

Curing of Epoxy Resin Using Imide-Amines

Pooja Sharma,¹ Veena Choudhary,² A. K. Narula¹

¹School of Basic & Applied Sciences, Guru Gobind Singh Indraprastha University, Kashmere Gate, Delhi, India

²Centre for Polymer Science & Engineering, Indian Institute of Technology, Hauz Khas, New Delhi, India

Received 28 September 2005; accepted 21 March 2006

DOI 10.1002/app.24580

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

ABSTRACT: The curing behavior of diglycidyl ether of bisphenol-A (DGEBA) was investigated by differential scanning calorimetry, using varying molar ratios of imide-amines and 4,4'-diaminodiphenyl sulfone (DDS). The imide-amines were prepared by reacting 1 mol of pyromellitic dianhydride (P) with excess (2.5 mol) of 4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl methane (M), or 4,4'-diaminodiphenyl sulfone (S) and designated as PE, PM, PS. Structural characterization was done using FTIR, ¹H NMR, ¹³C NMR spectroscopic techniques and elemental analysis. The mixture of imide-amines and DDS at ratio 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. The multiple heating rate method (5, 10, 15, and 20°C/min) was used to study the curing kinetics of

epoxy resins. The peak exotherm temperature was found to be dependent on the heating rate, structure of imide-amine, and also on the ratio of imide-amine : DDS used. Activation energy was highest in case of epoxy cured using a mixture of DDS : imide-amine of a ratio of 0.75 : 0.25. Thermal stability of the isothermally cured resins was also evaluated in a nitrogen atmosphere using dynamic thermogravimetry. The char yield was highest in case of resins cured using mixture of DDS : PS (0.25 : 0.75; EPS-3), DDS : PM (0.25 : 0.75; EPM-3), and DDS : PE (0.75 : 0.25; EPE-1). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3503–3510, 2006

Key words: curing kinetics; DGEBA; imide-amine; diaminodiphenylsulfone; thermal properties

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 improving the thermal and flame resistance of these resins such as incorporation of halogen and/or phosphorus into the epoxy polymer skeleton or by *in situ* formation of imide.^{1–8} Currently, the incorporation of halogen into epoxy polymers is not preferred for environmental reasons; therefore, phosphorous containing amines of varying structure have been used to investigate the effect of structure on thermal stability.⁹

Imide polymers are known for their high thermal stability and it is well reported in the literature that if chemical structures of the cured epoxy polymers are constituted with aromatic and/or heterocyclic rings, their thermal resistance is superior to those based on flexible or aliphatic chains. The reaction of diglycidyl ether of bisphenol-A (DGEBA) with trialkyl or aryl phosphate followed by curing with 4, 4'-diaminodiphenylsulfone gave products with good thermal stability and resistance.¹⁰ The reaction of DGEBA with an

amide-amine with both silicon and phosphorous gave products with good thermal stability and flame resistance.¹¹ Imide compounds and polymers, which contain aromatic and/or heterocyclic rings, can offer desirable high temperature stability. Therefore, using imide groups to modify the structure of epoxy to enhance its thermal resistance has received great attention in the research community.¹² To improve thermal resistance of the epoxy resin, curing agent containing imide groups such as hydroxyl-terminated imide compounds,¹³ imide-acid,^{14,15} imide-amine or imide-anhydride was used.

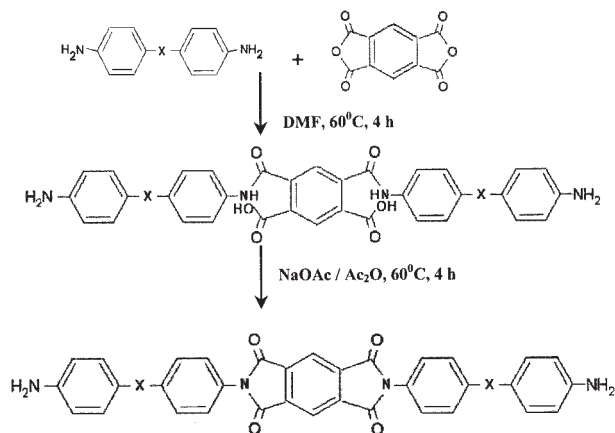
The primary objective of this study focused on improving the thermal and flame resistance of an epoxy resin via structural modification of the cured epoxy network by using aromatic diamines having preformed imide rings. Polymers with a sulfone group are known to have good oxidative, thermal and hydrolytic stability, and good mechanical properties.^{16,17} Hence, a modifier with a sulfone group will have an additional effect on the properties of a modified network. So, we thought it is interesting to use a mixture of imide-amine and diaminodiphenyl sulfone (DDS) as a curing agent for DGEBA.

