Curing and Thermal Behavior of Epoxy Resin in the Presence of Silicon-Containing Amide Amines

Parveen Khurana,[1] S Aggarwal,[1] A. K. Narula,[1] Veena Choudhary[2]

[1]*GGS, Indraprastha University, Kashmere Gate, Delhi 110 006, India*
[2]*Centre for Polymer Science and Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India*

ABSTRACT: The article describes the synthesis and characterization of silicon-containing amide amines obtained by the reaction of bis(4-chlorobenzoyl)dimethylsilane with 4,4′-diaminodiphenyl ether, 4,4′-diaminodiphenyl methane, 4,4′-diaminodiphenyl sulfone/3,3′-diaminodiphenyl sulfone, bis(3-aminophenyl)methyl phosphine oxide, and tris(3-aminophenyl)phosphine oxide with dimethyl acetamide as a solvent. Structural characterization of amide amines was done with Fourier transform infrared and ¹H-NMR spectroscopy. We used these aromatic amide amines as curing agents to investigate the effect of structure and molecular size on the curing and thermal behavior of diglycidyl ether of bisphenol A (DGEBA). The curing behavior of DGEBA in the presence of stoichiometric amounts of silicon-containing aromatic amide amines was investigated by differential canning calorimetry. A broad exothermic transition in the temperature range of 200–300°C was observed in all the samples. The peak exotherm temperature was lowest in the case of phosphorus-containing amides and was highest in the case of ether-containing amides. Thermal stability of the isothermally cured resins was evaluated with dynamic thermogravimetry in a nitrogen atmosphere. A significant improvement in the char yield was observed with silicon-containing amines, and it was highest in case of samples with both silicon and phosphorus as flame-retarding elements. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1345–1353, 2003

INTRODUCTION

Epoxy resins are the most important class of thermosetting resins and find applications in surface coatings, composite matrices, castings, adhesives, encapsulation of electronic components, and aerospace industries[1] because of their easy processing, superior properties, and low cost. The processing is convenient because it is possible to formulate compositions with required rheological properties such as low viscosity. Also, the epoxy resins can be crosslinked without the evolution of volatile products, and such resins have relatively low shrinkage during curing. However, their major drawback is their brittleness because of their highly crosslinked structure. However, the property of brittleness can be improved by modification of the structure of the epoxy resin or the nature and the molecular weight of the curing agent. Brittleness can also be reduced by the incorporation of elastomers. The limitations of epoxy resins are their poor high-temperature performance and flaming resistance.

Polyimides are widely used for applications that require higher thermal stability, better mechanical properties, and chemical resistance.[2,3] Polyimide and polyamide have also been blended with epoxies to improve toughness and heat and chemical resistance. However, the physical blending of epoxy with polyamide had very little effect on thermal stability. Polyimide and polyamide acid end-capped with amines have been used as curing agents for epoxies to impart higher thermal stability and flame resistance. Hay et al.[4] studied the molding of linear unreactive polyimide for toughening the epoxy–diaminodiphenyl sulfone system. They achieved an increase in the fracture toughness with no loss of modulus, but there was little influence on the thermal capability across the range of modifying polyimides. Another example is the incorporation of polyimide–siloxane in the epoxy to form protective coatings with high heat and chemical resistance.[5] Recently, Kakimoto and colleagues[6,7] developed a novel epoxy system cured with poly(amide acid) followed by thermal imidization.

Flame-resistant epoxy resins can extend the use of such resins to a variety of applications where high-temperature performance is of great concern. Flame-resistant resins can be obtained by the incorporation of flame-retarding elements, such as halogens, nitrogen, phosphorus, boron, and silicon, either at the polymerization stage or with a flame-retardant additive, which retards the flaming degradation by interfering with combustion process. The curing process can be initiated with a wide range of curing agents such as amines, amides, anhydrides, isocyanates, and amino formaldehyde resins.[8,9] The aim of this work was to develop nonhalogen flame-resis-

tant epoxy resins with silicon-containing amide amines as curing agents.

In this study, the curing and thermal behavior of diglycidyl ether of bisphenol A (DGEBA) was investigated with amide amines as curing agents. This article describes the synthesis and characterization of amide amines with molecular weights in the range of 650–900 obtained with commercial diamines or diamines and triamines synthesized in the laboratory with acid chlorides having silicon. The effect of the structure and molecular weight of amide amines on the curing and thermal behavior was evaluated with differential scanning calorimetry (DSC) and dynamic thermogravimetry.

