Multifunctional Epoxy Resins

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SYNOPSIS

The curing behavior of epoxy resins prepared by reacting epichlorohydrin with 4,4'-diaminodiphenyl methane (DADPM)/4,4'-diaminodiphenyl ether (DADPE) or 4,4'-diaminodiphenyl sulfone (DDS) was investigated using DDS and tris-(m-aminophenyl)phosphine oxide (TAP) as curing agents. A broad exothermic transition with two maxima were observed in the temperature range of 100–315°C when TAP was used as the curing agent. The effect of varying DDS concentration on curing behavior of epoxy resin was also investigated. Peak exotherm temperature (T_{exo}) decreased with increasing concentration of DDS, whereas heat of curing (ΔH) increased with an increase in amine concentration up to an optimum value and then decreased. Thermal stability of the resins, cured isothermally at 200°C for 3 h, was investigated using thermogravimetric analysis in a nitrogen atmosphere. Glass fiber-reinforced multifunctional epoxy resin laminates were fabricated and the mechanical properties were evaluated. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Multifunctional epoxy resins based on 4,4'-diaminodiphenyl methane have been used in the past for the fabrication of advanced fiber-reinforced composites for demanding applications. The literature reveals several applications of N,N,N',N'-tetraglycidyl methylene dianiline (M–M) cured by 4,4'-diaminodiphenyl sulfone. However, very little is known about the physical properties of the cured resins if the methylene group of M–M is replaced by other groups.[1,2] In this paper, we wish to report the effect of replacing the methylene group in M–M resin by ether or sulfone linkage on the curing behavior of the resin using 4,4'-diaminodiphenyl sulfone and tris(m-aminophenyl)phosphine oxide. Thermal stabilities of the cured resins were also evaluated.

EXPERIMENTAL

Materials

Epichlorohydrin (Sarabhai Chemicals), 4,4'-diaminodiphenyl methane (DADPM) (Fluka), 4,4'-di-

aminodiphenyl ether (DADPE) (Fluka), 4,4'-diaminodiphenyl sulfone (DDS) (Fluka), acetone (Aldrich), and methyl ethyl ketone (MEK) (Aldrich) were used as such. Ethanol was purified by distillation before use. E-glass woven mat (RP-6, plain weave, weighing 2.5 g/cm²) procured from Pilkington fiber glass was used for the fabrication of laminates. Tris(m-aminophenyl)phosphine oxide (TAP) was synthesized in the laboratory according to the method reported elsewhere.[3]

Synthesis of Multifunctional Epoxy Resins

The resins were synthesized by reacting the corresponding diamine with excess of epichlorohydrin. The structure of the resins can be depicted as follows:
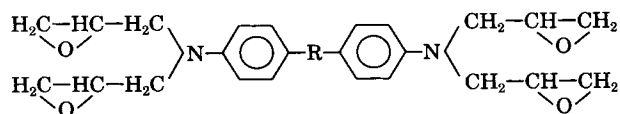
where R = —CH₂— [M–M], —O— [M–E], and —SO₂— [M–S]. The letters within brackets represent the designation for various resins.

Procedure

In a typical reaction for the synthesis of M–M resin, 0.05 mol of DADPM was dissolved in 30 mL ethanol

in a three-necked flask equipped with a nitrogen inlet, reflux condenser, and stirrer. Epichlorohydrin, 1.5 mol, was then added and the solution was heated to 55°C and held at that temperature for 3 h. After cooling the reaction mixture to 45°C, 20 mL of 40% sodium hydroxide solution was added dropwise over a period of 1 h. The contents were held for another 0.5 h at 45°C, followed by distillation under vacuum. The residue was extracted with MEK and washed several times with water. The water layer was removed by decantation and the organic layer was distilled under vacuum at 65°C. A viscous liquid was obtained in a 90% yield. The yield of M–E and M–S resins obtained was 89 and 60%.

