Curing and Thermal Behavior of DGEBA in Presence of Dianhydrides and Aromatic Diamine

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ABSTRACT: The article describes the curing behavior of diglycidyl ether of bisphenol-A using benzophenone 3,3′, 4,4′-tetracarboxylic acid dianhydride (BTDA)/naphthalene 1,4,5,8-tetracarboxylic dianhydride (NTDA)/or mixture of BTDA and 4,4′- diaminodiphenyl sulfone (DDS)/ or NTDA and DDS in varying molar ratio as curing agent. Differential scanning calorimetry was used to investigate the cure kinetics by recording DSC scans at heating rates of 5, 10, 15, and 20 °C/min. The peak exotherm temperature was found to be dependent on the heating rate, structure of the dianhydride as well as on the DDS/dianhydride molar ratio. Activation energy of curing reaction as determined in ac- cordance to Ozawa's method was found to be dependent on the structure of anhydride as well as on the ratio of an- hydride to amine. Thermal stability of the isothermally cured resins was evaluated using dynamic thermogravime- try in nitrogen atmosphere. The char yield was highest in case of resins cured using DDS/BTDA mixture or DDS/ NTDA one (0.75 : 0.25; sample EB-1/or EN-1). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3802–3808, 2007

Key words: diglycidy ether of bisphenol-A (DGEBA); cure kinetics; thermosetting resins; aromatic amines; epoxy res- ins; anhydrides

INTRODUCTION

In recent years, the range of potential applications of thermosetting resins and especially epoxy resins, is rapidly expanding from classical applications as a cover for surfaces and electronic components, pow- der moldings and as matrix resins for advanced composites in the automobile and aeronautical industries.[1] The versatility in formulation also makes epoxy resins widely applicable industrially for sur- face coatings, adhesives, pottings, laminates, encap- sulants for semiconductors and insulating materials for electrical devices, etc.[2–5] Several approaches have been reported[6–9] to modify the epoxy backbone for enhancing its thermal characteristics.

Linear epoxy resins can be converted into three- dimensional crosslinked thermoset network during cure. Various chemical reactions that take place dur- ing cure determine the resin morphology, which, in turn, determines the properties of the cured formula- tion. An accurate description of the curing kinetics and these materials is needed to establish process- ing-morphology property relationships in thermosets and their composites.[10] An accurate description of

the cure kinetics and the properties of these materi- als is the most important aspect of the practical model and fundamental theory. The mechanism and kinetics of curing reaction about different epoxy res- ins have been studied by many researchers.[11–13]

Cyclic anhydrides are some of the most important high temperature curing agents used for the conver- sion of epoxy resins to highly crosslinked, glassy, three-dimensional networks.[14–16] Especially for elec- trical applications, anhydride hardeners show some outstanding properties, i.e., low exotherm and shrink- age during curing, as well as low water absorption and almost internal stress free systems after curing. Therefore, anhydride-cured systems are widely used as electrical insulating materials at all voltage levels. The challenge is to achieve low temperature process- ing and curing of anhydride/DDS systems and also attain the advanced property profile of systems cured at higher temperatures. Curing and thermal behavior of DGEBA using phthalic anhydride and pyromellitic dianhydride was investigated in our laboratory[17] and it was observed that structure and amount of anhy- dride has a large effect on the curing characteristics. It was therefore considered of interest to investigate sys- tematically the curing behavior of DGEBA in presence of other anhydrides.

The present article describes the systematic studies on the curing of DGEBA using DDS/BTDA or DDS/ NTDA in the molar ratio of 0 : 1, 0.25 : 0.75, 0.5 : 0.5,

0.75 : 0.25 and 1 : 0. Thermal stability of the resins cured isothermally by heating in an air oven was evaluated by dynamic thermogravimetry in nitrogen atmosphere.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol-A (DGEBA, Grade LY556, epoxy equivalent = 177; Hindustan Ciba Geigy, Delhi, India); methyl ethyl ketone, benzophenone 3,3′, 4,4′-tetracarboxylic acid dianhydride (BTDA), naphthalene 1,4,5,8-tetracarboxylic dianhydride (NTDA), and 4,4′-diaminodiphenyl sulfone (DDS) (all from Merck) were used as received and their structures are shown below:


