

Curing and Thermal Behavior of Diglycidyl Ether of Bisphenol A in the Presence of a Mixture of Amines

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ABSTRACT: The curing behavior of diglycidyl ether of bisphenol A (DGEBA) was investigated by differential scanning calorimetry with mixtures of silicon-containing amide-amines and diaminodiphenyl sulfone (DDS). Silicon-containing amide-amines were prepared by the reaction of 2.5 mol of 4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl methane (M), 3,3'-diaminodiphenyl sulfone (mS), 4,4'-diaminodiphenyl sulfone (pS), bis(3-aminophenyl) methyl phosphine oxide (B), or tris(3-aminophenyl) phosphine oxide (T) with 1 mol of bis(4-chlorobenzoyl) dimethyl silane. Mixtures of the amide-amines and DDS at ratios of 0:1, 0.25:0.75, 0.5:0.5, 0.75:0.25, and 1:0 were used to investigate the curing behavior of DGEBA. A single exotherm was observed on curing with a mixture of amide-amine and DDS. This clearly shows that the mixture participated in the cocuring reaction. The peak exotherm temperature de-

pended on the structure and the molar ratio of amide-amines. With all of the amide-amines and DDS, a significant decrease in the kick-off temperature of the curing exotherm was observed on the incorporation of a 0.25 molar fraction of amide-amines. Thus, with the mixture, the curing temperatures were reduced and were lowest for ether-containing amide-amines and highest for methylene-containing amide-amines. The char yield was almost similar in the samples cured with amide-amines (E, pS, or mS) or DDS. The char yield was higher than for either of the constituents when a mixture was used. A synergistic behavior was observed when a mixture of E, M, mS, or pS and DDS was used, whereas mixture of B or T and DDS showed antagonism in the char yield. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1739–1747, 2003

Key words: curing of polymers; thermal properties; resins

INTRODUCTION

To extend the applications of epoxy resins as electronic materials and in the aerospace industry, it is crucial to improve their flame and thermal resistance. Several approaches have been reported in the literature for the improvement of the flame resistance and thermal stability 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.¹ Fire hazards and the environmental concerns of the use of halogen-based systems, which have been publicized by political movements, have necessitated the search for new, halogen-free fire retardant agents. With safety and environmental concerns in mind, epoxy polymers that are flame resistant and halogen-free have been the focus of attention by researchers in recent years.^{2,3}

Earlier studies with addition polyimides have shown that the incorporation of phosphorus/nitrogen

in the polymer backbone improves flame resistance.^{4–9} An improvement in the flame and thermal resistance of epoxy resins by the incorporation of phosphorus was also reported in the literature.^{10–12} The reaction of diglycidyl ether of bisphenol A (DGEBA) with trialkyl or aryl phosphate followed by curing with 4,4'-diaminodiphenyl sulfone (pS) gave products with good thermal stability and resistance.¹³ The reaction of DGEBA with an amide-amine with both silicon and phosphorus gave products with good thermal stability and resistance.¹⁴ Polymers with a sulfone group are known to have good oxidative, thermal, and hydrolytic stability and good mechanical properties.^{15,16} Hence, a modifier with a sulfone group will have an additional effect on the properties of a modified network along with its flexibilizing effect. So we thought it interesting to use a mixture of amide-amine and diaminodiphenyl sulfone (DDS) as a curing agent for DGEBA.

EXPERIMENTAL

Materials

DGEBA (grade LY556, epoxy equivalent = 177) was procured from Hindustan Ciba Geigy, Ltd. The following were used as received: nitric acid and sulfuric acid (Merck); palladium charcoal and methyl iodide

