



Curing Kinetics and Thermal Behaviour of N,N'-Diglycidyl Benzophenone Tetracarboxydiimide in the Presence of Mixture of Imide-Amines of Pyromellitic Dianhydride and 4,4'-Diaminodiphenyl sulfone

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The curing study of N,N'-diglycidyl benzophenone tetracarboxydiimide was investigated by differential scanning calorimetry using varying molar ratios of imide-amines and diaminodiphenyl sulfone. The imide-amines are obtained by reacting pyromellitic dianhydride with excess of 4,4'-diaminodiphenyl ether or 4,4'-diaminodiphenyl methane or 4,4'-diaminodiphenyl sulfone. Thermal stability of the isothermally cured resins was also evaluated using dynamic thermogravimetry in nitrogen atmosphere.

Key Words: Curing study, N,N'-Diglycidyl benzophenone tetracarboxydiimide, Thermal properties.

INTRODUCTION

In order to extend the applications of epoxy resins as electronic material and in the aerospace industry, it is crucial to improve their flame and thermal resistance. Several approaches have been reported in the literature for improving the thermal and flame resistance of these resins. Epoxy-imide polymers have received increasing attention during recent years in attempts to enhance their thermal properties¹⁻³.

The incorporation of halogen and/or phosphorous into the epoxy polymer skeleton can improve its flame properties. Currently, the incorporation of halogen into epoxy polymers is not preferred for environmental reasons. To avoid this problem, epoxy polymers have been modified by the introduction of phosphorous into the molecular structure, which improves its flammability properties^{4,5}.

If the chemical structures of the cured epoxy polymers are constituted with aromatic and/or heterocyclic rings, their thermal resistance is superior to those of constituents with flexible or aliphatic chains. Imide compounds and polymers, which contain aromatic and/or heterocyclic rings, can offer desirable high temperature stability. Therefore, using imide groups to modify the structure of epoxy to enhance its thermal resistance has received great attention in the research community⁶. In order to improve thermal resistance of the epoxy resin, curing agent containing imide groups such as hydroxyl-terminated imide compounds⁷, imide-acid^{8,9}, imide-amine or imide-anhydride *etc.*, was used.

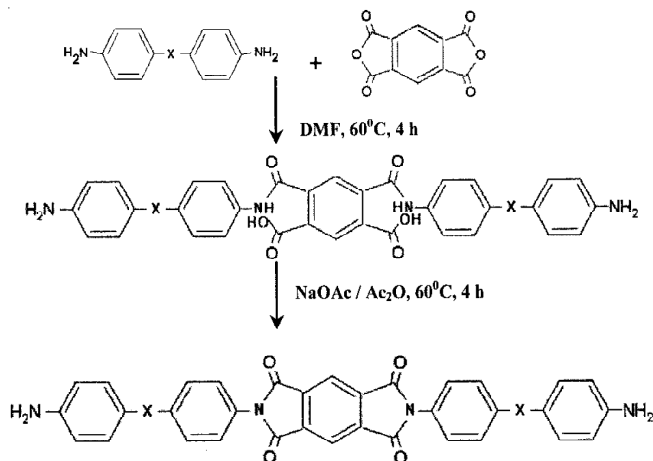
The primary objective of this study focused on improving the thermal and flame resistance of an epoxy system *via* structural modifications of the epoxy and curing agents. Improvement in thermal properties was achieved by use of imide groups to modify the backbone structure of the curing agents. The reaction of epoxy resin with trialkyl or aryl phosphate followed by curing with 4,4'-diaminodiphenyl sulfone gave products with good thermal stability and resistance¹⁰. The reaction of epoxy resin with an amide-amine having both silicon and phosphorous gave products with good thermal stability and resistance¹¹. Polymers with a sulfone group are known to have good oxidative, thermal and hydrolytic stability and good mechanical properties^{12,13}. Hence, a modifier with a sulfone group will have an additional effect on the properties of a modified network along with its flexibilizing effect. So, we thought it is interesting to use a mixture of imide-amine and diaminodiphenyl sulfone (DDS) as a curing agent for N,N'-diglycidyl benzophenone tetracarboxydiimide (DGBT) epoxy resin.