Characterization

Purity of the resins was determined by using a Waters HPLC with an ODS column at room temperature. A flow rate of 1.2 mL/min and a UV detector was used with chloroform as a solvent. The structure of the resins was characterized using a Digilab BioRad FTS-40 FTIR spectrophotometer.

The epoxide equivalent was determined by titration of resin (0.2 g) in a HCl–dioxane solution (25 mL) against $0.1N$ methanolic sodium hydroxide using cresol red as an indicator. The molecular weight of the resins was determined using a Knauer Model II vapor pressure osmometer.

Thermal Behavior

The curing behavior of the resins in static air was investigated using a DuPont 9900 thermal analyzer having a 910 DSC module. A heating rate of 10°C/min and a sample size of 5 ± 1 mg was used in each experiment.

For DSC studies, samples were prepared by mixing accurately weighed resin with a known amount of curing agent in MEK. The solvent was then removed by heating at 60°–70°C in air-circulating oven. The mixture was then immediately used for curing studies.

The exothermic transition associated with curing was characterized by determining the following temperatures:

T_i Kick-off temperature of polymerization, the temperature where the first detectable heat was released, and it was determined by the initial deviation in the base line.

T_o The onset temperature of curing. T_o was calculated by extrapolating the front side of the exothermic transition to the base line.

T_{exo} Exothermic peak temperature.

T_f Temperature for the completion of reaction.

The thermal stability of the cured resins (cured at 200°C for 3 h in an air oven) in N_2 atmosphere was evaluated using a DuPont 1090 thermal analyzer having a 951 TG module. A heating rate of 10°C/min and a sample size of 10 ± 1 mg was used in each experiment.

Fabrication of Laminates

Nine pieces of glass cloth (6 × 6 in.) were coated uniformly with a homogeneous solution of resin and 4,4'-DDS (100 : 25 w/w) in MEK. The coated plies were dried in air followed by drying in an air oven at 80°C for 1 h. After drying, the prepregs were stacked together between two Teflon sheets and placed between the heated platens of the compression-molding machine (Carver, laboratory press). Initially, contact pressure was applied at 100°C for 1 h, then increased to 50 psi at 140°C, and these conditions were maintained for 1 h. Finally, the temperature was increased to 190°C and pressure to 100 psi and kept under these conditions for 2 h. After cooling, the laminates were removed from the press and the postcuring was done at 200°C for 14 h in an air oven.

Evaluation of Properties

The resin content of the laminates was determined by pyrolysis in a muffle furnace. A known quantity (~ 1 g) of the laminate was heated in a silica crucible at 600°C for 6 h and the residual fibers were weighed. Density and void content of the laminates was determined according to ASTM D792-66 & ASTM D2734-70.

Flexural properties of the laminates was evaluated according to ASTM D790-71 using an Instron Model 1122. A span-to-depth ratio of 32 : 1, crosshead speed of 10 mm/min, and a chart speed of 100 mm/min was used.

Interlaminar shear strength (ILSS) was evaluated according to ASTM D2344-76. A span-to-depth ratio of 5 : 1, length-to-depth ratio of 7 : 1, crosshead speed of 1 mm/min, and a chart speed of 100 mm/min was used in each experiment. Izod impact strength (ASTM D256-70) of the notched specimens (notch angle 45°) was determined using an Impact testing machine Model IT-042 that had an energy range of 0–0.42 kg.

Glass transition temperature (T_g) of the laminates was determined by using polymer laboratories DMTA Model MK II. A heating rate of 5°C/min and a frequency of 10 Hz was used.

Aging Studies

Thermal aging of glass fabric-reinforced multifunctional epoxy/DDS laminates was carried out at 200°C for 200 h. The change in strength was monitored by determination of ILSS. Effect of humidity on long-term application of these laminates was determined by accelerated aging. For this purpose, the laminates were kept in boiling water for 200 h and the change in weight and ILSS was determined.

