Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 2, 495–501

STUDIES ON THE CURING KINETICS OF EPOXY RESINS USING MIXTURE OF NADIC/OR MALEIC ANHYDRIDE AND 4,4'-DIAMINODIPHENYL SULFONE

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Curing kinetics of diglycidyl ether of bisphenol-A (DGEBA) in the presence of maleic anhydride (MA)/or nadic anhydride (NA) or mixture of MA/NA: 4,4'-diaminodiphenyl sulfone (DDS) in varying molar ratios were investigated using differential scanning calorimetry. Curing behaviour of DGEBA in the presence of varying amounts of DDS:MA/NA was evaluated by recording DSC scans at heating rates of 5, 10, 15 and 20°C min^{-1}. The peak exotherm temperature depends on the heating rate, structure of the anhydride as well as on the ratio of anhydride: DDS. Thermal stability of the isothermally cured resins was evaluated by thermogravimetry. The char yield was highest in case of resins cured using mixture of DDS:MA (0.75:0.25; sample EM-1) and DDS:NA (0.75:0.25, sample EN-1).

Keywords: *curing kinetics, diglycidyl ether of bisphenol-A (DGEBA), maleic anhydride, nadic anhydride, thermal stability*

Introduction

Epoxy resins are one of the most versatile polymers and are thus widely used in technical applications such as coatings, encapsulations, structural composites, casting and adhesives [1]. Today, epoxy systems can be generally classified with respect to their curing temperatures i.e. low temperature curing and high temperature curing systems [2]. Epoxies requiring curing temperatures beyond 120°C belong to the group of high temperature curing systems and involve hardeners such as cycloaliphatic or aromatic amines, polyphenols, dicyandiamides, isocyanates and carboxylic anhydrides. On the other hand, epoxy resins that are curable at room or slightly higher temperature (<120°C), are known as low temperature-curing formulations, with commonly used hardeners being primary and secondary aliphatic amines, polyaminoamides or thiols [3].

Carboxylic acid anhydrides are some of the most important high temperature curing agents used for the conversion of the epoxy resins to highly cross-linked, glassy, three dimensional networks [4–7]. Especially for electrical applications, anhydride hardeners show some outstanding properties, i.e. low exotherm and shrinkage 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 disadvantage of anhydride-curing agents is that they require high curing temperatures to initiate the curing reaction and to reach the advanced property/performance profile required in terms of glass transition temperature and mechanical and thermal stabilities at evaluated temperatures. High curing temperature results in high-energy consumption, long processing cycles and difficult handling of tools and moulds. On the other hand, low temperature curing systems usually have an inadequate property profile at elevated temperature, which often limit their technical usage. The challenge is to achieve low temperature processing and curing of anhydride/DDS systems and also attain the advanced property profile of systems cured at higher temperatures.

In the late 1970's, Graham and co-workers suggested that this could be achieved with epoxy/anhydride systems cured at low temperature [8, 9]. Vohwinkel [10] carried out further work on the investigation of various resins and hardener combinations based on amino-glycidyl/anhydride systems cured at temperature below 120°C. The mechanism of complex, non-catalysed epoxy-anhydride curing reactions has been extensively studied [11–14]. Curing and thermal behaviour of DGEBA using phthalic anhydride and pyromellitic dianhydride was investigated in our laboratory [15] and it was observed that structure and amount of anhydride has a large affect on the curing characteristics. It was therefore considered of interest to investigate systematically the curing behavior of DGEBA in presence of other anhydrides.

The present paper describes the systematic studies on the curing mixture of DDS:MA/NA in the ratio of

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1388–6150/$20.00

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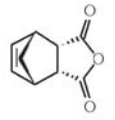
0:1, 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0. The epoxy samples cured using mixture of DDS:MA and DDS:NA have been designated as EM and EN respectively followed by a numerical suffix. For example epoxy cured using of mixture of DDS:MA in the ratio of 0:1, 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 have been designated as EM, EM-3, EM-2, EM-1and EM-0, respectively. Similarly samples cured using mixture of nadic anhydride and DDS were designated.

