

# Studies of the Curing Kinetics and Thermal Stability of Epoxy Resins Using a Mixture of Amines and Anhydrides

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Received 9 November 2004; accepted 14 April 2005

DOI 10.1002/app.22769

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This article describes the curing and thermal behavior of diglycidyl ether of bisphenol A with phthalic anhydride (PA)/pyromellitic anhydride/diaminodiphenyl sulfone (DDS) or a mixture of anhydrides and amines in varying ratios as curing agents. The kinetics of the curing behavior was investigated with a multiple-rate method. The activation energy of the curing reaction as determined in accordance with Ozawa's method was found dependent on the structure of the anhydride and on the ratio of amines to anhydrides. The activation energy was highest with sample

DP3 (0.25 : 0.75) and DM3 (0.25 : 0.75). We evaluated the thermal stability of epoxy resin, cured isothermally, by recording thermogravimetric traces in a nitrogen atmosphere. The char yield was highest for resins cured with a mixture of DDS and PA (0.5 : 0.5) and a mixture of DDS and pyromellitic dianhydride (0.25 : 0.75). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3919–3925, 2006

**Key words:** curing of polymers; kinetics (polym.); thermal properties

## INTRODUCTION

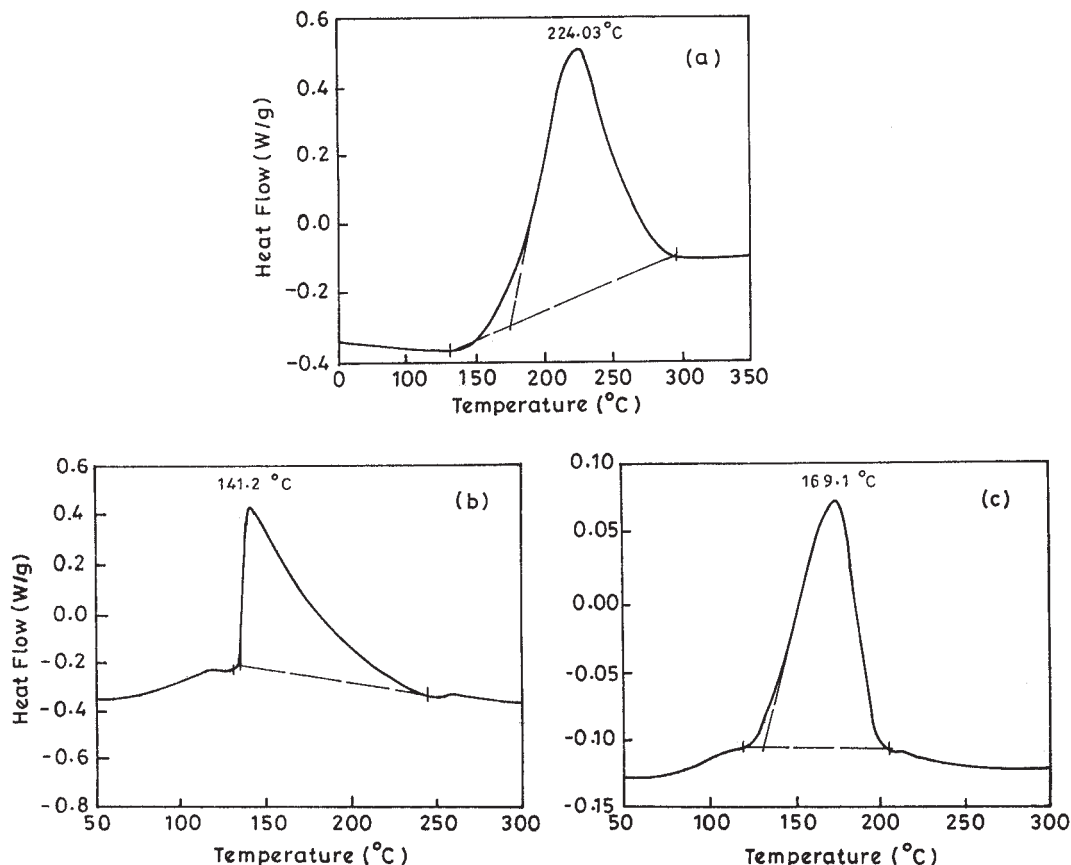
The properties and performance of epoxy resins are dependent on the type of epoxy resin, the curing agent, and the curing conditions. If the chemical structure of cured epoxy polymers are constituted of an aromatic and/or heterocyclic ring, their thermal resistance is superior to those with constituents with flexible or aliphatic chains. Imide compounds and polymers that contain aromatic and/or heterocyclic groups can offer desirable high-temperature stabilities. Therefore, the use of imide groups to modify the structure of epoxy to enhance its thermal resistance has received great attention in the research community.<sup>1</sup> The curing of epoxy resin has been extensively investigated with amines of varying structure and with acid/anhydrides as curing agents.<sup>2–4</sup> However, conventional epoxy resins are inefficient for satisfying the required properties in the field of advanced materials that require high thermal and flame resistances.<sup>5,6</sup>