RESULTS AND DISCUSSION

The epoxy equivalent weight determined by the titration method was 111.6, 105.5, and 165 for M–M, M–E, and M–S, respectively. The molecular weight of the resins determined by VPO was 416, 437, & 346.6 for M–M, M–E, and M–S, respectively. From the epoxy equivalent, the number of epoxy groups were 4, 3.8, and 2.9 in M–E, M–M, and M–S resins, respectively. The commercially available resin has an average functionality of 3.28.[1]

In the IR spectrum of various resins (Fig. 1), the characteristic absorption band due to the epoxide group was observed at 905 cm^{-1}. In M–M and M–S resins, a broad absorption band was observed
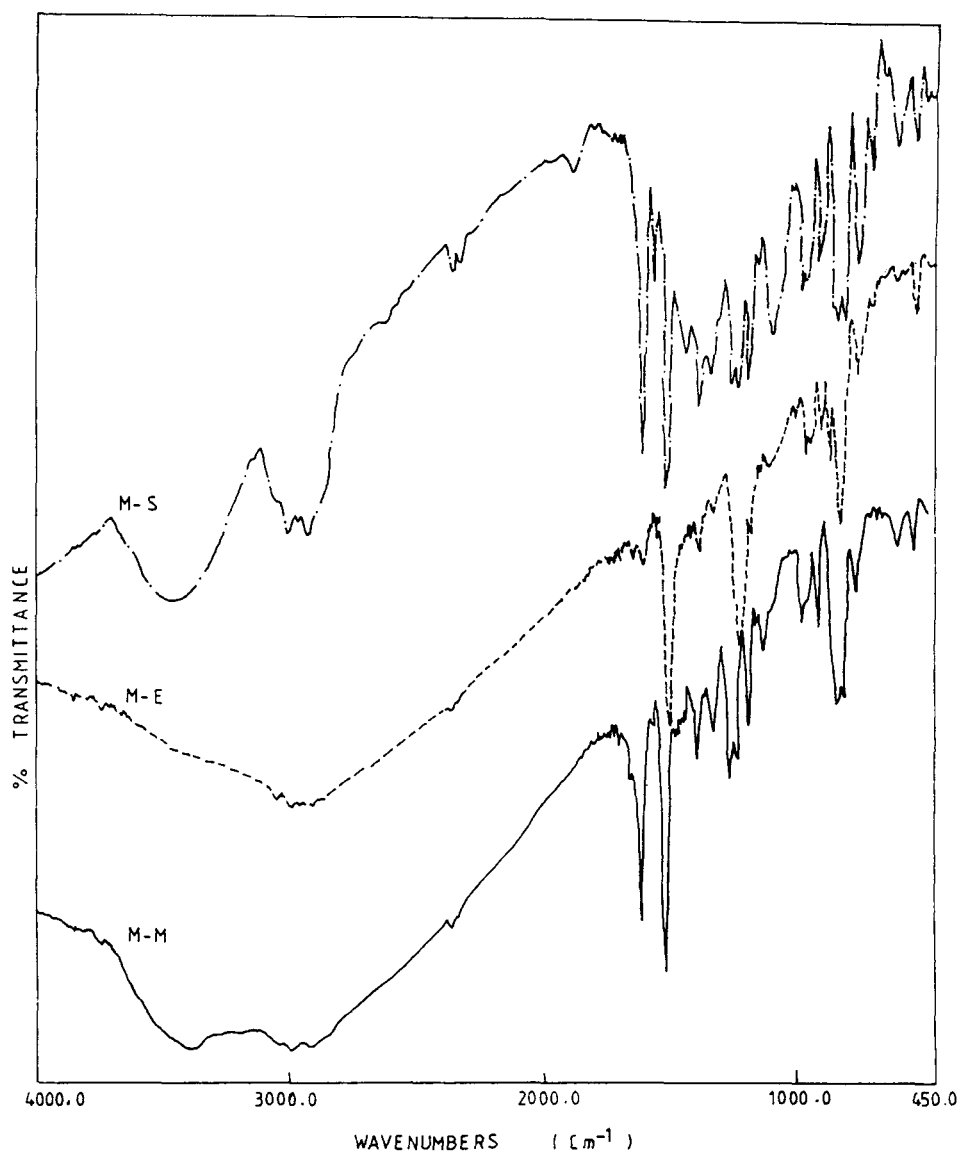