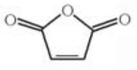
Experimental

Materials

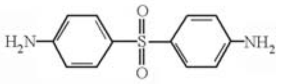
Diglycidyl ether of bisphenol-A (DGEBA, Grade LY556 having an epoxy equivalent 177) was procured from Hindustan Ciba Geigy Ltd. Methyl ethyl ketone, maleic anhydride (MA), nadic anhydride (NA) and 4,4'-diaminodiphenyl sulfone (DDS) (all of Merck) were used as such and their structures are shown below:



nadic anhydride (NA)



maleic anhydride (MA)



4,4'-diaminodiphenylsulfone (DDS)

Methods

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^{-1}. For curing studies, samples were obtained by mixing DGEBA with stoichiometric amounts of DDS/anhydride/or a mixture of DDS:anhydride in varying molar ratio dissolved in methyl ethyl ketone. After thorough mixing, the solvent was removed 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 400°C. 5±2 mg of sample was used in each experiment.

Thermal stability

Thermal stability of the resins cured isothermally by heating 300±50°C for 2 h in an air oven in the presence of DDS/MA/NA or a mixture of DDS:MA/NA in varying molar ratio was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 cm^3 min^{-1}) using a Rheometric Scientific module. A heating rate of 20°C min^{-1} and powdered samples of 10±2 mg were used in each experiment.

Results and discussion

In the DSC scans of all the samples, a broad exothermic transition was observed. Typical DSC scans of samples EM, EM-1 and EN-1, EN-2 are shown in Figs 1 and 2. The curing of epoxy resin depends on the structure of the curing agents and its stoichiometry. In the present work, we did not change the stoichiometry, however the ratio of amine:anhydride was varied to evaluate its effect on the curing behaviour. 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.
- T_p=temperature of peak position of exotherm.
- T_f=temperature of the end of curing exotherm.
- ΔH=heat of curing, calculated by measuring the area under the exothermic transition.

The results are summarized in Tables 1 and 2. The curing exotherm were characterized by noting T_i, T_{onset}, T_p and T_f. All these temperatures were dependent on the structure of anhydride as well as on the ra-

