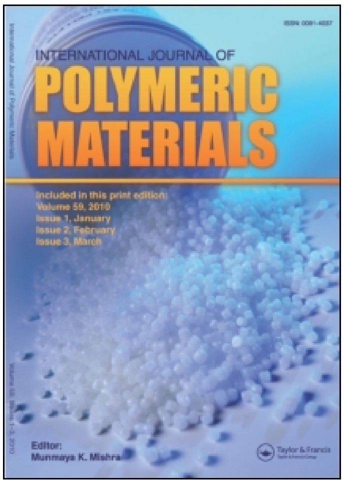

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Poly(Amido-Imide)s Based on Amino Terminated Oligomides

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An amino-terminated oligoimide was prepared by Michael addition reaction of 1,1′-(methylene-di-4,1-phenylene)bismaleimide (MDPBM) and 4,4′-diamino diphenyl methane (DDM) at MDPBM:DDM molar ratio of 1:2. The poly(amido-imide)s (PAI)s were prepared by condensation of this MDPBM:DDM oligoimide with various aliphatic bisesters. The resultant PAIs were characterized by elemental analysis, IR spectral studies, number average molecular weight ($\bar{M}n$) estimated by nonaqueous conductometric titration and thermogravimetry. The curing of epoxy resin namely; diglycidyl ether of bisphenol-A (DGEBA)-PAI system was monitored by Differential Scanning Calorimetry (D.S.C.). The glass and carbon fibre reinforced laminates of PAI-epoxy resin system have also been prepared and characterized.

Keywords: Diamino diphenyl methane; epoxy resin; poly(amido-imide)s; Differential Scanning Calorimetry; thermogravimetric analysis

INTRODUCTION

Bismaleimide-based polymers are potential candidates, as matrix resins for high-performance composites [1,2]. To achieve specific combination properties, different types of reactants and reaction routes been used to synthesize tailored bismaleimide resins [3–8]. The resins based on the Michael addition reaction using high molar ratios of bismaleimide to diamine have been well documented [6–8]. The curing of the resin is achieved with maleimido double bonds. Thermally

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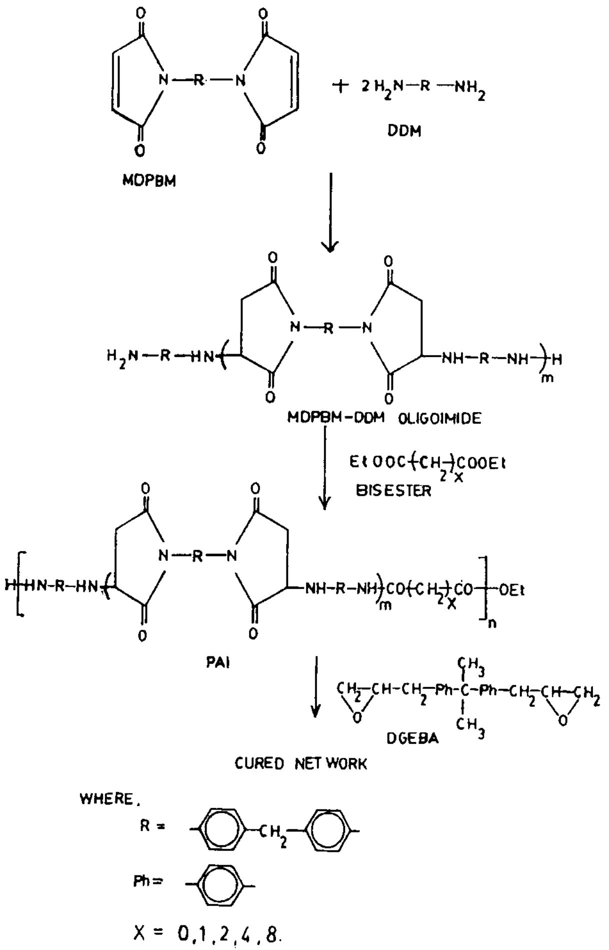
stable materials are also obtained by using an equimolar ratio of bismaleimide and diamine [9]. Use of a high molar ratio of diamine to bismaleimide can provide oligoimides having terminal amino groups, which make them suitable for further reaction like amidation. The amidation of amino terminated oligoimides can afford poly(amido-imide)s. Only few reports are available on PAIs based on trimetallic anhydride and amino-terminated polyamides [10–12]. The PAI known as 'Torlon' [1] received more attention individually. It is melt-processable and can be injection moulded to a wide variety of objects including gears, pistons and ball bearings.