NTDA   **BTDA**   **DDS**
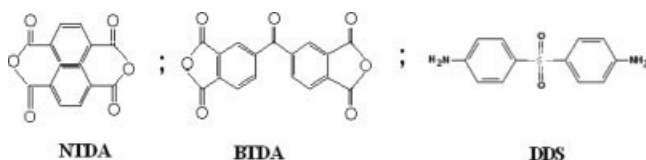
Curing studies

TA 2100 thermal analyzer having a 910 DSC module was used to record DSC scans at a heating rate of 5, 10, 15, and 20°C/min. For this purpose, samples were prepared by mixing required amounts of DGEBA with dianhydrides or DDS or DDS/dianhydride mixture with different molar ratios using methyl ethyl ketone as solvent. After thorough mixing, the solvent was evaporated under vacuum and the freshly prepared samples were used for recording DSC traces in static air atmosphere at a programmed heating rate from room temperature up to 350°C. The sample size was ranged from 3 to 7 mg.

The epoxy samples cured using mixture of DDS/BTDA or DDS/NTDA have been designated as EB and EN respectively, followed by a numerical suffix. For example epoxy resin cured using mixture of DDS/BTDA (sample EB) in the ratio of 0.25 : 0.75, 0.5 : 0.5, and 0.75 : 0.25 have been designated as EB-3, EB-2, and EB-1 respectively. Similarly samples cured using mixture of DDS/NTDA were designated as EN-3, EN-2, and EN-1 respectively. Epoxy resins cured using DDS, BTDA, or NTDA alone have been designated as ED, EB, or EN respectively.

Thermal studies

The thermal stability of epoxy resins cured isothermally (by heating in an air oven at 120°C and 240°C for 2 h) in presence of DDS/BTDA and DDS/NTDA mixture respectively, was evaluated using a Rheometric Scientific Thermal Analyzer having TG1500 − module. Thermogravimetric traces in nitrogen atmosphere (flow rate 60 cm^3/min) were recorded at a heating rate of 20°C/min. Powdered
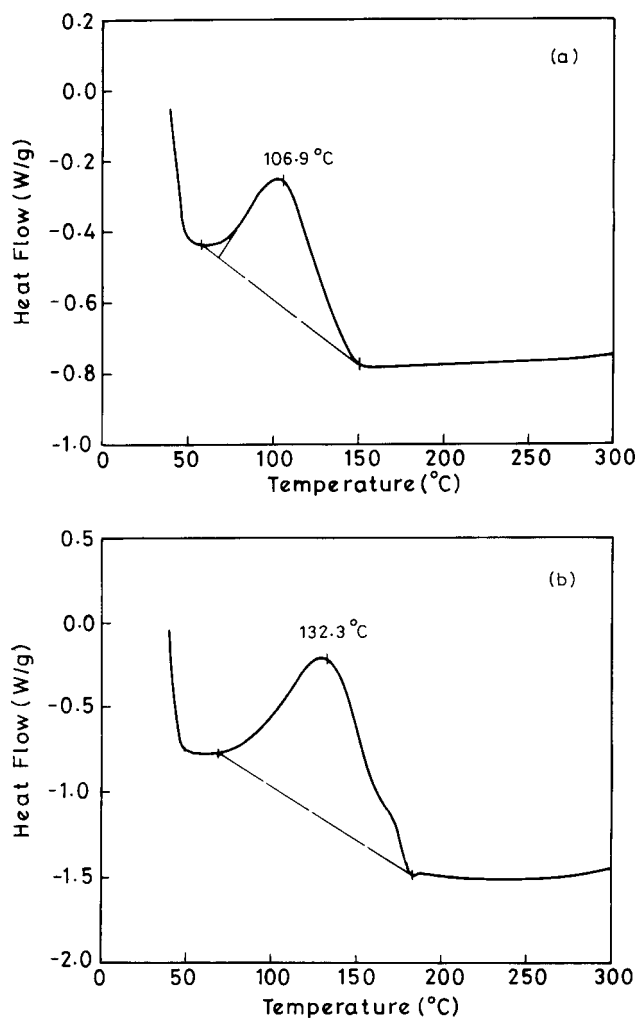
Figure 1 DSC scans of DGEBA in presence of DDS/BTDA mixture at a heating rate of 10°C/min (a) EB-1 and (b) EB-3.

samples ranging from 10 to 15 mg in each experiment were used.

