Journal of Thermal Analysis, Vol. 49 (1979) 367-373

CURING STUDIES OF EPOXY RESIN WITH NADIC ENDCAPPED PHOSPHORYLATED AMINES

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Abstract

Polyimides have aromatic moieties in the backbone structure which are responsible for their increased thermal stability. If phosphorus is introduced in the main chain structure of polyimides, there is further improvement in the thermal stability. This has been proved by the work carried out in our group. The polyimide having amine termination can be used for crosslinking of epoxy resins.

In the present study amine terminated phosphorus containing nadicimide were taken as curing agent for DGEBA resins. The curing characteristics of DGEBA resin were studied by DSC using different amounts of nadic endcapped phosphorylated amines. DSC thermogram showed the heat of polymerization was lower as compared to system cured with aromatic amines.

Keywords: curing, epoxymodified resin, endcapping

Introduction

Epoxy resin find applications in wide range of fields such as electrical, electronics, protective coating, construction industry, composites and others, owing to its outstanding properties, encompassing electrical, mechanical and chemical resistance [1]. Amines, polyamides anhydrides, BF3-amine complexes etc. have been commonly used as curatives for epoxy resin [2]. In recent years, studies have been focussed on development of novel curators containing imide groups, such as bis (hydroxy phthalimide), anhydride terminated polyimides etc. for epoxy resin systems with a view to improve performance of various properties at elevated temperatures [3]. Nadicimides are a class of compound which have excellent thermal stability [4]. These compounds react with aromatic amines to form an additive with amine termination. In the present study, work has been carried out by using amine terminated nadicimide as curative for epoxy resin.

The curing behaviour and reaction energies are important parameters which can be used for characterization of polymers. DSC has been extensively used for studying heat and kinetics of cure reactions of thermosetting resins [3]. In this paper curing characteristics of epoxy-amine were studied using DSC.

Mass loss of cured product after subjecting the materials at 400°C for 12 h were also studied.

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Experimental

(a) Synthesis of tri(3-aminophenyl) phosphine-oxide

Nitration of triphenyl phosphine-oxide was carried out below 10°C. The resulting yellow coloured solution was further stirred for 3 h at room temperature and then slowly poured, with stirring into approx. 4 litre ice water to yield yellow precipitate of trinitro derivative.

The trinitro derivative was further reduced with palladium charcoal in ethanol. Hydrazine hydrate was added to mixture slowly and temperature maintained at less than 20°C. The solution was further refluxed and filtered. Tris-(3-aminophenyl) hosphine crystals were obtained on cooling. *Mp*: 258–260°C.

(b) Synthesis of nadic endcapped phosphorylated amine

Nadic anhydride was added to tris-(3-aminophenyl) phosphine-oxide in molar ratio (1:1) and refluxed for 12 h at 120°C in glacial acetic-acid/DMAc. The nadic endcapped phosphorylated amine was recovered by precipitation in ice water.

Both the amines were characterised by elemental analysis, IR spectroscopy and ^{1}H-NMR spectroscopy.

Epoxy resin LY556 (DGEBA) [Epoxide Equivalent=190±5] supplied by M/S Hindustan Ciba Geigy was used as such.

DSC analysis was performed using DuPont module 2920 thermal analyzer.

Curing of the epoxy resin with the amines was carried out using epoxy and amine in different stoichiometric ratios (1:0.6, 1:0.8, 1:1.0, 1:1.2, 1:1.4). The sample were prepared by mixing thoroughly at room temperature.

DSC analysis was carried out at heating rate of 10°C min^{-1}.

Result and discussion

IR spectra of tris-(3-aminophenyl) phosphine-oxide showed an absorption band at 3224–3384 cm^{-1} due to NH_2. The absorption band due to P–C_6H_5 and >P=O were observed at 1420 cm^{-1} and 1180 cm^{-1} respectively. In the IR spectra of nadicimide endcapped phosphorylated amine characteristic bands due to imide group appear at 1748 cm^{-1} and 1723 cm^{-1}.

The presence of NH_2 group is indicated by NH stretching at 3220 cm^{-1}. The C=O, >P=O and P–C_6H_5 bands were observed at 1680 cm^{-1}, 1185 cm^{-1} and 1430 cm^{-1}.

DSC curve of neat nadicimide endcapped phosphorylated amine and tris-(3-aminophenyl) phosphine-oxide are shown in Fig. [1] .

It was observed that tris-(3-aminophenyl) phosphine oxide showed a sharp endothermic peak at 265.78°C. Nadicimide endcapped amine showed no DSC endothermic peaks but a broad exothermic peak between 306.13–380°C [4].

