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Curing Kinetics of Diglycidyl Ether of Bisphenol-A using Mixture of Alkylaryltindihydride and 4,4'-Diaminodiphenylmethane

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Curing kinetics of diglycidyl ether of bisphenol-A in presence of varying molar ratios of alkylaryltindihydrides and 4,4'-diaminodiphenylmethane was investigated by the dynamic differential scanning calorimetry. The thermal stability of the isothermally cured resins was also evaluated using dynamic thermogravimetry in a nitrogen atmosphere.

Key Words: Curing kinetics, Diglycidyl ether of bisphenol-A, Epoxy resins, 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 and versatility in formulation make epoxy resins 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].

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[4-7]. 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, amide, urethane[8], or heterocyclic groups, such as hydroxyl-terminated imide compounds[9,10] and imide-acid[11-12].

In this article, we have prepared the various heterocyclic derivatives of tin by reacting the stannanes with biguanide. 4,4'-Diaminodiphenylmethane is generally used as hardener for curing of epoxies. The incorporation of derivatives along with the 4,4'-diaminodiphenylmethane was expected to affect the curing behaviour and the thermal stability of the cured network. Therefore these derivatives have been used as epoxy curing agents for investigating the curing behaviour and resultant thermal stability of diglycidyl ether of bisphenol-A (DGEBA) with mixture of derivatives and 4,4'-diaminodiphenylmethane (DDM).

EXPERIMENTAL

Tetramethyltin, tetraethyltin, tetrabutyltin. phenyltintrichloride, ethylmethylketone (Aldrich) were used as such. The derivatives of tin were prepared according to the literature method[13].

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 ºC min^{-1}. 5 ± 2 mg of sample was used in each experiment. For curing studies, the samples were obtained by mixing stoichiometric amounts of derivatives and 4,4'-diaminodiphenylmethane with diglycidyl ether of bisphenol-A 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 ethylmethylketone solvent. After thorough mixing, the solvent was evaporated under vacuum and the freshly prepared samples

TABLE-1
RESULTS OF DSC SCANS OF DGEBA IN THE PRESENCE OF MIXTURE OF
BPETH DERIVATIVE AND DDM AT VARYING HEATING RATES

Sample designation	Moles of BPETH	Heating rate (^{0}C min^{-1})	T_i (ºC)	T_o (ºC)	T_p (ºC)	T_f (ºC)	ΔH (J g^{-1})
ED	0	5	139.2	178.2	230.2	294.4	275.1
		10	151.5	194.7	244.2	315.6	284.5
		15	163.9	201.6	252.3	314.5	245.4
		20	210.1	218.3	266.4	331.9	206.5
EBPETH-1	0.25	5	134.2	189.5	200.2	308.5	304.7
		10	138.5	200.5	212.4	307.5	296.7
		15	154.2	203.9	218.3	306.2	245.5
		20	158.6	209.4	223.8	304.5	258.3
EBPETH-2	0.5	5	125.6	196.8	203.2	286.3	229.6
		10	137.4	207.3	212.6	306.3	204.6
		15	147.4	214.1	217.8	305.6	171.3
		20	149.8	214.9	223.7	299.2	215.4
EBPETH-3	0.75	5	190.9	199.6	210.8	263.6	94.3
		10	192.7	204.7	216.6	264.5	74.7
		15	195.7	227.3	233.6	314.8	154.1
		20	201.5	232.7	237.5	279.5	127.5
EBPETH-0	1	5	191.3	213.6	216.8	253.8	68.6
		10	199.6	214.5	220.4	241.6	95.8
		15	209.6	220.9	235.1	301.3	117.5
		20	210.9	222.4	235.9	287.8	78.5

TABLE-2
RESULTS OF DSC SCAN OF DGEBA IN THE PRESENCE OF MIXTURE OF
BPMTH DERIVATIVE AND DDM AT VARYING HEATING RATES

Sample designation	Moles of BPMTH	Heating rate (^{0}C min^{-1})	T_i (ºC)	T_o (ºC)	T_p (ºC)	T_f (ºC)	ΔH (J g^{-1})
EBPMTH-1	0.25	5	123.3	154.5	211.8	302.9	314.9
		10	145.4	181.6	232.8	310.5	166.5
		15	167.5	199.6	235.9	309.8	252.5
		20	170.8	215.2	241.9	339.5	283.6
EBPMTH -2	0.5	5	143.5	175.4	222.6	309.9	240.9
		10	153.6	189.3	236.7	320.7	244.5
		15	161.3	202.6	237.2	327.5	245.4
		20	175.6	211.4	240.3	330.7	248.6
EBPMTH-3	0.75	5	150.5	180.6	215.4	300.6	250.6
		10	166.9	193.3	226.3	302.4	251.6
		15	172.4	195.9	229.9	303.9	217.4
		20	183.9	202.6	232.9	304.7	197.8
EBPMTH-0	1	5	145.5	155.8	227.4	258.7	253.4
		10	165.3	174.6	237.9	285.5	218.6
		15	175.6	190.5	240.9	309.4	293.5
		20	180.4	212.6	243.3	318.8	288.4

were used for recording DSC traces in the static air atmosphere at a programmed heating rate from room temperature up to 350 ºC. The epoxy samples have been designated by adding prefix E to BPETH/BPMTH/BPBTH followed by a numerical suffix. For example, epoxy cured using mixture of BPETH:DDM in the ratio of 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 has been designated as EBPETH-1, EBPETH-2, EBPETH-3 and EBPETH-0. The sample with diglycidyl ether of bisphenol-A and DDM has been designated as ED. Similarly samples cured using mixture of BPMTH /BPBTH and DDM were designated.