EXPERIMENTAL

Materials

DGEBA (grade LY556, having an epoxide equivalent of 177) was procured from Hindustan Ciba Geigy Ltd.

Correspondence to: A. K. Narula (narulaipu@indiatimes.com).



Scheme 1 Synthesis of aromatic imide-amines. X = —O— (PE); —CH₂— (PM); —SO₂— (PS). Letters within parenthesis represents the designation of imide-amines.

4,4'-Diaminodiphenyl sulfone (S), 4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl methane (M), and pyromellitic dianhydride (P) all were purchased from

Aldrich and used as received. *N,N'*-Dimethyl formamide (DMF, Qualigens) was dried by keeping it over calcium hydride for 72 h followed by distillation under reduced pressure. Ethanol (Merck) and sodium acetate (Qualigens) were used as received. Acetic anhydride (Qualigens) was distilled before use.

The imide-amines were prepared according to Scheme 1.

The detailed procedure for the synthesis and characterization of imide-amines has been reported elsewhere.¹⁸

Curing studies

TA 2100 thermal analyzer having 910 DSC module was used for recording DSC scans at heating rates of 5, 10, 15, and 20°C/min. About 5 ± 2 mg of sample was used in each experiment. For curing studies, the samples were obtained by mixing stoichiometric amounts of imide-amines, DDS, or mixture of imide-amines and DDS in molar ratio of 0:1, 0.25:0.75, 0.5:0.5,