The DSC analysis of epoxy resin cured with varying amounts tris-(3-aminophenyl) phosphine-oxide and nadicimide endcapped are shown in Table 1 and Table 2. DSC curves are shown in Figs 1, 2.

Table 1 DSC data of epoxy-amine tris-(3-aminophenyl) phosphine-oxide

Composition epoxy:amine	T_{onset}/ °C	Extrapolated T/ °C	T_{max}/ °C	T_{end}/ °C	Curing time range	Curing/ min	Heat of reaction/ J g^{-1}
1:0.6	146.77	170.57	186.86	263.83	117.06	11.07	137.10
1:0.8	146.70	170.42	188.72	258.00	111.30	11.13	149.10
1:1.0	133.31	171.66	185.91	247.46	114.15	11.42	135.10
1:1.2	144.55	166.46	184.55	253.77	109.22	10.92	105.00
1:1.4	130.02	164.89	181.11	240.35	110.33	11.03	107.70

Table 2 DSC data of epoxy-nadicinamide endcapped phosphorylated amine

Composition epoxy:amine	T_{onset}/ °C	Extrapolated T/ °C	T_{max}/ °C	T_{end}/ °C	Curing time range	Curing/ min	Heat of reaction/ J g^{-1}
1:0.6	245.95	276.47	302.85	336.34	90.39	9.04	79.17
1:0.8	256.11	275.72	302.56	337.6	80.89	8.09	89.10
1:1.0	236.96	272.77	290.56	320.65	83.69	8.37	65.60
1:1.2	234.84	258.44	287.90	320.83	86.00	8.60	66.60
1:1.4	211.66	250.35	298.02	322.22	110.56	11.05	46.16

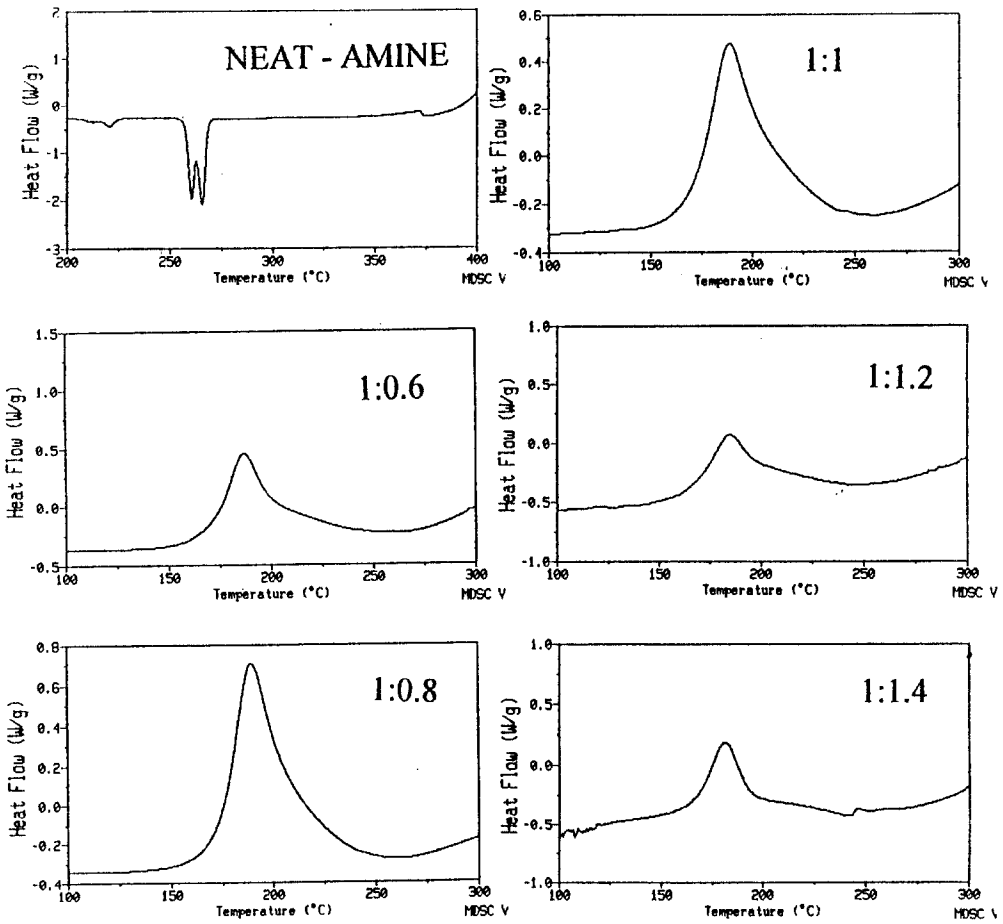

Fig. 1 DSC of epoxy+tris-(3-aminophenyl) phosphine-oxide

DSC scans showed an onset of exothermic transition at 140±10°C extrapolation temperature at 167±5°C and T_{max} in the range of 185±4°C for tris-(3 aminophenyl) phosphine-oxide cured epoxy resin. DSC scans for epoxy resin cured by nadicimide endcapped phosphorylated amine showed an onset at 245±10°C. Extrapolation temperature of 274±2°C for 1:0.6 and 1:0.8 compositions 258.44°C for 1:1 and 1:1.2 composition and 250.35° for 1:1.4 compositions were observed. T_{max} temperature was 295±7° C for all the compositions.