EXPERIMENTAL

N,N'-Diglycidyl benzophenone tetracarboxydiimide (DGBT), grade LY559, having an epoxy equivalent 178) was procured from Hindustan Ciba Geigy Ltd. 4,4'-Diaminodiphenyl sulfone (S), 4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl methane (M), pyromellitic dianhydride (P) 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 according to literature method¹⁴. The reaction scheme for synthesis is as follows:



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. 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 DGBT 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 ethanol as solvent. The epoxy samples have been designated

by adding prefix D to PS/PM/PE followed by a numerical suffix. For example, epoxy cured using mixture of PS:DDS in the ratio of 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 has been designated as DPS-1, DPS-2, DPS-3 and DPS-4. The sample with DGBT and DDS has been designated as DPS-0, DPE-0 and DPM-0. Similarly samples cured using mixture of PE/PM and DDS were designated. 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 430 °C.

Thermal stability: Thermal stability of the resins cured isothermally by heating 250 ± 50 °C for 3 h in an air oven in the presence of DDS/PS/PM/PE or a mixture of DDS:PS/PE/PM in varying molar ratio was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 cm³/min). Rheometric Scientific Module TG1500 module was used for recording TG/DTG traces. A heating rate of 20 °C/min and powdered samples of 10 ± 2 mg were used in each experiment.

RESULTS AND DISCUSSION

Curing kinetics: The curing reaction of epoxy resins depends on the structure and reactivity of the curing agent. The exothermic transition associated with curing was characterized by the following parameters: 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).

TABLE-1
RESULTS OF DSC SCAN OF DGBT IN THE PRESENCE OF PS IMIDE-AMINES AT VARYING HEATING RATES

Sample designation	Molar ratio of imide:DDS	Heating rate (°C/min)	T _i (°C)	T _{onset} (°C)	T _p (°C)	T _f (°C)	ΔH (J/g)	E _a (KJ/mol)
DPS-0	0:1	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	
DPS-1	0.25:0.75	5	128.9	179.8	194.1	330.1	358.5	113.8
		10	127.6	192.8	204.9	297.4	257.7	
		15	124.0	199.8	212.1	296.1	220.1	
		20	122.6	201.6	217.0	294.7	212.2	
DPS-2	0.5:0.5	5	100.9	181.0	194.7	298.7	429.4	110.3
		10	136.5	193.4	206.0	253.4	174.5	
		15	165.6	200.6	211.0	267.6	166.5	
		20	120.8	207.6	217.4	294.8	173.3	
DPS-3	0.75:0.25	5	45.8	51.9	64.8	116.9	174.2	56.9
		10	132.9	140.0	186.4	283.6	316.6	
		15	55.4	59.2	70.3	119.4	127.0	
		15	136.8	154.2	208.6	292.5	302.5	
		20	57.6	60.7	73.1	121.9	108.7	
DPS-4	1:0	15	138.6	160.1	224.6	296.0	310.9	93.1
		20	72.1	77.4	88.7	121.9	36.8	
		10	140.7	170.4	222.6	293.9	254.4	
		5	133.1	149.9	193.4	284.0	248.1	
		10	183.4	209.2	218.3	274.7	160.1	
15	141.4	176.9	224.4	296.0	271.2			
20	142.5	183.0	232.5	294.7	419.7			

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 DGBT at different heating rates in the presence of imide-amine, DDS and mixture of DDS:PS/PE/PM 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^{15,16} 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, R is the gas constant.

Assuming a constant conversion at the peak exotherm temperature, a plot of $\log \phi$ versus $1/T_p$ was obtained. From the slope of these lines, activation energy was calculated for exotherm and results are given in the Tables 1-3. Activation energy was highest for DPS-1, DPE-1 and DPM-1.