Figure 1 FTIR spectra of M–M, M–E, and M–S resins.

around 3450 cm^{-1}, which may be due to the —NH— stretch. Absorption in this region was absent in the M–E resin. As mentioned earlier, the epoxy equivalent in M–M and M–S was lower than 4. The lower functionality may therefore arise due to the presence of an unreacted —NH— group in these resins. The presence of the —NH— group is further confirmed by the appearance of a strong absorption band at 1633 cm^{-1} due to —NH— bending in M–M and M–S resins (Fig. 1).

Effect of Resin Structure on the Curing Behavior

Curing studies of multifunctional epoxies with DDS revealed two curing exotherms (Fig. 2) in the temperature range of 101–202 and 202–306°C in M–S resin, whereas in M–M and M–E resins, only one exotherm in the temperature range of 136–276°C was observed (Table I and Fig. 2). A single exotherm observed in the M–M/M–E–DDS resin system can be supported by the results reported by Barton,[4] thereby indicating that activation energy for linear polymerization and cross-linking reactions are equal. The appearance of the first exotherm at lower temperature in the M–S/DDS system can be attributed to the presence of an electron-withdrawing sulfone group in M–S resin. Such an —I and —R group will enhance the electron deficiency at the oxirane carbon, thereby favoring the nucleophillic attack of an —NH group of DDS:
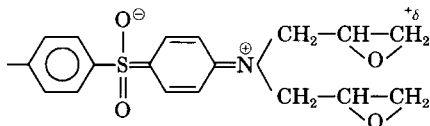
The second exotherm arises due to the attack of a secondary amino group with the oxirane ring. The reactivity of this group is expected to be low due to the presence of the —SO$_2$ group in M–S.

Table I DSC Results of Epoxy Resins Cured with 25 Phr of DDS

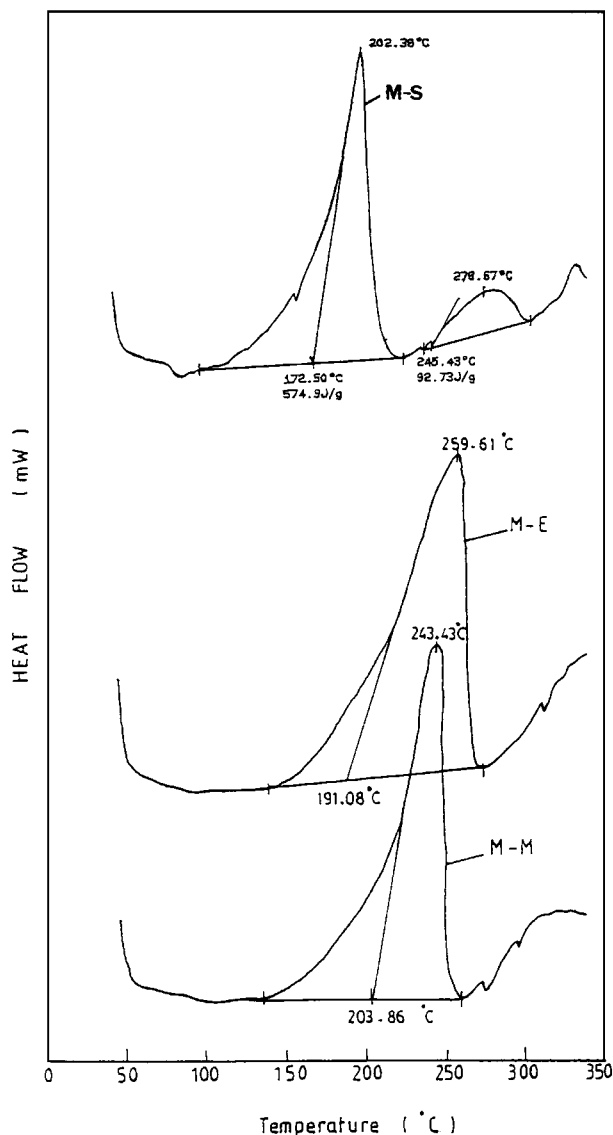| Curing Characteristics	Resin Designation		
	M–M	M–E	M–S
T_i (°C)	136.6	141.0	101.6
T_o (°C)	203.8	191.0	172.5
T_{exo-1} (°C)	243.4	259.6	202.3
T_{exo-2} (°C)	—	—	278.6
T_f (°C)	260.0	276.6	306.6
ΔH (J/g)	714.9	818.2	667.6