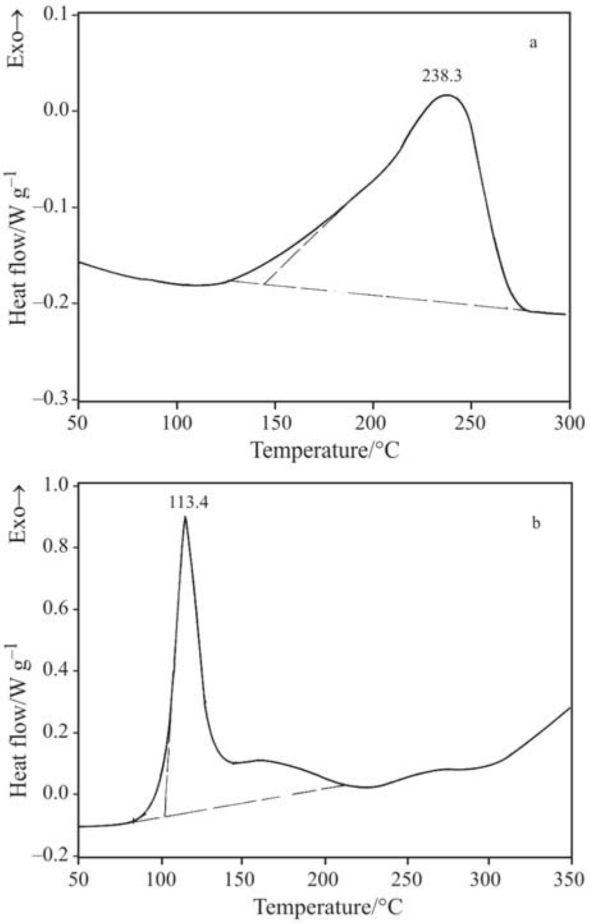


Fig. 1 DSC scans of a – EM and b – EM-1 at 10°C min^{-1}

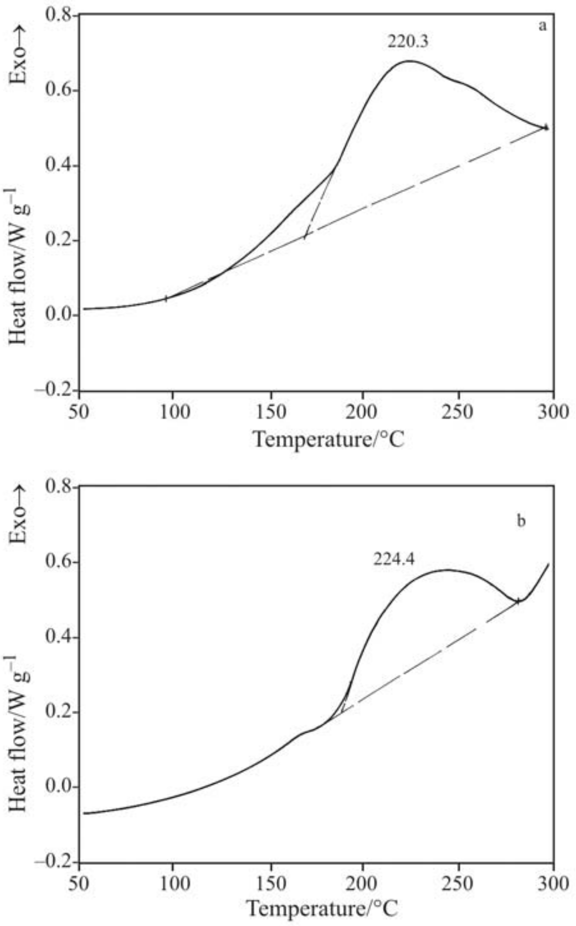


Fig. 2 DSC scans of a – EN-1 and b – EN-2 at 10°C min^{-1}

tio of anhydride to amine. The curing reaction started directly after adding the hardener mixture to the epoxy resin and a visible change in colour from light yellow to deep red green was observed.

In the presence of MA alone (i.e. sample EM), a broad exothermic transition in the temperature range of 128–276°C was observed (heating rate 10°C min^{-1}) whereas in the presence of NA (i.e. sample EN), a major exothermic transition was observed in the temperature range of 276–366°C. In case of DGEBA cured with DDS (i.e. sample EM-0 or EN-0), a broad exothermic transition in the temperature range of 131–296°C was observed. Anhydrides are often used where thermal stability is of importance, however curing in the presence of anhydride gave diffused exotherm. It was therefore investigated the curing of DGEBA in the presence of mixture i.e. amine and anhydride to get an optimum combination of curing and thermal stability.

In case of DGEBA cured using mixture of DDS:MA, two exothermic transitions were observed in samples having higher/equal amounts of MA (i.e. in samples EM-2 and EM-3) whereas it showed a single exotherm in samples having higher amount of DDS (EM-1). In case of samples EM-2 and EM-3, first exotherm peak temperature decreased significantly with increasing amount of MA whereas peak exotherm temperature due to second exotherm increased. A sharp exothermic transition followed by a broad diffused exotherm was observed in all the samples. T_i, T_{onset}, T_p and T_f showed a significant decrease at the molar ratio of DDS:MA (sample EM-1). This clearly showed that partial replacement of DDS by MA i.e. sample EM-1 (DDS:MA molar ratio 0.75:0.25) resulted in a significant reduction in the curing temperature.

The curing behavior of EN-3 sample was very close to EN-0. An endothermic peak at 174°C followed by a diffused exotherm in the temperature range of 174–278°C. Major exothermic transition was observed in the temperature range of 278–374°C followed by an exotherm due to degradation. In EN-2, a very broad and diffused exotherm was observed. A significant decrease in the curing temperatures was observed when mixture of DDS:NA was used in ratio of 0.75:0.25. These results clearly showed that addition of mixture of DDS:NA at molar ratio of 3:1 and 1:1 gave a single exotherm and curing temperature was lowered significantly in sample EN-1.