RESULTS AND DISCUSSION

Curing studies

DSC scans of samples (a) EB-1 and (b) EB-3 are shown in Figure 1. The curing of epoxy resin depends on the structure of curing agents and its stoichiometry. In the present work, we did not change the stoichiometry; however the ratio of amine/dianhydride was varied to evaluate its effect on the curing behavior. The curing exotherm was characterized by noting the following temperatures:

T_i = kick- off temperature, where the curing starts.

T_{onset} = temperature where the first detectable heat is released. It was obtained by extrapolation of the steepest portion of curve.
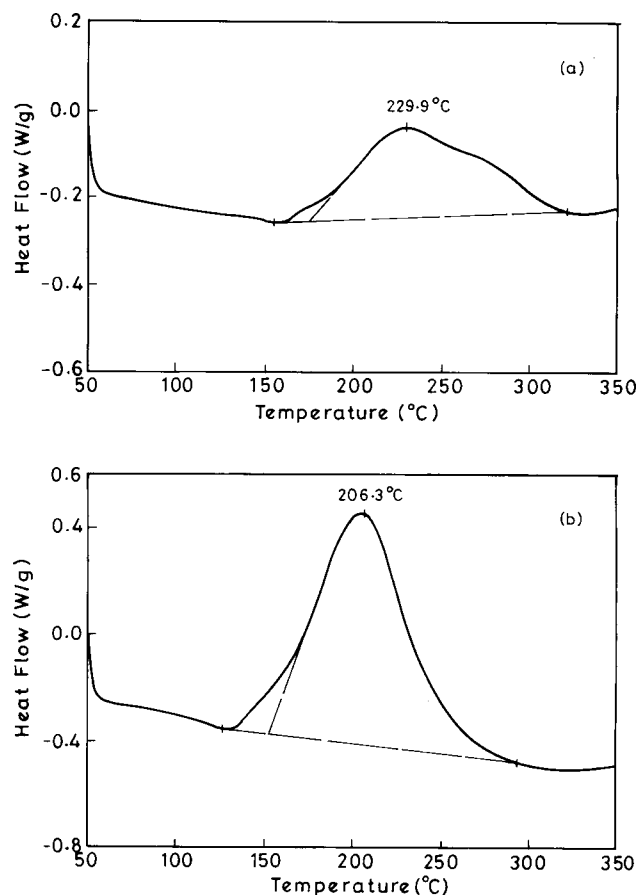
Figure 2 DSC scans of DGEBA in presence of DDS/NTDA mixture at a heating rate of 10°C/min (a) EN-3 and (b) EN-1.

T_p = temperature of peak position of exotherm.

T_f = temperature of the end of curing exotherm. This was taken as the temperature where the exotherm levels off with the base line.

ΔH = heat of curing, calculated by measuring the area under the exothermic transition.

Figures 1 and 2 show the DSC scans of DGEBA in presence of mixture of DDS/BTDA (EB-1 and EB-3) and DDS/NTDA (EN-3 and EN-1) respectively. The results of DSC scans are summarized in Table I. The characteristic curing temperatures i.e., T_i, T_{onset}, T_p, and T_f showed the effect of dianhydride structure (Tables I and II). In the presence of BTDA (EB sample) or DDS (sample ED) alone, a broad exothermic transition due to curing was observed in the temperature range of 92–220°C (EB) and 131–295°C (ED) in the DSC scans recorded at 10°C/min. On the other hand EN sample showed exothermic transition at much higher temperature i.e., in the range of 271–385°C. These temperatures increased with increasing heating rate. These curing chararacterstic clearly indicate that NTDA is the least reactive and much higher temperature are needed to cure the resin. The structure of anhydride was also investigated by Patel and Patel[18] indicating that hexahydrophthalic anhydride (HHPA) is more reactive than phthalic anhydride (PA). The uncatalyzed cure of epoxy-anhydride has been reported to begin through the reaction of these anhydride groups with hydroxyl groups, which are present in oligomers or as impurities[11] leading to the formation of monoester and a carboxylic group. The monoester reacts with the