Figure 2 DSC traces of M–M, M–E, and M–S resins cured with 25 phr of DDS.

Effect of Amine Concentration

The concentration of DDS was varied from 15 to 60 phr to investigate the effect of concentration on the curing characteristics of M–M and M–E resins (Table II), which has almost a similar functionality. In M–E resin, increase in the concentration of DDS resulted in a decrease in the characteristic curing temperatures (T_i, T_o, T_{exo}). The heat of curing (ΔH) increased with increase in DDS concentration (up to 25 phr) and reduced on further increase of DDS. No such regular trend was observed in the curing temperature of M–M resin. ΔH values reached an optimum value at an amine concentration between

Table II   DSC Results of Epoxy Resins Cured with Varying Amounts of DDS

Resin Designation	Ratio of Epoxy Groups to Amino Hydrogen	T_i (°C)	T_o (°C)	T_{exo} (°C)	T_f (°C)	ΔH (kcal/mol Equiv. Epoxide)
M–M	3.96	150.0	225.0	255.0	268.0	19.7
	2.37	136.6	203.8	243.4	260.0	22.4
	1.98	143.3	207.9	228.3	298.3	23.3
	1.06	128.3	165.9	211.3	281.6	21.5
	0.91	133.8	164.7	209.6	231.6	21.3
M–E	3.75	170.0	245.5	276.6	288.3	24.7
	2.25	141.6	191.0	259.6	276.6	27.1
	1.87	140.0	182.5	235.8	266.6	25.1
	0.97	136.6	175.5	220.0	256.6	27.4
	0.86	131.6	170.4	213.5	250.0	27.0

25 and 30 phr in M–M resin. The heat of reaction (ΔH) per mol equivalent epoxide group was also calculated and the values range from 20 to 23 kcal/mol in M–M and 25 to 27 kcal/mol equiv. epoxide group in M–E resin (Table II). ΔH values of the 24–26 kcal/mol epoxide group have been reported for the amine–epoxide reaction.[1]

The concentration of amine at which the maximum ΔH is observed is basically a nonstoichiometric amount. It is quite possible that the mobility of functional groups becomes restricted as the crosslink density increases. This therefore makes the curing reaction a diffusion-controlled process and the amino group is not able to approach the oxirane ring due to the resistance on segmental mobility in a high-viscosity medium. Hence, the increase in concentration of amine does not facilitate curing; instead, it acts as a diluent. Residual epoxy groups in these resin systems can perhaps be cured by isothermal heating for prolonged periods of time.

Effect of Amine Structure on Curing Behavior

TAP (25 phr) and DDS was used to investigate the effect of amine structure on the curing behavior of multifunctional epoxy resins. With TAP, two exothermic transitions were observed in all the resin systems (Fig. 3). An intense exotherm was present in the temperature range of 110–239°C, followed by a small exotherm in the temperature range of 239–315°C (Table III).