EXPERIMENTAL

Materials

DGEBA (Araldite grade LY556, epoxy equivalent 177) was procured from Hindustan Ciba Geigy Ltd. and was used as such. 4,4'-Diaminodiphenyl methane (M), 4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl sulfone (pS), 3,3'-diaminodiphenyl sulfone (mS), dichlorodimethyl silane, lithium metal, triphenyl phosphine, 4-bromotoluene, and triphenyl phosphine oxide were purchased from Aldrich and were used as received. Pyridine (CDH), thionyl chloride (Thomas Baker), and potassium permanganate (Qualigens) were used as such. We dried N,N'-dimethylacetamide (DMAc; Thomas Baker) by keeping it over phosphorus pentaoxide for 24 h and then vacuum distilling it. It was then stored in a sealed dark flask over molecular sieves. Amide amines were synthesized by the following reaction scheme:
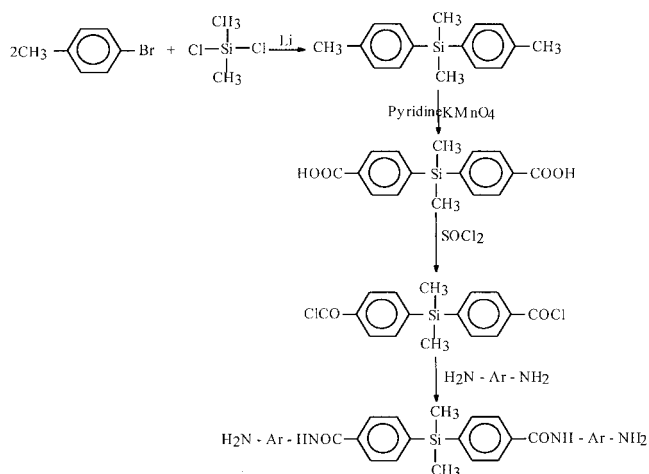
where Ar is
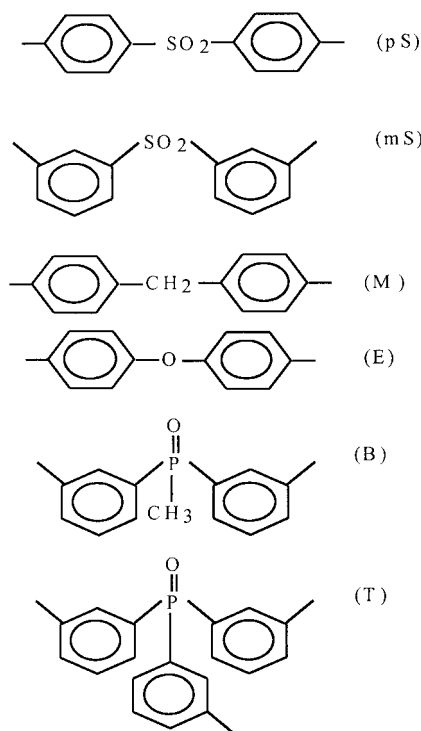
The letters within the parenthesis represents the designation of the amide amines.

Procedure

Preparation of diamine/triamine

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

Diphenyl methyl phosphine oxide was synthesized by the reaction of triphenyl phosphine (39.3 g, 0.15 mol) with methyl iodide (10 mL) with a mixture of chloroform (130 mL) and petroleum ether (200 mL) as the 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 evolved benzene was collected with a Dean Stark apparatus. The reaction mixture was cooled to room temperature and washed with 100 mL of toluene (5–6 times) with a separating funnel. All the toluene extracts were collected and dried overnight over anhydrous MgSO$_4$. The solvent was distilled under vacuum [yield = 80%, melting temperature (T_m) = 110–113°C].

Diphenyl methyl phosphine oxide was nitrated with 75 mL of concentrated H_2SO_4 and 75 mL of concentrated HNO_3 at 0°C. The nitrating mixture on cooling was added to a solution of diphenyl methyl phosphine oxide (22 g) in concentrated H_2SO_4 (85 mL) at ice temperature over a period of 2 h, with the temperature maintained below 10°C. The ice bath was then removed, and stirring was continued for about 2 h. The reaction mixture was poured slowly with 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%, T_m = 202°C).

An ethanolic solution of dinitro compound (10% w/v) was reduced catalytically with 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 the removal of ethanol under reduced pressure. On cooling, white crystals of diamine B were obtained (yield = 60%, T_m = 157°C).

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

Synthesis of bis(4-carboxyphenyl)dimethyl silane

The reaction was carried out in a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a condenser with a calcium chloride guard tube. Dry ether (15 mL) was added to the flask containing 2.4 g of lithium metal. 4-Bromotoluene (30 g, 0.18 mol) was added slowly with stirring, and the temperature was controlled at −5°C. After complete addition, the mixture was stirred at room temperature for 5 h, and then dichlorodimethyl silane (11.32 g, 0.09 mol) was added dropwise at −5°C. The mixture was then stirred overnight at room temperature. Unreacted metal and metal chloride were removed by filtration followed by washing with dry ether. The filtrate was then concentrated with a rotary vacuum evaporator, and bis(4-methylphenyl)dimethyl silane was obtained as a solid (20 g), which was then oxidized to produce bis(4-carboxyphenyl)dimethyl silane with pyridine as a solvent and $KMnO_4$ as an oxidizing agent. The reaction was carried out by refluxing the mixture for 8 h. Unreacted $KMnO_4$ was destroyed by the addition of methanol, and the MnO_2 formed was removed by filtration. It was washed several times with hot methanol to remove $KMnO_4$ completely. To the filtrate a small amount of activated charcoal was added and then decanted. The filtrate was then acidified with diluted HCl to precipitate the acid. The product was purified by dissolution in dilute alkali followed by precipitation. It was further purified by recrystallization with an ethanol:water (1:1) mixture and was then dried in a vacuum oven at 80°C (yield = 75%, T_m = 274°C).

Synthesis of bis(4-chlorobenzoyl)dimethyl silane

Bis(4-chlorobenzoyl)dimethyl silane was obtained by the reaction of bis(4-carboxyphenyl)dimethyl silane (10 g, 0.03 mol) with thionyl chloride (30 mL). The mixture was refluxed for 6 h, and then the excess of thionyl chloride was removed by distillation, first by simple distillation and then by the use of dry benzene. Bis(4-chlorobenzoyl)dimethyl silane was recrystallized from n-hexane and was then dried in a vacuum oven (yield = 80%, T_m = 80°C).