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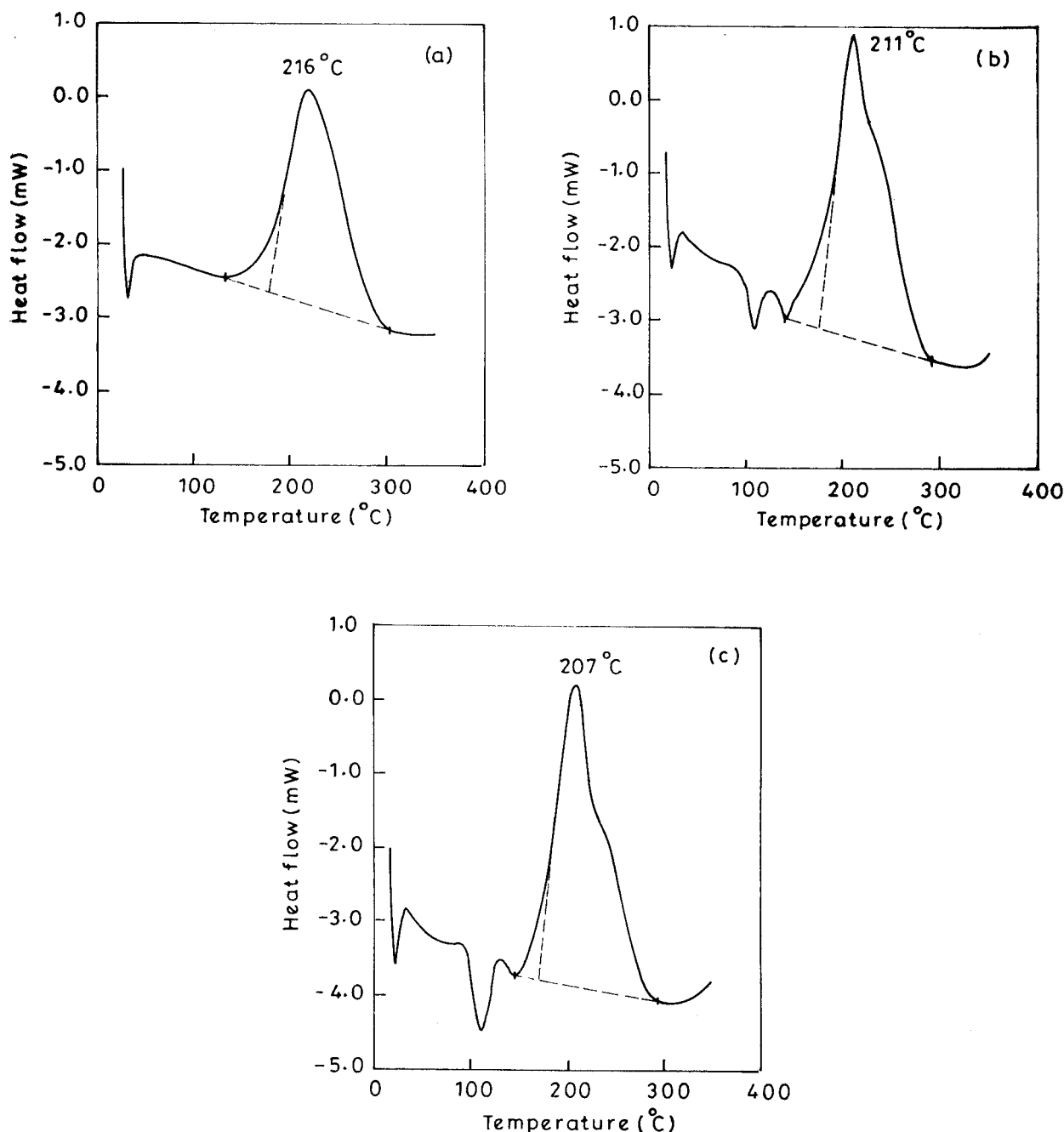


Figure 1 DSC scans of DGEBA in the presence of pS/DDS: (a) EpS1, (b) EpS2, and (c) EpS3.

(CDH); hydrazine hydrate, chloroform, toluene, potassium hydroxide, and hydrochloric acid (Qualigens, AR grade); petroleum ether (S.D. Fine Chemicals); thionyl chloride (Thomas Baker); triphenyl phosphine oxide (Fluka); triphenylphosphine (Sisco); and pS, 3,3'-diaminodiphenyl sulfone (mS), 4,4'-diaminodiphenyl methane (M), and 4,4'-diaminodiphenyl ether (E; Aldrich). *N,N'*-dimethyl formamide and *N,N'*-dimethyl acetamide (CDH) were dried over phosphorus pentoxide for 24 h and were then vacuum-distilled and stored in sealed dark flask over molecular sieves.

Diethyl ether (E-Merck) was dried by being passed over sodium wire. The amines bis(3-aminophenyl) methyl phosphine oxide (B) and tris(3-aminophenyl) phosphine oxide (T) were prepared in a laboratory according to a procedure reported elsewhere.^{17,18}

Curing studies

A Rheometric Scientific thermal instrument with a differential scanning calorimetry (DSC)-SP module was used to record DSC scans in a static air atmo-