It was observed from DSC data that onset, extrapolation and T_{max} temperature were lower for epoxy resins cured by tris-(3-aminophenyl) phosphine-oxide than nadicimide endcapped phosphorylated amine. But the curing range was higher for tris-(3-aminophenyl) phosphine-oxide.

From the Tables it was observed that heat of reaction values increases with increase in amine concentration upto 1:0.8 stoichiometric composition and decreases afterwards with increase in amine content for both the amines.

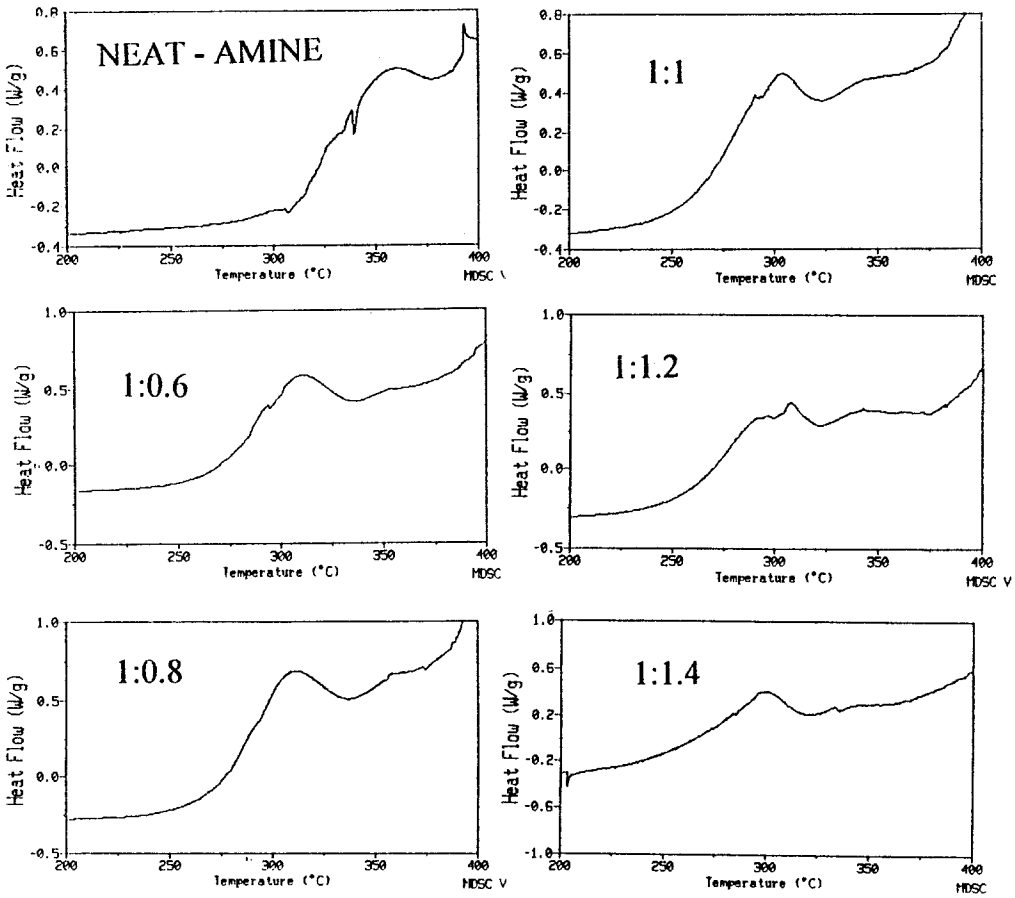

Fig. 2 DSC of epoxy+nadicimide endcapped phosphorylated amine

Tris-(3-aminophenyl) phosphine-oxide possess three primary amino group, which are acting as nucleophile for oxirane group and hence a very sharp exotherm was observed in DSC curve.

DSC curves of epoxy resin cured by different amounts of nadicimide endcapped phosphorylated amine showed a single broad exothermic peak. This indicates that nadicimide is undergoing polymerization simultaneously along with epoxy-amine reaction. Epoxy nadicimide endcapped phosphorylated amine of various compositions were isothermally cured at 300°C for 8 h. The DSC curves of two cured compositions (1:0.6 and l: 1) are shown in Fig. 3. The DSC curve shows no exothermic peak indicating that crosslinking reaction is complete.