Synthesis of amide amines

To the well-stirred solution of 4,4'diaminodiphenyl sulfone (4.9 g, 0.02 mol) in 50 mL of dry N,N'-dimethyl acetamide, bis(4-chlorobenzoyl)dimethyl silane (3.3 g, 0.01 mol) was added dropwise, and then, it was further stirred for a period of 6–7 h at room temperature. We precipitated the amide amines by pouring the reaction mixture into ice-cold water with stirring. The product was washed repeatedly with dilute sodium bicarbonate to remove unreacted acid; it was then washed with water until it was neutral, and it was washed finally with methanol. It was then dried in vacuum oven at 80°C overnight. Similarly, all other amide amines were prepared by the reaction of bis(4-chlorobenzoyl)dimethyl silane with appropriate diamines.

Characterization

Structural characterization of amide amines

The structural characterization of amide amines was done with Fourier transform infrared (FTIR) and ^{1}H-NMR spectroscopic techniques. IR spectra were recorded in KBr pellets with a Shimadzu FTIR 8700 spectrophotometer.^{1}H-NMR spectra were recorded on Bruker 300 spectrophotometer with dimethyl sulfoxide (DMSO)–d_6 as a solvent and tetramethylsilane as an internal standard.

Curing studies

For curing studies, the samples were obtained by the mixture of stoichiometric amounts of amide amines with DGEBA with a minimum amount of a suitable solvent. The samples were designated by adding the prefix E to the sample designation of amide amines. For example, DGEBA mixed with M and T amide

TABLE I
Results of C,H,N Analyses and Amine Equivalents of Amide Amines

Sample designation	Carbon[a] (%)	Hydrogen[a] (%)	Nitrogen[a] (%)	Amine equivalent[a]
EM	75.60 (76.30)	5.75 (6.06)	7.80 (8.49)	655 (660)
EE	55.96 (54.22)	4.80 (5.42)	8.60 (8.43)	660 (664)
EpS	46.50 (47.36)	5.25 (5.42)	8.25 (8.43)	755 (760)
EmS	45.80 (47.36)	5.24 (5.42)	8.30 (8.43)	755 (760)
EB	65.42 (66.66)	5.30 (5.55)	7.60 (7.41)	750 (755)
ET	67.55 (68.35)	5.60 (5.26)	8.65 (9.20)	910 (913)

[a] Figures in parentheses represent the calculated values.

amines were designated as EM and ET, respectively. The solvent was evaporated under vacuum, and the freshly prepared samples were used to record DSC traces in static air atmosphere. A TA 2100 thermal analyzer with a 910 DSC module was used to record DSC traces. A heating rate of 10°C/min and a sample size of 10 ± 1 mg was used in each experiment. DSC scans of isothermally cured samples were also recorded to determine the effect of network structure on the glass-transition temperature.

Thermal stability

We investigated the thermal stability of the isothermally cured resins (cured at 250 ± 20°C in an air oven for 3 h) by recording TG/DTG traces in a nitrogen atmosphere (with a flow rate maintained at 60 mL/min) with a TA 2100 thermal analyzer with a 951 TG module. A heating rate of 20°C/min and a sample size of 11 ± 1 mg was used in each experiment.

