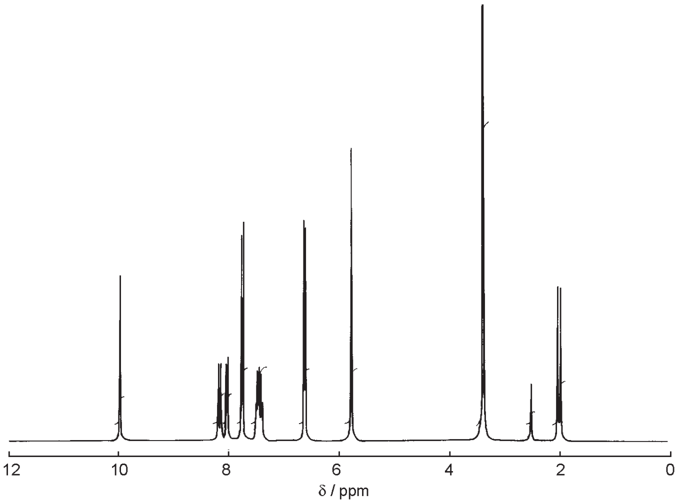


Fig. 1c ^{1}H-NMR spectrum of bis[3(4'-aminobenzamido phenyl)]methyl phosphine oxide (PB)

In the ^{1}H-NMR spectra, the proton resonance signals for amide, aromatic, amine and methyl protons were observed (Figs 1b and 1c) thereby confirming the structure of these amines.

MB-δ=10.2 (2H, –NH–CO–), 6.7–8.2 (16H, aromatic),
5.3 (4H, $-NH_2$), 2.0 (3H, CH_3)

PB-δ= 9.9 (2H, –NH–CO–), 6.5–8.2 (16H, aromatic),
5.7(4H, $-NH_2$), 2.0 (3H, CH_3)

MT-δ=10.3 (3H, –NH–CO–), 6.7–8.2 (24H, aromatic),
5.3 (6H, $-NH_2$)

PT-δ=10.0 (3H, –NH–CO–), 6.5–8.2 (24H, aromatic),
5.7 (6H, $-NH_2$)

Thermal behaviour of resins

The thermal behaviour of DGEBA with P-containing amines and 4,4'-diaminodiphenyl sulfone was investigated by evaluating the curing characteristics (DSC) and thermal stability of cured network (TG). Mixed amines (P-containing and D) formulations were also investigated. Thermal studies with single amines will be described first and mixed amine formulations i.e. D and P-containing amines of varying composition will be described later.

Curing of DGEBA with single amines

In the DSC scans of DGEBA containing stoichiometric amounts of phosphorus containing amines an exotherm due to curing reaction was observed in the temperature range of 90–300°C (Table 2, Fig. 2). The curing of epoxy resin proceeds by the nucleophilic attack of amine on the oxirane carbon. The curing reaction would thus depend on nucleophilic character of amines. The temperature of onset of curing is expected to be lower when amines with higher nucleophilicity are used. In the present studies the onset temperature of curing (T_i and T_o) of DGEBA depended on the amine structure and were in the order MT≈MB<PT<PB<D. The exotherm appeared at a

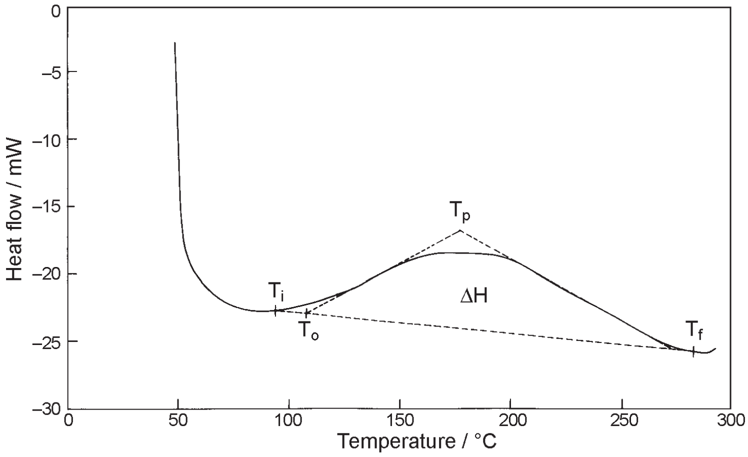


Fig. 2 DSC scan showing exothermic transition due to curing of DGEBA with stoichiometric amount of amine PT (static air, heating rate=10°C min^{-1})

