Effect of Structure of Aromatic Imide–Amines on Curing Behavior and Thermal Stability of Diglycidyl Ether of Bisphenol-A

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ABSTRACT: The curing behavior of diglycidyl ether of bisphenol-A (DGEBA) with aromatic imide–amines having aryl ether, sulfone, and methylene linkages was studied using differential scanning calorimetry (DSC). Six imide–amines of varying structure were synthesized by reacting 1 mol of naphthalene 1,4,5,8-tetracarboxylic dianhydride (N) or 4,4′-oxodiphthalic anhydride (O) with excess (>2 mol) of 4,4′-diaminodiphenylether [E] or 4,4′-diaminodiphenyl methane [M] or 4,4′-diaminodiphenyl sulfone [S]. The imide–amines prepared by reacting O or N with S, M, and E have been designated as OS/NS; OM/NM, and OE/NE, respectively. Structural characterization of imide–amines was done using FTIR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The curing behavior of DGEBA in the presence of stoichiometric amount of imide–amines was investigated by recording DSC scans. A broad exothermic transition was observed and the peak exotherm temperature was found to be dependent on the structure of imide–amines. The peak exotherm temperature (T_p) was lowest in case of imide–amines OE and highest in case of imide–amines NS/OS. Thermal stability of isothermally cured DGEBA in the presence of imide–amines was evaluated by dynamic thermogravimetry. The char yield was highest for resin cured with imide–amines NE. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1946–1953, 2008

Key words: diglycidyl ether of bisphenol-A; imide–amines; curing; thermal properties

INTRODUCTION

Epoxy resins have excellent moisture, solvent and chemical resistance, low shrinkage on cure, superior electrical and mechanical properties, and good adhesion to many substrates. The versatility in formulation also makes epoxy resins widely applicable industrial materials, as pottings, composites, laminates, encapsulants for semiconductors, and insulating materials for electric devices, etc.[1–4] However, the common epoxy systems cannot satisfy field applications that require high thermal and flame resistance. Several approaches for the modification of the epoxy backbone to enhance the thermal properties of epoxy resins have been reported.[5–8] These include varying the epoxy resin/curing agent functional group ratio, using a difunctional epoxy prepolymer with a different average chain length and varying the molecular size and structure of the difunctional curing agent.

Curing of the most commonly used epoxy resin, i.e., diglycidyl ether of bisphenol-A (DGEBA), with a variety of aromatic diamines has been extensively reported in the literature.[9–14] In recent years, attention has been focused on the development of novel curators containing imide group for epoxy resins[15,16] with a view to improve the performance at elevated temperatures. Imide compounds and polymers[17–21] that contain aromatic and/or heterocyclic groups can offer desirable high temperature stability. The paper describes the synthesis and characterization of aromatic imide–amines of varying structure obtained by reacting dianhydride [naphthalene 1,4,5,8-tetracarboxylic dianhydride (NTDA)/or 4,4′-oxodiphthalic anhydride (ODPA)] with diamines [4,4′-diaminodiphenylether(DDE)/or 4,4′-diaminodiphenyl methane (DDM)/or 4,4′-diaminodiphenyl sulfone (DDS)]. The curing behavior of epoxy resin in the presence of imide–amines of varying structure was investigated using differential scanning calorimetry (DSC). Thermal stability of DGEBA cured isothermally was evaluated using dynamic thermogravimetry (TGA) in nitrogen atmosphere.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA, grade LY556, having an epoxide equivalent of 177) was
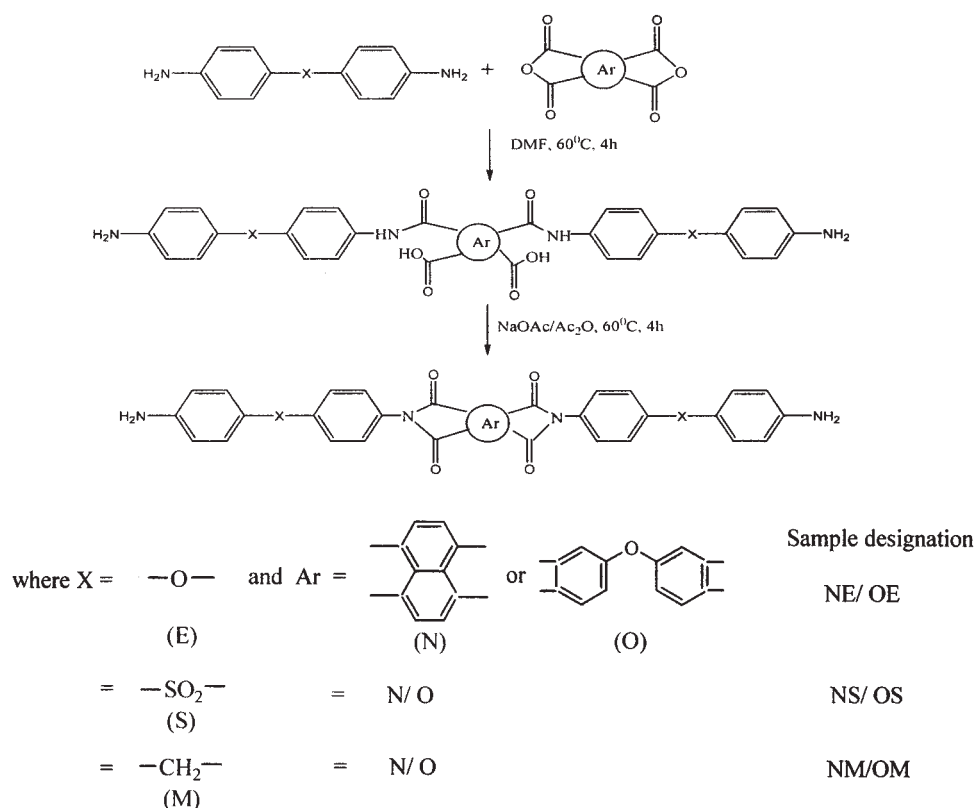
Scheme 1 Synthesis of aromatic imide–amines.