TABLE I
Results of DSC Scans of DGEBA in Presence of DDS/BTDA Mixture

Sample designation	DDS : BTDA molar ratio	Heating rate (°C/min)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (kJ/mol)
EB	0 : 1	5	77.5	95.1	159.7	215.7	259.6	139.0
		10	92.0	105.3	165.5	220.1	203.5	
		15	113.4	115.3	169.2	222.4	208.7	
		20	127.5	130.1	175.2	230.1	205.4	
EB-3	0.25 : 0.75	5	65.2	69.5	119.9	162.6	129.8	49.0
		10	78.4	81.2	132.3	182.9	181.9	
		15	90.1	96.3	145.6	195.4	179.3	
		20	102.1	108.4	157.3	215.1	177.0	
EB-2	0.5 : 0.5	5	54.7	58.5	119.7	174.6	184.5	64.0
		10	56.0	64.4	122.4	182.4	123.0	
		15	59.3	67.5	132.8	189.4	120.2	
		20	64.1	73.2	144.6	195.2	125.0	
EB-1	0.75 : 0.25	5	43.9	50.3	88.2	138.5	151.0	36.0
		10	58.9	68.7	106.9	151.3	123.1	
		15	62.2	71.8	119.5	165.4	120.4	
		20	72.3	80.2	132.1	176.1	90.1	
ED	1 : 0	5	119.8	158.1	210.1	274.4	255.0	74.0
		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	

TABLE II
Results of DSC Scans of DGEBA in Presence of DDS/NTDA Mixture

Sample designation	DDS : NTDA molar ratio	Heating rate (°C/min)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (kJ/mol)
EN	0 : 1	5	258.1	261.5	324.4	375.2	168.4	135.0
		10	271.1	275.4	335.2	385.1	164.1	
		15	285.2	301.5	347.7	404.7	163.5	
		20	290.1	304.4	355.2	415.5	160.1	
EN-3	0.25 : 0.75	5	145.0	165.2	209.4	294.8	100.4	82.0
		10	155.1	174.6	229.9	315.4	101.0	
		15	160.2	181.2	235.2	316.1	83.7	
		20	164.1	186.1	240.2	320.4	79.6	
EN-2	0.5 : 0.5	5	113.7	141.5	197.6	273.0	274.6	105.0
		10	125.6	149.2	200.5	255.4	260.2	
		15	130.6	152.2	211.0	292.3	273.7	
		20	135.4	158.3	218.8	296.2	250.1	
EN-1	0.75 : 0.25	5	114.8	125.1	187.4	267.0	240.6	64.0
		10	130.5	152.2	206.3	280.2	335.1	
		15	135.1	166.1	217.2	285.3	315.8	
		20	140.2	169.5	225.6	296.9	178.7	

epoxide to form a diester. The concentration of hydroxyl group increases and may produce an autocatalytic effect. In NTDA it is a six membered anhydride whereas a five membered anhydride ring is presented in BTDA. The lower reactivity of NTDA could be due to its rigid structure because of the presence of naphthalene moiety and more stability of six member ring as compared to five member ring.