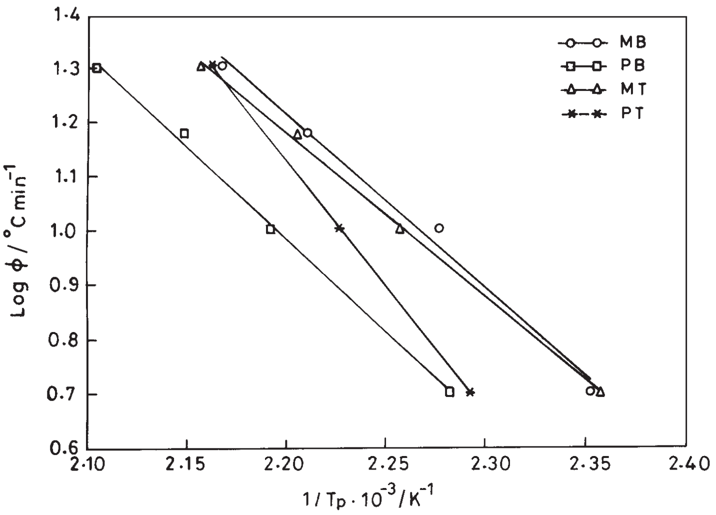


Fig. 3 Evaluation of activation energy for the curing of DGEBA with P-containing amide-amines

much higher temperature with amine D. The sulphone group is a very strong electron-withdrawing group and is in direct conjugation with amino group compared to phosphine oxide thereby leading to a significant reduction in the nucleophilicity of the amine. In amine MB and MT the amino group is at *m*-position with respect to electron withdrawing carbonyl group (amide) while in PB and PT it is at *p*-position. Therefore only inductive effect (-*I*) will be significant in MB and MT while in PB and PT both resonance and inductive effects will affect the nucleophilic character. Thus observed trend in onset temperatures of curing of DGEBA can be explained on the basis of changes in the nucleophilicity of the amines.

Table 2 Results of DSC scans of DGEBA in the presence of stoichiometric amounts of amide-amines

Amine	D	MB	PB	MT	PT
T_i/°C	165	81	98	81	91
T_o/°C	184	101	124	94	108
T_P/°C	224	166	183	170	176
T_F/°C	310	272	270	272	278
ΔH/J g^{-1}	173	313	308	327	327
Activation energy/kJ mol^{-1}	68.7	60.4	64.8	56.6	84.6

The exothermic peak temperature T_p also depended on the nature of amine and order was D>PB>PT>MT≈MB. Thus T_p value was the lowest in P-containing amines having *m*-linkage. The viscosity of DGEBA resin increases with resin advancement and in later stages of curing the diffusion of amines to the reactive site will be impor-

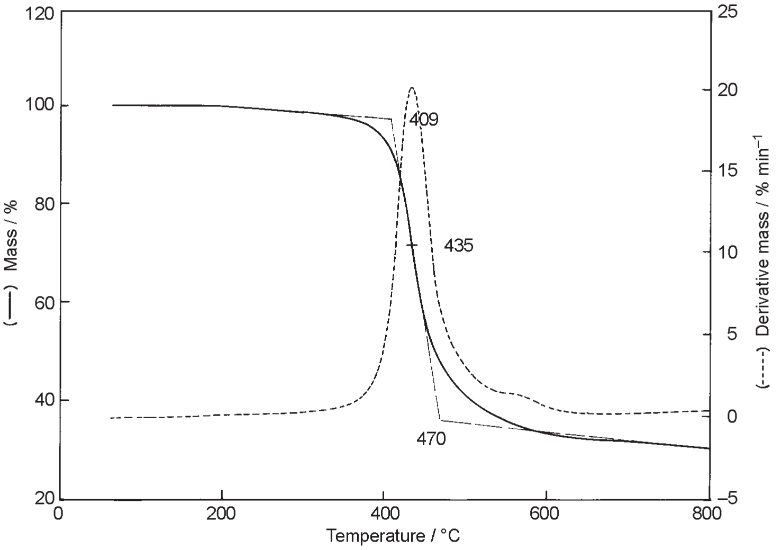


Fig. 4 TG/DTG curves of DGEBA cured isothermally with amine MT

tant. The presence of *m*-linkages increases the flexibility of the amine and also leads to a reduction in the melting point thereby facilitating the diffusion of amines. Thus the observed lowest value of T_p in MB and MT can be attributed to their flexibility.

Activation energy of curing (Table 2) was also higher in amine PB and PT as compared to amines MB and MT (Fig. 3). The temperature dependence of the curing reaction was more in amines having para linkage compared to amines with meta linkage.

Thermal stability of cured network

TG/DTG traces of isothermally cured epoxy resins with various amines were recorded in N_2 atmosphere (Fig. 4). The initial decomposition temperature (T_i), final decomposition temperature (T_f) and temperature of maximum rate of mass loss (T_{max}) were noted from TG and DTG traces respectively.

Table 3 Thermal behaviour of isothermally cured DGEBA with amide-amines (heating rate 20°C min^{-1})

Amine	Phosphorus content/g of resin	Decomposition temperature/°C			Char yield at 800°C/%
		T_i	T_{max}	T_f	
D	0	424	442	461	15.5
MB	0.026	402	435	470	22.91
PB	0.026	408	438	464	21.82
MT	0.0178	409	435	470	30.37
PT	0.0178	405	433	465	28.89

DGEBA cured with phosphorus containing amide-amines showed similar decomposition temperatures. However, in DGEBA cured with amine D, the decomposition temperatures were marginally higher (Table 3). Significant changes in the mass loss at different temperatures were observed. The order of char residue at 800°C was MT≈PT>MB≈PB>D. Amine D cured DGEBA had zero P-content and char residue was lowest (15.5%). Incorporation of 0.026 g of phosphorus/g of cured epoxy network (calculated on the basis of amine and DGEBA taken initially) increased the char yield to ≈22%. The phosphorus content of the cured resin network was the highest when MB and PB were used as curing agent yet the char yield was lower compared to MT or PT system. This may be due to the fact that in amines MB and PB a methyl group is present while in MT or PT a thermally stable phenyl group is present.