RESULTS AND DISCUSSION

Characterization of amide amines

The amines were obtained in 80% yield. These amide amines were insoluble in acetone, methyl ethyl ketone, and chloroform but were soluble in dimethylformamide, DMAc, and DMSO. Table I shows the results of
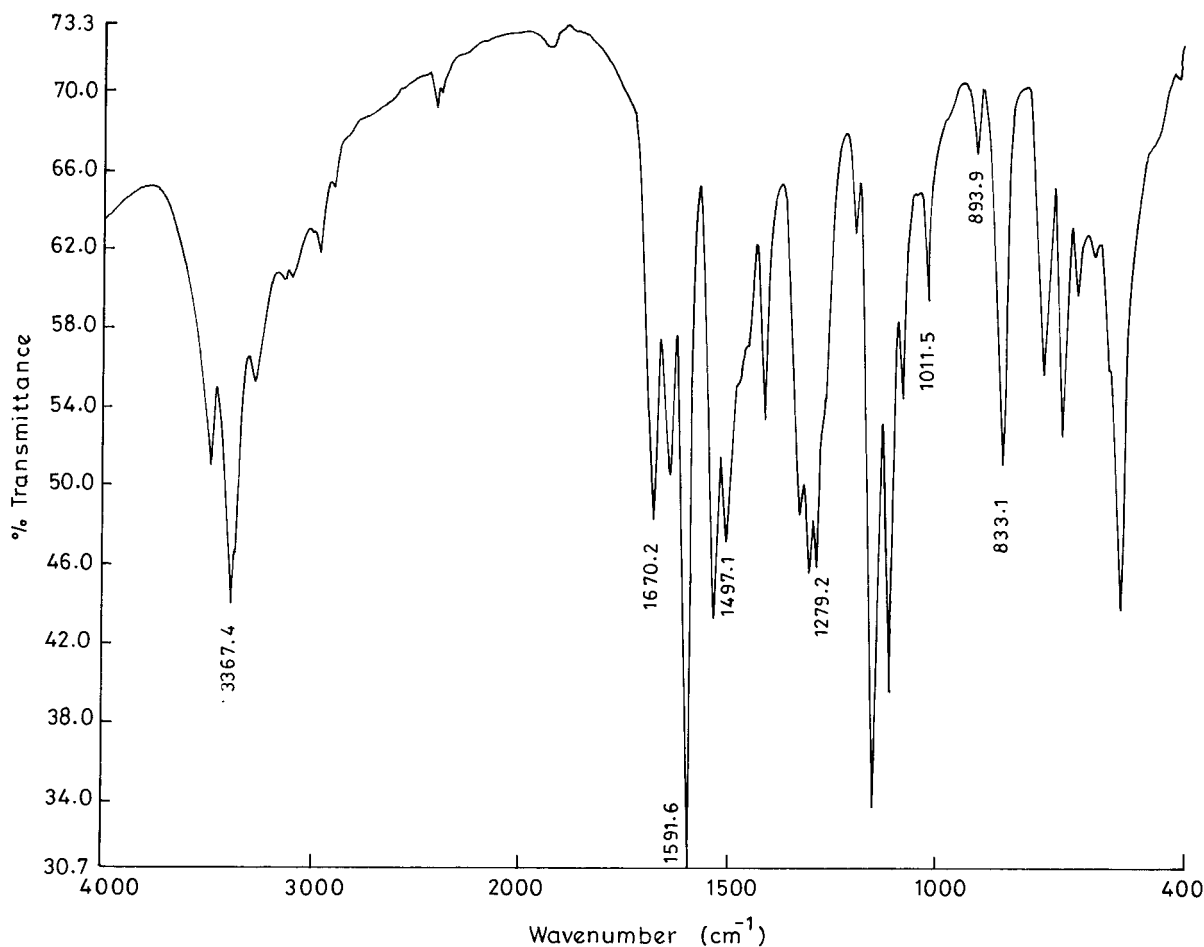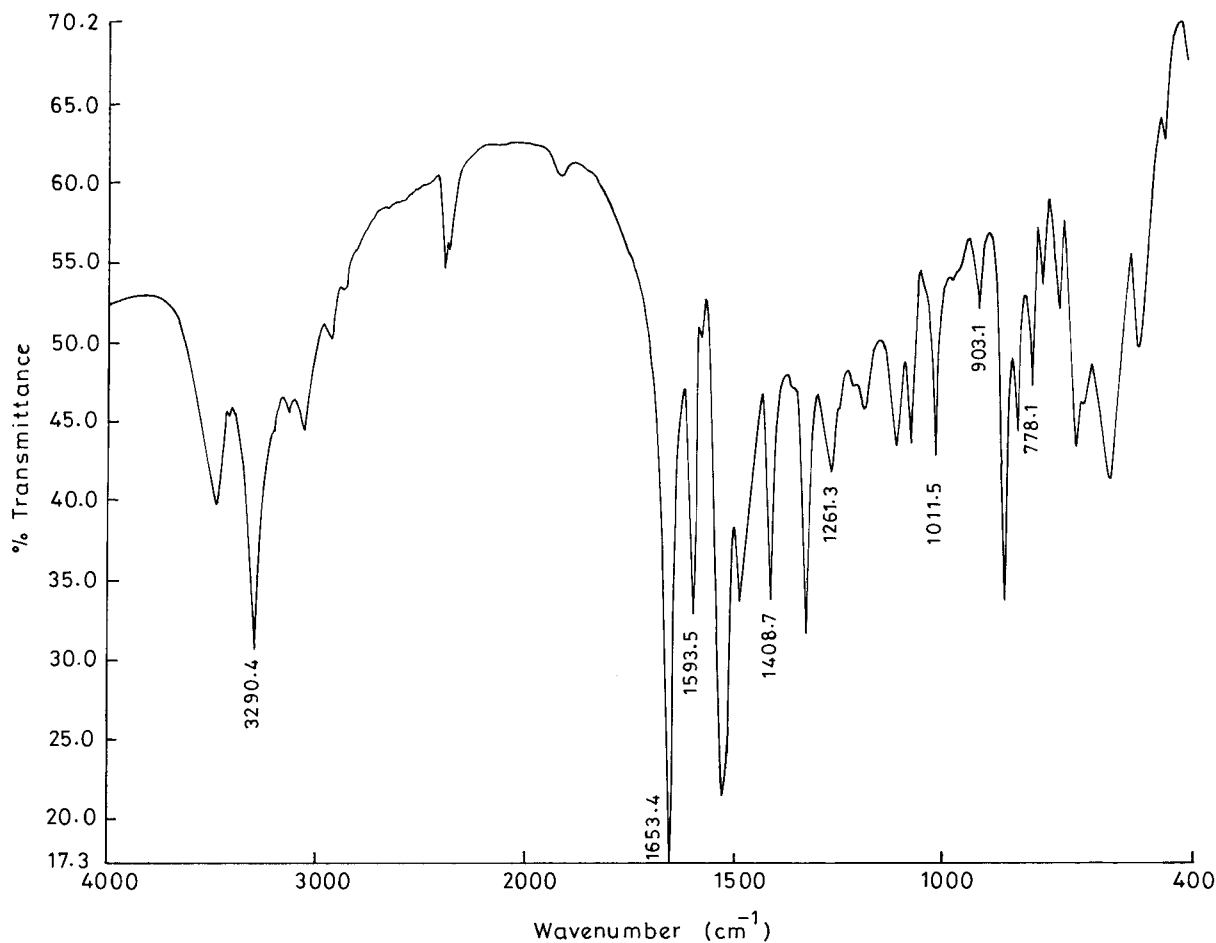

Figure 1 FTIR spectrum of amide amine (sample pS).

Figure 2 FTIR spectrum of amide amine (sample B).

CHN analyses and amine equivalents of these amide amines. The calculated values of CHN and amine equivalents agreed well with the experimentally determined values.