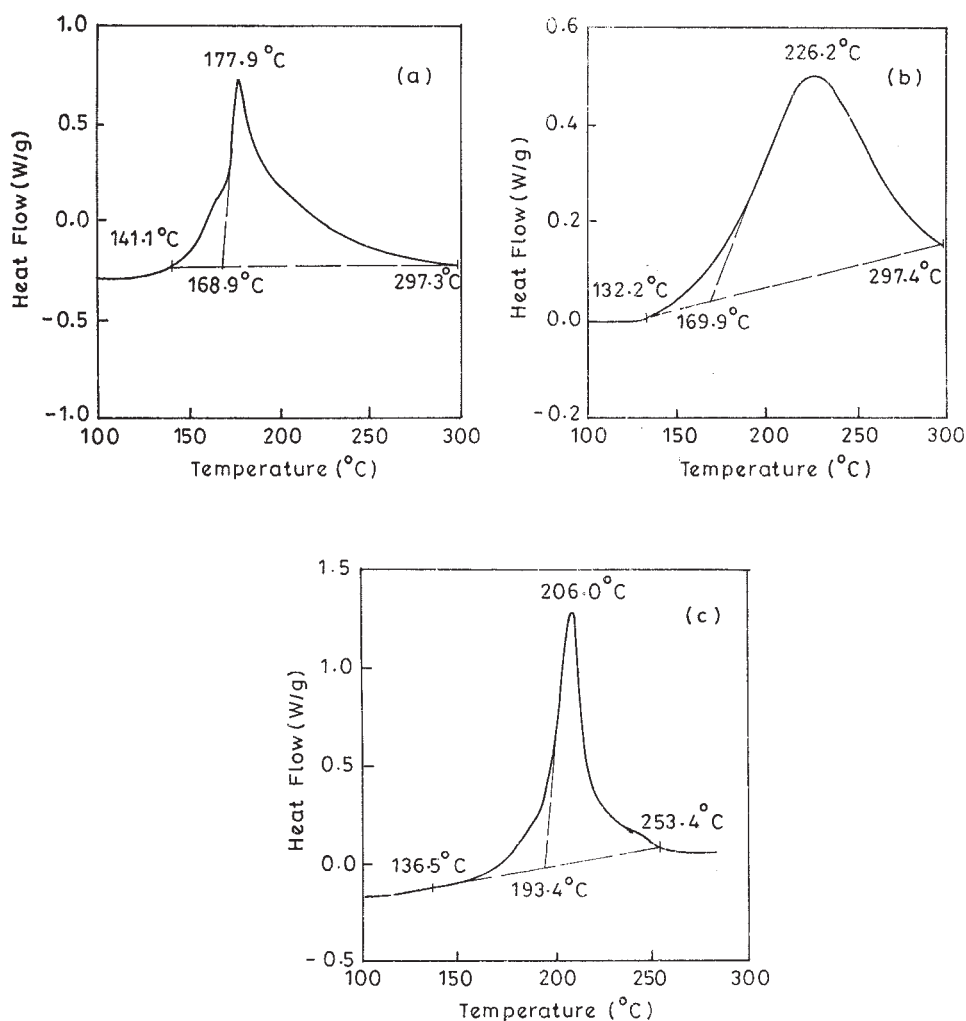


Figure 1 DSC scans of DGEBA with mixture of imide-amines and DDS of (a) EPM-3, (b) EPE-1, and (c) EPS-2 at 10°C/min.

TABLE I
Results of DSC Scan of DGEBA in the Presence of Imide-Amines (PS), DDS, and Its Mixture in Varying Molar Ratios at Different Heating Rates

Sample designation	Molar ratio of PS : DDS	Heating rate (°C/min)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (kJ/mol)
ED	0 : 1	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	
EPS-1	0.25 : 0.75	5	136.9	179.8	194.1	330.1	358.5	113.8
		10	138.4	192.8	204.9	297.4	257.7	
		15	152.4	199.8	212.1	296.1	220.1	
		20	160.2	201.6	217.0	294.7	212.2	
EPS-2	0.5 : 0.5	5	122.8	181.0	194.7	298.7	429.4	110.3
		10	136.5	193.4	206.0	253.4	174.5	
		15	165.6	200.6	211.0	267.6	166.5	
		20	181.6	207.6	217.4	294.8	173.3	
EPS-3	0.75 : 0.25	5	45.8	51.9	64.8	116.9	174.2	56.9
			132.9	140.0	186.4	283.6	316.6	93.1
		10	55.4	59.2	70.3	119.4	127.0	
			136.8	154.2	208.6	292.5	302.5	
			57.6	60.7	73.1	121.9	108.7	
EPS-0	1 : 0	5	133.1	149.9	193.4	284.0	248.1	68.3
		10	136.5	160.5	218.3	274.7	160.1	
		15	141.4	176.9	224.4	296.0	271.2	
		20	142.5	183.0	232.5	294.7	419.7	

0.75 : 0.25, and 1 : 0 with DGEBA, using minimum amount of ethanol as solvent. The solvent was removed by vacuum stripping and the freshly prepared samples were used for recording DSC traces in static air atmosphere. The epoxy samples were designated by adding prefix E to letter designation of imide-

amines (PS/PM/PE) followed by a numerical suffix indicating the molar ratio of imide-amines. For example, epoxy cured using mixture of PS:DDS in the ratio of 0.25 : 0.75, 0.5 : 0.5, 0.75 : 0.25, and 1 : 0 has been designated as EPS-1, EPS-2, EPS-3, and EPS-0 respectively. The epoxy cured using DDS alone has been

TABLE II
Results of DSC Scan of DGEBA in the Presence of Imide-Amines (PE), DDS, and Its Mixture in Varying Molar Ratios at Different Heating Rates

Sample designation	Mole ratio of PE : DDS	Heating rate (°C/min)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (kJ/mol)
EPE-1	0.25 : 0.75	5	131.2	166.4	214.3	284.6	142.8	117.4
		10	136.8	169.2	225.3	297.4	170.0	
		15	139.2	174.5	232.1	296.2	181.8	
		20	146.4	184.9	237.5	294.8	187.8	
EPE-2	0.5 : 0.5	5	143.2	184.4	199.6	270.8	193.1	101.8
		10	148.9	187.4	209.7	282.4	222.4	
		15	150.7	195.7	215.3	296.1	209.8	
		20	181.6	205.6	223.4	294.7	214.9	
EPE-3	0.75 : 0.25	5	145.6	180.4	182.3	270.6	166.5	92.2
		10	150.3	188.9	201.7	277.2	182.7	
		15	158.1	189.2	202.7	282.4	179.4	
		20	162.1	184.5	208.4	294.7	188.6	
EPE-0	1 : 0	5	148.9	170.8	179.2	227.5	150.9	109.2
		10	156.4	180.4	186.4	281.5	344.8	
		15	161.4	179.2	192.9	258.4	177.3	
		20	174.9	191.0	196.3	276.9	196.2	