procured from Hindustan Ciba Geigy (Mumbai, India). 4,4′-Diaminodiphenyl sulfone (S), 4,4′-diaminodiphenyl ether (E), 4,4′-diaminodiphenyl methane (M), naphthalene 1,4,5,8-tetracarboxylic dianhydride (N), and 4,4′-oxodiphthalic dianhydride (O) all purchased from Aldrich and were used as received. N, N′-dimethyl formamide (DMF, Qualigens, Mumbai, India) was dried by keeping it over phosphorous pentoxide for 72 h followed by distillation under reduced pressure. Ethanol (Merck, Germany) was used as such. Acetic anhydride (Qualigens) was distilled before use. Sodium acetate (Qualigens) was fused before using.

Aromatic imide–amines[22] were prepared by reacting 1 mol of dianhydride with excess of aromatic amine (2.5 mol), according to the reaction in Scheme 1.

Procedure

To the well-stirred solution of 4, 4′-diaminodiphenyl sulfone (S) (0.0025 mol, 0.62 g) in dry N, N′-dimethyl formamide, naphthalene 1,4, 5,8-tetracarboxylic dianhydride (0.001 mol, 0.218 g) was added in small parts and heated for a period of 4 h at 60°C. To the amide-acid solution, fused sodium acetate (0.9 g) and acetic anhydride (7 mL) were added. The reaction mixture was heated for another 4 h. The imide–

amine was precipitated by pouring the reaction mixture into ice-cold water with stirring. The product was separated by filtration and washed with aqueous sodium bicarbonate solution and finally washed with water till neutral. It was then dried in vacuum oven at 80°C. The imide–amines were purified by recrystallisation in ethanol solution.

Similarly, all other imide–amines were prepared by reacting 4,4′-diaminodiphenyl methane (M)/4,4′-diaminodiphenyl ether (E) with naphthalene 1,4,5,8-tetracarboxylic dianhydride (N)/4,4′-oxodiphthalic dianhydride (O). The imide–amines obtained by reacting N/O with E/M/S have been designated as NE/OE, NM/OM, and NS/OS respectively.

Structural characterization of imide–amines

Structural characterization of imide–amines was done using FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopic techniques. IR spectra were recorded in KBr pellets using Shimadzu FTIR 8700 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 spectrophotometer using DMSO-d_6 as solvent and tetramethyl silane as an internal standard. Elemental analysis was carried out using EURO EA 3000 elemental analyser. Amine equivalent weight was also determined by the acetylation method.[23]

TABLE I
Analytical Data of Synthesized Imide–Amines

Sample designation	Formula	Molecular weight	Yield (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Amine equivalent
NS	$C_{38}H_{24}N_4S_2O_8$	728	59.0	62.0 (62.6)	3.0 (3.3)	7.4 (7.7)	359 (364)
NM	$C_{40}H_{28}N_4O_4$	628	61.3	75.8 (76.4)	4.3 (4.5)	8.5 (8.9)	309 (314)
NE	$C_{38}H_{24}N_4O_6$	632	59.3	71.5 (72.2)	3.4 (3.8)	8.5 (8.9)	311 (316)
OS	$C_{40}H_{26}N_4S_2O_9$	770	65.4	61.9 (62.3)	3.3 (3.4)	6.9 (7.3)	379 (385)
OM	$C_{42}H_{30}N_4O_5$	670	70.9	74.8 (75.2)	4.2 (4.5)	8.1 (8.4)	328 (335)
OE	$C_{40}H_{26}N_4O_7$	674	58.7	70.9 (71.7)	3.5 (3.7)	7.9 (8.2)	339 (343)

The numerical values within parenthesis represent calculated values.