The DSC scans of the isothermally cured samples were recorded at 10°C min^{-1}. There is significant increase in T_g when amount of DDS is replaced by NA i.e., EN-1 (DDS:NA; 0.75:0.25). Further increase of NA content in the mixture of the samples i.e., EN-2 and EN-3, decrease in T_g was observed. One would have expected the increase of T_g values with increasing amount of NA in the mixture. However the decrease in T_g was observed, this could be due to the decrease in the crosslink density. The DSC scans of the cured samples containing NA or MA alone and DDS:MA mixture, no shift in the baseline was observed in the temperature range up to 350°C. The T_g values are summarized in the Tables 1 and 2. Sample cured using NA alone did not show any T_g in the DSC scans whereas DGEBA cured with DDS alone showed a T_g of 112°C. T_g of DBEBA resins cured using mixture of DDS and NA was found to be independent on the ratio and it decreased with increasing amounts of NA. Maximum T_g was observed when ratio of DDS:NA was taken as 0.75:0.25. In the DSC scans of DGEBA cured using MA alone or mixture of DDS and MA, no shift in the base line was observed in the temperature range of investigation.

Curing kinetics

The kinetic parameters of the curing reaction can be obtained from dynamic DSC scans or isothermal experiments. The dynamic method was used in the pres-

Table 1 Results of DSC scans of DGEBA in the presence of maleic anhydride or mixture of DDS:MA at varying heating rate

Sample designation	Molar ratio of DDS:MA	Heating rate/ °C min^{-1}	T_i/ °C	T_{onset}/ °C	T_p/ °C	T_f/ °C	ΔH/ J g^{-1}	E_a/ kJ mol^{-1}	T_g/ °C
EM	0:1	5	125.5	156.3	219.2	280.1	97.0	57.5	–
		10	128.7	143.8	238.3	275.8	72.1		
		15	130.1	185.2	247.8	293.9	104.1		
		20	154.6	220.9	271.7	294.7	51.7		
EM-3	0.25:0.75	5	81.7	87.7	110.9	138.6	6.8	64.0	–
			155.7	173.1	184.7	219.6	56.9	134.0	
		10	91.3	98.2	123.6	153.5	6.4		
			167.0	182.1	193.3	244.9	77.7		
		15	95.9	101.9	133.4	168.1	7.4		
			178.4	189.0	198.9	255.9	50.6		
		20	102.7	105.9	141.7	172.0	4.0		
			184.1	192.1	202.4	250.6	38.8		
EM-2	0.5:0.5	5	124.7	131.9	139.7	156.0	20.4	136.5	–
			156.0	160.3	173.2	198.7	39.2	136.6	
		10	132.2	139.6	145.8	166.0	12.8		
			166.0	170.3	182.8	215.4	15.1		
		15	136.8	144.8	151.0	170.0	10.0		
			170.0	173.6	186.8	229.2	24.0		
		20	137.9	148.0	154.0	172.0	8.3		
			172.0	176.2	190.6	229.2	30.8		
EM-1	0.75:0.25	5	81.6	96.9	107.5	203.6	201.3	145.0	–
		10	82.4	101.4	113.4	203.2	150.3		
		15	84.5	103.0	116.1	225.6	203.7		
		20	88.7	105.5	119.1	231.0	169.0		
EM-0	1:0	5	119.8	158.1	210.1	274.4	255.0	60.0	112.2
		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 2 Results of DSC scans of DGEBA in the presence of nadic anhydride or mixture of DDS:NA at varying heating rate