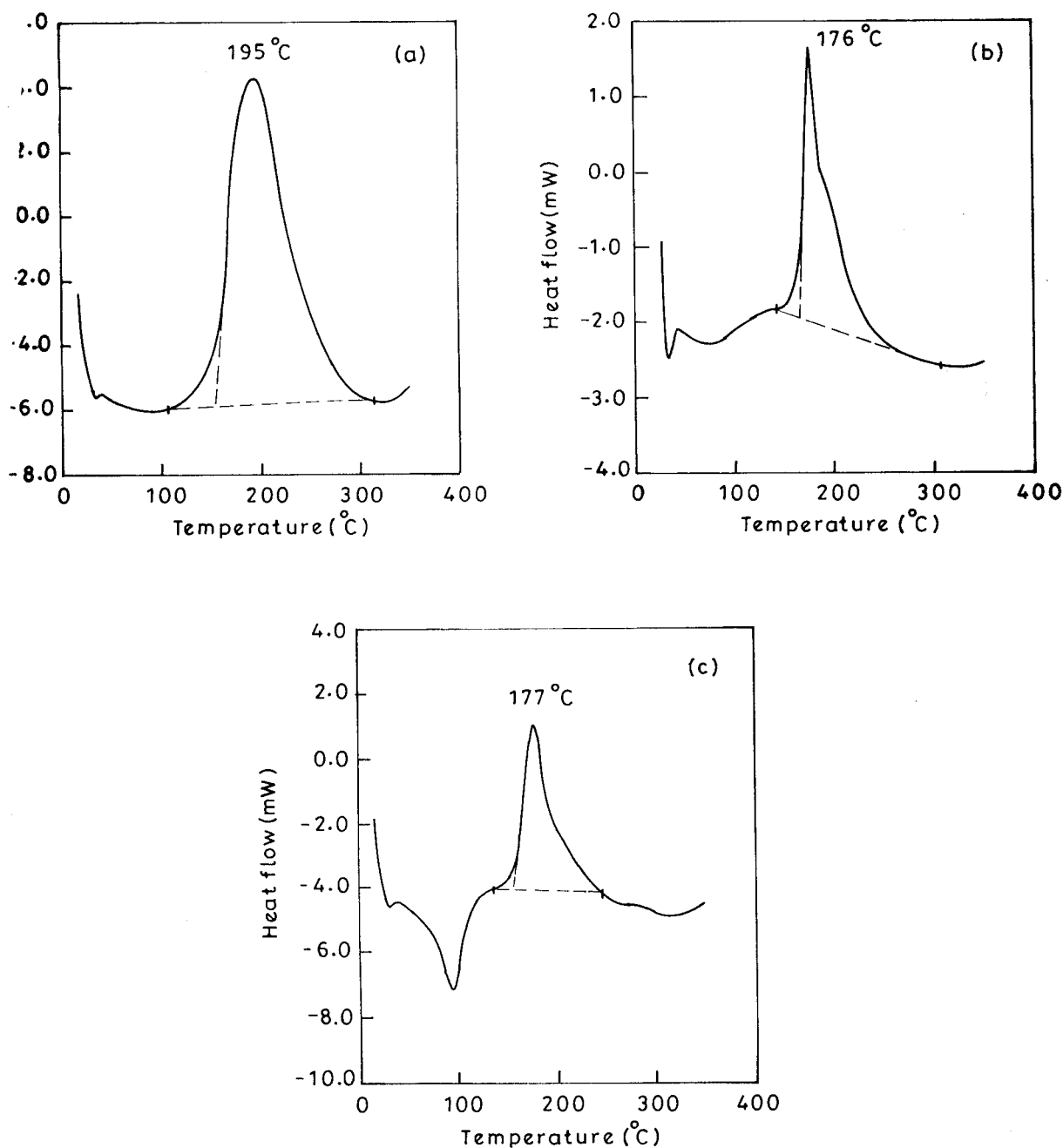


Figure 2 DSC scans of DGEBA in the presence of B/DDS: (a) EB1, (b) EB2, and (c) EB3.

sphere. A heating rate of $10^{\circ}\text{C min}^{-1}$ and a sample size of 5 ± 3 mg was used in each experiment. For curing studies, the samples were prepared by the dissolution of a known weight of amide-amine and the conventional curing agent DDS at ratios of 0.25:0.75, 0.5:0.5, and 0.75:0.25 in methyl ethyl ketone and addition to DGEBA. This was done to facilitate a uniform mixing of curing agents in DGEBA. The solvent was then removed by vacuum-stripping. These samples were designated by adding the suffix 1, 2, or 3 to the designation of amide-amine plus DGEBA. For exam-

ple, DGEBA cured with an M/DDS mixture at molar ratios of 0.25:0.75, 0.5:0.5, and 0.75:0.25 were designated EM1, EM2, and EM3, respectively. The sample with DDS and DGEBA was designated ED.

Thermal stability

We evaluated the thermal stability of samples cured isothermally in a hot-air oven (at $200 \pm 10^{\circ}\text{C}$ for 2 h) by recording TG/DTG traces in a nitrogen atmosphere (flow rate = $10 \text{ cm}^3/\text{min}$). A Rheometric Scientific