TABLE-2
RESULTS OF DSC SCAN OF DGBT IN THE PRESENCE OF PE IMIDE-AMINES AT VARYING HEATING RATES

Sample designation	Mole ratio of PE:DDS	Heating rate (°C/min)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (KJ/mol)
DPE-0	0:1	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	
DPE-1	0.25:0.75	5	131.2	166.4	214.3	284.6	142.8	117.4
		10	136.8	169.2	225.3	297.4	170.0	
		15	139.2	174.5	232.1	296.2	181.8	
		20	146.4	184.9	237.5	294.8	187.8	
DPE-2	0.5:0.5	5	143.2	184.4	199.6	270.8	193.1	101.8
		10	148.9	187.4	209.7	282.4	222.4	
		15	150.7	195.7	215.3	296.1	209.8	
		20	181.6	205.6	223.4	294.7	214.9	
DPE-3	0.75:0.25	5	145.6	180.4	182.3	270.6	166.5	92.2
		10	150.3	188.9	201.7	277.2	182.7	
		15	158.1	189.2	202.7	282.4	179.4	
		20	162.1	184.5	208.4	294.7	188.6	
DPE-4	1:0	5	148.9	170.8	179.2	227.5	150.9	136.5
		10	156.4	180.4	186.4	281.5	344.8	
		15	161.4	179.2	192.9	258.4	177.3	
		20	174.9	191.0	196.3	276.9	196.2	

TABLE-3
RESULTS OF DSC SCAN OF DGBT IN THE PRESENCE OF PM IMIDE-AMINES AT VARYING HEATING RATES

Sample designation	Mole ratio of PE:DDS	Heating rate (°C/min)	T_i (°C)	T_{onset} (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	E_a (KJ/mol)
DPM-0	0:1	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	
DPM-1	0.25:0.75	5	138.6	169.1	187.8	287.2	294.6	99.3
		10	148.2	180.7	198.0	285.8	209.3	
		15	150.7	190.6	220.7	296.0	217.0	
		20	152.1	193.1	222.2	294.8	256.2	
DPM-2	0.5:0.5	5	138.2	175.9	181.2	248.4	222.5	91.0
		10	150.0	185.6	192.2	296.8	276.1	
		15	149.3	193.1	201.5	294.7	347.9	
		20	153.5	197.9	206.4	294.8	338.2	
DPM-3	0.75:0.25	5	135.6	163.0	158.8	290.4	213.0	55.2
		10	141.1	168.9	177.9	297.3	218.5	
		15	148.9	192.7	188.5	296.0	218.5	
		20	156.4	177.0	198.6	294.8	212.7	
DPM-4	1:0	5	142.5	166.6	175.1	205.8	81.7	92.6
		10	146.4	174.2	185.7	282.2	396.3	
		15	153.4	183.8	190.0	285.3	75.8	
		20	169.9	194.2	200.5	278.7	57.0	

TABLE-4
RESULTS OF THERMAL STABILITY OF ISOTHERMAL CURED EPOXY RESINS
(PS IMIDE-AMINES + DDS) AT 20 °C/min HEATING RATE

Sample designation	Mole ratio of PS:DDS	IDT (°C)	T _{max} (°C)	FDT (°C)	Char yield (%) at 800 °C
DPS-0	0:1	394.9	419.9	466.0	19.2
DPS-1	0.25:0.75	404.9	438.2	461.8	21.8
DPS-2	0.5:0.5	386.9	424.6	456.2	27.6
DPS-3	0.75:0.25	355.9	372.4	396.1	17.5
DPS-4	1:0	392.2	433.6	465.0	20.9