Sample designation	Molar ratio of DDS:NA	Heating rate/ °C min^{-1}	T_i/ °C	T_{onset}/ °C	T_p/ °C	T_f/ °C	ΔH/ J g^{-1}	E_a/ kJ mol^{-1}	T_g/ °C
EN	0:1	5	274.3	281.4	313.5	346.5	160.5	101.0	–
		10	276.6	298.0	328.7	366.1	366.1		
		15	283.7	303.3	339.0	386.2	386.2		
		20	316.2	321.8	350.1	399.8	399.8		
EN-3	0.25:0.75	5	170.6	171.4	198.9	236.9	37.4	32.1	127.7
			236.9	274.2	303.7	319.9	128.6		
		10	171.2	174.0	205.8	279.0	45.3	109.3	
			279.0	291.8	327.9	344.6	244.2		
		15	178.9	207.9	229.5	261.3	18.4		
			290.2	305.6	331.3	347.1	79.2		
		20	221.8	232.5	248.2	271.9	5.8		
			292.4	304.0	338.8	369.7	158.7		
EN-2	0.5:0.5	5	179.1	180.0	192.5	236.4	48.7	65.0	135.6
		10	181.5	183.4	224.4	280.4	56.6		
		15	187.5	204.5	227.7	281.4	12.3		
		20	202.4	210.0	231.9	282.6	20.2		
EN-1	0.75:0.25	5	93.1	141.4	196.5	285.1	221.8	72.8	152.2
		10	96.7	169.7	220.3	297.4	161.5		
		15	126.5	183.1	229.7	296.1	117.8		
		20	148.6	190.0	238.3	294.8	78.0		
EN-0	1:0	5	119.8	158.1	210.1	274.4	255.0	60.0	112.2
		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		

ent study and the DSC scans were recorded at different heating rates for the samples. Figures 3 and 4 show DSC scans for resin samples EM-3 and EN-3 using different heating rates. The characteristic curing temperatures for the DGEBA at different heating rates in the presence of anhydride, DDS and mixture of DDS:MA/or NA are summarized in Tables 1 and 2. As expected in all the samples, curing temperatures increased with the increasing heating rate. The activation energy of the curing reaction was calculated using Ozawa's method [16, 17] assuming that

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

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

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

where ϕ is the heating rate, E_a the activation energy, R the gas constant. Assuming a constant conversion at the peak exotherm temperature, a plot of $\log\phi$ *vs.* $1/T_p$ was obtained and the results are given in Tables 1 and 2. Activation energy of sample containing both mixtures of DDS:MA or DDS:NA was higher as compared to sample containing either MA/NA or DDS alone.

Thermal stability

Figures 5 and 6 show TG/DTG traces of isothermal cured epoxy resins (a) EM (b) EM-3 and (a) EN-3 (b) EN-2 respectively. 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 800°C. The results are summarized in Tables 3 and 4. The EM and EN samples were cured isothermally by heating at 200±10 and 320±10°C for 3 h, respectively. DGEBA cured with MA alone or using mixture of DDS:MA in varying molar ratios had higher values of IDT, T_{max}, and as compared to EM-0. Char yield was found to be maximum in EM-1 0.75:0.25 (DDS:MA) and was much higher than the theoretical value (16.4) calculated on the basis of additively rule. These results clearly show that at a molar ratio of 0.75:0.25 (DDS:MA) a narrow curing exothermic