In the DSC scans of DGEBA cured using mixture of BTDA or NTDA with DDS in varying molar ratio, a broad exothermic transition due to curing was observed. The presence of small amount of amine in a mixture resulted in a significant decrease in the peak exothermic temperature. All the temperatures were lower than either of the curing agent used alone (Tables I and II). The decrease in the curing temperature of DGEBA upon addition of small amount of DDS to either BTDA or NTDA can be explained on the basis of catalytic action of amines, which might accelerate the curing. The catalytic

action of tertiary amine on the curing of epoxies in the presence of HHPA has been reported by Matejka et al. and Steinmann.[19,20]

Curing kinetics

The kinetic parameters of the curing reaction can be obtained from dynamic DSC scans (i.e., multiple heating rate method) or using 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 3 and 4 show DSC scans for resin samplesEB and EN-2 recorded at different heating rates. The characteristic curing temperatures for DGEBA at different heating rates in the presence of dianhydride, DDS, and mixture of DDS/BTDA or DDS/NTDA are summarized in Tables I and II. As expected, curing temperatures increased with increasing heating rate. The activation energy of the curing reaction was calculated using Ozawa's method[21,22] assuming that
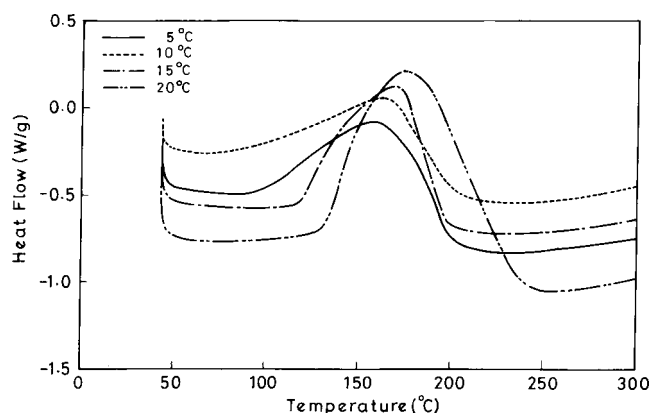

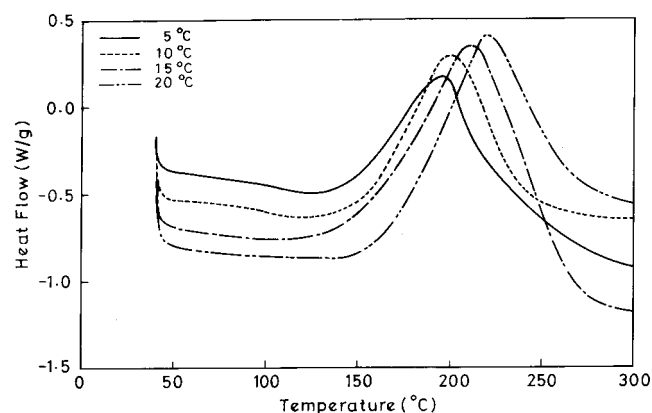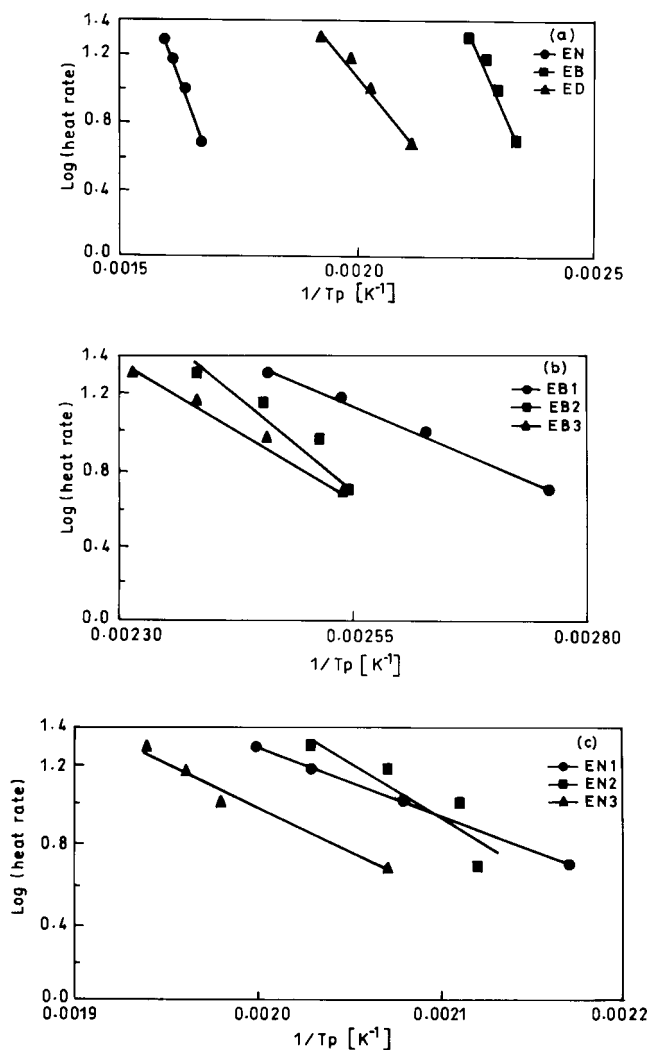**Figure 3** Effect of heating rate on the DSC scans of sample EB.

