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Curing and Thermal Behaviour of N,N'-Diglycidyl benzophenone Tetracarboxydiimide Resin Using Mixture of Nadic/or Maleic Anhydride and 4,4'-Diaminodiphenylsulphone

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Curing studies of N,N'-diglycidyl benzophenone tetracarboxydiimide epoxy resin in the presence of maleic anhydride/or nadic anhydride or mixture of maleic anhydride/nadic anhydride: 4,4'-diaminodiphenyl sulfone in varying molar ratios were investigated using differential scanning calorimetry. Thermal stability of the isothermally cured resins was evaluated by thermogravimetry.

Key Words: Epoxy resin, Curing behaviour, 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 ºC 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 ºC), 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[4,5]. 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. Graham and co-workers suggested that this could be achieved with epoxy/anhydride systems cured at low temperature[6,7]. Vohwinkel[8] carried out further work on the investigation of various resins and hardener combinations based on amino-glycidyl/anhydride systems cured at temperature below 120 ºC. The mechanism of complex, non-catalyzed epoxy-anhydride curing reactions has been extensively studied[9-12]. Curing and thermal behaviour of epoxy resin using phthalic anhydride and pyromellitic dianhydride was investigated by some co-workers[13]. 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 behaviour of N,N'-diglycidyl benzophenone tetracarboxydiimide (DGBT) epoxy resin in presence of some anhydrides.

The present paper describes the systematic studies on the curing mixture of 4,4'-diaminodiphenyl sulfone and maleic anhydride/nadic anhydride (DDS:MA/NA) in the ratio of 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 has been designated as DM and DN, 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 DM, DM-3, DM-2 and DM-1and DM-0, respectively. Similarly samples cured using mixture of nadic anhydride and DDS were designated.

EXPERIMENTAL

N,N'-Diglycidyl benzophenone tetracarboxydiimide (DGBT), grade LY559 having an epoxy equivalent 178) 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.

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 curing studies, samples were obtained by mixing DGBT with stoichiometric amounts of DDS/anhydride/or a mixture of DDS: anhydride in varying molar ratio dissolved in ethyl methyl 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) 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. The curing exotherm was characterized by noting the following temperatures: T_i (The kick-off temperature, where the curing starts), T_{onset} (the temperature where the first detectable heat was released, obtained by the extrapolation of steepest portion of the curve), 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 curve, ΔH (the heat of curing, calculated by the measurement of the area under the exothermic transition).

The results are summarized in Tables 1 and 2. In the presence of MA alone (*i.e.*, sample DM), a broad exothermic transition in the temperature range of 128-276 °C was observed (heating rate 10 °C/min) whereas in the presence of NA (*i.e.*, sample DN), a major exothermic transition was observed in the temperature range of 276-366 °C. In case of DGBT cured with DDS (*i.e.*, sample DM-0 or DN-0), a broad exothermic transition in the temperature range of 131-296 °C was observed.

In case of DGBT cured using mixture of DDS: MA, two exothermic transitions were observed in samples having higher/equal amounts of MA (*i.e.*, in samples DM-2 and DM-3) whereas it showed a single exotherm in samples having higher amount of DDS (DM-1). In case of samples DM-2 and DM-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 DM-1). This clearly showed that partial replacement of DDS by MA *i.e.*, sample DM-1 (DDS: MA molar ration 0.75:0.25) resulted in a significant reduction in the curing temperature.

The curing behaviour of DN-3 sample was very close to DN-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 DN-2, a very broad and diffused exotherm was observed. A significant decrease in the curing temperatures was observed

TABLE-1
RESULTS OF DSC SCANS OF DGBT 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	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (KJ/mol)	T_g (°C)
DM	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		
DM-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		
DM-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	25.1		
		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		
DM-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		
DM-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 SCAN OF DGBT IN THE PRESENCE OF NADIC ANHYDRIDE OR MIXTURE OF DDS:NA AT VARYING HEATING RATE

Sample designation	Molar ratio of DDS: NA	Heating rate	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (KJ/mol)	T_g (°C)
DN	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		
DN-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		
DN-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		
DN-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		
DN-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		

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 DN-1.

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 present study and the DSC scans were recorded at different heating rates for the samples. The characteristic curing temperatures for the DGBT 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[14,15] assuming that (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 are analyzed in accordance with the following equation:

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

where ϕ is the heating rate, E_a is the activation energy and R is the gas constant. Assuming a constant conversion at the peak exotherm temperature, a plot of log ϕ *versus* $1/T_p$ 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: 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 per cent char yield at 800 °C. The results are summarized in Tables 3 and 4. DGBT cured with MA alone or using mixture of DDS: MA in varying molar ratios had higher values of IDT, Tmax and as compared to DM-0.

In case of DN 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 DN-1 (DDS:NA in the ratio of 0.75:0.25). All the samples obtained using mixture DDS:NA had char yield higher than either of those cured using only NA (DN) or DDS (DN-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[16].

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 (%)
DM	404.7	454.3	472.8	13.7	23.0
DM-3	396.2	444.0	465.0	18.1	24.8
DM-2	401.4	428.5	452.0	19.2	25.2
DM-1	413.0	433.5	457.1	22.2	26.4
DM-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 ºC HEATING RATE IN NITROGEN ATMOSPHERE

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

$$\text{Limiting oxygen index (LOI)} = 17.5 + 0.4\text{CR}$$

where CR = char yield.

All the samples had limiting oxygen index values calculated based on their char yield was higher than 28. On the basis of limiting oxygen index values, such materials can be classified as self-extinguishing resin. Thermal stability of epoxy resin cured using mixture of DDS:NA (DN) 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[17]. The higher thermal stability of DGBT cured using mixture of DDS:NA could be due to the *in situ* formation of nadimides in the cured network.

Conclusion

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 DM-1 and DN-1.

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