Polyimides/polyamides have also been blended with epoxies to improve their toughness, heat, and chemical resistance. However, the physical blending of epoxy with polyamide has had a very little effect on its thermal stability. Polyimide/poly(amide acids)

end-capped with amines have been used as curing agents for epoxy to impart a higher thermal stability and flame resistance. Hay et al.<sup>7</sup> studied the molding of linear unreactive polyimide for the toughening of an epoxydiaminodiphenyl sulfone system. They achieved an increase in the fracture toughness without any change in the modulus, but there was little influence on the thermal capability across the range of the modifying polyimides. Another example is the incorporation of polyimide–siloxane in epoxy to form protective coatings with high heat and chemical resistance.<sup>8</sup> Recently, Kakimoto et al. developed a novel epoxy system cured with poly(amide acid) followed by thermal imidization.

The curing behavior of epoxy resins with amines, amides, anhydrides, isocyanates, and aminoformaldehyde resins<sup>9,10</sup> as curing agents is well documented in the literature. The curing of the epoxy resins in the presence of amines of varying structure is well reported in the literature.<sup>12–14</sup> However, to the best of our knowledge, no reports are available on the use of mixtures of amines and anhydrides. Therefore, the main aim of this study was to investigate the curing and thermal behavior of diglycidyl ether of bisphenol A (DGEBA) with a mixture of 4,4'-diaminodiphenyl sulfone (DDS)/phthalic anhydride (PA) and a mixture of DDS and pyromellitic dianhydride (PMDA) in the ratios of 1 : 0, 0.75 : 0.25, 0.5 : 0.5, 0.25 : 0.75, and 0 : 1. The thermal stability of the epoxy resin cured isothermally was analyzed with dynamic thermogravimetry (DTG).

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**Figure 1** DSC scans of epoxy resins in the presence of (a) DDS, (b) PMDA, and (c) PA at 10°C/min in stoichiometric ratios.

## EXPERIMENTAL

### Materials

DGEBA (grade LY556, epoxy equivalent = 177; Hindustan Ciba Geigy, Delhi, India); DDS, PMDA, and PA (all from Merck); and ethyl methyl ketone (Thomas Baker, Mumbai, India) were used as received.

### Curing studies

A thermal analyzer with a TA 1500 module and a Rheometric scientific thermal instrument with a DSC-SP module were used for recording differential scanning calorimetry (DSC) scans in a static air atmosphere at heating rates ( $\Phi$ 's) of 5, 10, 15, and 20°C/min, and a sample size of  $5 \pm 2$  mg was used in each experiment for the curing studies. The samples were prepared by the dissolution of stoichiometric amounts of DDS and PA/PMDA in methyl ethyl ketone and their addition to DGEBA. This was done to facilitate uniform mixing of curing agents in DGEBA. The solvent was then removed by vacuum stripping.

The samples we obtained by taking DGEBA and DDS plus PA in a ratio of 2 : 1 and by taking DDS and PA in different molar ratios of 1 : 0, 0.75 : 0.25, 0.5 : 0.5, 0.25 : 0.75, and 0 : 1 were designated as D, DP1, DP2, DP3, and P, respectively. Freshly prepared samples

were used to monitor the curing behavior of DGEBA in the presence of stoichiometric amounts of amines and anhydrides. The molar ratio of DDS/PMDA was also varied from 1 : 0, 0.75 : 0.25, 0.5 : 0.5, 0.25 : 0.75, and 0 : 1, and the samples were designated as D, DM1, DM2, DM3, and M, respectively.