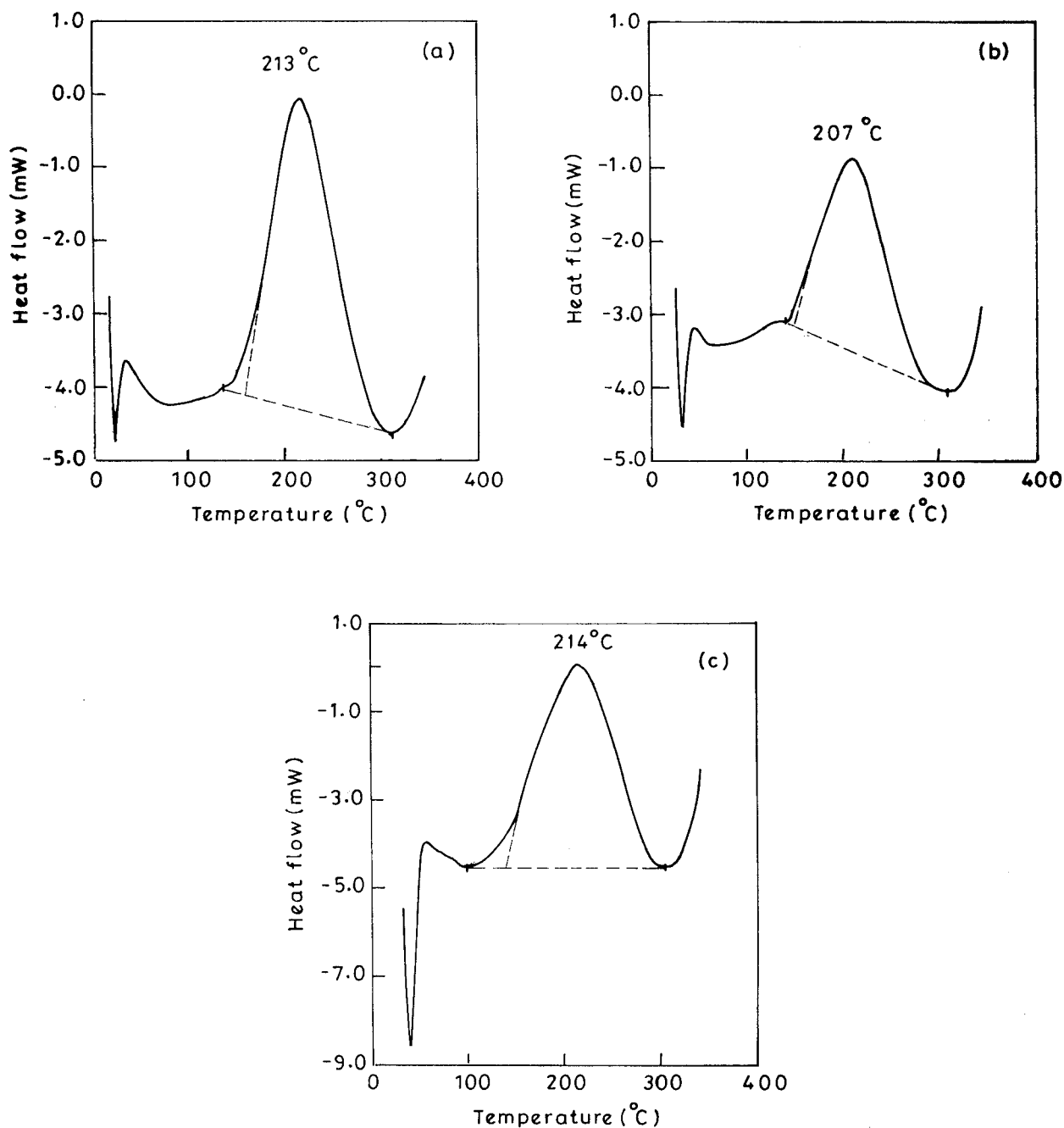


Figure 3 DSC scans of DGEBA in the presence of T/DDS: (a) ET1, (b) ET2, and (c) ET3.

thermal analyzer with a TG 1500 module was used to record TG/DTG traces at a heating rate of $20^{\circ}\text{C min}^{-1}$ with a sample size of 5 ± 3 mg.

RESULTS AND DISCUSSION

Structural characterization of amide-amines

The syntheses and structural characterization of the amide-amines were performed with the Fourier transform infrared and $^1\text{H-NMR}$ spectroscopic techniques

TABLE I
Results of the DSC Scans of DGEBA in the Presence of a Stoichiometric Amount of an Amide-Amine (E)DDS Mixture at a Heating Rate of $10^{\circ}\text{C min}^{-1}$

Sample designation	E (mol)	T_i ($^{\circ}\text{C}$)	T_{onset} ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH (J/g)
ED	0	165.0	184.0	225.3	310.0	173.0
EE1	0.25	105.3	174.3	263.4	315.7	216.5
EE2	0.5	111.5	197.8	269.5	317.7	257.6
EE3	0.75	93.8	96.2	163.6	217.7	152.4
EE	1.0	100.6	118.3	156.3	211.6	181.5

TABLE II
Results of the DSC Scans of DGEBA in the Presence of a Stoichiometric Amount of an Amide–Amine (M)DDS Mixture at a Heating Rate of 10°C min⁻¹

Sample designation	M (mol)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
EM1	0.25	109.8	165.7	224.5	330.5	374.8
EM2	0.5	98.6	115.9	230.2	330.5	349.8
EM3	0.75	103.2	118.3	164.9	296.5	360.2
EM	1.0	212.9	240.6	272.6	315.8	133.9

and elemental analysis, and the results were reported in an earlier work.¹⁴

Curing studies

The curing reaction of epoxy resins depends on the structure and reactivity of the curing agent. The onset of the curing exotherm depends on the nucleophilicity of the amino group. Aromatic amines containing electron donor substituents start the curing of epoxy resin at lower temperatures. The chemical structure of the amine is not the only factor; steric restrictions to the epoxy amine addition reaction, physical interactions among different functional groups of the constituent components, and the cure extension can also influence the cure kinetics. It was, therefore, necessary to understand the effect of amines on the curing behavior of DGEBA and the thermal stability of the cured network. The curing of epoxy resins in the presence of amines with various structures has been well reported in the literature.^{19–22}

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

The kick-off temperature (T_i), where the curing starts.

The temperature where the first detectable heat was released (T_{onset}). This was obtained by the extrapolation of the steepest portion of the curve.

The temperature of the peak position of the exotherm (T_p).