This curing behavior is in contrast to that observed with DDS. Onset of curing takes place at a lower temperature and two exotherms were observed in M–M and M–E resins when TAP is used, while the behavior of M–S resin with TAP and DDS is

similar. The occurrence of two exotherms in the M–M/M–E–TAP system can be explained on the basis of steric hinderance for amine–epoxide reactions.[5] The exotherm peak temperature (T_{exo-1}) was lower
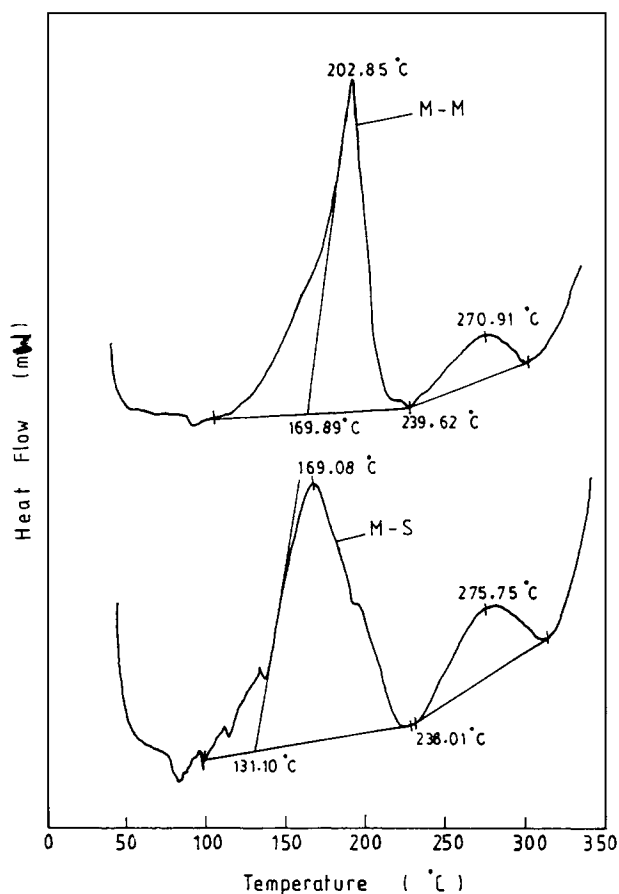

Figure 3   DSC traces of M–M and M–S resins cured with 25 phr of TAP.

Table III DSC Results of Epoxy Resins Cured with 25 phr of TAP

Curing Characteristics	Resin Designation		
	M–M	M–E	M–S
T_i (°C)	110.0	110.0	100.0
T_o (°C)	199.0	156.7	131.1
T_{exo-1} (°C)	202.8	188.1	169.0
T_{exo-2} (°C)	270.9	267.3	275.7
T_f (°C)	306.6	275.0	315.0
ΔH (J/g)	751.4	405.9	502.0

in the presence of TAP in all epoxy systems under investigation. These observations can be explained in terms of greater nucleophilicity of TAP, which contains an —I group at the m-position. Earlier studies with p- and m-DDS indicated greater reac-

tivity of amine having an [— I] SO_2 group in the m-position.[6] On a similar basis, higher reactivity of TAP can be explained. The secondary amino group, generated as a result of the reaction of the primary amino group with an oxirane ring, is less reactive and, hence, a second small exotherm is observed at higher temperature. This exotherm is not prominent because of the increased molecular weight and cross-link density.