TABLE III
Results of DSC Scan of DGEBA in the Presence of Imide-Amines (PM), DDS, and Its Mixture in Varying Molar Ratios at Different Heating Rates

Sample designation	Mole ratio of PM : DDS	Heating rate (°C/min)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (kJ/mol)
EPM-1	0.25 : 0.75	5	138.6	169.1	187.8	287.2	294.6	99.3
		10	148.2	180.7	198.0	285.8	209.3	
		15	150.7	190.6	220.7	296.0	217.0	
		20	152.1	192.3	222.2	294.8	256.2	
EPM-2	0.5 : 0.5	5	138.2	175.9	181.2	248.4	222.5	91.0
		10	150.0	185.6	192.2	296.8	276.1	
		15	149.3	193.1	201.5	294.7	347.9	
EPM-3	0.75 : 0.25	20	153.5	197.9	206.4	294.8	338.2	55.2
		5	135.6	163.0	158.8	290.4	213.0	
		10	141.1	168.9	177.9	297.3	218.5	
EPM-0	1 : 0	15	148.9	192.7	188.5	296.0	218.5	92.6
		20	156.4	177.0	198.6	294.8	212.7	
		5	142.5	166.6	175.1	205.8	81.7	
		10	146.4	174.2	185.7	282.2	396.3	
		15	153.4	183.8	190.0	285.3	75.8	
		20	169.9	194.2	200.5	278.7	57.0	

designated as ED. Similarly, samples cured using mixture of PE/PM and DDS were also designated.

Thermal stability

Thermal stability of the samples (cured isothermally by heating the DGEBA in the presence of DDS/PS/PM/PE or a mixture of DDS : PS/PE/PM in varying molar ratio) at $250 \pm 50^\circ\text{C}$ for 3 h in an hot air oven was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate $60 \text{ cm}^3/\text{min}$). Rheometric Scientific Module having TG1500 module was used for recording TG/DTG traces. A heating rate of $20^\circ\text{C}/\text{min}$ and powdered samples of $10 \pm 2 \text{ mg}$ were used in each experiment.

RESULTS AND DISCUSSION

Structural characterization of imide-amines

The imide-amines synthesized in the laboratory were characterized using FTIR, ^1H NMR, ^{13}C NMR spectroscopic techniques and elemental analysis. The detailed conditions for the synthesis and characterization are reported in our earlier paper.¹⁸

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 starts 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, interesting to understand the effect of structure of imide-amines on the curing behavior of DGEBA and the thermal stability of the cured network of varying structure. Figure 1(a–c) show the DSC traces of DGEBA cured using imide-amines and mixture of imide-amines and DDS at $10^\circ\text{C}/\text{min}$. In the DSC traces of all the samples, a broad exothermic transition associated with curing was observed. The exothermic transition was characterized by noting the following parameters: T_i (the kick-off temperature, where the curing starts), T_{onset} (the temperature of onset of exotherm, obtained by the extrapolation of steepest portion of the initial side of the exotherm), T_p (the temperature of the peak position of the exotherm), T_f (the temperature of the end of curing exotherm, obtained by the extrapolation of the end of the exothermic transition), and ΔH (the heat of curing calculated by the measurement area under the exothermic transition).

DDS is generally used as a hardener for curing epoxies. The incorporation of imide-amines along with DDS was expected to affect the curing behavior and the thermal stability of the cured network. Therefore, imide-amine and DDS mixtures, such as PS/DDS, PM/DDS, and PE/DDS, in varying molar ratio were used to investigate systematically the curing behavior of DGEBA in the presence of mixture.