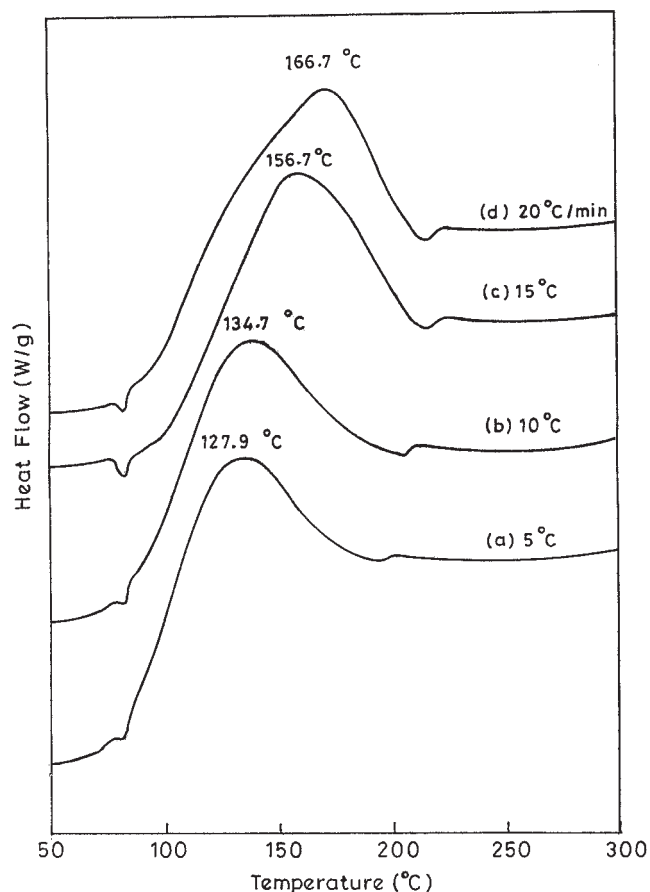
### Thermal studies

The thermal stability of samples cured isothermally in a hot-air oven (at  $150 \pm 10^\circ\text{C}$  for DDS/PA and at  $200 \pm 10^\circ\text{C}$  for the DDS/PMDA mixture for 2 h) was evaluated by thermogravimetry (TG)/DTG traces in a nitrogen atmosphere (flow rate =  $60 \text{ cm}^3/\text{min}$ ). A Rheometric scientific thermal analyzer with a TG 1500+ module was used to record TG/DTG traces at a  $\Phi$  of 20°C/min with a sample size of  $10 \pm 2$  mg.

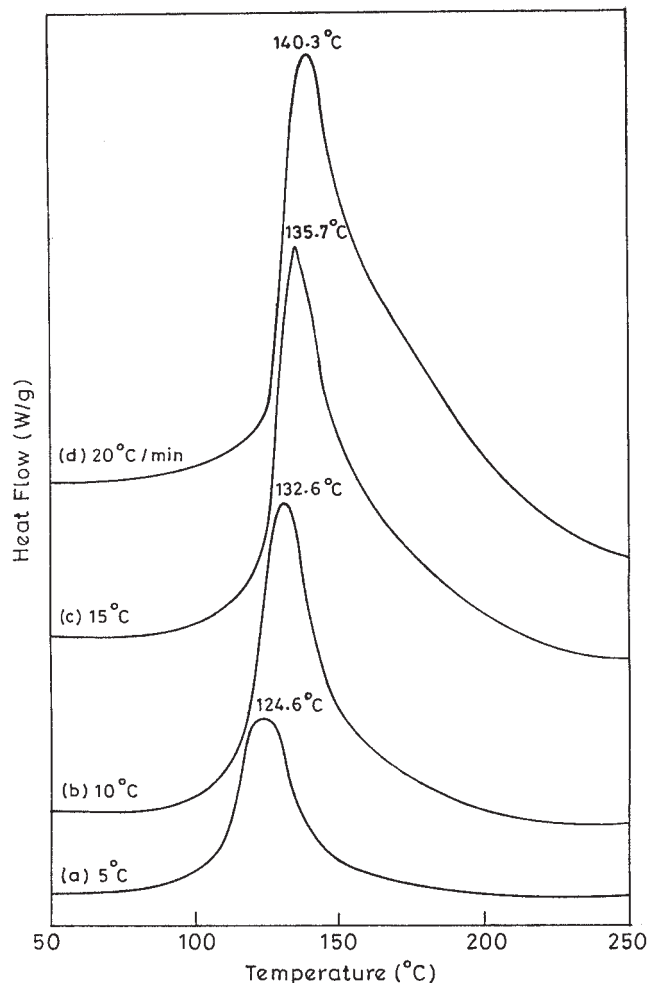
## RESULTS AND DISCUSSION

### Curing studies

The curing of epoxy resin depends on the nature of curing agents and on the stoichiometry. The exothermic transition associated with curing was characterized by the following parameters:



**Figure 2** DSC scans of the epoxy resins in the presence of a mixture of DDS and PA at a molar ratio of 0.75 : 0.25 at various  $\Phi$ 's.



**Figure 3** DSC scans of the epoxy resins in the presence of a mixture of DDS and PMDA at a molar ratio of 0.25 : 0.75 at various  $\Phi$ 's.

**TABLE I**  
Results of DSC Scans of DGEBA in the Presence of a Mixture of DDS and PA

Sample designation	DDS/PA molar ratio	Heating rate (°C/min)	$T_i$ (°C/min)	$T_{onset}$ (°C/min)	$T_p$ (°C/min)	$T_f$ (°C/min)	$\Delta H$ (J/g)	$E$ (kJ/mol)
D	1:0	5	119.8	158.1	210.1	274.4	255.0	60.0
		10	131.4	174.6	224.0	295.7	264.4	
		15	143.9	181.7	232.4	294.4	225.5	
		20	190.3	198.2	246.5	311.8	186.3	
DP1	0.75 : 0.25	5	82.1	82.3	127.9	190.7	143.0	49.9
		10	82.9	87.6	134.8	204.0	94.3	
		15	84.2	117.9	156.7	217.8	81.9	
		20	83.3	97.9	166.7	213.1	85.9	
DP2	0.5 : 0.5	5	67.5	92.9	124.8	212.9	84.6	22.5
		10	84.2	92.1	168.7	205.7	76.0	
		15	89.1	96.9	142.4	218.9	82.9	
		20	99.9	100.5	139.0	218.9	106.5	
DP3	0.25 : 0.75	5	62.6	133.1	146.8	180.0	81.2	79.2
		10	85.8	96.7	157.5	189.9	87.8	
		15	89.5	136.9	171.7	200.3	89.5	
		20	152.5	159.6	174.4	269.4	116.4	
P	0 : 1	5	116.2	129.5	173.6	169.1	206.1	21.1
		10	119.1	130.1	169.1	173.5	205.0	
		15	134.7	144.4	201.4	201.3	249.1	
		20	141.4	152.3	209.7	209.7	242.7	

TABLE II  
Results of DSC Scans of DGEBA in the Presence of a Mixture DDS and PMDA

Sample designation	DDS/PMDA molar ratio	Heating rate (°C/min)	$T_i$ (°C/min)	$T_{onset}$ (°C/min)	$T_p$ (°C/min)	$T_f$ (°C/min)	$\Delta H$ (J/g)	$E$ (kJ/mol)
D	1 : 0	5	119.8	158.1	210.1	274.4	255.0	60.0
		10	131.4	174.6	224.0	295.7	264.4	
		15	143.9	181.7	232.4	294.4	225.5	
		20	190.3	198.2	246.5	311.8	186.3	
DM1	0.75 : 0.25	5	97.4	126.0	137.7	183.4	228.6	109.2
		10	95.2	132.6	144.6	191.9	210.5	
		15	103.8	139.0	150.7	191.9	221.3	
		20	110.9	142.1	154.8	199.4	143.9	
DM2	0.5 : 0.5	5	77.1	113.4	123.8	213.3	296.5	91
		10	86.7	120.4	131.2	229.2	276.3	
		15	90.3	123.7	136.4	228.5	271.3	
		20	120.5	127.3	141.7	199.4	176.6	
DM3	0.25 : 0.75	5	74.3	108.3	124.6	199.0	281.8	112.8
		10	80.7	115.5	132.6	214.7	266.1	
		15	86.4	123.2	135.7	214.3	202.5	
		20	87.8	126.9	140.3	248.4	260.7	
M	0 : 1	5	119.4	124.9	134.9	230.3	224.4	33.4
		10	133.3	135.0	141.2	244.2	238.6	
		15	144.6	146.0	190.0	256.6	129.4	
		20	146.1	147.8	198.1	264.8	176.3	