Figure 4 Effect of heating rate on the DSC scans of sample EN-2.

Figure 5 Plot of log heating rate versus 1/Tp (a) (▲) ED (■) EB (●) EN, (b) (●) EB-1 (■) EB-2 (▲) EB-3 and (c) (●) EN-1 (■) EN-2 (▲) EN-3.

1. The peak exothermic temperature (T_p) represents a point of constant conversion.
2. The reaction follows the first order kinetics.
3. The temperature dependence of the reaction rate constant obeys Arrhenius equation.

The data from dynamic DSC measurements was analyzed in accordance to the following equation:

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

where ϕ = heating rate (°C/min)
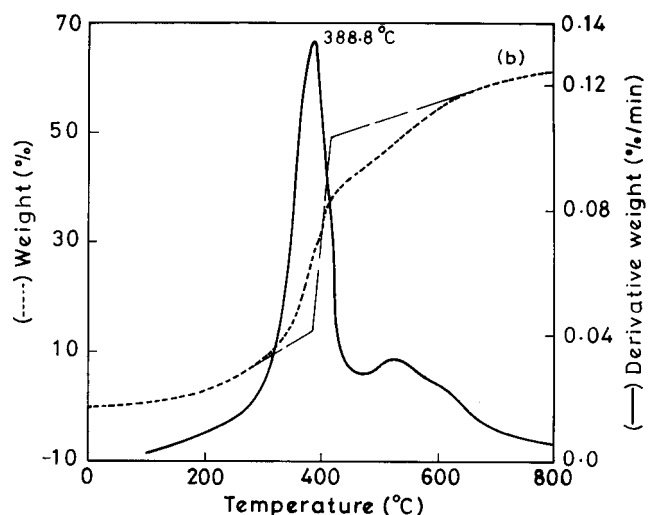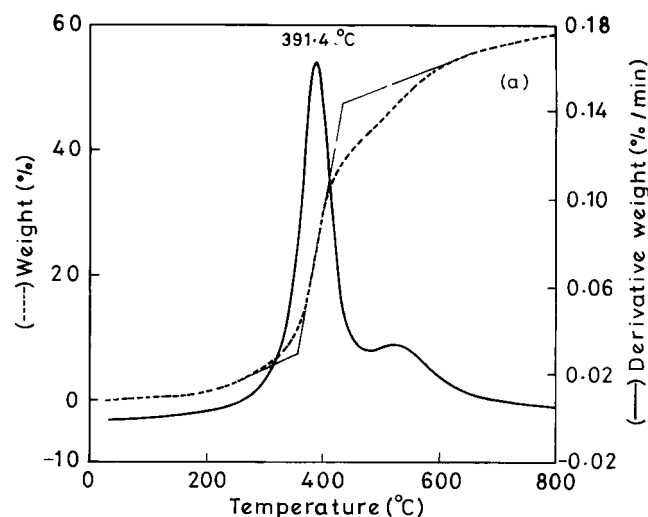
E_a = activation energy (kJ/mol)

R = gas constant (8.314 J/mol K)