In our earlier communications [13–16], we reported several amino terminated oligoimides prepared via Michael addition reaction of bismaleimides and diamines and their modification with epoxy resin. With a view of above objective it was thought interesting to study the poly(amido-imide)s (PAI) based on this amino terminated oligoimide and bis esters. The present paper comprises the synthesis and characterization of novel PAIs and the glass and carbon fibre reinforcement of PAI-epoxy resin system. The entire research work has been summarised in the Scheme I.

RESULTS AND DISCUSSION

All the PAIs presented in Table I are brown coloured and insoluble in almost all organic solvents. They do not melt upto 200°C, but above 200°C they soften and turn into either viscous liquid or black mass. The elemental analysis of all PAIs are consistent with their predicted structures (Scheme I). All the PAIs show positive the qualitative imide and amide tests.

IR spectra of all PAIs are identical in all aspects. The spectra show the bands due to imide groups (1710 cm^{-1}, 1650 cm^{-1}, 1050 cm^{-1}, 730 cm^{-1}) arising from oligoimide. The only discernible difference from oligoimide is that the spectra of PAIs comprise the bands due to the amide group (1530 cm^{-1}) and bands due to aliphatic moiety from diesters moiety. The spectrum of MDPBM-DDM oligoimides resemble to the spectrum reported by us in all aspects [13]. The number average molecular weights ($\bar{M}n$) of all PAIs are given in Table I. $\bar{M}n$ values varied because of the nature of polymers.



SCHEME 1

The TGA data of all PAIs are given in Table I. The PAIs start their decomposition around 200°C. The rate of decomposition increases between 270°C and 550°C, and PAIs lose almost 90% at 650°C.

The cure reaction of PAI-epoxy was studied for the molar ratio of 1:1. The data obtained from DSC scans are furnished in Table II. From the DSC thermograms obtained it was seen that all the PAIs-epoxy cured systems gave a single exothermic peak in the range

TABLE I Synthesis and characterization of PAIs

PAI Poly (amido-imides)*	*Oligoimide MDPBM: Diester* used (equimolar ratio)*	*Elemental Analysis*						$\bar{M}n$	*Weight loss from TGA at °C*				
		%C		*%H*		*%N*							
		Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*		*250*	*300*	*400*	*500*	*600*
PAI-1	DEO	71.88	71.8	6.11	6.1	10.26	10.2	2895	5	10	45	71	86
PAI-1	DEM	72.11	72.1	6.25	6.2	10.09	10.1	2930	7	13	47	76	90
PAI-3	DES	72.34	72.3	6.38	6.3	9.92	9.9	2955	9	16	50	77	92
PAI-4	DEA	72.93	72.9	6.65	6.6	9.63	9.6	3010	6	11	48	74	91
PAI-5	DESb	73.54	73.5	7.09	6.1	9.03	9.0	3075	8	14	51	78	89

*Diesters: DEO = Diethyloxalate, DES = Diethylsuccinate, DESb = Diethyl sebacate, DEM = Diethylmalonate, DEA = Diethyl adipate MDPBM = 1,1'-(Methylene-di-4, 1-phenylene) Bismaleimide-Diamino diphenyl methane Oligoimide.

TABLE II Curing characteristics of PAI epoxy cured (equimolar ratio) system

PAI	*Cure onset temperature* T_i *(°C)*	*Peak temperature* T_p *(°C)*	*Final temperature* T_f *(°C)*	*Activation energy* E_a*(kcal/mol)*
PAI-1	173	193	228	35.27
PAI-2	178	215	231	35.64
PAI-3	184	224	238	36.15
PAI-4	191	226	241	37.48
PAI-5	187	230	248	38.10

145–225°C. The typical DSC thermogram at 10 K/min shows that the cure onset temperature (T_i), peak exotherm temperature (T_p) and temperature of completion of curing (T_f) were obtained.

The curing temperature of the PAI-s epoxy system increases with an increase in the molecular weight of the PAI. This behaviour is probably due to the lower rate of diffusion of the high molecular weight PAIs as well as the reduced functionality, compared with the lower molecular weight PAIs. The activation energy (E_a) for such a system (Tab. II) increases with increase in the molecular weight of the PAI, indicating the lower reactivity of higher molecular weight PAI. The kinetic parameters such as E_a (activation energy) were calculated by assuming that the curing reaction obeys Arrhenius type kinetics and that the peak maximum represents a point of constant conversion.

