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CURING KINETICS AND THERMAL STABILITY OF DIGLYCIDYL ETHER OF BISPHENOL

Mixture of aromatic imide-amines of benzophenone 3,3’, 4,4’-tetra- carboxylic acid dianhydride and 4,4’-diaminodiphenylsulfone

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Curing kinetics of diglycidyl ether of bisphenol-A (DGEBA) in the presence of varying molar ratios of aromatic imide-amines and 4,4’-diaminodiphenylsulfone (DDS) were investigated by the dynamic differential scanning calorimetry. The imide-amines were prepared by reacting 1 mole of benzophenone 3,3’,4,4’-tetracarboxylic acid dianhydride (B) with 2.5 moles of 4,4’-diaminodiphenyl ether (E)/ or 4,4’-diaminodiphenyl methane (M)/ or 4,4’-diaminodiphenylsulfone (S) and designated as BE/ or BM/ or BS. 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 behaviour of DGEBA.

The multiple heating rate method (5, 10, 15 and 20°C min^{-1}) 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-amines as well as on the ratio of imide-amine: DDS used. A broad exotherm was observed in the temperature range of 180–230°C on curing with mixture of imide-amines and DDS. Curing of DGEBA with mixture of imide-amines and/or DDS resulted in a decrease in characteristic curing temperatures. Activation energy of curing reaction as determined in accordance to the Ozawa’s method was found to be dependent on the structure of amine. The thermal stability of the isothermally cured resins was also evaluated using dynamic thermogravimetry in a nitrogen atmosphere. The char yield was highest in case of resins cured using mixture of DDS: BS (0.25:0.75; EBS-3), DDS: BM (0.5: 0.5; EBM-2) and DDS: BE (0.5: 0.5; EBE-2).

Keywords: *curing kinetics, DGEBA, epoxy resins, imide-amines, thermal stability*

Introduction

Epoxy resins have been commercially available for about 45 years and are now used in many major industrial applications, especially where major technical advantages warrant their somewhat higher cost with respect to other thermosets. The characteristics of toughness, low shrinkage on curing, high adhesion to many substrates, good alkali resistance, versatility in formulation make epoxy resins widely used in adhesive, laminating, coating, and casting applications. The chemistry and technological applications of epoxy are voluminous, and there are many new developments each year. To meet some application requirements, several approaches have been used to enhance the thermal properties of epoxy resins [1, 2].

The full characterization of the cure process of an epoxy resin involves many factors, that is, the properties and performance of the cured epoxy resin, which are dependent on the type of epoxy resin, the curing agent, and the curing conditions used. If the chemical structures of cured epoxy resins are constituted with aromatic rings, heterocyclic rings, or both, their thermal resistance is superior to those of constituents with flexible or aliphatic chains [3–5].

To prepare high-performance epoxies, many researchers synthesized polymeric networks with a liquid-crystalline order. The resulting networks could use in new applications because of their mechanical, electrical, and optical properties [6–9]. Liquid-crystalline epoxy networks were obtained mostly by chemical reactions between epoxy groups contained in the liquid-crystalline compounds and the curing agent. Another way to improve the thermal resistance of epoxy resins is to use a curing agent containing imide, urethane [10], or heterocyclic groups, such as hydroxyl-terminated imide compounds [11, 12], and imide-acid [13–14].

Reaction of diglycidyl ether of bisphenol-A (DGEBA) with trialkyl or aryl phosphate followed by curing with 4,4’-diaminodiphenyl sulfone gave products with good thermal stability and flame resistance [15–17]. In this article, we synthesized the various imide-amines as epoxy curing agents and investigated the curing behaviour and resultant thermal stability of diglycidyl ether of bisphenol-A (DGEBA) with mixture of imide-amines and 4,4’-diaminodiphenylsulfone (DDS).

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Experimental

Materials

Diglycidyl ether of bisphenol A (DGEBA, grade LY556, having an epoxy equivalent 177) was procured from Hindustan Ciba Geigy Ltd. 4,4’-diaminodiphenyl sulfone (S), 4,4’-diaminodiphenyl ether (E), 4,4’-diaminodiphenyl methane (M), benzophenone 3,3’,4,4’-tetracarboxylic acid dianhydride (B) all purchased from Aldrich and were 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 such. Acetic anhydride (Qualigens) was distilled before use.

The imide-amines were synthesized and characterized in our earlier publication [18].