The results of DSC scans are summarized in Tables I–III. A single exotherm was obtained in case of sam-

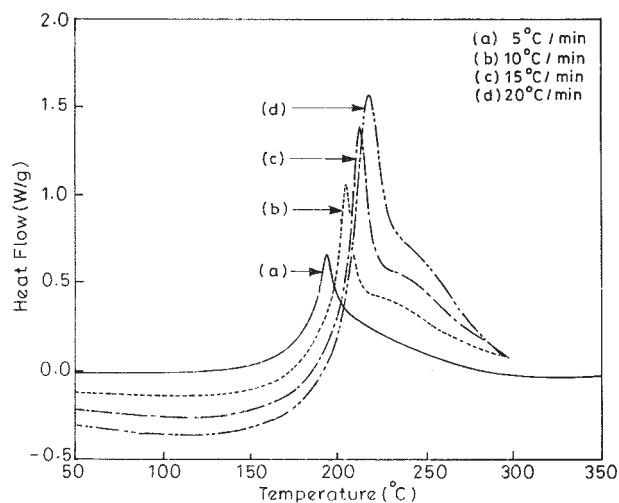


Figure 2 DSC scans of EPS-1 at different heating rates.

ples curing using DDS (sample ED), PS (EPS), PE (EPE), or PM (EPM) and mixture of DDS : PS/PM/PE in varying molar ratio except in sample EPS-3 when the molar ratio of DDS : PS was 0.25 : 0.75. In all the samples, a single curing exotherm was observed thus showing that the two amines act as cocuring agents. The peak exotherm was higher with DDS compared with that of imide-amines. Comparing imide-amines of varying structure, T_p was found to be higher in EPS-0 than that of samples EPE-0 or EPM-0. This could be due to the electron withdrawing nature of the $-\text{SO}_2-$ group, which in turn reduces the nucleophilicity of the amine and hence reduces the reactivity of the amine. A significant decrease in T_p was observed when part of DDS was replaced by imide-amine PS, PM, or PM (i.e., samples EPS-1, EPM-1, EPE-1). Further increase in imide-amine content did not show much effect on T_p .

Curing kinetics

Kinetic parameter of the curing reaction can be obtained from dynamic DSC scans or isothermal experiments. The dynamic method was used in the present study and the DSC scans were recorded at different heating rates for the samples. Figures 2– show DSC scans for resin samples EPS-1, EPE-2, and EPM-2 recorded at different heating rates. The characteristic curing temperatures for the DGEBA at different heating rates in the presence of imide-amine, DDS, and mixture of DDS : PS/PE/PM are summarized in Table I–III. As expected in all the samples, peak at curing temperature increased with the increasing heating rate. The activation energy of the curing reaction was calculated using Ozawa's method^{19,20} assuming that:

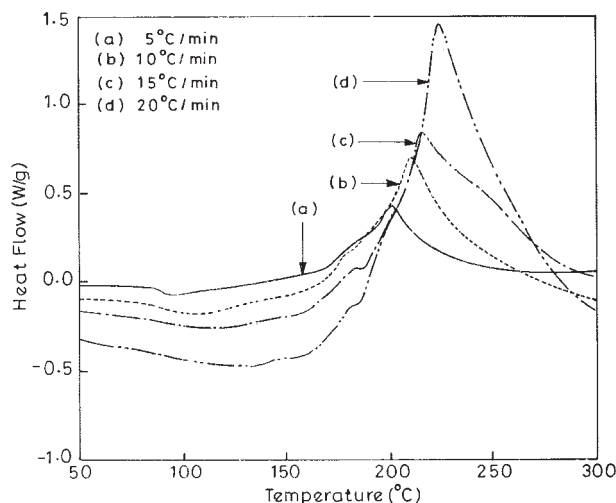


Figure 3 DSC scans of EPE-2 at different heating rates.

- i. the peak exothermic temperature T_p represents a point of constant conversion;
- ii. the reaction follows the first-order kinetics; and
- iii. the temperature dependence of the reaction rate constant obeys Arrhenius equation.

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

$$E_a = \frac{R\Delta \log \phi}{0.4567\Delta(1/T_D)}$$

where ϕ is the heating rate; E_a is the activation energy; R is the gas constant.