Thermal stability: Thermal stability of the epoxy resins cured isothermally by heating 200 ± 20 ºC for 3 h in an air oven in the presence of DDM/BPETH/BPMTH/BPBTH or a mixture of DDM: BPETH/BPMTH/BPBTH in varying molar ratio was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 cm^3 min^{-1}) using rheometric thermal analyzer. A heating rate of 20 ºC min^{-1} and powdered samples of 10 ± 2 mg were used in each experiment.

RESULTS AND DISCUSSION

Curing studies: The curing reaction of epoxy resins depends on the structure and reactivity of the curing agent. In the DSC traces of all the other samples, a broad exothermic transition associated with curing was observed. The exothermic transition associated with curing was characterized by the following parameters:

(1) The kick-off temperature (T_i), where the curing starts.

(2) 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.

(3) The temperature of the peak position of the exotherm (T_p).

(4) The temperature of the end of curing exotherm (T_f) obtained by the extrapolation of the curve.

(5) The heat of curing (ΔH), calculated by the measurement of the area under the exothermic transition.

The results of DSC scans are summarized in Tables 1-3. In all the samples, a single curing exotherm was observed upon

TABLE-3
RESULTS OF DSC SCAN OF DGEBA IN PRESENCE OF MIXTURE OF BPBTH DERIVATIVE AND DDM AT VARYING HEATING RATES

Sample designation	Moles of BPBTH	Heating rate (^{0}C min^{-1})	T_i (°C)	T_o (°C)	T_p (°C)	T_f (°C)	ΔH(J g^{-1})
EBPBTH-1	0.25	5	155.7	186.6	191.8	296.6	255.5
		10	158.4	188.6	200.6	298.5	265.4
		15	161.5	192.9	213.7	308.7	184.7
		20	162.4	195.7	215.6	322.9	197.9
EBPBTH -2	0.5	5	157.5	174.7	193.8	280.8	231.6
		10	160.6	184.6	199.6	287.6	232.5
		15	162.3	188.8	206.8	292.7	245.9
		20	165.7	191.4	208.4	299.4	249.6
EBPBTH-3	0.75	5	148.8	171.6	180.5	267.9	239.3
		10	154.9	178.5	193.4	272.7	226.7
		15	163.6	179.9	198.6	284.6	244.5
		20	167.8	180.5	203.4	284.8	214.8
EBPBTH-0	1	5	151.3	176.9	181.9	249.5	228.7
		10	156.4	180.6	189.5	257.5	243.8
		15	161.5	181.9	197.5	266.8	234.4
		20	164.7	184.5	198.6	269.6	228.3

curing with a mixture of derivatives and DDM. Comparing derivatives of varying structure, T_p was found to be higher in EBPMTH-0 as compared to samples EBPETH-0 or EBPBTH-0. This could be due to the relatively small induction effect (+I) of the methyl group which in turn does not increase much the nucleophilicity of the nitrogen atoms through C-Sn-N bond in the derivatives and hence also the reactivity of the derivatives.

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. The characteristic curing temperatures for the DGEBA at different heating rates in the presence of derivatives, DDM and mixture of DDM: BPETH/BPMTH/BPBTH are summarized in Tables 1-3. As expected in all the samples, peak at curing temperature increased with the increasing heating rate. The other curing parameters like T_i, T_o and T_f, increased as the heating rate was increased. However T_f and ΔH do not show the regular trend as the heating rate was increased. This may be due to the stearic factor imposed by derivative and hardener during the curing reaction.

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 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 up to 400 ± 20 °C and started loosing weight above this temperature. The degradation temperature was dependent on the structure of network. Char yield was higher than either of their constituents when mixture of derivatives and DDM 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[14].

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

where, CR = char yield

All the samples had LOI values greater than 28. These results thus clearly showed that flame resistant DGEBA resin can be obtained by using the stannanes derivatives as curing agents.

TABLE-4
RESULTS OF THERMAL STABILITY OF ISOTHERMAL CURED EPOXY RESINS (BPETH DERIVATIVES + DDM) AT 20 °C min^{-1} HEATING RATE

Sample designation	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield at 800 ^{0}C (%)	LOI (%)
ED	404.7	429.8	476.4	19.6	25.3
EBPETH-1	420.2	440.5	461.4	26.8	28.2
EBPETH-2	405.7	439.1	466.5	24.9	27.5
EBPETH-3	409.6	434.7	449.1	31.3	30.0
EBPETH-0	407.8	433.6	451.8	27.1	28.3

TABLE-5
RESULTS OF THERMAL STABILITY OF ISOTHERMAL CURED EPOXY RESINS (BPMTH DERIVATIVE + DDM) AT 20 °C MIN^{-1} HEATING RATE

Sample designation	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield at 800 °C (%)	LOI (%)
EBPMTH-1	423.1	454.8	476.4	24.9	27.5
EBPMTH -2	406.2	438.9	473.5	30.4	29.7
EBPMTH-3	408.1	447.2	469.4	29.6	29.3
EBPMTH-0	422.3	447.8	484.2	29.8	29.4

TABLE-6
RESULTS OF THERMAL STABILITY OF ISOTHERMAL CURED EPOXY RESINS (BPBTH DERIVATIVE + DDM) AT 20^{0}C min^{-1} HEATING RATE

Sample designation	IDT (°C)	T_{max} (°C)	FDT (°C)	Char yield at 800 °C (%)	LOI (%)
EBPBTH-1	416.8	444.7	470.3	27.1	28.3
EBPBTH-2	403.7	448.9	477.3	30.4	29.7
EBPBTH-3	414.3	448.7	473.5	28.3	28.8
EBPBTH-0	378.8	434.6	474.6	29.2	29.2

Conclusion

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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