Figures 1 and 2 show the FTIR spectra of amide amines pS and B, respectively. Absorption bands due to amide I and amide II were observed in all the samples at 1650 ± 20 and $1595 \pm 4 \, cm^{-1}$, respectively. Symmetrical stretching due to the —NH_2 group was observed in the range of $3290–3370 \, cm^{-1}$ Out-of-plane NH wagging was responsible for a broad band of medium intensity in the range of $800–666 \, cm^{-1}$. Absorption bands due to C—N stretching was observed at $1408–1497 \, cm^{-1}$, and Si—C stretching was observed at 840 and $1210–1250 \, cm^{-1}$. An FTIR spectrum of a model compound obtained by the reaction of aniline with bis(4-chlorobenzoyl)dimethyl silane was also recorded (Fig. 3). The IR spectrum of the model compound showed similar absorption bands, and symmetrical stretching due to —NH_2 was absent.

^{1}H-NMR studies

In the ^{1}H-NMR spectra of amide amines, a characteristic signal due to amino protons was observed at δ $= 4.8 \pm 0.5$ ppm, NH protons of amide group at δ $= 10.2 \pm 0.3$ ppm and a multiplet due to aromatic protons was observed in the range of $\delta = 6.5–8.0$ ppm. The P—CH_3 was also observed at $\delta = 3.3$ ppm in the case of B. The integration was used to calculate the number of protons. The appropriate coupling constants for various hydrogens, such as $J_{H—H}$, $J_{P—H}$, and $J_{C—H}$, were also observed. A representative NMR spectrum of sample E is shown in Figure 4.

Curing studies

Figures 5 and 6 show the DSC scans of DGEBA in the presence of stoichiometric amounts of amide amines EB and EpS, respectively. A broad exotherm due to the curing reaction was observed in the temperature range of 150 ± 20 to $300 \pm 20°C$. The curing exotherms were characterized by determination of

Kick-off temperature (T_i), where the curing started.
The temperature where the first detectable heat was released (T_{onset}). It was obtained by extrapolation of the steepest portion of curve.
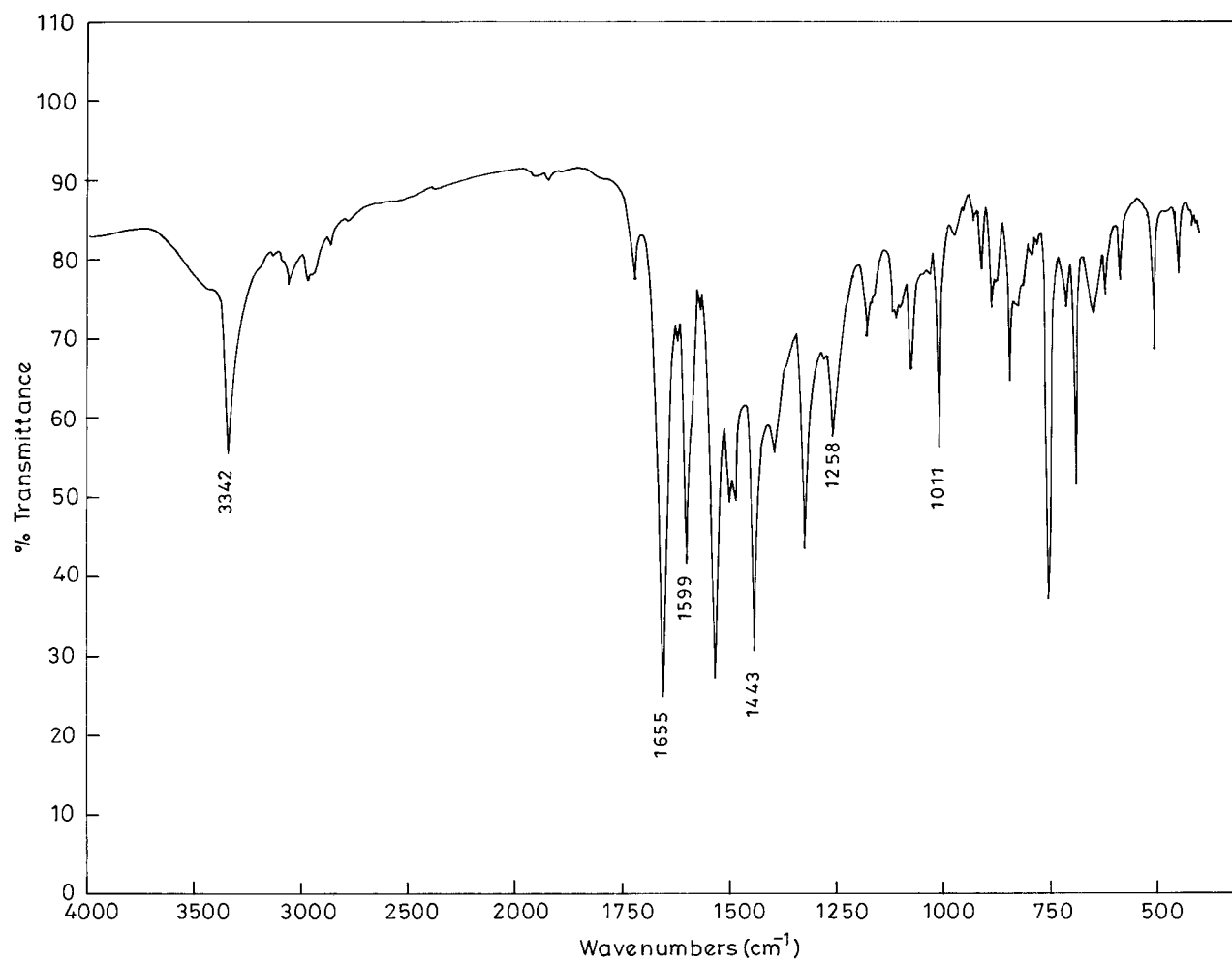The peak exotherm temperature (T_p).