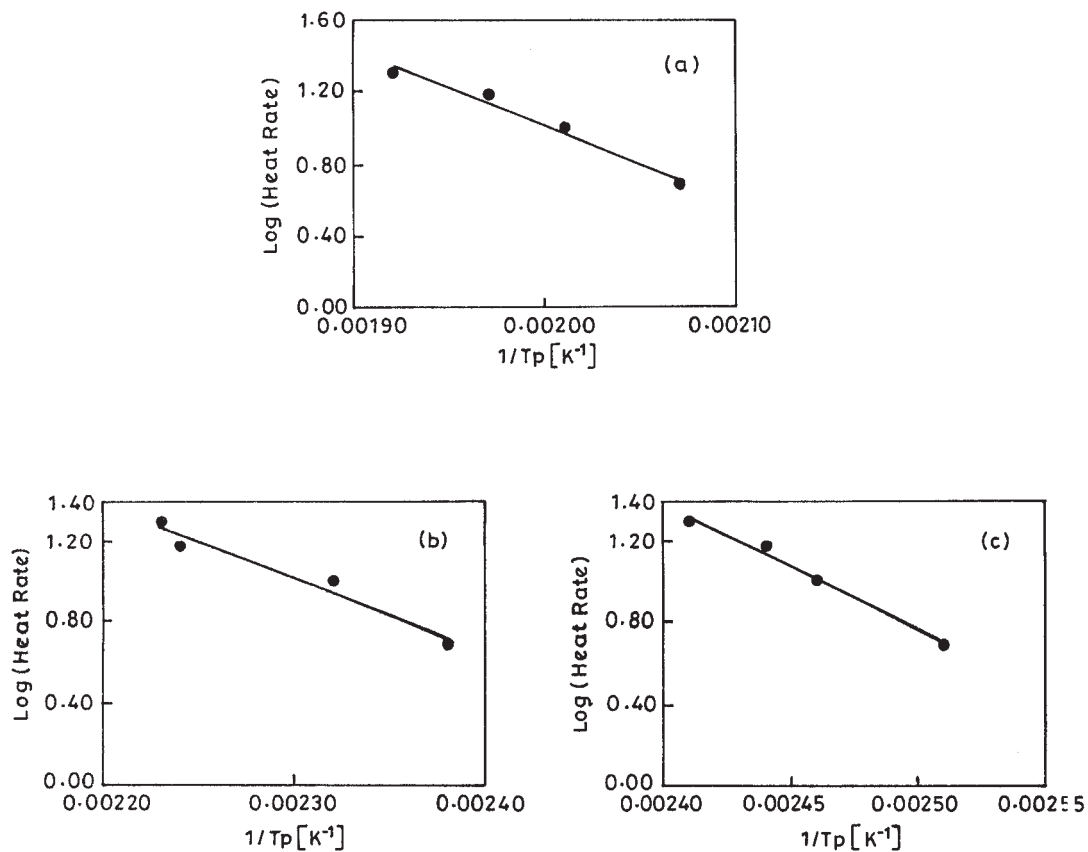
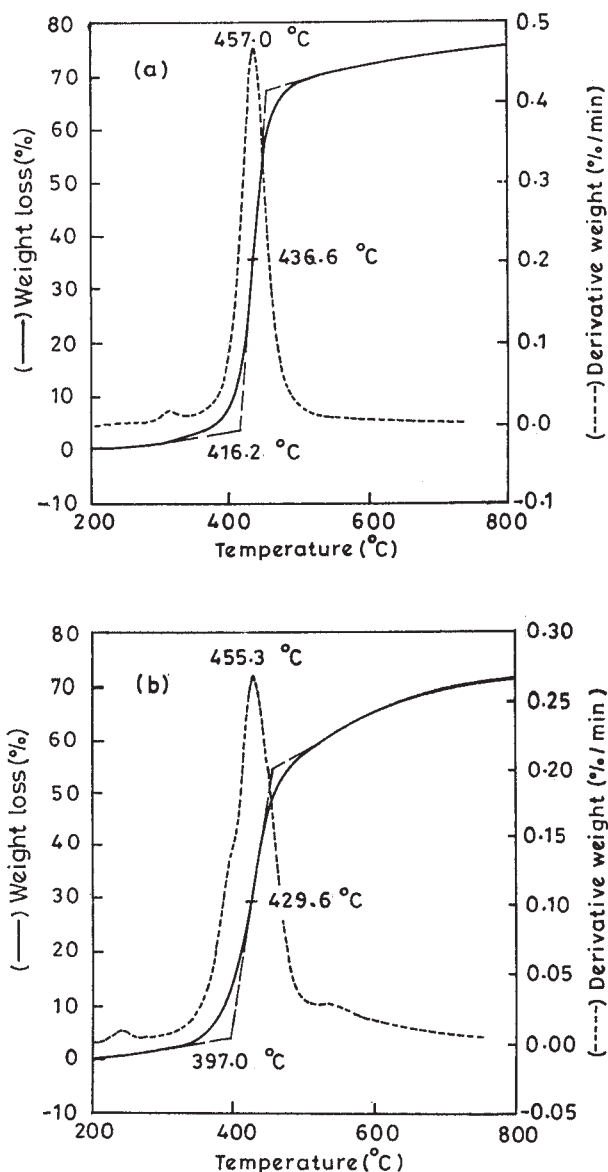