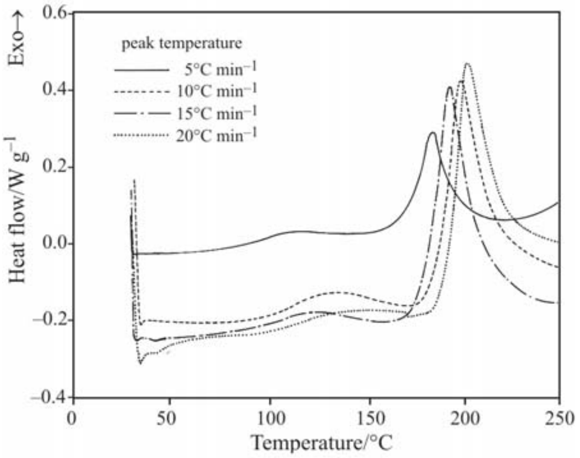


Fig. 3 DSC scans of EM-3 at different heating rates

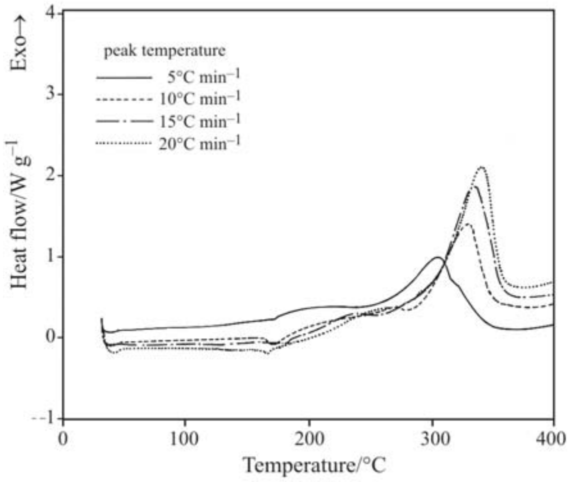


Fig. 4 DSC scans of EN-3 at different heating rates

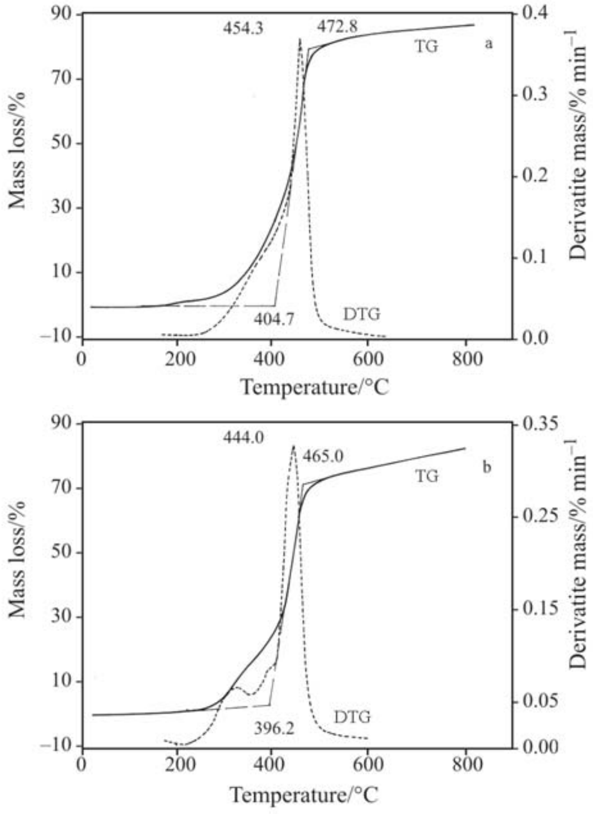


Fig. 5 TG traces of a – EM and b – EM-3 at 20°C min^{-1}

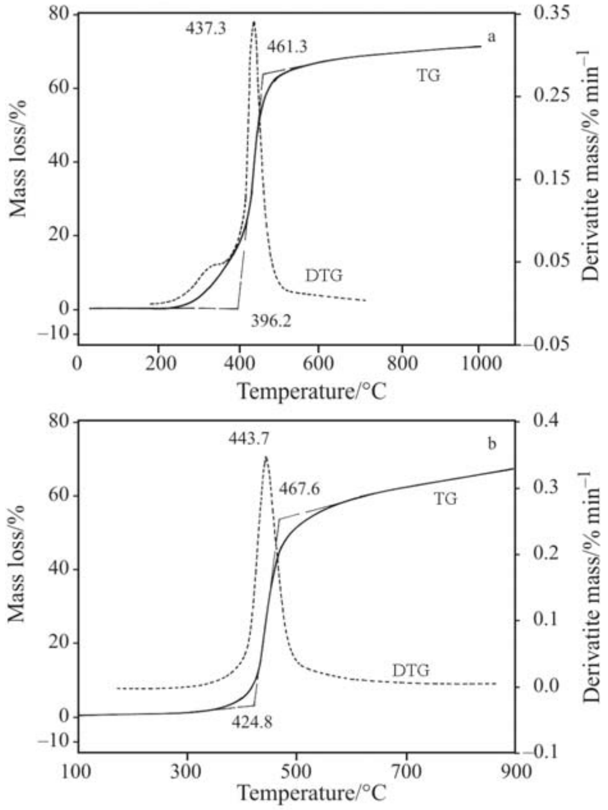


Fig. 6 TG traces of a – EN-3 and b – EN-2 at 20°C min^{-1}

along with a better thermal stability could be due to the formation of modified network structure. Several reactions are possible when a mixture of amine, anhydride and DGEBA are reacted together such as formation of more stable imide structure, cross linking through the double bond present in MA/NA or opening of epoxy by MA/NA/amine. At a molar ratio of DDS:MA (0.75:0.25) showed the formation of more compact network with better thermal stability can be explained on the basis of all the reaction occurring during curing.