Isothermal ageing of cured epoxy nadicimide endcapped phosphorylated amines was carried out at 400°C in a muffle furnace. Weight retention for all the compositions are tabulated in Table 3. It was observed that as the nadicimide amine content

increased the thermal stability of system increased. This is due to the increased imide linkages in the network of the system. From Table 3 it was observed that weight retention of epoxy:nadicimide endcapped phosphorylated amine of composition 1:1 and above are in the range of 80±2% even after 12 h.

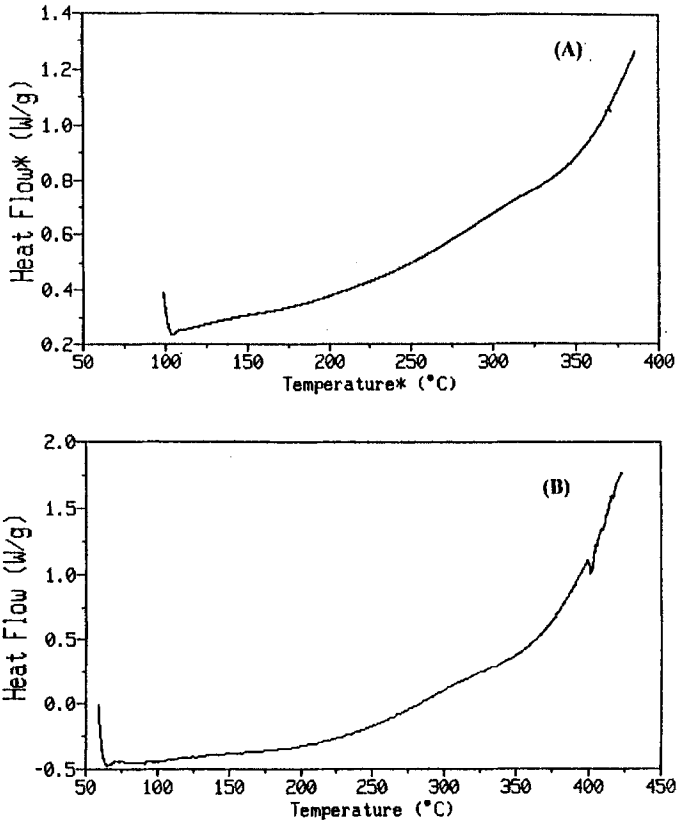

Fig. 3 Cured epoxy + nadicimide endcapped phosphorylated amine (A)1:0.6; (B)1:1

Table 3 Isothermal ageing of epoxy:nadicimide endcapped phosphorylated amines at 400°C

Composition	After 4 h	After 8 h	After 12 h
DDM	80.40	75.43	70.02
1:0.6	74.02	70.42	63.51
1:0.8	77.60	75.39	70.36
1:1	84.75	82.81	70.60
1:1.2	85.38	83.75	81.38
1:1.4	86.77	85.52	82.10

In case of DDM cured epoxy the weight retention at 400°C after 12 h is reduced to 70% and material becomes black due to charring. The nadicimide amine cured epoxy composition below 1:1 also show reduction in weight retention after 12 h like DDM.

Hence compositions of 1:1 and above can be suggested for improving the thermal stability of epoxy resins.

Conclusion

Curing parameters were studied using DSC which was useful for optimization of cure cycles and for prediction of thermal response during cure and exposure to higher temperature.

Heat of reaction increased upto 1:0.8 composition for both amines but decreased as the stoichiometric ratio increased from 1:1 composition. The lowering of heat of reaction in case of nadicimide end-capped phosphorylated amines is due to simultaneous polymerization of nadicimide.

Compositions of 1:1 and above can be suggested for improving the thermal stability of epoxy resin. Studies on thermal stability by TG technique is in progress.

References

1 E. M. Woo, L. B. Chen and J. C. Seferis, J. Mater. Sci., 22 (1987).
2 R. Hou Wink and G. Solomon, Adhesion & Adhesives, Elsevier, Amsterdam 1965.
3 V. L. Rao, K. Krishnan, R. Ramaswamy and K. N. Ninan, Proceedings of the National Symposium on Thermal Analysis, Kanpur 1995.
4 Sarfaraz Alam, L. D. Kandpal and I. K. Varma, J. Appl. Poly. Sci. 53 (1994) 1073.
5 Eli. Shiow-Chinglin and M. Pearce, High-Performance Thermosets Chemistry, Properties, Applications, page 204.