TABLE III
Results of the DSC Scans of DGEBA in the Presence of a Stoichiometric Amount of an Amide–Amine (mS)DDS Mixture at a Heating Rate of 10°C min⁻¹

Sample designation	mS (mol)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
EmS1	0.25	115.5	157.0	210.6	294.4	343.2
EmS2	0.5	133.6	153.5	212.6	296.6	275.0
EmS3	0.75	100.8	145.3	222.3	296.5	344.9
EmS	1.0	141.7	167.9	207.1	268.2	202.1

TABLE IV
Results of the DSC Scans of DGEBA in the Presence of a Stoichiometric Amount of an Amide–Amine (pS)DDS Mixture at a Heating Rate of 10°C min⁻¹

Sample designation	pS (mol)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
EpS1	0.25	132.4	178.2	216.0	303.4	378.6
EpS2	0.5	140.6	175.5	211.0	290.9	395.1
EpS3	0.75	145.6	170.8	206.9	294.4	373.9
EpS	1.0	174.9	188.3	207.5	277.5	146.7

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

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

DDS is generally used as a hardener for curing epoxies. The incorporation of amide–amines along with DDS was expected to affect the curing behavior and the thermal stability of the cured network. Therefore, amide–amine and DDS mixtures, such as B/DDS, M/DDS, mS/DDS, pS/DDS, E/DDS, and T/DDS were used to cure DGEBA. Figures 1(a–c), 2(a–c), and 3(a–c) show the DSC scans of DGEBA with mixtures of amide–amines and DDS in varying proportions. The molar fraction of these amide–amines was varied from 0 to 1.0 to study the effect of the structure and molar ratio on the curing behavior. The results are tabulated in Tables I–VI.

A single exotherm was observed on curing with a mixture of amide–amine and DDS. This clearly shows that the mixture participated in the cocuring reaction. With all of the amide–amines, a significant decrease in T_i was observed on the incorporation of a 0.25 molar fraction of amide–amine.

T_p of amide–amines also decreased with the addition of DDS. The curing of DGEBA was initiated at a higher temperature with amide–amine alone as compared to that with a mixture (amide–amine and DDS). With the mixture, the curing temperatures were reduced and were lowest for ether-containing amide–amines and highest for methylene-containing amide–amines. All of the characteristic curing temperatures

TABLE V
Results of the DSC Scans of DGEBA in the Presence of a Stoichiometric Amount of an Amide–Amine (B)DDS Mixture at a Heating Rate of 10°C min⁻¹

Sample designation	B (mol)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
EB1	0.25	105.9	153.9	195.3	316.4	388.1
EB2	0.5	142.5	164.2	175.9	307.8	251.5
EB3	0.75	135.8	157.2	176.9	245.8	232.6
EB	1.0	210.4	222.4	251.1	277.1	52.3

TABLE VI
Results of the DSC Scans of DGEBA in the Presence of
a Stoichiometric Amount of an Amide-Amine (T)DDS
Mixture at a Heating Rate of $10^{\circ}\text{C min}^{-1}$

Sample designation	T (mol)	T_i ($^{\circ}\text{C}$)	T_{onset} ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH (J/g)
ET1	0.25	134.7	156.6	213.4	310.2	393.8
ET2	0.5	141.5	145.3	206.8	308.9	265.5
ET3	0.75	98.5	137.2	213.8	304.4	393.2
ET	1.0	123.8	147.9	203.9	292.1	233.6

were lower and ΔH was higher when a mixture of amide-amines and DDS was used as the curing agent. These studies clearly indicated that the curing of epoxy resins can be tailored and controlled with a mixture of amines as hardeners.

Thermal stability

TG analysis was performed to assess the relative thermal stability of the cured epoxy resins. We obtained TG traces by plotting the percentage residual weight against temperature. Percentage char yield at 650°C and following characteristic temperatures were noted from the TG/DTG traces:

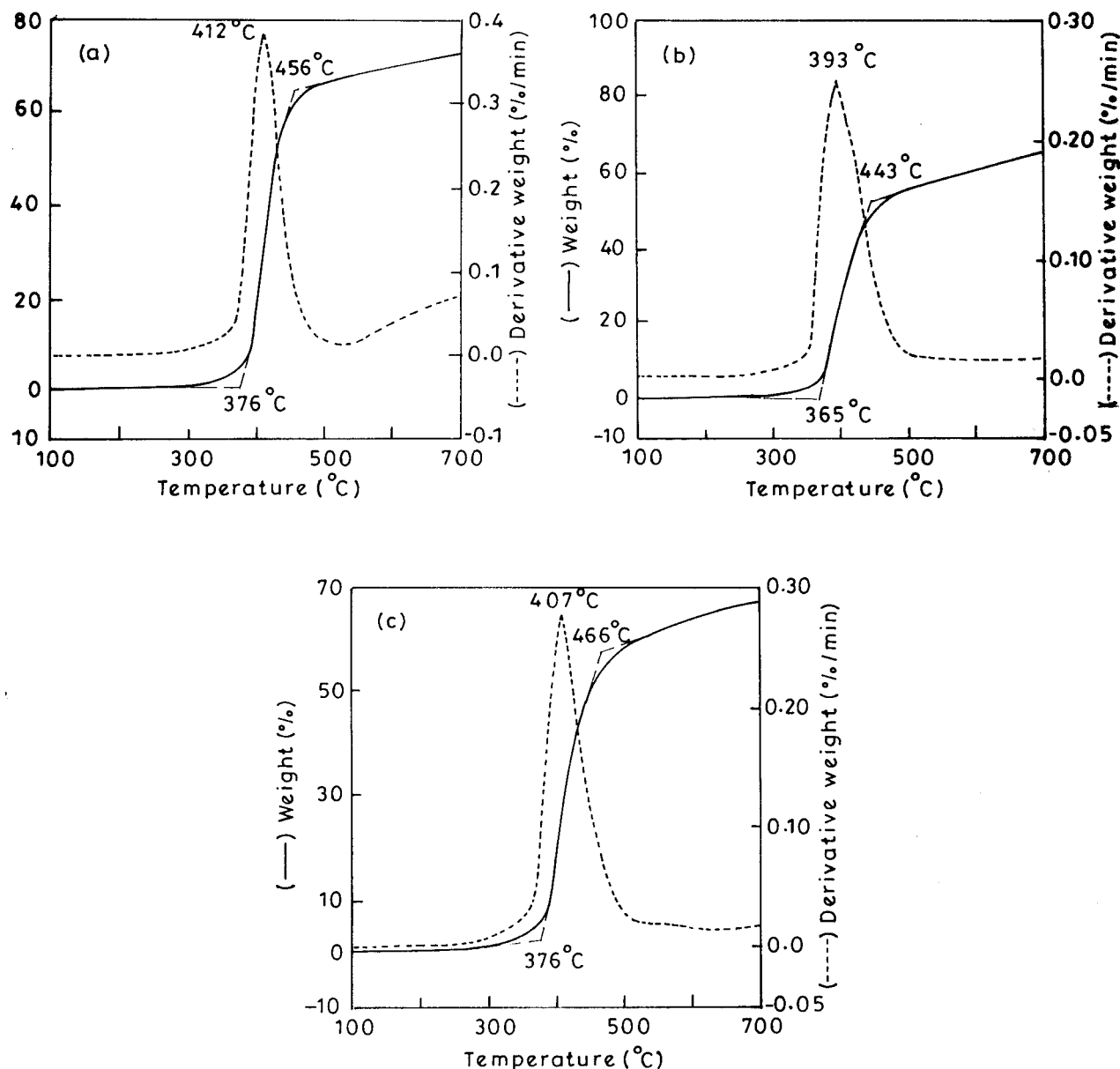


Figure 4 TG/DTG traces of cured epoxy resins in a nitrogen atmosphere (heating rate = $20^{\circ}\text{C min}^{-1}$): (a) EpS1, (b) EpS2, and (c) EpS3.