To obtain information about the properties of unreinforced crosslinked materials, larger cured specimens were prepared using the same proportions and temperatures (i.e. T_p) as stated in Table II. The unreinforced cured oligoimide-epoxy samples are dark brown, hard materials. They are insoluble in all common organic solvents including formic acid. Thermogravimetric analysis Table III of all the reinforced crosslinked materials reveals that they all degrade in a single step and start their decomposition at around 250°C. Degradation becomes faster between 300°C and 500°C. The IR spectrum of the unreinforced cured products clearly shows the disappearance of the oxirane ring (910 cm^{-1}). The inflections at 1170 cm^{-1} in the spectra of the unreinforced products obtained by using a higher proportion of epoxy may be due to the ether linkage arising from the homopolymerization of

TABLE III TGA of unreinforced PAI-Epoxy-cured (equimolar-ratio) materials

PAI	*% weight loss at °C from TGA*				
	250	300	400	500	600
PAI-1	2	8	41	67	89
PAI-2	3	10	38	71	86
PAI-3	2	9	37	73	90
PAI-4	4	11	39	70	91
PAI-5	3	10	43	69	88

epoxy resin is only possible in the presence of tertiary amine catalyst at elevated temperature [17].

The glass and carbon reinforced PAI epoxy laminates (i.e. composites) were in form of dark brown and black sheets respectively. The density was 1.33–1.80 g.cm for glass laminates (Tab. IV) and 1.55–1.90 g.cm for carbon laminates (Tab. V). Results indicate that there is no appreciable change in the density with the nature of the PAI at the processing temperature. Chemical resistance studies at room temperature indicated that the PAI glass and fibre laminates were not affected by immersion in organic solvents for 24 hours (alcohols, ketones DMSO, 1,4-dioxane, THF). No change in weight or thickness was observed. It was also noted that concentrated hydrochloric acid (25% v/v) did not affect the laminates. However exposure to concentrated alkali (25% w/v NaOH) resulted in changes in thickness and weight (Tabs. IV and V). The high chemical resistance of all the laminates indicates that the oligoimide moiety might contribute to the high level of crosslinking of epoxy resin with PAI during laminates fabrication. The mechanical properties of glass and carbon reinforced laminates are given in (Tabs. IV and V). The result shows that the glass laminates had better properties than the carbon ones. This may be due to glass laminates have been prepared by using glass cloth while carbon laminates have been prepared by using carbon filaments. The values are also quite comparable with those from other resin system (phenolics, amino resin). Few poly(amido-imide)s are commercially available and of these only Torlon has superior properties. Comparison of the mechanical properties of laminates PAIs 1–5 with those of Torlon [1] reveals laminates PAIs 1–5 have lower values (Tab. VI). In some cases the values are only slightly lower. The

TABLE IV Mechanical and chemical properties of glass reinforced composites based on PAI-Epoxy (equimolar ratio) system

PAI	*Percentage change on exposure to 25% (w/v) NaOH*		*Density g. cm*$^{-3}$	*Flexaral strength (MPa)*	*Compressive strength (MPa)*	*Impact strength (MPa)*	*Rockwell hardness (R)*	*Breakdown potential (in air) (KV/mm)*
	thickness	*weight*						
PAI-1	0.9	1.1	1.3	245	215	235	135	12.0
PAI-2	1.2	0.9	1.5	260	195	190	120	14.5
PAI-3	1.1	1.0	1.7	235	230	185	130	13.0
PAI-4	1.0	1.1	1.6	250	170	210	140	11.5
PAI-5	1.3	1.0	1.4	270	195	210	125	15.0

TABLE V Mechanical and chemical properties of carbon reinforced composites based on PAI-Epoxy (equimolar ratio) system