Curing studies

For curing studies, freshly prepared samples obtained by mixing stoichiometric amounts of imide–amines with DGEBA were used for recording DSC traces. DSC scans of freshly prepared DGEBA and imide–amine mixture were recorded using TA 2100 thermal analyzer having 910 DSC module. A heating rate of 10°C/min and a sample size of 5 ± 1 mg was used in each experiment. For this purpose, known amount of imide–amine was dissolved in ethanol, which was then added to DGEBA. The solvent was removed under vaccum and the epoxy resins cured with stoichiometric amounts of imide–amines have been designated by introduction of prefix E to the letter designation of imide–amines. For example, DGEBA cured using NE and OE have designated as ENE and EOE, respectively. DSC scans of isothermally cured samples were also recorded to determine the effect of network structure on the glass transition temperature. For this purpose, mixtures of DGEBA and the corresponding amine (stoichiometric amount) were cured isothermally by heating in an air oven at (165 ± 20)°C for 3 h. Then samples were used for recording DSC scans at a heating rate of 10°C/min using 6 ± 2 mg of powdered samples.

Thermal stability

Thermal stability of the samples cured isothermally by heating in the hot air-oven at (165 ± 20)°C for 3 h was investigated by recording TG/DTG traces in nitrogen atmosphere (flow rate, 60 mL/min). A Rheometric Scientific thermal analyzer having TG1500 module was used for recording TG/DTG traces using powdered samples. A heating rate of 20°C/min and a sample size of 11 ± 1 mg was used in each experiment.

RESULTS AND DISCUSSION

Structural characterization of imide–amines

The aromatic imide–amines were of white to orange in color and insoluble in acetone and chloroform but were soluble in DMF and DMSO. The formula molecular weight, percentage yield, and results of elemental analysis and amine equivalents of imide–amines are reported in Table I. The calculated values of CHN and amine equivalent agreed well with the experimentally determined values. The experimented values are marginally lower ($\sim$ 1–2%) than the theoretical calculated values.

FTIR

In the FTIR spectra of all aromatic imide–amines, the absorption bands because of imide stretching and vibration were observed at 1782, 1720 and 1379, 1105, 725 cm^{-1}, respectively.[24] Stretching bands because of —NH_2 was also observed in the range of 3260 ± 30 cm^{-1}. An absorption band because of C—N stretching was observed at 1408–1497 cm^{-1}. In the FTIR spectra of imide–amine (NS and OS), strong absorption bands were observed at 1320 cm^{-1} and 1149 cm^{-1}, which have been attributed to asymmetric and symmetric stretching vibration of the sulfone group (—SO_2—). In imide–amine NE and OE, strong absorption band because of Ar—O—Ar linkage was observed at 1013 cm^{-1}. The broad peak around 1580–1660 cm^{-1} implies the C=C stretch in benzene ring. All other characteristic absorption bands due to imide and aromatic stretching were observed at their usual position. A typical FTIR spectrum of OS is shown in Figure 1.

^{1}H NMR

In the ^{1}H NMR spectrum of imide–amines, a characteristic signal because of —NH_2 protons was observed at δ = 3.6 ppm (singlet) and a multiplet because of aromatic protons was observed in the range of δ = 6.8–8.2 ppm. In NM and OM samples, a singlet due to methylene protons was also observed at 1.6 ppm. The integration was used to calculate the number of protons. The position of signals observed in the ^{1}H NMR spectra of all the imide–amines along with their assignment are given in Table II. A representative ^{1}H NMR spectrum of OM is shown in Figure 2.
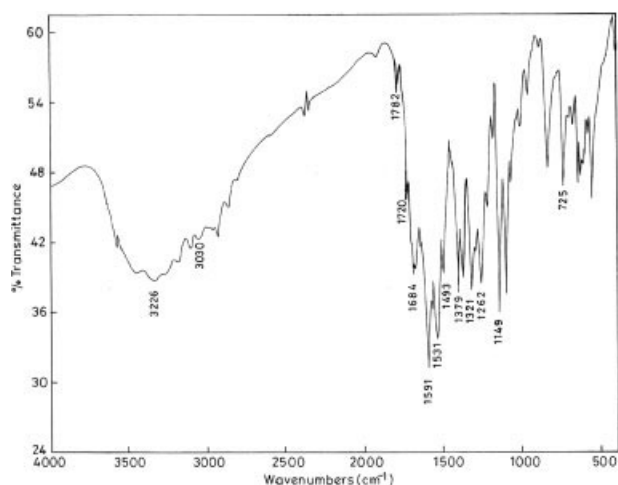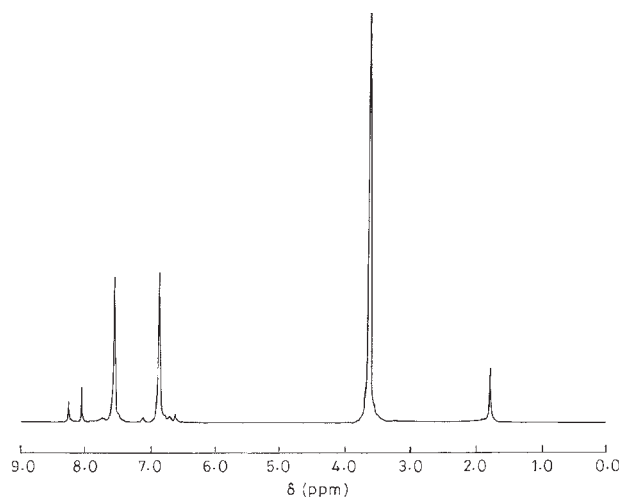
Figure 1 FTIR spectrum of OS imide–amine.