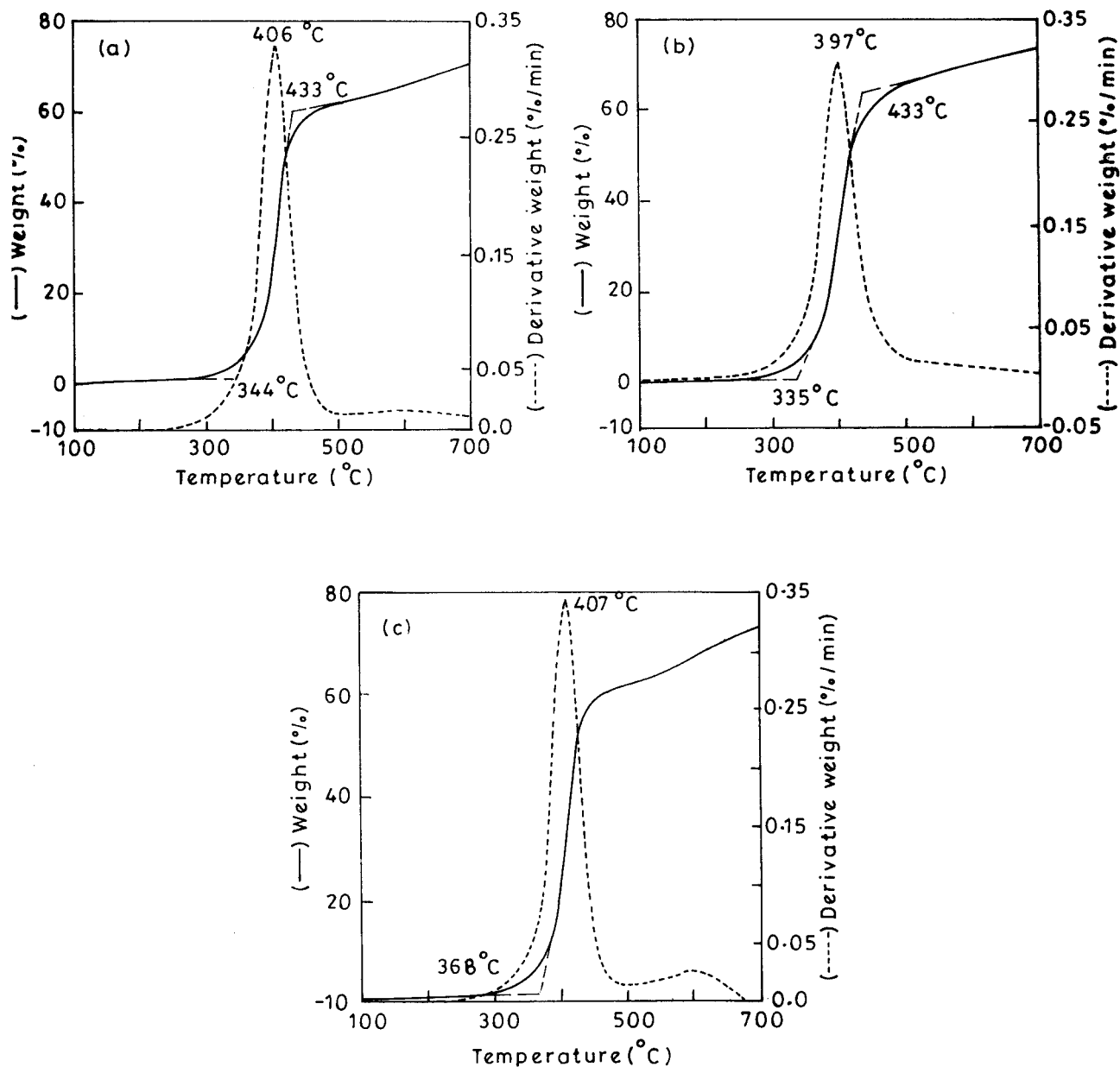


Figure 5 TG/DTG traces of cured epoxy resins in a nitrogen atmosphere (heating rate = 20°C min⁻¹): (a) EB1, (b) EB2, and (c) EB3.

TABLE VII
Results of the TG Studies of DGEBA Cured with a Mixture of Amide-Amines (E) and DDS

Sample designation	E (mol)	IDT (°C)	T _{max} (°C)	FDT (°C)	Char yield at 650°C (%)
EE1	0.25	373.6	395.1	437.8	35.5
EE2	0.5	369.1	405.3	435.6	46.5
EE3	0.75	360.1	392.4	450.3	36.7
EE	1.0	369.5	398.0	424.8	27.8

TABLE VIII
Results of the TG Studies of DGEBA Cured with a Mixture of Amide-Amines (M) and DDS

Sample designation	M (mol)	IDT (°C)	T _{max} (°C)	FDT (°C)	Char yield at 650°C (%)
EM1	0.25	370.6	410.0	437.3	29.1
EM2	0.5	357.7	399.7	421.2	33.8
EM3	0.75	357.5	402.1	441.7	37.5
EM	1.0	342.8	395.5	433.3	34.9
		490.0	563.0	631.8	