Figure 4 Plot of  $\log \Phi$  versus  $1/T_p$ : (a) D (DGEBA/DDS = 2 : 1), (b) DP3 (DDS/PA = 0.25 : 0 : 75), and (c) DM3 (DDS/PMDA = 0.25 : 0.75).



**Figure 5** TG/DTG traces of the cured epoxy resins (a) DP2 (DDS/PA = 0.5 : 0.5) and (b) DM3 (DDS/PMDA = 0.25 : 0.75) at a  $\Phi$  of 20°C/min in a nitrogen atmosphere.

- $T_i$  = the kickoff temperature where the curing started.
- $T_{\text{onset}}$  = the temperature where the first detectable heat was released. It was obtained by

extrapolation of the steepest portion of the curve.

- $T_p$  = the temperature of the peak position of the exotherm.
- $T_f$  = the temperature of the end of the curing exotherm obtained by extrapolation.
- $\Delta H$  = the heat of curing, calculated by measurement of the area under the exothermic transition.

Figure 1(a,c) shows the DSC scans of epoxy resins in the presence of DDS and PA at 10°C/min in a stoichiometric ratio. The DSC scans of epoxy resins in the presence of the DDS/PA mixture in varying molar ratios at 10°C/min are shown in Figure 2. The results of the DSC scans are summarized in Table I. The DSC scans of the samples cured isothermally (at 150 ± 10°C in the hot-air oven for 2 h) showed no residual exotherm. A broad exothermic transition was observed in the temperature range 110–311°C, which was dependent on  $\Phi$ , the nature of curing agent, and the molar ratio of amine/PA. With DDS (sample D),  $T_p$  was higher than with PA (sample P). For samples cured with a mixture of amines and anhydrides, a single exotherm was observed, which thus indicated that they acted as cocuring agents and did not show separate curing exotherms. With the incorporation of PA into the system containing DDS, significant reductions in  $T_i$ ,  $T_{\text{onset}}$ ,  $T_p$ , and  $T_f$  were observed, which decreased with increasing amounts of PA up to 0.5 (DP2) and was followed by an increase. All of the temperatures were still lower than either of the two. This showed that the use of DDS/PA catalyzed the curing thermal reaction.

Figure 1(b) shows the DSC scan of the epoxy resin in the presence of DDS/PMDA at 100°C/min in stoichiometric ratios. The DSC scans of epoxy resins in the presence of a mixture of DDS and PMDA at a molar ratio of 0.25 : 0.75 at varying  $\Phi$  are shown in Figure 3, and the results are summarized in Table II. In all these samples, a single exotherm was observed in the presence of the mixture, and the curing temperatures were dependent on the molar ratios. There was little effect on the heat of polymerization. The DSC scans of samples cured isothermally (at 200 ± 10°C in a hot-air oven for 2 h) showed no residual exotherm.  $T_p$  was

**TABLE III**  
Results of the Thermal Stability of Isothermally Cured Epoxy Resins (DDS + PA) at a Heating Rate of 20°C/min