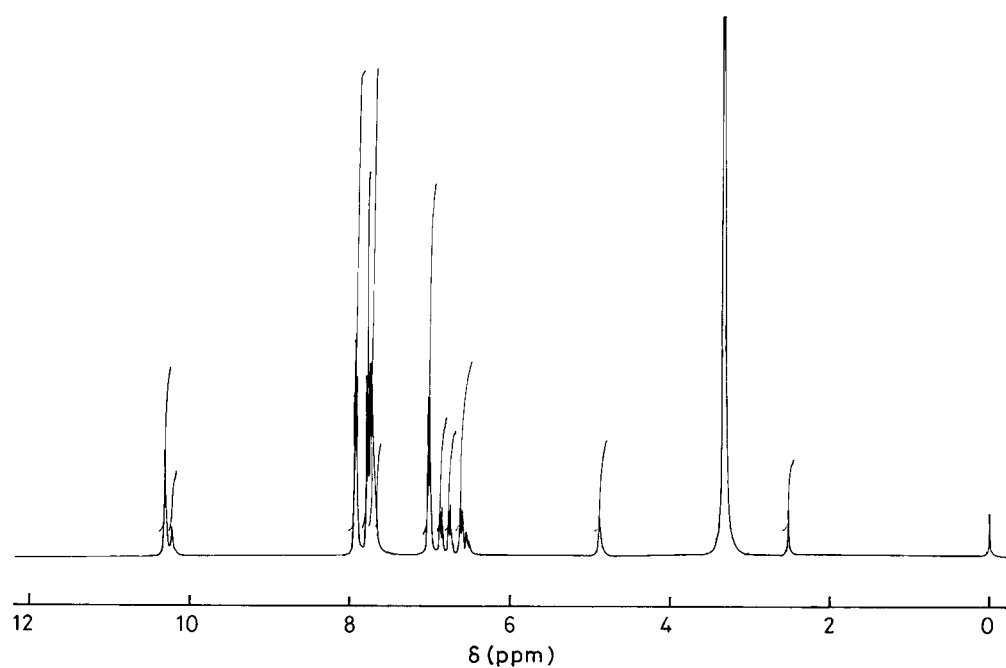**Figure 3**   FTIR spectrum of model compound.

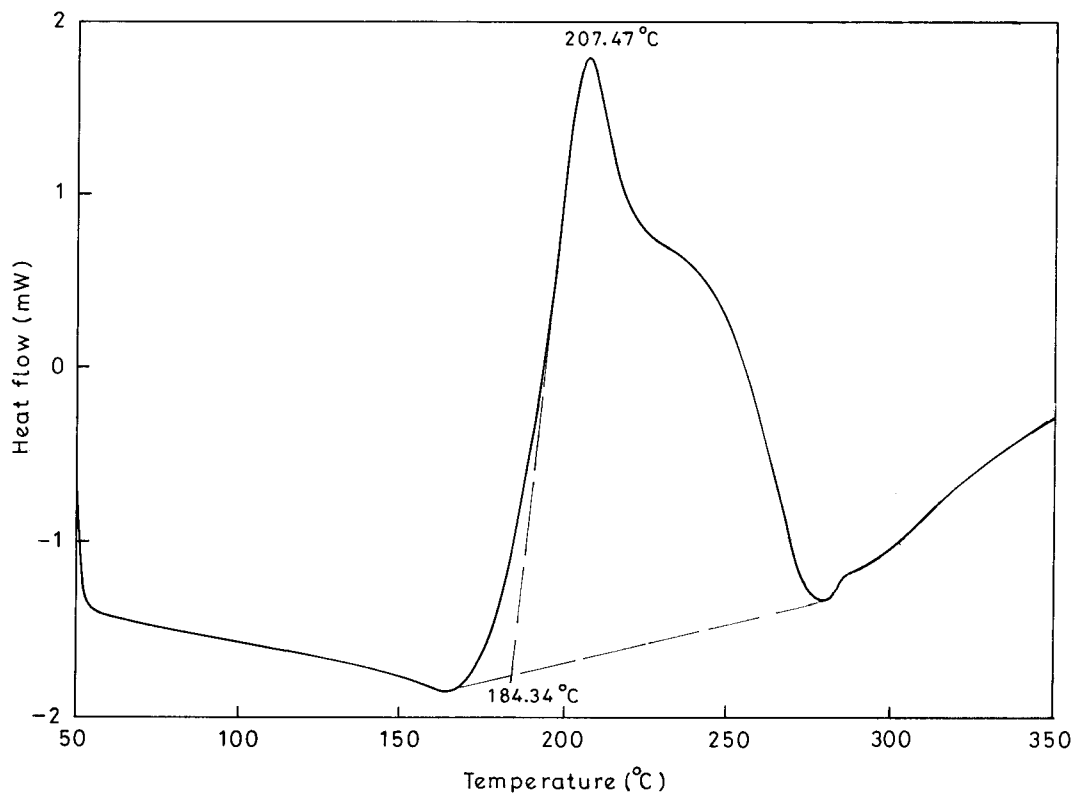**Figure 4** ^{1}H-NMR spectrum of amide amine (sample E).