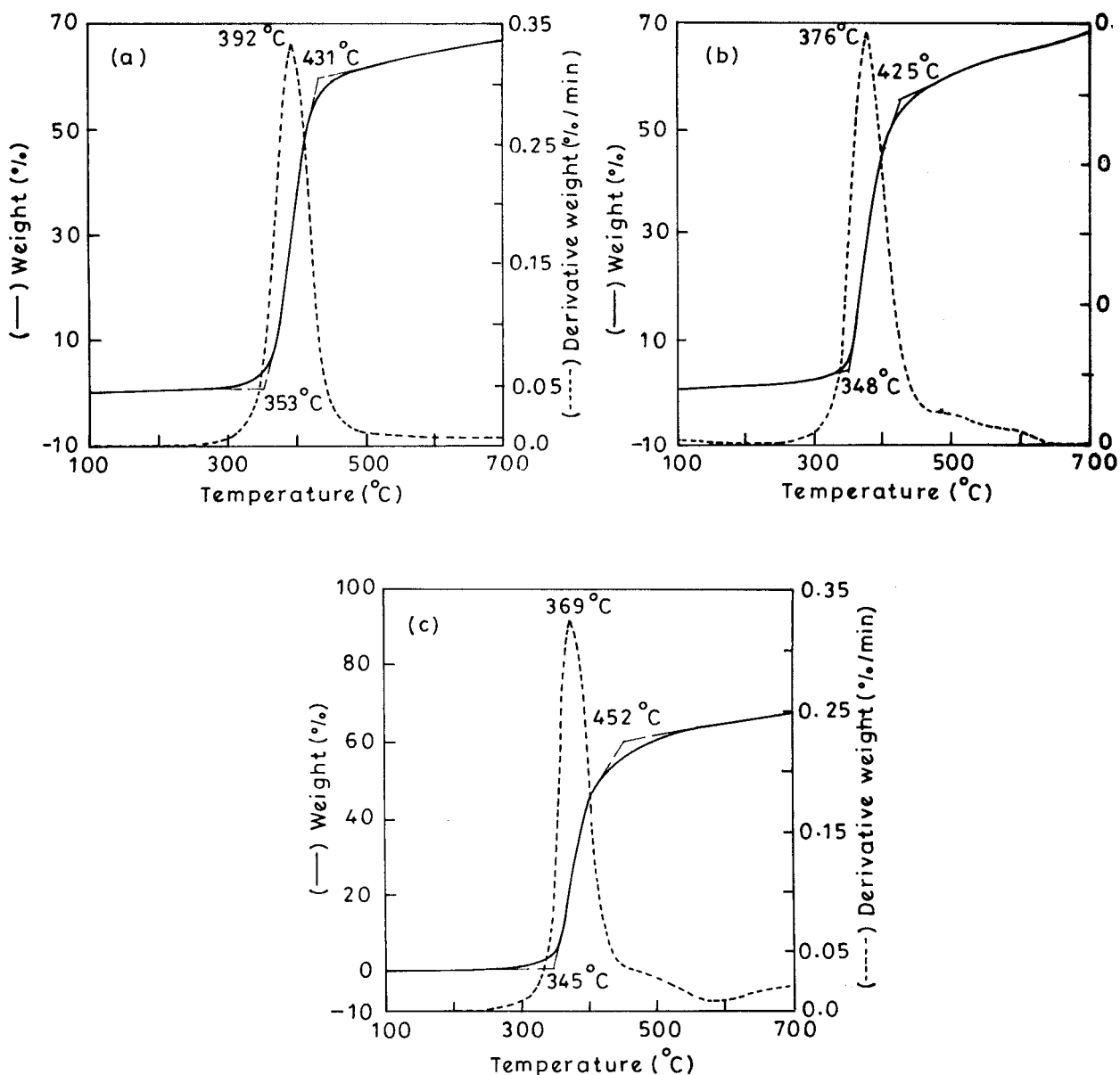


Figure 6 TG/DTG traces of cured epoxy resins in a nitrogen atmosphere (heating rate = $20^{\circ}\text{C min}^{-1}$): (a) ET1, (b) ET2, and (c) ET3.

TABLE IX
Results of the TG Studies of DGEBA Cured with a Mixture of Amide-Amines (mS) and DDS

Sample designation	mS (mol)	IDT ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	FDT ($^{\circ}\text{C}$)	Char yield at 650°C (%)
EmS1	0.25	342.9	403.4	434.8	31.2
EmS2	0.5	344.8	389.3	425.6	30.8
EmS3	0.75	334.3	384.1	432.8	32.3
EmS	1.0	369.9	387.1	428.2	16.4

TABLE X
Results of the TG Studies of DGEBA Cured with a Mixture of Amide-Amines (pS) and DDS

Sample designation	pS (mol)	IDT ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	FDT ($^{\circ}\text{C}$)	Char yield at 650°C (%)
EpS1	0.25	375.9	411.8	456.3	28.4
EpS2	0.5	365.3	393.1	443.0	36.6
EpS3	0.75	376.4	407.3	466.5	33.8
EpS	1.0	362.7	413.4	438.1	22.2

The initial decomposition temperature (IDT) is the temperature at which the sample starts decomposing. It was determined by extrapolation with the steep portion of the weight loss curve and the initial base line.

The final decomposition temperature (FDT) is the temperature at which the weight loss is complete. It was also obtained by extrapolation.

The temperature at which the rate of weight loss was maximum (T_{\max}) was obtained from DTG traces. The temperature corresponding to the peak position in DTG trace was taken as T_{\max} .

Figures 4(a–c), 5(a–c), and 6(a–c) show the TG/DTG traces of DGEBA cured isothermally (cured at 200°C for 2 h) with a mixture of amide–amines and DDS. The results are summarized in Tables VII–XII. A single-step decomposition was observed in all of the samples. Char yields were almost similar in the samples cured with amide–amines (E, pS, or mS) or DDS. Char yields were higher than either of their constituents when mixtures of amide–amines and DDS was used. A synergistic behavior was observed when mixtures of E, M, mS, or pS and DDS was used, whereas a mixture of B or T and DDS showed antagonism in char yield.

CONCLUSIONS

The addition of a 0.25 molar fraction of D to amide–amines decreased T_i significantly. T_{onset} and T_p also showed a decrease on the addition of D. These studies clearly indicate that the curing of an epoxy resin can be controlled and tailored with a mixture of amines as hardeners. Novel silicon-containing amide–amine curing agents in combination with a conventional curing agent, that is, 4,4' DDS, showed the effects of structure on curing behavior and thermal stability.

TABLE XI
Results of the TG Studies of DGEBA Cured with a Mixture of Amide–Amines (B) and DDS

Sample designation	B (mol)	IDT (°C)	T_{\max} (°C)	FDT (°C)	Char yield at 650°C (%)
EB1	0.25	343.9	405.7	433.6	31.8
EB2	0.5	334.9	397.1	433.5	28.2
EB3	0.75	367.5	406.7	433.6	29.4
EB	1.0	314.9	363.3	382.3	50.8
		382.3	477.3	554.5	

TABLE XII
Results of the TG Studies of DGEBA Cured with a Mixture of Amide–Amines (T) and DDS

Sample designation	T (mol)	IDT (°C)	T_{\max} (°C)	FDT (°C)	Char yield at 650°C (%)
ET1	0.25	352.6	392.2	431.8	34.1
ET2	0.5	348.1	376.2	425.2	33.8
ET3	0.75	344.7	369.5	457.5	33.4
ET	1.0	333.2	362.1	407.7	38.2

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