Methods

Curing studies

TA 2100 thermal analyzer having 910 DSC module was used for recording DSC traces at heating rate of 5, 10, 15 and 20°C min^{-1}. 5±2 mg of sample was used in each experiment. For curing studies, the samples were obtained by mixing stoichiometric amounts of imide-amines and DDS with DGEBA in the varying molar ratio of 0:1, 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 using minimum amount of low boiling solvent. After thorough mixing, the solvent was evaporated under vacuum and the freshly prepared samples were used for recording DSC traces in the static air atmosphere at a programmed heating rate from room temperature upto 350°C. The epoxy samples have been designated by adding prefix E to BS/BM/BE followed by a numerical suffix. For example, epoxy cured using mixture of BS:DDS in the ratio of 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 has been designated as EBS-1, EBS-2, EBS-3 and EBS-0. The sample with DGEBA and DDS has been designated as ED. Similarly samples cured using mixture of BE/BM and DDS were designated.

Thermal stability

Thermal stability of the epoxy resins cured isothermally by heating 200±20°C for 3 h in an air oven in the presence of DDS/BS/BM/BE or a mixture of DDS: BS/BE/BM in varying molar ratio was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 cm^3 min^{-1}) using 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

Structural characterization of imide-amines

The imide-amines synthesized in the laboratory were characterized using FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopic techniques and elemental analysis and the results were reported in an earlier work [18].

Curing studies

The curing reaction of epoxy resins depends on the structure and reactivity of the curing agent. Figures 1a–c shows the DSC scans of DGEBA with mixture of imide-amines and DDS in varying proportions at 10°C min^{-1}. In the DSC traces of all the samples, a broad exothermic transition associated with curing was observed and it was characterized by the following parameters:

- The kick-off temperature (T_i), where the curing starts.
- The temperature of onset of exotherm where the first detectable heat was released (T_o). This was obtained by the extrapolation of steepest portion of the curve.

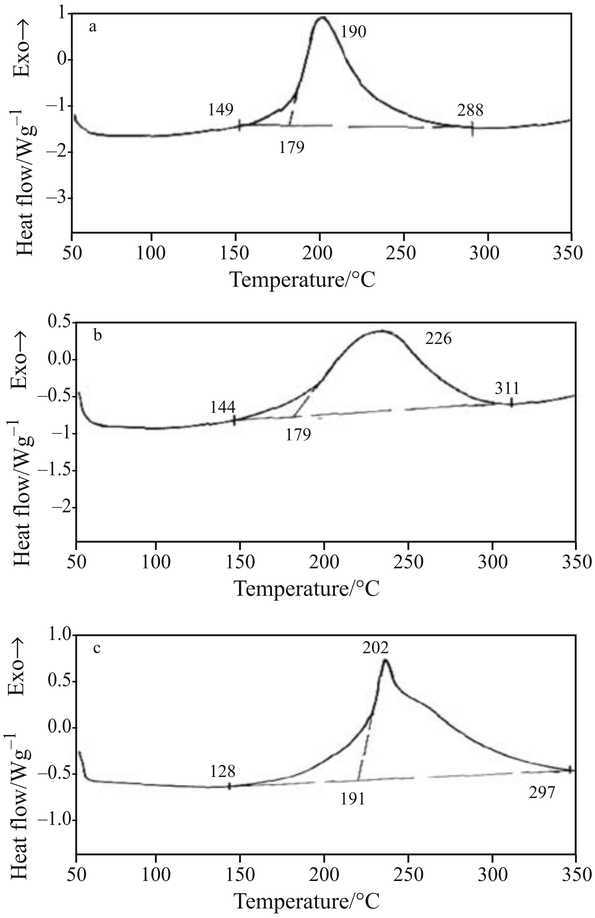

Fig. 1 DSC scans of epoxy resin with mixture of imide-amines and DDS at heating rate 10°C min^{-1} of a – EBM-1, b – EBE-2 and c – EBS-1

- The temperature of the peak position of the exotherm (T_p).
- The temperature of the end of curing exotherm (T_f) obtained by the extrapolation of the curve.
- The heat of curing (Δ*H*), calculated by the measurement of the area under the exothermic transition.