A plot of $\log \phi$ versus $1/T_p$ was obtained and then activation energy was calculated using standard procedure. Activation energy of curing was found to be dependent on the structure of amines and was

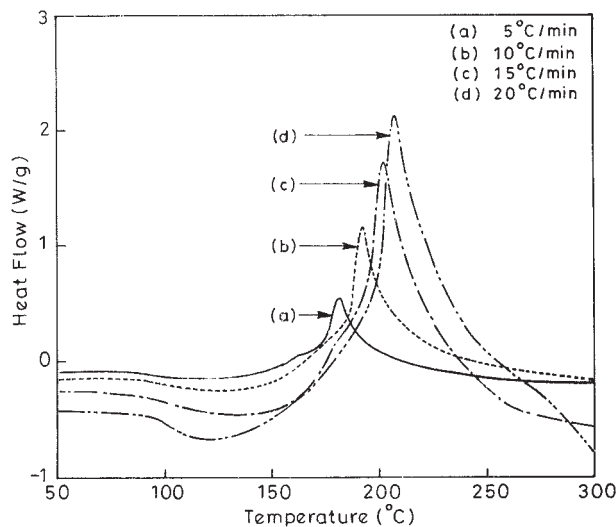


Figure 4 DSC scans of EPM-2 at different heating rates.

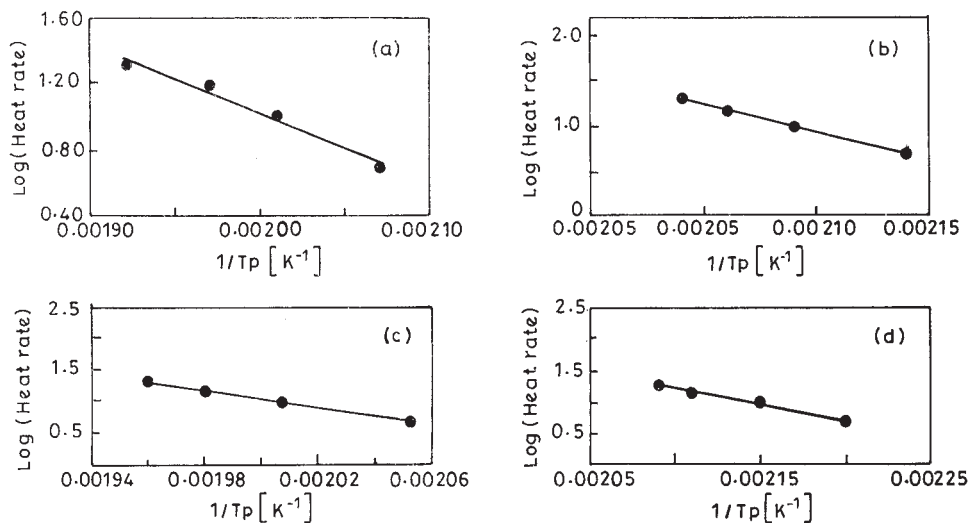


Figure 5 Activation energy plot of $\log \phi$ versus $1/T_p$ of samples (i) ED, (ii) EPS-1, (iii) EPE-1, and (iv) EPM-2.

found to be highest when PE (imide-amine) was used as the curing agent. Activation energy was also found to be dependent on the molar ratio of imide-

amines : DDS in case of samples where mixture was used. In case of EPE and EPM samples, E_{act} decreased as the amount of PE or PM was increased in