Thermal Stability

Thermogravimetric traces of multifunctional epoxy resins cured with 25 phr of DDS and TAP are shown in Figure 4. From the TG traces, the relative stability of the cured resins was assessed by noting the initial decomposition temperature (IDT), integral procedural decomposition temperature (IPDT), the temperature of the maximum rate of weight loss (T_{max}),
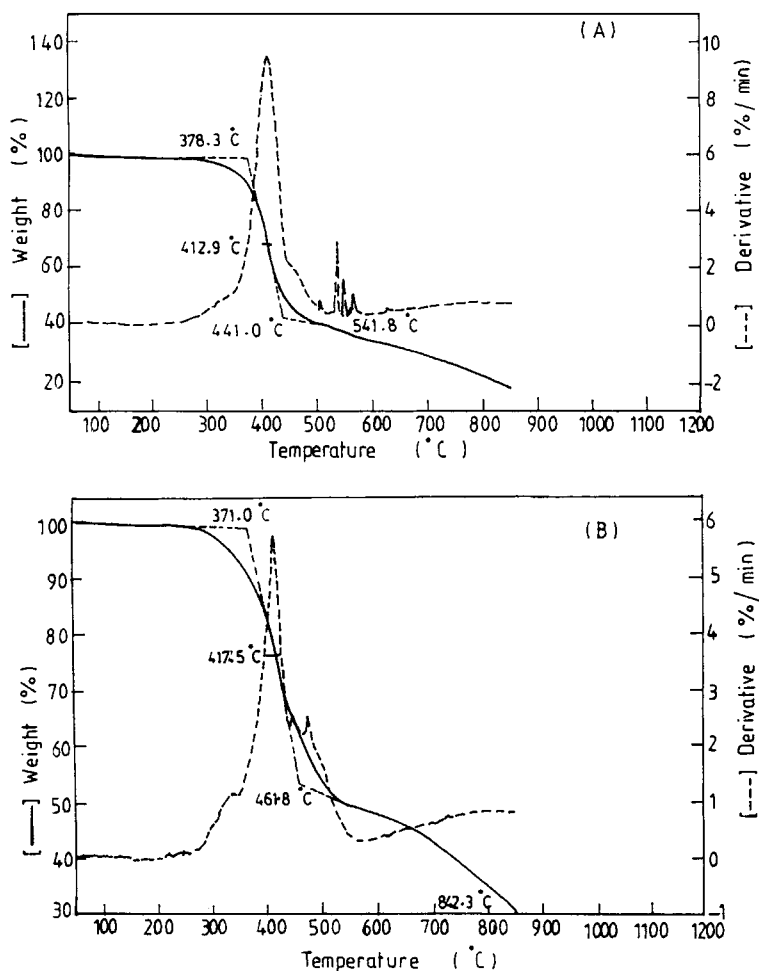

Figure 4 TG traces of M–E resin cured by using (A) DDS (25 phr) and (B) TAP (25 phr) as hardeners.

Table IV   Thermogravimetric Results of Isothermally Cured Epoxy Resins in N₂ Atmosphere

Sample Designation	Amine	IDT (°C)	T_{max-1} (°C)	T_{max-2} (°C)	FDT (°C)	IPDT (°C)	Char Yield (%)
M–M	TAP	287.6	331.3	472.0	500	528	37.5
	DDS	291.0	331.2	471.3	500.3	440	28.0
M–E	TAP	371.0	417.5	—	461.8	530	35.0
	DDS	378.0	412.9	—	441.0	471	22.0
M–S	TAP	370.0	425.6	—	493.7	531	34.5
	DDS	378.9	414.0	—	442.1	476	24.0

and final decomposition temperature (FDT). IDT and FDT were obtained by extrapolation and IPDT was calculated according to the method of Doyle.[7] The results of TG studies are summarized in Table IV.

In case of M–M/DDS or TAP resins, a two-step degradation was observed, whereas a single-step degradation was observed in all other samples. Char yield at 800°C was higher when TAP was used as a curing agent for multifunctional epoxy resins. This observation is similar to what has been reported earlier[8-10] and can be attributed to the increase in condensed-phase reactions.