DDS is generally used as hardener for curing of epoxies. The incorporation of imide-amines along with DDS was expected to affect the curing behaviour and the thermal stability of the cured network. Therefore, imide-amine and DDS mixtures, such as BS/DDS, BM/DDS and BE/DDS, in varying molar ratio were used to cure DGEBA. The results of DSC scans are summarized in Tables 1–3. In all the samples, a single curing exotherm was observed upon curing with a mixture of imide-amine and DDS. These results thus clearly showed that the two amines act as co-curing agents. Comparing imide-amines of varying structure, T_p was found to be higher in EBS-0 (210.2°C) as compared to samples EBE-0 or EBM-0. This could be due to the electron withdrawing nature of the $-SO_2$-group which in turn reduces the nucleophilicity of the amine and hence reduces the reactivity of the amine. Addition of 0.25 mole fraction of imide-amines to DDS decreased T_i significantly. These studies clearly indicate that curing of epoxy resin and tailored by using a mixture of amines and hardener. The curing of DGEBA was initiated at

Table 1 Results of DSC scan of DGEBA in the presence of mixture of BS imide-amines and DDS at varying heating rates

Sample designation	BS/mol	Heating rate/ °C min^{-1}	T_i/°C	T_o/°C	T_p/°C	T_f/°C	Δ*H*/J g^{-1}	E_a/kJ mol^{-1}
ED	0	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	
EBS-1	0.25	5	124.7	179.3	190.0	298.6	294.5	101.8
		10	128.3	190.8	202.3	297.3	286.9	
		15	144.0	193.7	208.2	296.0	235.2	
		20	148.2	199.1	213.9	294.7	248.0	
EBS-2	0.5	5	115.5	186.7	193.1	276.2	219.3	122.7
		10	127.2	197.6	202.5	296.1	194.4	
		15	137.2	204.5	207.9	295.4	161.1	
		20	139.7	204.6	213.4	289.0	205.1	
EBS-3	0.75	5	180.8	189.5	200.6	253.4	84.4	84.1
		10	182.9	194.4	206.4	254.9	64.5	
		15	185.5	217.4	223.0	304.5	144.6	
		20	191.3	222.9	227.1	269.0	117.2	
EBS-0	1	5	181.2	203.4	206.5	243.6	58.4	101.7
		10	189.4	204.8	210.2	231.4	85.9	
		15	199.7	210.7	225.0	291.1	107.0	
		20	200.8	212.2	225.9	277.6	68.0	

Table 2 Results of DSC scan of DGEBA in the presence of mixture of BE imide-amines and DDS at varying heating rates

Sample designation	BS/mol	Heating rate/ °C min^{-1}	T_i/°C	T_o/°C	T_p/°C	T_f/°C	Δ*H*/J g^{-1}	E_a/kJ mol^{-1}
EBE-1	0.25	5	113.2	144.6	201.5	292.7	304.4	82.6
		10	135.2	171.7	222.5	300.2	156.7	
		15	157.6	189.2	225.6	299.4	242.0	
		20	160.5	205.7	231.8	329.2	273.1	
EBE-2	0.5	5	133.8	165.4	212.4	299.8	230.6	148.9
		10	143.9	179.1	226.4	310.6	234.7	
		15	151.2	192.3	227.0	317.7	235.7	
		20	165.9	201.1	230.1	320.9	238.3	
EBE-3	0.75	5	140.3	170.4	205.2	290.2	240.2	147.8
		10	156.7	183.5	216.1	292.7	241.1	
		15	162.8	185.3	219.6	293.4	207.2	
		20	173.7	192.4	222.7	294.8	187.6	
EBE-0	1	5	135.8	145.5	217.2	248.8	243.6	152.9
		10	155.0	164.3	227.9	275.1	208.8	
		15	165.3	180.2	230.8	299.6	283.2	
		20	170.1	202.4	233.1	308.4	278.3	

Table 3 Results of DSC scan of DGEBA in the presence of mixture of BM imide-amines and DDS at varying heating rates

Sample designation	BS/mol	Heating rate/ °C min^{-1}	T_i/°C	T_o/°C	T_p/°C	T_f/°C	ΔH/J g^{-1}	E_a/kJ mol^{-1}
EBM-1	0.25	5	145.6	176.2	181.5	286.1	245.3	89.5
		10	148.8	178.8	190.0	288.2	255.2	
		15	151.7	182.8	203.4	298.5	174.5	
		20	152.2	185.5	205.8	312.7	187.6	
EBM-2	0.5	5	147.3	164.5	183.0	270.2	221.8	149.2
		10	150.5	174.9	189.4	277.4	222.1	
		15	152.4	178.2	196.5	282.4	235.4	
		20	155.5	181.6	198.9	289.0	239.4	
EBM-3	0.75	5	138.9	161.4	170.1	257.5	229.1	98.2
		10	144.7	168.7	183.1	262.9	216.5	
		15	153.4	169.3	188.8	274.1	234.8	
		20	157.6	170.8	193.1	274.9	204.3	
EBM-0	1	5	141.1	166.6	171.6	239.3	218.3	120.9
		10	146.1	170.9	179.2	247.0	233.1	
		15	151.7	171.4	187.8	256.4	224.6	
		20	154.5	174.8	188.0	259.8	218.7	

higher temperature with mixture (imide-amine and DDS) as compared to imide-amine alone. 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 and 3 show DSC scans for resin samples EBE-1 and EBS-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: BS/BE/BM are summarized in Tables 1–3. 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:

- The peak exothermic temperature T_p represents a point of constant conversion.

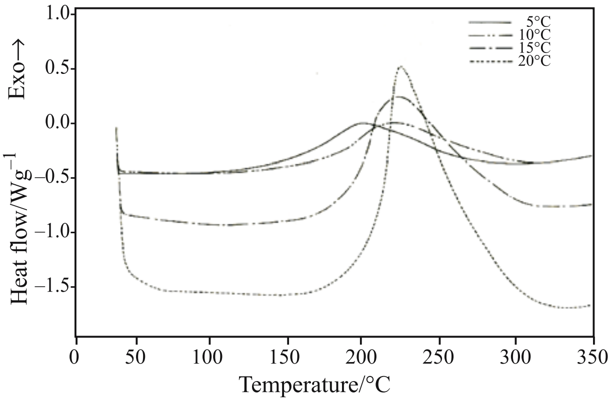

Fig. 2 DSC scans of EBE-1 sample at different heating rates 5, 10, 15 and 20°C min^{-1}

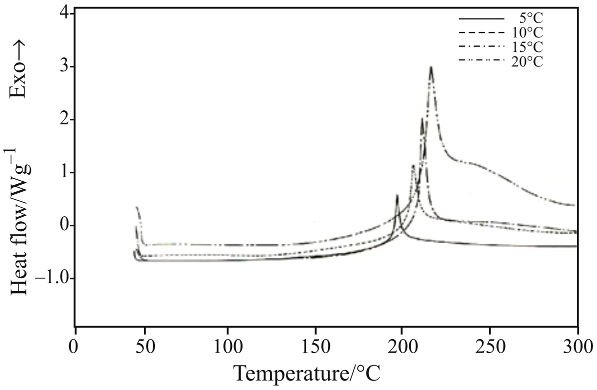

Fig. 3 DSC scans of EBS-2 sample at different heating rates 5, 10, 15 and 20°C min^{-1}

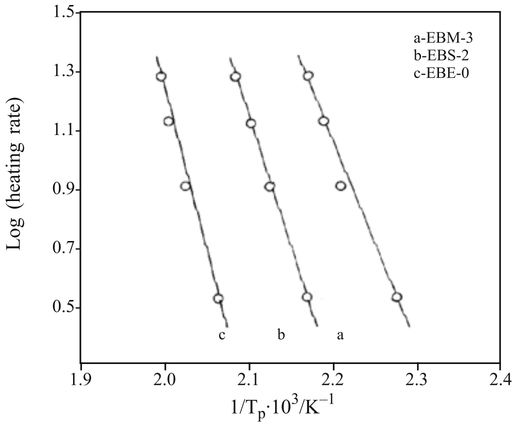

Fig. 4 Plots of logϕ *vs.* $1/T_p$ for a – EBM-3, b – EBS-2 and c – EBE-0

Table 4 Results of thermal stability of isothermal cured epoxy resins (BS imide-amines+DDS) at 20°C min^{-1} heating rate

Sample designation	IDT/ °C	T_{max}/ °C	FDT/ °C	Char yield at 800°C/%	LOI/ %
ED	394.9	419.9	466.0	19.2	25.2
EBS-1	410.0	430.2	451.2	26.5	28.1
EBS-2	395.8	429.6	456.7	24.6	27.3
EBS-3	399.9	424.6	439.4	30.8	29.8
EBS-0	397.1	423.5	441.5	26.5	28.1

Table 5 Results of thermal stability of isothermal cured epoxy resins (BE imide-amines+DDS) at 20°C min^{-1} heating rate

Sample designation	IDT/ °C	T_{max}/ °C	FDT/ °C	Char yield at 800°C/%	LOI/ %
EBE-1	413.0	444.7	466.3	24.7	27.4
EBE-2	396.3	428.9	463.3	30.2	29.6
EBE-3	398.2	437.3	459.6	29.3	29.2
EBE-0	412.1	437.9	474.1	29.5	29.3