Figure 5   DSC scan of DGEBA in the presence of a stoichiometric amount of amide amine B (heating rate = 10°C/min).
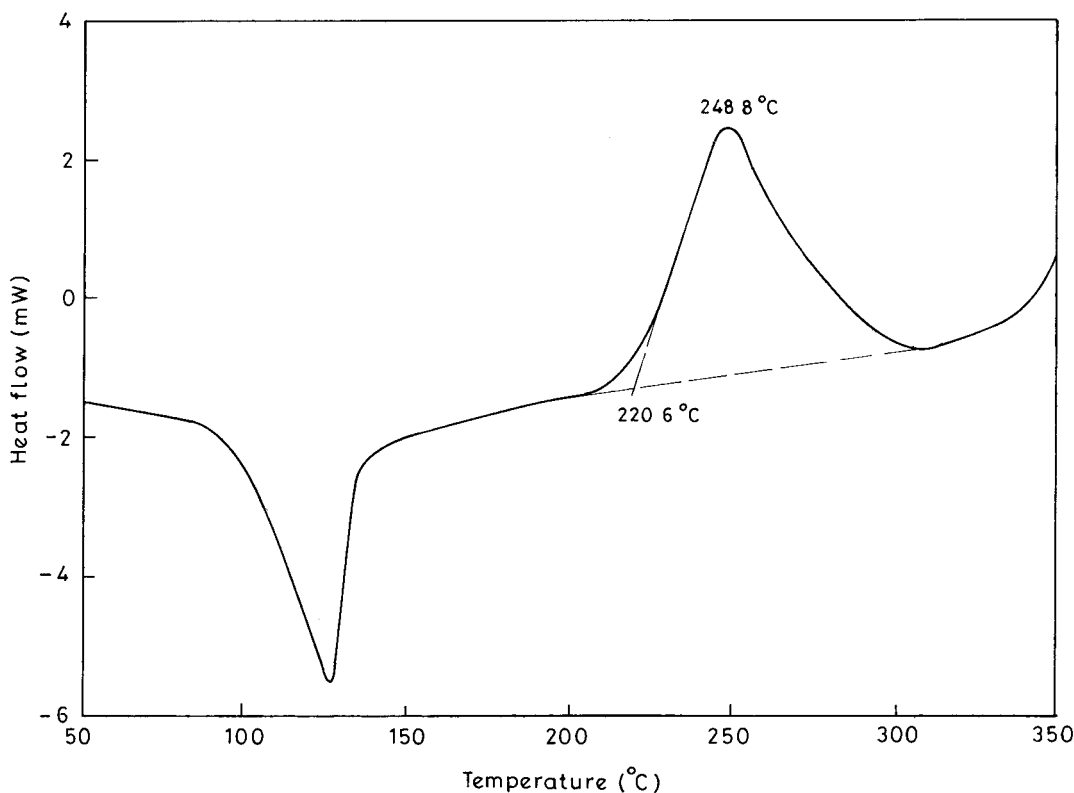

Figure 6   DSC scan of DGEBA in the presence of a stoichiometric amount of amide amine pS (heating rate = 10°C/min).

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

Sample designation	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
EM	211.8	241.6	272.6	304.9	111.6
EE	228.3	240.0	279.1	321.9	156.3
EpS	193.1	220.6	248.8	306.2	182.3
EmS	125.1	185.3	201.7	286.0	89.7
EB	166.9	184.3	207.4	278.9	196.2
ET	150.0	155.1	200.6	268.2	163.1

The temperature of the end of exotherm curing (T_f), obtained by extrapolation of the curve.

Heat of curing (ΔH), calculated by measurement of the area under the exothermic transition.

The results of the DSC scans are summarized in Table II. The curing of epoxy resin proceeded by the nucleophilic attack of amine on the oxirane ring. The curing of epoxy resin thus depended on the nucleophilicity of amide amines. In these studies, T_p depended on the structure of amide amines and were in the order

$$EE > EM > EpS > EB > EmS > ET$$

T_i, T_{onset}, T_p, and T_f were highest when amine E was used and lowest with amine T. DSC scans of samples cured isothermally (at 250 ± 20°C in an air oven for 3 h) showed no residual exotherm.

Thermal behavior

TG/DTG traces of epoxy resins cured isothermally with stoichiometric amounts of different amide amines were recorded in a nitrogen atmosphere. Typical TG/DTG traces for samples EmS and EM are shown in Figures 7 and 8. A single-step decomposition was observed in all the samples. The relative thermal stability of the cured resins was assessed by comparison of the initial decomposition temperature (T_i), the temperature of the maximum rate of weight loss (T_{max}), the final decomposition temperature (T_f), and percentage char residue at 600°C. T_i and T_f were obtained by extrapolation. These results are summarized in Table III. All the samples were stable up to 300°C, and significant weight loss occurred only beyond this temperature. The degradation temperatures were dependent on the structure of the network, and T_{max} was found to be at a maximum in the case of sample EE and at a minimum in the case of sample ET. All others had T_{max} of 385 ± 5°C. Higher char yields were obtained in the case of samples cured with diamides containing both phosphorus and silicon, that is, for samples EB and ET. The EB sample showed higher char yields than did ET.
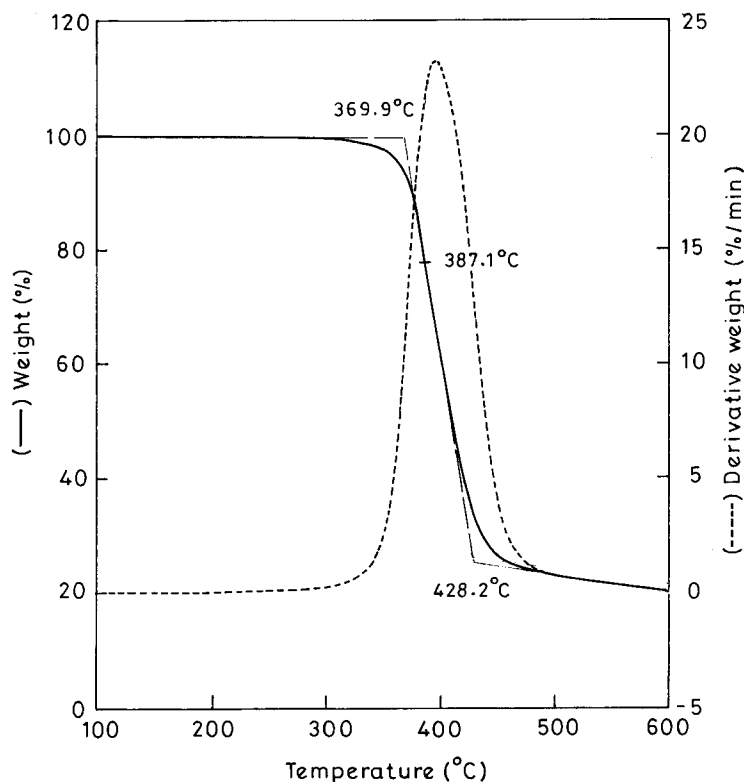