Figure 2 ^{1}H NMR spectrum of OM imide–amine.

^{13}C NMR

Figure 3 shows ^{13}C NMR spectra of OS imide–amine. In the ^{13}C NMR spectra of imide–amines, a characteristic signal due to Ar—NH$_2$ and imide carbon was observed at 160 ppm and 169 ppm, respectively. In NS and OS samples, a singlet due to Ar—SO$_2$ was observed at 144 ppm. In NE and OE samples, a singlet due to Ar—O— was also observed at 153 ppm. In NM and OM samples, a triplet due to Ar—CH$_2$ was observed at 134 ppm. The structure of aromatic imide–amines thus synthesized was confirmed by using FTIR and NMR spectroscopy.

Curing studies

The curing behavior of epoxy resin depends on the structure and molecular size of the imide–amines investigated by recording DSC traces. In the DSC scan of DGEBA alone, no exothermic transition was seen in the temperature range of 50–350°C thereby indicating the absence of curing or crosslinking. In the DSC scans of DGEBA in the presence of imide–

amines, a broad exothermic transition in the temperature range of (165 ± 20)°C–(290 ± 30)°C was obtained. The exothermic transition associated with crosslinking or curing was characterized by noting the following temperatures.

T_i, kick-off temperature, where the curing starts; T_{onset}, temperature of onset of exotherm obtained by extrapolating the steepest portion of the exotherm to the base line; T_p, temperature of peak position of exotherm; T_f, temperature of end of curing exotherm, and this was taken as the temperature where the exotherm levels with the base line in the final stage of curve; ΔH, heat of curing reaction, obtained from the area under the exothermic transition.

Figure 4 shows the DSC scans of DGEBA in the presence of stoichiometric amount of imide–amines (a) NS, (b) NM, and (c) OE recorded at a heating

TABLE II
Results of ^{1}H NMR Spectra Along with Their Assignment

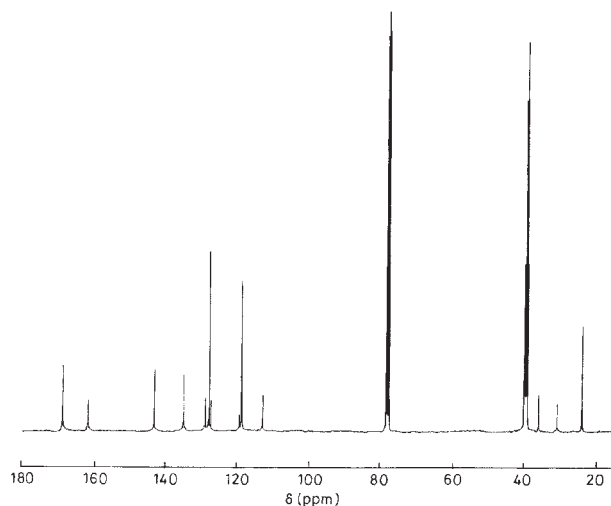| Sample designation	δ (ppm)		
	—NH$_2$	Aromatic H's	—CH$_2$—
NS	3.4 (4H)	6.8–7.9 (20H)	–
NE	3.4 (4H)	6.8–8.3 (20H)	–
NM	3.4 (4H)	6.8–7.6 (20H)	2.1 (4H)
OS	3.6 (4H)	6.6–8.2 (22H)	–
OE	3.4 (4H)	6.9–8.2 (22H)	–
OM	3.6 (4H)	6.9–8.2 (22H)	2.1 (4H)