Curing of DGEBA with mixed amines

A broad exothermic transition in the temperature range of 85 to 297°C was observed in DSC when DGEBA was cured with mixed amine formulations containing amine D and P-containing amines. The kick-off temperature of curing exotherm (T_i) which was 165°C with amine D reduced by more than 50°C by the addition of 0.25 mole fraction of phosphorus containing amide amines (Table 4). Initially the T_p value, which was 224°C with amine D and 165–185°C with phosphorus containing amines reduced by 20°C. Further increase in mole fraction of P-containing amines reduced the characteristic curing temperatures of DGEBA with amine D. None of the resin formulations showed a bimodal exothermic transition indicative of independent curing of DGEBA with the mixed amines. These studies thus indicate that curing exotherm can be manipulated by using mixed amines of varying nucleophilicity thereby reducing the sharpness of the exotherm which creates a problem of temperature dissipation specially in thick moldings and laminates.

Table 4 Results of DSC scans of DGEBA in the presence of stoichiometric amounts of phosphorylated amines (MB, PB, MT and PT) and amine D

Amine formulation	T_i/°C	T_o/°C	T_p/°C	T_f/°C	ΔH/J g^{-1}
MB_1	115	146	200	271	298
MB_2	99	135	188	290	292
MB_3	85	117	178	285	288
PB_1	121	152	205	294	285
PB_2	112	146	198	287	288
PB_3	101	129	190	284	298
MT_1	108	121	200	290	334
MT_2	95	122	188	277	279
MT_3	90	109	176	267	262
PT_1	111	126	205	297	265
PT_2	105	124	201	294	274
PT_3	93	105	177	286	298

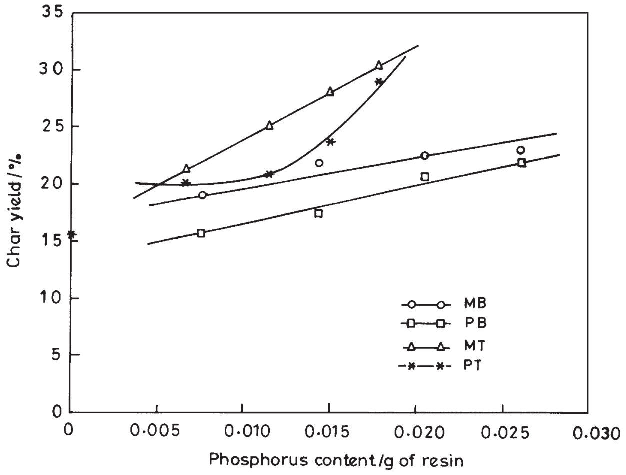


Fig. 5 Effect of phosphorus content on char yield of isothermally cured DGEBA with mixture of P-containing amide-amines and amine D

Thermal stability

Addition of amine D to phosphorylated amines resulted in a reduction in the char yield of cured DGEBA (Table 5). Changing the ratio of amine D and phosphorus containing amines used as curing agents for DGEBA could easily vary phosphorus content of the cured resin. A linear dependence of char yield on the phosphorus content of cured epoxy network was observed when amine formulations based on MB, PB, MT and D were used for curing of DGEBA (Fig. 5).

Table 5 Thermal behaviour of isothermally cured DGEBA with mixed amines MB/PB/MT/PT and D (heating rate 20°C min^{-1})

Amine formulation	Phosphorus content/g of resin	Decomposition temperature/°C			Char yield at 800°C/%
		T_i	T_{max}	T_f	
MB_1	0.0076	415	438	415	19.00
MB_2	0.0144	408	436	462	21.80
MB_3	0.0250	410	440	466	22.40
PB_1	0.0076	415	443	466	15.60
PB_2	0.0144	416	442	463	17.30
PB_3	0.0250	409	440	463	20.54
MT_1	0.0067	418	433	465	21.40
MT_2	0.0115	410	437	467	25.17
MT_3	0.0150	410	437	468	28.15
PT_1	0.0067	416	445	469	20.00
PT_2	0.0115	413	435	465	20.73
PT_3	0.0150	411	435	466	23.60

Conclusions

Curing of DGEBA with phosphorus containing amines could be carried out at lower temperatures than the conventionally used curing agent 4,4'-diaminodiphenyl sulfone. The nucleophilic character of the amine and flexibility of the backbone structure were two controlling parameters for curing. Using mixed amine formulations and molar ratio of such amines could control the curing exotherm. A linear relationship between char residue and P-content was observed.

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