Figure 7   TG/DTG trace of DGEBA cured isothermally with amide amine M (sample EM).
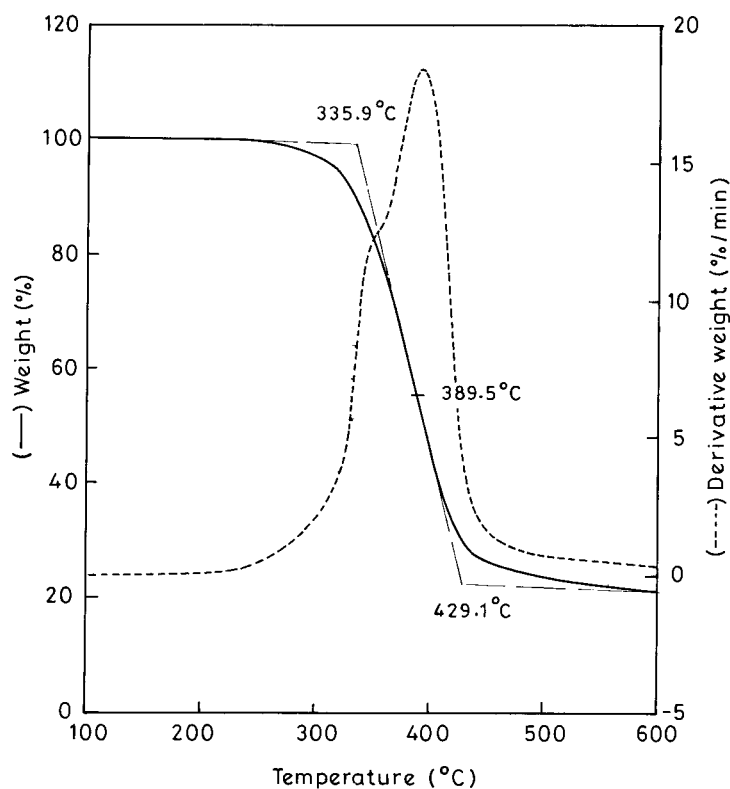
Figure 8 TG/DTG trace of DGEBA cured isothermally with amide amine mS (sample EpS).

CONCLUSIONS

The curing of epoxy resin depended on the structure of amide amines. Cured resins with higher thermal stability could be obtained with amide amines having both phosphorus and silicon atoms.

TABLE III
Thermal Behavior of DGEBA Cured Isothermally with Stoichiometric Amounts of Amide Amines

Sample designation	T_i (°C)	T_{max} (°C)	T_f (°C)	Char yield at 600°C (%)
EM	335.9	389.5	429.1	19.1
EE	384.8	419.8	442.7	30.5
EpS	346.2	386.2	425.9	19.9
EmS	369.9	387.1	428.2	16.3
EB	348.2	380.5	410.3	44.5
ET	333.2	362.1	407.7	38.1

References

1. Feldman, D.; Barbalata, A. Synthetic Polymers: Technology, Properties and Applications; Chapman & Hall: London, 1996; Chapter 8.
2. King, F. A.; King, J. J. Engineering Thermoplastics; Marcel Dekker: New York, 1985; p 351.
3. Ghosh, K. L.; Mittal, K. L. Polyimides Fundamentals and Applications; Marcel Dekker: New York, 1996.
4. Hay, J. N.; Woodfine, B.; Davies, M. High Perform Polym 1996, 8, 35.
5. Ishikawa, S.; Nakatani, M.; Fukuda, H.; Yamamoto, S. Jpn. Pat. 08253677 (1996).
6. Gaw, K.; Kikei, M.; Kakimoto, M.; Imai, Y. React Funct Polym 1996, 30, 85.
7. Gaw, K.; Jikei, M.; Kakimoto, M.; Imai, Y. Polymer 1997, 38, 4413.
8. Ashcroft, W. R. Chemistry and Technology of Epoxy Resin; Ellis, B., Ed.; Chapman & Hall: London, 1993; Chapter 2.
9. Bucknall, C. B.; Toughened Plastics; Wiley: New York, 1977.
10. Varma, I. K.; Fohlen, G. M.; Parker, J. A. J Polym Sci Polym Chem Ed 1983, 19, 209.