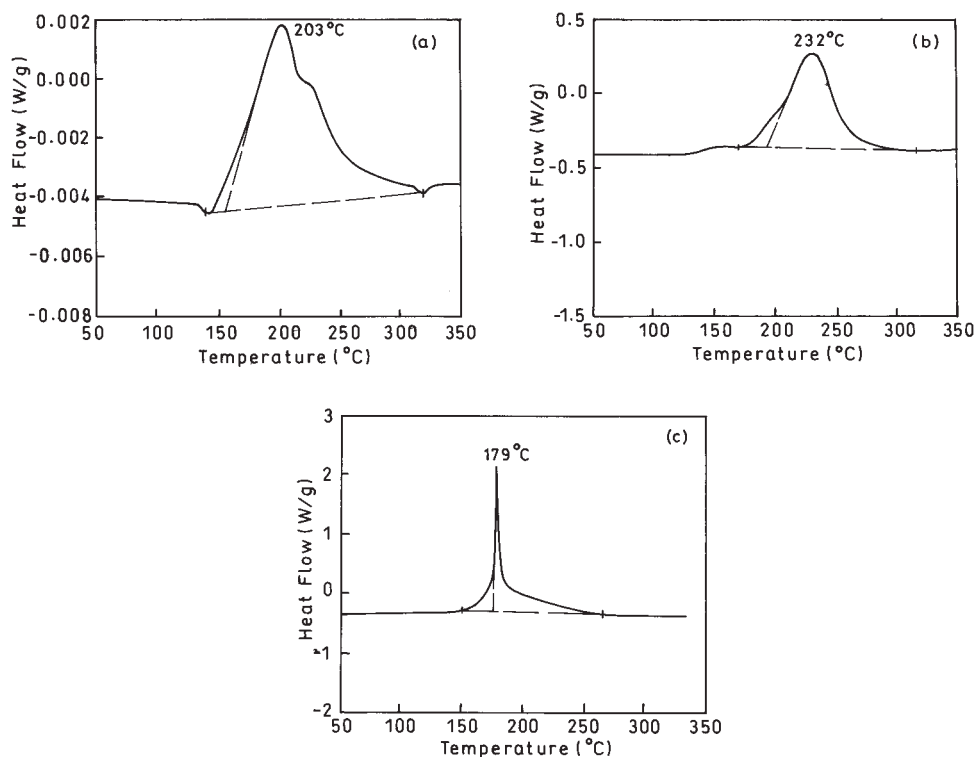Figure 3 ^{13}C NMR spectrum of OS imide–amine.

Figure 4 DSC scans of DGEBA in the presence of stoichiometric amount of imide–amines (a) NM, (b) NS, and (c) OE at heating rate 10°C/min.

rate of 10°C/min, respectively. The results of DSC scans are summarized in Table III. The curing temperatures were dependent upon the structure of dianhydride or diamine used in the preparation of imide–amines. Comparing the curing behavior, the following trend in T_i was observed as:

$$ENM < EOM \sim EOE < ENE < ENS < EOS$$

Reaction of an amine with an oxirane ring is a nucleophilic addition and the presence of an electron withdrawing group is expected to reduce the nucleophilicity of amine. This is obvious from T_p value, which was highest in the case of DGEBA/NTDA-DDS (ENS) or DGEBA/ODPA-DDS (EOS) samples

TABLE III
Results of DSC Scans of DGEBA in the Presence of Imide–Amines

Sample designation	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	T_g (°C)
ENS	170.8	194.0	231.7	317.2	179.8	194.3
ENM	140.1	155.2	203.0	320.5	112.4	165.4
ENE	156.7	182.2	198.9	260.0	137.8	116.3
EOS	185.8	196.4	223.1	308.5	177.1	189.4
EOM	149.3	154.2	183.9	260.0	115.3	125.6
EOE	150.9	176.4	179.2	265.8	181.5	120.8

Stoichiometric amount at heating rate 10°C/min.

because of the decreased nucleophilcity of imide–amines (NS or OS) due to the presence of electron withdrawing (SO$_2$) group. The value of ΔH was in the range of 112–182 J/g.