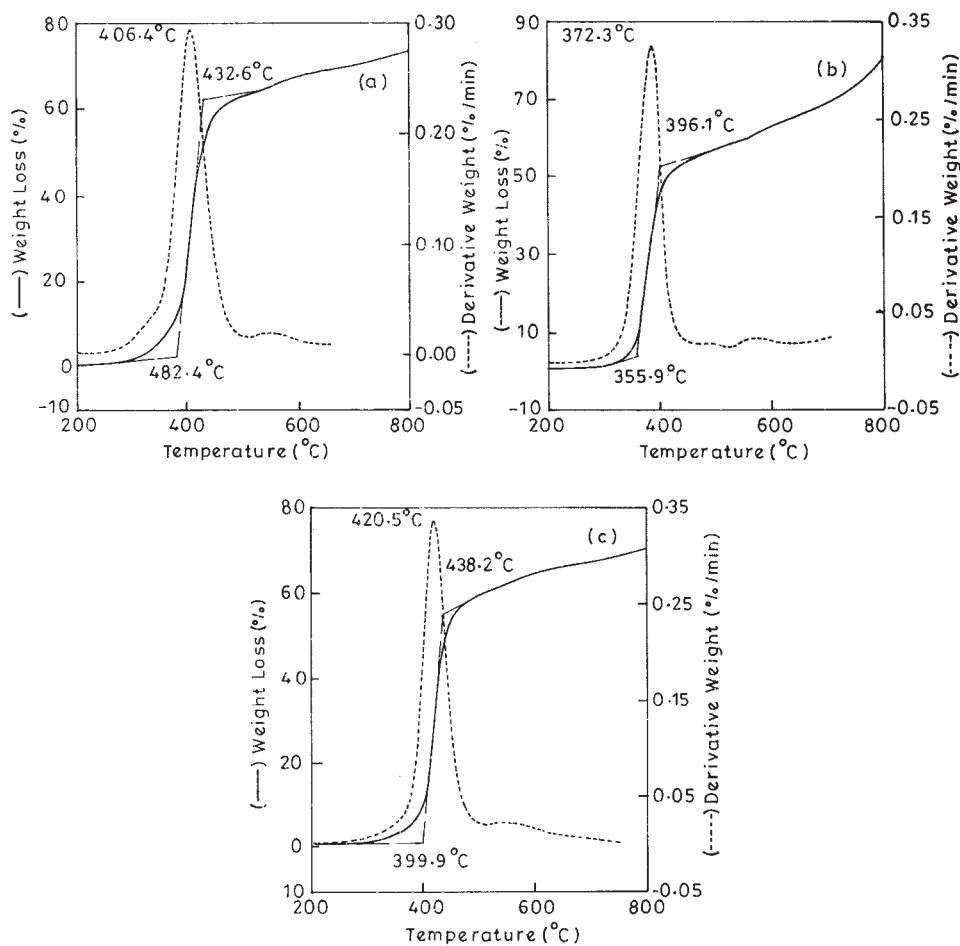


Figure 6 TG trace of (a) EPM-1, (b) EPS-3, and (c) EPE-1 at 20°C/min.

TABLE IV
Results of Thermal Stability of DGEBA Cured Isothermally Using PS, DDS, or Mixture in Nitrogen Atmosphere
(heating rate = 20°C/min)

Sample designation	Mole ratio of PS : DDS	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield (%) at 600°C	LOI (%)
ED	0 : 1	394.9	419.9	466.0	19.2	25.2
EPS-1	0.25 : 0.75	404.9	438.2	461.8	27.6	28.5
EPS-2	0.5 : 0.5	386.9	424.6	456.2	33.0	30.7
EPS-3	0.75 : 0.25	355.9	372.4	396.1	34.6	31.4
EPS-0	1 : 0	392.2	433.6	465.0	30.9	29.9

TABLE V
Results of Thermal Stability of DGEBA Cured Isothermally Using PE, DDS, or Mixture in Nitrogen Atmosphere
(heating rate= 20°C/min)

Sample designation	Mole ratio of PE : DDS	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield (%) at 600°C	LOI (%)
EPE-1	0.25 : 0.75	400.0	420.5	438.2	33.8	31.0
EPE-2	0.5 : 0.5	399.6	422.4	447.4	30.2	29.6
EPE-3	0.75 : 0.25	396.3	422.3	441.3	31.8	30.2
EPE-0	1 : 0	392.1	422.3	447.2	30.0	29.5

the mixture. Plots of $\log \phi$ versus $1/T_p$ are shown in Figure 5(a–d).

Thermal stability

Figure 6(a–c), respectively, show TG/DTG traces of epoxy resins EPS-3, EPM-1, and EPE-1 cured isothermally by heating in an air-oven. The relative thermal stability of the cured resins was evaluated by comparing initial decomposition temperature (IDT), temperature of maximum rate of mass loss (T_{max}), final decomposition temperature (FDT), and percent char yield at 600°C. The results are summarized in Table IV–VI. A single step decomposition was observed in all the samples. All the cured resins were stable up to $380 \pm 20^\circ\text{C}$ and started losing weight above this. Percent char yield increased significantly when one-fourth of DDS is being replaced by imide-amines. Increase in the imide-amine content in the mixture did not affect the char yield.