In order to prove the network formation and its compactness, we investigated the isothermal curing of DGEBA in the presence of varying molar ratio of DDS:MA/NA or by using DDS/MA/NA separated. Isothermal curing was done by heating the mixture of DGEBA with curing agent (DDS/NA/MA or mixture of DDS:MA/NA) in an air oven at T_{onset} obtained from DSC scan. The samples were taken out at regular intervals of heating time and % gel content was calculated. Gel content was calculated by determining the percent solubility in DMF.

Samples cured using MA alone (sample EM-0 at 210°C for 60 min) or DDS:MA mixture in the ratio of 0.25:0.75 (sample EM-3 at 190°C for 30 min), 0.5:0.5 (sample EM-2 at 140°C for 30 min) remain in the form of liquid or semi-solid and were completely soluble in DMF and DMSO. Solid samples were obtained after isothermal aging for 120 min and were completely insoluble. On the other hand DGEBA cured with DDS:MA mixture (0.75:0.25) after heating at 105.5°C became solid after 15 min (100% gel content), which became completely insoluble after 30 min of heating. From these results, it can be concluded that network formation is very much dependent upon their nature and the composition of the curing agents.

In case of EN samples, a similar trend was observed i.e. IDT, $T_{\max}$ and FDT increased with increase molar ratio of NA in the mixture, however the char yield at 800°C was found to be maximum in sample EN-1 (DDS:NA in the ratio of 0.75:0.25). All the samples obtained using mixture DDS:NA had char yield higher

Table 3 Results of thermal stability of isothermal cured epoxy resins (DDS:maleic anhydride) at 20°C heating rate in nitrogen atmosphere

Sample designation	IDT/°C	$T_{\max}$/°C	FDT/°C	Char yield at 800°C	LOI/%
EM	404.7	454.3	472.8	13.7	23.0
EM-3	396.2	444.0	465.0	18.1	24.8
EM-2	401.4	428.5	452.0	19.2	25.2
EM-1	413.0	433.5	457.1	22.2	26.4
EM-0	394.9	419.9	466.0	19.2	25.2

Table 4 Results of thermal stability of isothermal cured epoxy resins (DDS:nadic anhydride) at 20°C heating rate in nitrogen atmosphere

Sample designation	IDT/°C	$T_{\max}$/°C	FDT/°C	Char yield at 800°C	LOI/%
EN	413.8	442.0	472.3	27.9	28.7
EN-3	424.8	443.7	467.6	35.0	31.5
EN-2	398.4	437.3	461.3	30.0	29.5
EN-1	413.9	433.5	449.1	38.2	32.8
EN-0	394.9	419.9	466.0	19.2	25.2

than either of those cured using only NA (EN) or DDS (EN-0). Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins in accordance with Van Krevelen and Hoftyzer equation [18].

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

where CR=char yield.

All the samples had LOI values calculated based on their char yield was higher than 28. On the basis of LOI values, such materials can be classified as self-extinguishing resin. Thermal stability of epoxy resin cured using mixture of DDS:NA (EN) was higher as compared to DDS:MA at all molar ratios. Nadimides are reported to have better thermal stability and higher T_g as compared to maleimides [19]. The higher thermal stability of DGEBA cured using mixture of DDS:NA could be due to the in-situ formation of nadimides in the cured network.

Conclusions

From these results, it can be concluded that the curing behaviour 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 using mixture of nadic anhydride and DDS gave cured resins having much higher thermal stability as compared to resin obtained using mixture of DDS and MA. Composition of the mixture had a large effect on the curing and thermal behaviour. Optimum curing characteristics with excellent thermal stability was obtained in case of sample EM-1 and EN-1.

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Received: July 5, 2006
Accepted: September 5, 2006
OnlineFirst: June 1, 2007

DOI: 10.1007/s10973-006-7793-x