The isothermally curing of DGEBA in the presence of stoichiometric amounts of imide–amines was done by heating in an air oven (165°C ± 20°C for 3 h), which was then used for the determination of the glass transition temperature using DSC. In the DSC scans of isothermally cured samples, absence of exothermic transition indicates the completion of curing. However, a shift in the baseline corresponding to the glass transition was observed. The glass transition temperature was noted as midpoint inflexion and the results are summarized in Table III. Glass transition temperature is dependent on the rigidity of polymer backbone as well as on the crosslink density. Since in all these samples, the curing was done using stoichiometric amount of amines with molecular weight ranging from 628 to 770, therefore it is expected that all these samples may have the same crosslink density. However, T_g was found to be highest in samples cured using sulfone-containing imide–amines DGEBA/NTDA-DDS (ENS) or DGEBA/ODPA-DDS (EOS) and lowest in samples cured using ether imide–amines DGEBA/NTDA-DDE (ENE) or DGEBA/ODPA-DDE (EOE). This can be explained on the basis of rigidity being imparted by sulfone containing amines.
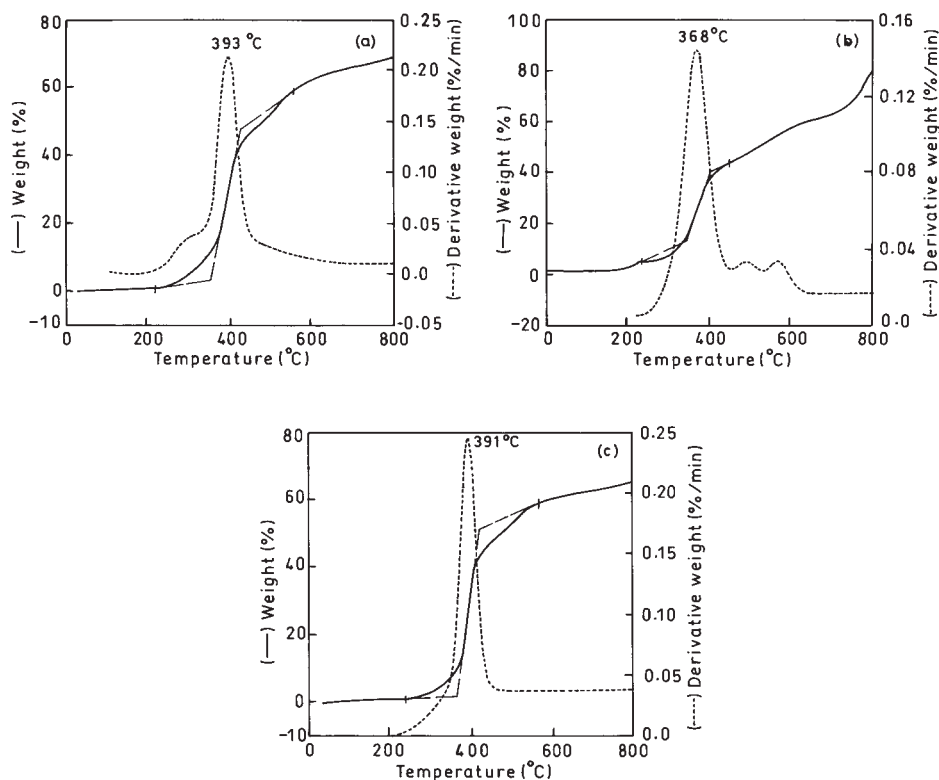
Figure 5 TG/DTG traces of DGEBA cured isothermally with imide–amine (a) NE, (b) OS, and (c) NM.

Thermal behavior

The thermal stability of epoxy resin samples cured isothermally with a stoichiometric amount of imide–amines was determined by recording TG/DTG derivative traces in nitrogen atmosphere. Figure 5 shows TG/DTG traces of epoxy resin samples, i.e., ENM, EOS, and ENE. The relative thermal stability of the cured resins was compared by noting initial decomposition temperature (IDT), final decomposition temperature (FDT), temperature of maximum rate of weight loss (T_{max}), and percent char yield at 800°C. The results are summarized in Table IV.

TABLE IV
Results of TG/DTG Traces of DGEBA Cured Isothermally with Stoichiometric Amount of Imide–Amines in Nitrogen Atmosphere

Sample designation	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield (%) at 800°C	LOI (%)
ENS	353.0	386.7	414.4	28.3	28.8
ENM	362.4	390.7	417.5	34.5	31.3
ENE	353.2	393.4	424.8	35.2	31.6
EOS	340.2	367.9	400.5	20.5	25.6
EOM	382.7	402.3	426.1	30.4	29.7
EOE	369.9	400.4	427.5	32.1	30.3

Heating rate 20°C/min.

Integral procedural decomposition temperature

The integral procedural decomposition temperature (IPDT) which sums the shape of the primary thermogravimetric traces (TG) was calculated according to the method of Doyle.[25] IPDT provides the most valid comparison of diverse polymeric materials, when TG traces of all polymer samples were obtained under identical conditions.

From the TG traces, area under the curve was obtained by counting the squares under TG trace. The ratio of area under the TG trace and the area of rectangular plot bounded by TG trace gave the value of A^*. A^* was correlated to IPDT by the following relation:

$$IPDT = A^*(T_f - T_i) + T_i \tag{1}$$

where A^* is the area under the TG trace/area bounded by TG trace; T_f, final decomposition temperature; and T_i, initial decomposition temperature.