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins in accordance with Van Krevelen and Hoftyzer equation.²¹

$$\text{LOI} = 17.5 + 0.4 \text{ CR}$$

where CR = char yield.

All the samples had LOI values greater than 28. These results clearly show that flame resistant DGEBA resin can be obtained by using imide-amines as curing agents.

CONCLUSIONS

From these results, it can be concluded that the curing behavior of epoxy resins can be altered by changing the molar ratio of curing agents in a mixture and by the nature of the curing agents. Thermal stability of the cured material was found to be dependent on the structure of network. Composition of the mixture had a large effect on the curing and thermal behavior. Higher activation energy observed in the curing of epoxy with imide-amines could be due to the high molecular weight of amines; thus needs higher stoichiometric amine concentration of imide-amines as compared to DDS, which may increase the viscosity of

TABLE VI
Results of Thermal Stability of DGEBA Cured Isothermally Using PM, DDS, or Mixture in Nitrogen Atmosphere
(heating rate= 20°C/min)

Sample designation	Mole ratio of PM : DDS	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield (%) at 600°C	LOI (%)
EPM-1	0.25 : 0.75	382.5	406.4	432.6	31.3	30.0
EPM-2	0.5 : 0.5	370.1	400.0	430.5	32.9	30.7
EPM-3	0.75 : 0.25	366.1	392.4	424.9	33.8	31.0
EPM-0	1 : 0	394.1	413.9	433.6	31.2	30.0

the system, and availability of amino groups for reaction with epoxy decreases. In the case of DGEBA cured with mixture both diffusion and solubility of the chains may be controlling the curing reactions.

References

1. Martinez, P. A.; Cadiz, V.; Mantecon, A.; Serra, A. *Angew Makromol Chem* 1985, 133, 97.
2. Mantecan, A.; Cadiz, V.; Serra, A.; Martinez, P. A. *Eur Polym Mater* 1987, 23, 481.
3. Serra, A.; Cadiz, V.; Martinez, P. A.; Mantecan, A. *Angew Makromol Chem* 1986, 140, 113.
4. Soler, H.; Cadiz, V.; Serra, A. *Angew Makromol Chem* 1987, 152, 55.
5. Mantecon, A.; Cadiz, V.; Serra, A.; Martinez, P. A. *Angew Makromol Chem* 1988, 156, 37.
6. Rao, B. S. *J Polym Sci Part C: Polym Lett* 1988, 26, 3.
7. Shau, M. D.; Chin, W. K. *J Polym Sci Part A: Polym Chem* 1993, 31, 1653.
8. Ichino, T.; Hasuda, Y. *J Appl Polym Sci* 1987, 34, 1667.
9. Jain, P.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 2002, 84, 2235.
10. Deronet, D.; Morren, F.; Brosse, J. C. *J Appl Polym Sci* 1996, 62, 1855.
11. Khurana, P.; Aggawal, S.; Narula, A. K.; Choudhary, V. *J Appl Polym Sci* 2002, 87, 1345.
12. Chin, W. K.; Shaun, M. D. In *Polymeric Materials Encyclopedia*, Vol. 3, D-E; CRC Press: Boca Raton, FL, 1996; p 2210.
13. Sasaki, S.; Hasuda, Y. *J Polym Sci Part C: Polym Lett* 1987, 25, 377.
14. Serra, A.; Cadiz, V.; Mantecan, A. *Angew Makromol Chem* 1987, 155, 93.
15. Adhinarayanan, K.; Packirisamy, R. *J Appl Polym Sci* 1991, 43, 783.
16. Jurek, M. J.; McGrath, J. E. *Polymer* 1989, 30, 1552.
17. Johnson, R. N.; Franham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. L. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 2375.
18. Sharma, P.; Kukreja, P.; Narula, A. K.; Choudhary V. *Indian J. Eng Mater Sci* 2005, 12, 259.
19. Ozawa, T.; Duswalt, A. A. *Thermal Anal* 1970, 2, 301.
20. Duswalt, A. A. *Thermochim Acta* 1974, 8, 54.
21. Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers*; Elsevier: New York, 1976; p 529.