Sample designation	DDS/PA molar ratio	IDT (°C)	$T_{\text{max}}$ (°C)	FDT (°C)	Char yield at 800°C
D	1 : 0	394.9	419.9	466.0	19.2
DP1	0.75 : 0.25	420.8	443.8	464.9	17.7
DP2	0.5 : 0.5	416.2	438.6	457.0	24.7
DP3	0.25 : 0.75	380.5	438.3	463.0	17.0
P	0 : 1	361.3	414.4	456.5	22.3

TABLE IV  
Results of the Thermal Stability of Isothermally Cured Epoxy Resins (DDS + PMDA) a Heating Rate of 20°C/min

Sample designation	DDS/PMDA molar ratio	IDT (°C)	$T_{\max}$ (°C)	FDT (°C)	Char yield at 800°C
D	1 : 0	394.9	419.9	466.0	19.2
DM1	0.75 : 0.25	412.5	430.5	454.1	25.3
DM2	0.5 : 0.5	394.2	434.0	461.4	23.8
DM3	0.25 : 0.75	397.1	429.6	455.4	28.6
M	0 : 1	390	420.4	454.3	18.0

lower for DGEBA cured with PMDA (sample M) compared to with DDS (sample D). A significant decrease in curing temperature was observed when we used a small amount of anhydrides in the DGEBA/DDS system. A further increase in PMDA content resulted in an increase in  $T_p$ .

### Curing kinetics

Kinetic parameters of curing reactions can be obtained from dynamic DSC scans or isothermal experiments.

The dynamic method was used in this study, and the DSC scans were recorded at different  $\Phi$ 's for the samples. Typical DSC scans for samples DP3 and DM3 obtained at different  $\Phi$ 's are shown in Figures 2 and 3. The characteristic curing temperatures for the DGEBA at different  $\Phi$ 's in the presence of different amines and anhydrides are summarized in Tables I and II. As expected for all of the samples, the curing temperatures increased with increasing  $\Phi$ . The activation energy ( $E$ ) of the curing reaction was calculated with Ozawa's<sup>15,16</sup> method with the following assumptions:

1.  $T_p$  represented a point of constant conversion.
2. The reaction followed the first-order kinetics.
3. The temperature dependence of the reaction rate constant obeyed an Arrhenius equation.

The data from the dynamic DSC measurements were analyzed in accordance with the following equation:

$$\log \phi = 1/2.303 \times \ln \phi = -0.4567E/RT + \log AE/R - \log f(\alpha) - 2.315 \quad (1)$$

where  $\Phi$  is the heating rate,  $E$  is the activation energy,  $R$  is the gas constant,  $T$  is the temperature in Kelvin,  $A$  is the arrhenius constant, and  $f(\alpha)$  is the conversion-dependent term.

Assuming a constant conversion at  $T_p$ , we obtained plots of  $\log \Phi$  versus  $1/T_p$ ; these are shown in Figure

4(a–c). From the slope of these lines,  $E$  was calculated for the exotherm, and the results are given in Tables I and II.  $E$  was highest with DP3 (0.25 : 0.75) and DM3 (0.25 : 0.75).

### Thermal stability

Figure 5(a,b) shows the TG/DTG traces of samples DP2 and DM3. In all of the samples, a single-step decomposition was observed. The relative thermal stability of the cured resins was evaluated by a comparison of the initial decomposition temperature (IDT), the temperature of maximum rate of weight loss ( $T_{\max}$ ), the final decomposition temperature (FDT), and the percentage char at 800°C.

The results of TG/DTG scans are summarized in Tables III and IV. All of the samples were stable up to  $390 \pm 15^\circ\text{C}$ . The degradation temperatures were dependent on the structure of the network. IDT, FDT, and  $T_{\max}$  were lower when either DDS or PA was used as the curing agent in samples D or P (cured with DDS or PA alone) compared to samples cured with a mixture of DDS and PA. Similar behavior was observed for the DM samples cured with a mixture of DDS and PMDA. Char yield was higher in the DM samples compared to the DP samples.

### CONCLUSIONS

From these studies, we concluded that thermally stable thermosetting matrices with lower curing temperatures can be obtained with a mixture of amines and anhydrides. The thermal stability of the cured network was higher in the presence of PMDA than in the presence of PA.

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