Mechanical Properties

The mechanical properties of the various glass fabric-reinforced resins cured with 25 phr of p-DDS were evaluated and the results are summarized in Table V. DMTA traces of glass fabric-reinforced laminates at a frequency of 10 Hz are shown in Figure 5. Glass transition temperature (T_g) of laminates was determined from the peak position of the loss modulus curve and was found to be 265, 245, and 202 for M–M, M–E, and M–S, respectively. The lower T_g observed in the case of M–S can be explained on the basis of low network density as the
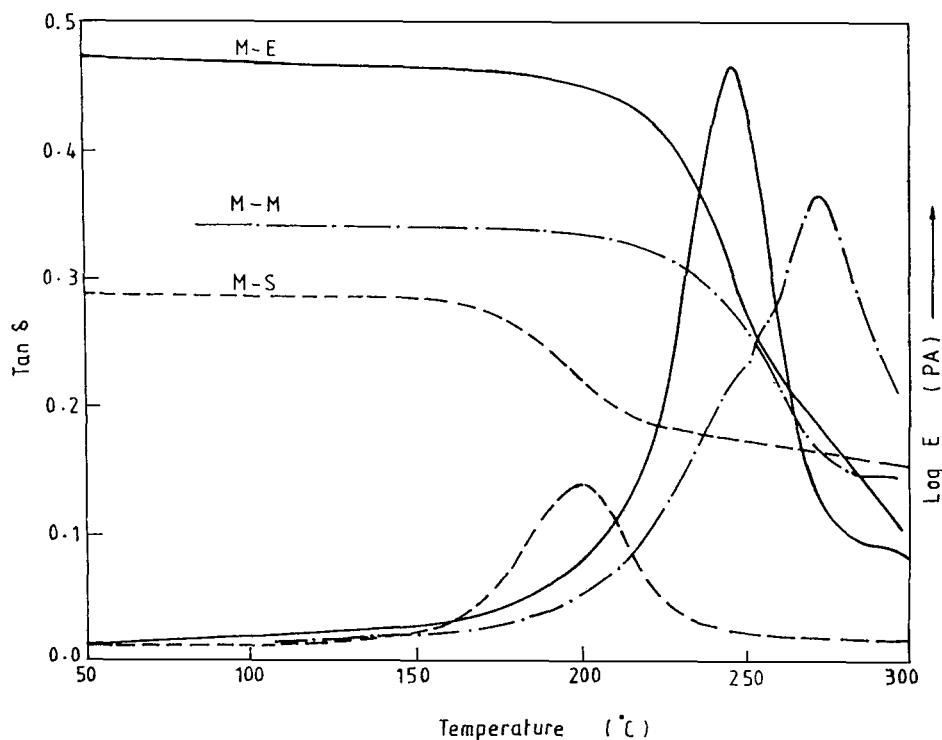

Figure 5   DMTA traces of epoxy–glass fabric laminates based on multifunctional epoxy/DDS resins.

Table V Mechanical Properties of the Laminates Fabricated Using Multifunctional Epoxy/DDS Resins

Sample No.	Property Tested	Resin Designation		
		M–M	M–E	M–S
1.	Resin content (wt %)	32	33	35
2.	Flexural strength (MN/m^2)	695	893	773
3.	ILSS (MN/m^2)	40.5	37.1	55.8
4.	Impact strength (kg cm/cm)	65	54	47
5.	Void content (%)	1.0	1.1	1.3

epoxy functionality is 2.9 as compared to 4.0 and 3.8 of M–E and M–M, respectively.

Thermal aging of laminates at 200°C for 200 h showed a decrease in ILSS. A loss of 30 ± 5% in ILSS was observed in these laminates. Results of boiling water treatment also showed a 15 ± 5% decrease in ILSS. The lowering in ILSS on treatment with boiling water can be due to the plasticizing effect of the water at the resin–fiber interface. The % gain in weight on boiling water treatment for 200 h in all the resins was 1.5%.

CONCLUSIONS

These results thus clearly indicate that the multifunctional epoxy resins containing an electron-withdrawing group in the backbone can be cured at lower temperatures. Alternatively, the curing temperature of the epoxy resins can be reduced by taking more reactive amines. Epoxies cured with amines containing phosphine oxide groups gave better char yields, thereby indicating higher flame resistance in these samples.

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