Activation energy of decomposition

Activation energy of decomposition (E) can also be used as a criteria for comparing the thermal stability of polymers. The rate constant of a reaction depends upon energy difference between the transition and initial states. This shows that if the energy difference

is higher (i.e., activation energy is higher) the compound will be more stable.

Several expressions for the determination of activation energy from the TGA data have been reported in the literature.[26–29] Dharwadkar and Kharkhanawala[30] have given a modified equation for the calculation of activation energy, which is independent of sample size and heating rate.

$$\ln\left[\ln\left(1-\alpha\right)^{-1}\right] = \frac{E100\,\theta}{RT_i^2(T_f - T_i)} + C \qquad (2)$$

where α, fraction reacted; T_i, the temperature of inception of reaction; T_f, temperature at the point of inflection on the thermogram; $\theta = (T - T_s)$ (where T is the temperature under consideration and T_s is the maximum temperature); C, constant; R, gas constant.

A plot of $\ln\left[\ln\left(1-\alpha\right)^{-1}\right]$ versus θ gave a straight line. The slope of the line was equal to

$$m = \frac{100E}{RT_i^2(T_f - T_i)} \qquad (3)$$

From this equation E was calculated.

All the samples were stable upto 350°C and a significant weight loss occurred only beyond this temperature. The char yield was found to be dependent on the structure of imide–amines and it was highest for ENE and lowest for EOS. Lower char yield observed in case of EOS, ENS compared with other samples in a particular series such as EOM or EOE/ENM or ENE could be due to the loss of SO_2, which is present in the imide–amines. Imide–amines based on NTDA gave resins with higher char yield as compared with those based on ODPA. This can be explained on the basis of compact network structure in the presence of naphthalene based imide–amines. Increased char formation can limit production of combustible carbo-containing gases, decrease the exothermicity due to pyrolysis reactions, as well as decrease the thermal conductivity of the surface of burning materials.[31] The solid-state aromatization reactions in these imide–amines may be facilitated by the formation of additional cross-links through the reaction of carbonyl and trapped/unreacted amino groups at elevated temperatures.

Char yield can be used as a criteria for evaluating limiting oxygen index (LOI) of the resin in accordance with Van Krevelen and Hoftyzer equation[32] [eq. (4)].

$$LOI = 17.5 + 0.4CR \qquad (4)$$

where CR is char yield.

All the samples had LOI values calculated based on their char yield was higher than 28 except for

TABLE V
Thermal Behavior of Cured Epoxy Resin in Nitrogen Atmosphere

Sample designation	Decomposition temperature (°C) at % weight loss of				IPDT (°C)
	10	20	30	40	
ENS	348	372	390	400	601.1
ENM	350	386	400	412	765.8
ENE	332	355	386	400	702.1
EOS	320	360	387	430	641.6
EOM	376	400	410	423	600.8
EOE	360	399	409	431	573.9

DGEBA/ODPA-DDS (EOS). On the basis of LOI values, such materials can be classified as self-extinguishing resin and flame resistant DGEBA resin can be obtained by using imide–amines as curing agents.

The thermal stability of epoxy network was also compared by comparing the decomposition temperature at various % weight loss as well as by calculation of IPDT. IPDT, which sums up the shape of the TG trace was calculated according to Doyle's method using eq. (1) in the temperature range of 300–800°C and the results are given in Table V. Comparing imide–amines based on ether/methylene/sulfone amine and different anhydrides, the trend in IPDT was

$$ENE > EOE$$

$$ENM > EOM$$

$$EOS > ENS$$

This clearly shows that the trend of thermal stability changes with the nature of anhydride/amine. For example with ether containing amine, IPDT value was highest with NTDA based anhydride. The trend with methylene or sulfone containing amines was different.

The activation energy of decomposition (E) was calculated according to eqs. (2) and (3) and the values are given in Table VI. On comparing the activation energy in a series of imide–amines based on DDM/DDE/DDS keeping anhydride constant, the following trend in activation energy was seen.

$$ENM > ENE > ENS$$

$$EOE > EOM > EOS$$

In case of NTDA-based imide–amines, activation energy was highest for DDM (ENM) based amines and lowest with sulfone containing amines (ENS).