T_p = peak exothermic temperature (K)
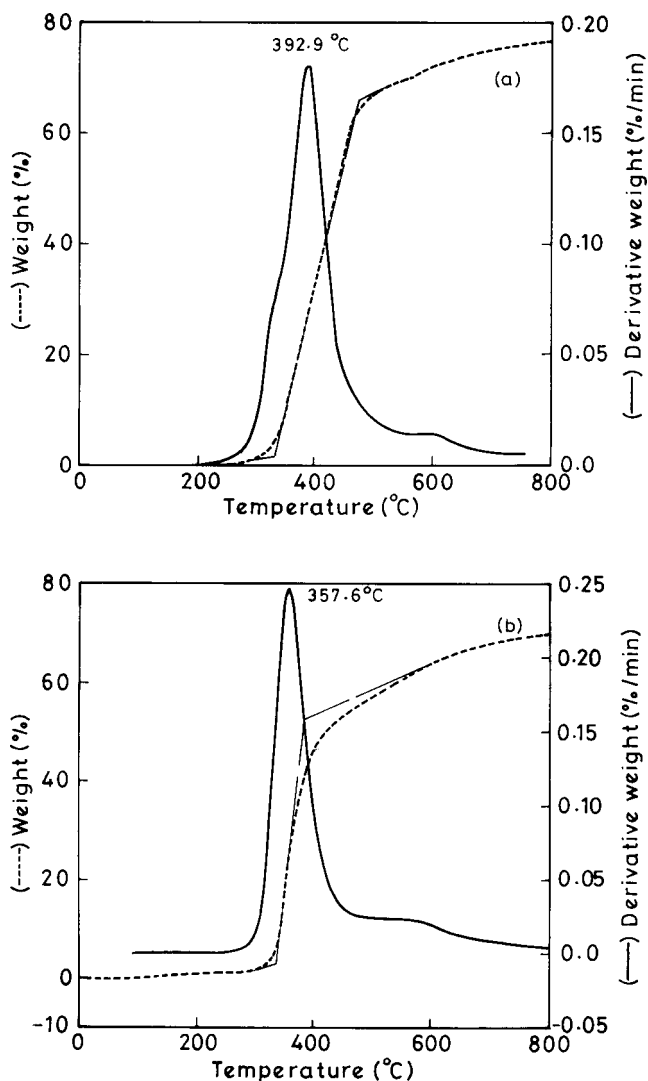
Assuming a constant conversion at the peak exotherm temperature, plots of log ϕ versus $1/T_p$ were

obtained and the activation energy was calculated using standard procedure. Plots of log ϕ versus $1/T_p$ are shown in Figure 5. Activation energy of curing was found to be dependent on the structure of dianhydride and on the molar ratio of DDS/BTDA or DDS/NTDA. Activation energy was higher for anhydride-cured system 135 kJ/mol (EN), 139 kJ/mol (EB) as compared to DDS cured system 74 kJ/mol (ED) (Tables I and II). In case of EB and EN samples, a significant decrease in activation energy was observed upon addition of 0.25 mol of DDS to DDS/BTDA system (EB-3). Further increase of DDS content did not show any definite trend in the activation energy.

Activation energy for system cured using mixture of anhydride and amine is lower than the samples cured using either anhydrides (EB, EN) or DDS alone (ED) (Tables I and II). This could be due to the more complex mechanism of curing DGEBA in presence of mixture as reported earlier for catalyzed epoxy-anhydride curing system.[23] Considering the

Figure 6 TG/DTG traces of the cured DGEBA resin with BTDA and DDS/BTDA mixture (a) EB and (b) EB-3.

Figure 7 TG/DTG traces of the cured DGEBA resin with NTDA and DDS/NTDA mixture (a) EN and (b) EN-2.

In the DSC scans of isothermally cured samples (curing done by heating at 120 ± 10°C for DDS/BTDA (EB samples) and at 240 ± 10°C for DDS/NTDA (EN samples) in an air oven for 2 h), no shift in the base line was observed in the temperature range upto 350°C. Absence of exothermic transition indicated the completion of curing. It was not possible to determine the glass transition temperature of the cured resins from the DSC scans as no shift in base line was observed under the experimental conditions.