Table 6 Results of thermal stability of isothermal cured epoxy resins (BM imide-amines+DDS) at 20°C min^{-1} heating rate

Sample designation	IDT/ °C	T_{max}/ °C	FDT/ °C	Char yield at 800°C/%	LOI/ %
EBM-1	406.7	434.6	460.4	26.8	28.2
EBM-2	393.9	438.8	467.1	30.2	29.6
EBM-3	404.0	438.8	463.2	28.1	28.7
EBM-0	368.9	424.5	464.2	28.9	29.1

- 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 analyzed in accordance with the following equation:

$$E_{\mathrm{a}} = \frac{R\Delta\log\phi}{0.4567\Delta(1/T_{\mathrm{p}})}$$

where ϕ is the heating rate, E_{a} is the activation energy, R is the gas constant.

Assuming a constant conversion at the peak exotherm temperature, plots of $\log\phi$ *vs.* $1/T_{\mathrm{p}}$ were obtained and then activation energy was calculated using standard procedure. Plots of $\log\phi$ *vs.* $1/T_{\mathrm{p}}$ are shown in Fig. 4. Activation energy of curing was found to be dependent on the structure of amines and the molar ratio of imide-amines: DDS used in case of samples where mixture was used.

Thermal stability

Figures 5a–c show TG/DTG traces of isothermal cured epoxy resins in the presence of mixture of different imide-amines and DDS. 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 of TG/DTG scans are summarized in Tables 4–6. A single step decomposition was observed in all the samples. All the samples were stable upto 400±20°C and started loosing mass above this temperature. The degradation temperature was dependent on the structure of network. Percent char yield increased significantly when one-forth of imide-amines is being replaced by DDS. Char yield was higher than either of their constituents when mixture of imide-amine and DDS was used.

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].

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

where CR=char yield.

The values are summarized in Tables 4–6. All the samples had LOI values greater than 28. These results thus clearly show that flame resistant DGEBA resin can be obtained by using imide-amines as curing agents.

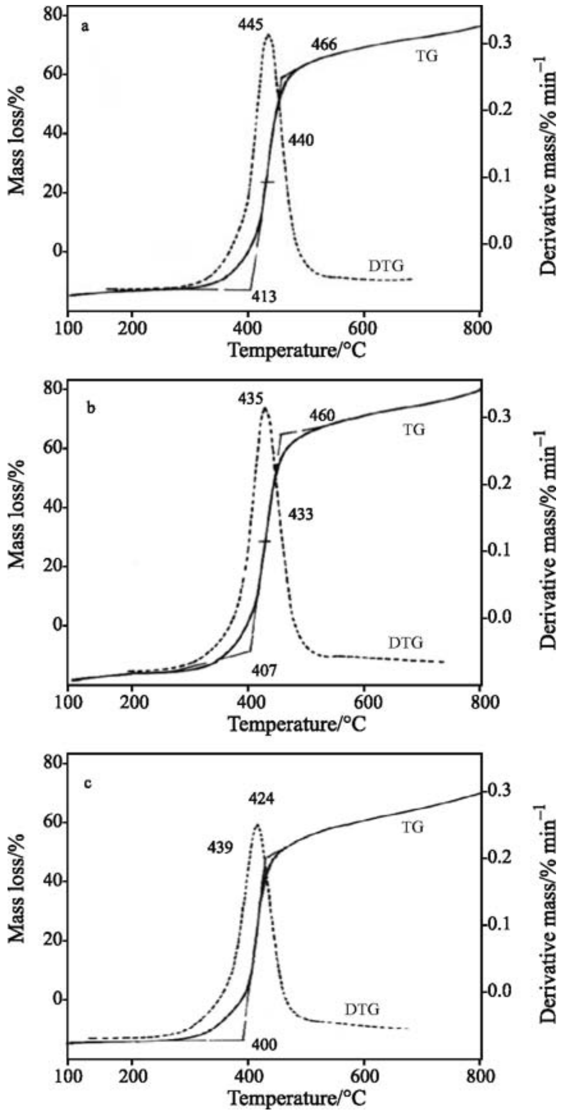

Fig 5 TG/DTG traces of cured epoxy resins in nitrogen atmosphere at heating rate 20°C min^{-1} of a – EBE-1, b – EBM-1 and c – EBS-3

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 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 behaviour.

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