TABLE VI
Activation Energy Values for the Thermal
Decomposition of Cured Epoxy Resin

Sample designation	Temperature range (°C)	E (KJ/mol)
ENS	260–486	148.7
ENM	230–584	301.8
ENE	221–550	234.2
EOS	230–451	174.4
EOM	250–552	223.6
EOE	226–570	247.5

CONCLUSIONS

From these results, it can be concluded that the crosslinking of epoxy resin by aromatic imide–amines containing aryl ether, sulfone, and methylene linkages was influenced by the structure of imide–amines. The peak temperature of exothermic transition depends on the nucleophilicity of imide–amines and it was found to be highest for DGEBA/NTDA-DDS (ENS) and DGEBA/ODPA-DDS (EOS) due to the presence of electron withdrawing group (sulfone group). The glass transition temperature (T_g) of the cured resin depended on the structure of the epoxy network and it was highest for epoxy resin cured with sulfone containing imide–amines. Higher char yields were obtained with epoxy resins cured with imide–amines based on NTDA as compared with ODPA-based imide–amines. The highest char yield was observed in case of DGEBA/NTDA-DDE (ENE) and lowest with DGEBA/ODPA-DDS (EOS).

References

1. Wang, C. S.; Shieh, J. Y.; Kinjo, N. J Appl Polym Sci 1999, 3, 353.
2. Iijima, T.; Horiba, T.; Tomoi, M. Eur Polym J 1991, 27, 851.
3. Lin, S. C.; Pearce, E. M. High Performance Thermosets, Chemistry, Properties, Applications; Hanser Publishers: Germany, 1993, p 247.
4. Ho, T. H.; Wang C. S. J Appl Polym Sci 1994, 54, 13.
5. Deng, J.; Wenfang, S. Eur Polym J 2004, 40, 1137.
6. Liu, Y. L.; Hsiue, G. H.; Lan, C. W.; Chiu, Y. S. Polym Degrad Stab 1997, 56, 291.
7. Martinez, P. A.; Cadiz, V.; Mantecaon, A.; Serra, A. Angew Makromol Chem 1985, 133, 97.
8. Chin, W. K.; Hsau, M. D.; Tsai, W. C. J Polym Sci Polym Chem Ed 1995, 33, 373.
9. Mezzenga, R.; Boogh, L.; Manson, J. A. E.; Pettersson, B. Macromolecules 2000, 33, 4373.
10. Jain, P.; Choudhary, V.; Varma, I. K. Eur Polym J 2002, 39, 181.
11. Iijima, T.; Hamakawa, S.; Tomoi, M. Polym Int 2001, 50, 1214.
12. Gupta, N.; Varma, I. K. J Appl Polym Sci 1998, 68, 1759.
13. Jain, P.; Choudhary, V.; Varma, I. K. J Appl Polym Sci 2001, 81, 390.
14. Khurana, P.; Aggarwal, S.; Marula, A. K.; Choudhary, V. J Appl Polym Sci 2002, 87, 1345.
15. Lee, S. D.; Ahn, B. H.; Lee, K. G.; Kim, W. H. Kongop Hwahak 2004, 15, 646.
16. Barral, L.; Cano, J.; Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Ramirez, C.; Torres, A.; Abad, M. J. Thermochim Acta 2000, 344, 137.
17. Chin, W. K.; Shau, M. D.; Salamone, J. C. Polymeric Materials Encyclopedia; CRC Press: London, 1996; Vol. 3, p 2210.
18. Abraham, G.; Packirisamy, S.; Ramaswamy, R. Int J Polym Mater 2006, 55, 121.
19. Yang, S. J.; Lee, C.; Jang, W.; Kwon, J.; Sundar, S.; Han, H. J Polym Sci Part B: Polym Phys 2004, 42, 4293.
20. Hwang S. H.; Jung, J. C. J Appl Polym Sci 2001, 81, 279.
21. Abraham, G.; Packirisamy, S.; Vijayan, T. M.; Ramaswamy, R. J Appl Polym Sci 2003, 88, 1737.
22. Mathur, A.; Varma, I. K.; Polymer 1992, 33, 4845.
23. Vogel, A. I. Elementary Practical Organic Chemistry, Part III; ELBS: London, 1971.
24. Behniafar, H.; Haghighat, S. Eur Polym J 2006, 42, 3236.
25. Doyle, C. D., Anal Chem 1961, 33, 77.
26. Freeman, E. S.; Caroll, B. J Phys Chem 1958, 62, 394.
27. Coats, A. W.; Redfern, J. R. Nature 1964, 68, 201.
28. Horowitz, H. H.; Metzger, G. Anal Chem 1963, 35, 1464.
29. Reich, L. J Polym Sci 1965, B-3, 231.
30. Dharwadkar, S. R.; Kharkhanawala, M. D. In Thermal Analysis in Inorganic Materials and Physical Chemistry; Schwenker, R. P., Garn, P. D., Eds.; Academic Press: New York, 1969; Vol. 2.
31. Shieh, J. Y.; Wang, C. S. Polymer 2001, 42, 7615.
32. Van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers, 2nd ed.; Elsevier: New York, 1976, p 529.