Thermal stability

Figures 6 [(a) EB and (b) EB-3] and 7 [(a) EN and (b) EN-2] show the TG/DTG traces of isothermally cured epoxy resins. Isothermal curing of epoxy resin i.e., EB (DDS/BTDA mixture) and EN (DDS/NTDA mixture) samples was done by heating in an air oven for 2 h at 120 ± 10°C and at 240 ± 10°C respectively. All the samples were stable up to 360 ± 20°C and started losing weight above this temperature.

The relative thermal stability of the cured resins was evaluated by comparing initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{max}), final decomposition temperature (FDT) and percent char at 800°C. The results of TG/DTG scans are summarized in Tables III and IV. DGEBA cured with BTDA alone or using mixture of DDS/BTDA in varying molar ratio (samples EB-1, EB-2, and EB-3) had lower values of IDT, T_{max} and FDT as compared to ED; however the char yield was much higher in all the samples as compared to ED. Char yield was found to be maximum in EB-1 (DDS/BTDA in the ratio of 0.75/0.25). Several reactions are possible when a mixture of amine, dianhydride, and DGEBA are reacted together, such as: formation of more stable imide structures or crosslinking through reaction of BTDA/NTDA with hydroxyl group. Thermal stability of the resin is dependent on the structure of network, degree of crosslinking etc, which in turn is dependent on the nature and amount of curing agent.

In case of EN samples, a similar trend was observed i.e., IDT, T_{max} and FDT decreased as the

complex nature of curing reaction, the activation energy is an overall value including various steps of curing reaction. Activation energy for samples cured using of DDS/NTDA mixture was higher as compared to those cured using DDS/BTDA mixture. This can be explained on the basis of higher rigidity of NTDA, which might be responsible for the decreased mobility.

TABLE III
Results of TG/DTG Traces of Cured Epoxy Resins in Nitrogen Atmosphere [DGEBA Cured Isothermally in Presence of DDS/BTDA Mixture by Heating in an Air Oven at 120 ± 10°C for 2h]

Sample designation	DDS : BTDA molar ratio	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield at 800°C	LOI (%)
EB	0 : 1	358.1	391.4	433.7	41.5	34.1
EB-3	0.25 : 0.75	386.6	388.8	418.3	38.9	33.1
EB-2	0.5 : 0.5	341.2	383.8	460.7	32.6	30.5
EB-1	0.75 : 0.25	338.4	380.1	460.1	65.4	43.7
ED	1 : 0	394.9	419.9	466.0	19.2	25.2

TABLE IV
Results of TG/DTG Traces of Cured Epoxy Resins in Nitrogen Atmosphere [DGEBA Cured Isothermally in Presence of DDS/NTDA Mixture by Heating in an Air Oven at 240 ± 10°C for 2h]

Sample designation	DDS : NTDA molar ratio	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield at 800°C	LOI (%)
EN	0 : 1	333.2	392.9	465.1	23.7	27.0
EN-3	0.25 : 0.75	350.2	366.1	381.3	37.0	32.3
EN-2	0.5 : 0.5	338.7	357.6	384.6	30.2	29.6
EN-1	0.75 : 0.25	329.8	356.1	402.2	48.6	36.9

amount of NDTA in the mixture decreased; however the char yield at 800°C was found to be maximum in sample EN-1 (DDS/NTDA in the ratio of 0.75/0.25). All the samples obtained using mixture of NTDA/DDS had char yield higher than those cured using only NTDA (EN). Char yield can be used as a criteria for evaluating limiting oxygen index (LOI) of the resins in accordance to Van Krevelen and Hoftyzer equation.[24]

$$LOI = 17.5 + 0.4CR$$

where CR = char yield.

All the samples had LOI values, calculated based on their char yield, higher than 28. On the basis of LOI values, such materials can be classified as self-extinguishing resin.

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 and nature of curing agents. Thermal stability of the cured material was found to be dependent on the structure of network. Epoxy resins obtained with BTDA alone gave cured resins having much higher thermal stability as compared to resin obtained using NTDA alone. Composition of the mixture had a large effect on the curing and thermal behavior. Optimum curing characteristics with excellent thermal stability was obtained in case of samples EB-1 and EN-1. Inspite of more rigid structures because of naphthalene rings, lower stability in EN could due to the low crosslink density.

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