TABLE-5
RESULTS OF THERMAL STABILITY OF ISOTHERMAL CURED EPOXY RESINS
(PE IMIDE-AMINES + DDS) AT 20 °C/min HEATING RATE

Sample designation	Mole ratio of PE:DDS	IDT (°C)	T _{max} (°C)	FDT (°C)	Char yield (%) at 800 °C
DPE-0	0:1	394.9	419.9	466.0	19.2
DPE-1	0.25:0.75	400.0	420.5	438.2	30.6
DPE-2	0.5:0.5	399.6	422.4	447.4	28.7
DPE-3	0.75:0.25	396.3	422.3	441.3	25.5
DPE-4	1:0	392.1	422.3	447.2	20.9

TABLE-6
RESULTS OF THERMAL STABILITY OF ISOTHERMAL CURED EPOXY RESINS
(PM IMIDE-AMINES + DDS) AT 20 °C/min HEATING RATE

Sample designation	Mole ratio of PM:DDS	IDT (°C)	T _{max} (°C)	FDT (°C)	Char yield (%) at 800 °C
DPM-0	0:1	394.9	419.9	466.0	19.2
DPM-1	0.25:0.75	382.5	406.4	432.6	26.2
DPM-2	0.5:0.5	370.1	400.0	430.5	24.6
DPM-3	0.75:0.25	366.1	392.4	424.9	26.3
DPM-4	1:0	394.1	413.9	433.6	25.8

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. All the samples were stable upto 380 ± 20 °C. The degradation temperatures were dependent on the structure of network. The char yield was higher in case of DPE samples as compared to DPS and DPM.

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 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. The thermal stability of the cured was higher in presence of PE as compared to PM and PS imide-amines.

REFERENCES

1. A. Mantecon, V. Cadiz, A. Serra and P.A. Martinez, *Angew Makromol. Chem.*, **156**, 37 (1988).
2. B.S. Rao, *J. Polym. Sci. C: Polym. Lett.*, **26**, 3 (1988).
3. M.D. Shau and W.K. Chin, *J. Polym. Sci. A: Polym. Chem.*, **31**, 1653 (1993).
4. T. Ichino and Y. Hasuda, *J. Appl. Polym. Sci.*, **34**, 1667 (1987).
5. T.S. Wang, J.F. Yeh and M.D. Shau, *J. Appl. Polym. Sci.*, **59**, 215 (1996).
6. W.K. Chin and M.D. Shaun, Epoxy-Imide, Phosphorylated Epoxy-Imide Polymers in The Polymeric Materials Encyclopedia, J.C. Salamone, CRC Press, Vol. 3, D-E, p. 2210 (1996).
7. S. Sasaki and Y. Hasuda, *J. Polym. Sci. C Polym. Lett.*, **25**, 377 (1987).
8. A. Serra, V. Cadiz and A. Mantecan, *Angew. Makromol. Chem.*, **155**, 93 (1987).
9. K. Adhinarayanan and R. Packirisamy, *J. Appl. Polym. Sci.*, **43**, 783 (1991).
10. D. Deronet, F. Morren and J.C. Brosse, *J. Appl. Polym. Sci.*, **62**, 1855 (1996).
11. P. Khurana, S. Aggawal, A.K. Narula and V. Choudhary, *J. Appl. Polym. Sci.*, **87**, 1345 (2002).
12. M.J. Jurek and J.E. McGrath, *Polymer*, **30**, 1552 (1989).
13. R.N. Johnson, A.G. Franham, R.A. Clendinning, W.F. Hale and C.L. Merriam, *J. Appl. Polym. Sci. A-1 Polym. Chem.*, **5**, 2375 (1967).
14. P. Sharma, P. Kukreja, A.K. Narula and V. Choudhary, *Indian J. Engg. Mat. Sci.*, **12**, 259 (2005).
15. T. Ozawa and A.A. Duswalt, *Thermal Anal.*, **2**, 301 (1970).
16. A.A. Duswalt, *Thermochim. Acta*, **8**, 54 (1974).