PAI	*Percentage change on exposure to 25% (w/v) NaOH*		*Density g. cm*$^{-3}$	*Flexaral strength (MPa)*	*Compressive strength (MPa)*	*Impact strength (MPa)*	*Rockwell hardness (R)*	*Breakdown potential (in air) (KV/mm)*
	thickness	*weight*						
PAI-1	1.0	1.2	1.4	225	205	145	145	11.5
PAI-2	1.1	1.1	1.3	240	160	150	125	13.5
PAI-3	1.2	1.0	1.5	235	185	165	110	12.0
PAI-4	0.9	1.2	1.2	225	170	185	135	11.0
PAI-5	1.1	1.3	1.6	230	180	170	120	15.5

TABLE VI Comparison of mechanical properties of PAIs with Torlon [1] at 23 °C

Properties	*Torlon*	*PAI-1*	*PAI-2*	*PAI-3*	*PAI-4*	*PAI-5*
Flexural strength (MPa)	249	180	164	125	170	175
Tensile strength (MPa)	198	160	175	158	170	160
Flexural modulas (MPa)	52	30	44	47	41	46

difference may be due to the crosslinked network. However Torlon has a linear and symmetrical polymeric structure.

The neated cured products obtained from the PAI/epoxy resin system were dark brown, amorphous powders. They did not melt up to 300°C and were insoluble in mineral acid and organic solvents. The film or cast of system is too brittle and therefore the hardness is not presented.

The electrical breakdown potential of all composites are presented in Tables IV and V for glass and carbon laminates respectively. The values for the present composites are low. This could imply the presence of a charred path, over which subsequent discharge could take place more and readily. Additionally minute leakage of current may arise from surface contamination.

EXPERIMENTAL

Materials

4,4′-Diamino diphenyl methane was obtained from CIBATUL Ltd., India. 1,1′-(methylene-di-4,1-phenylene) bismaleimide [MPDBM] was prepared by a method reported earlier [18]. A commercial epoxy (DGEBA) resin was obtained from Sympol Products Pvt. Ltd., Ahmedabad, India. The epoxy resin specifications were: epoxy equivalent weight, 190–210; viscosity at 25°C, 4–10 p; density at 25°C, 1.16–1.17 g/cm^3. E glass woven fabric (PI compatible) of 0.25 mm thick (Unnati Chemicals, India) of areal weight 270 g/m^2 was used for composite preparation. Carbon fibre (12 K) obtained from Indian Petrochemicals Corporation Limited (Baroda). Bisesters and all other chemicals used were of laboratory grade.

Synthesis of Oligomide

MPDBM-DDM oligoimide was prepared by using the 1:2 molar ratio of MPDBM:DDM following the method reported in our earlier communication [13].

Synthesis of Poly(amido-imide)s

A mixture of MDPBM-DDM oligoimide (0.01 mole), an aliphatic bisester (listed in Scheme I, Tab. I) (0.01 mole) and potasium hydroxide in THF-ethanol (70:30 v/v) mixture (50 cm^3) was refluxed for 4–5 h on a water bath. The product was then cooled and poured into a large quantity of water:methanol (75:25 v/v) mixture, filtered and washed with THF (10 cm^3) and then with DMF (10 cm^3) to remove unreacted reactants. Thus the poly(amido-imide)s were obtained in the form of a dark brown amorphous powder. The details of all PAIs are furnished in Table I.

Composite Fabrication

The glass and carbon fibre reinforced laminates based on the PAI-epoxy system were prepared by the procedure reported in our earlier communications [13]. A mixture of equimolar PAI and epoxy resin (40% wt. of total glass cloth) in dioxane was stirred well for 2 to 5 min. The suspension was then applied with a brush on to a 150 mm x 150 mm polyimide-compatible fibre glass cloth and the solvent was allowed to evaporate. Once dried, the 10 plies of prepreg thus prepared were stacked one on prepared the top of another, pressed between steel plates coated with a Teflon film release, and compressed in a flat plate press under about 70 psi(mPa) pressure. The prepreg stack was cured by heating in the press 170°C–180°C for 12 h. The laminates so obtained were cooled to 45°C before the pressure was released. Test specimens were made by cutting the laminates and machining them to final dimensions.

The carbon fibre laminates were prepared by using 30 tows of (30 cms each) carbon fibre, wherein the fibres were allowed to pass through the suspensions and were then compression moulded under similar moulding conditions to those used for glass fibre laminates. The final glass and carbon fibre to PAI epoxy resin ratio were in the range of 60:40 (w/w).

MEASUREMENTS

The C, H, N and S content of all PAIs were estimated using an Elemental Analyzer made by Carlo Erba, Italy.

The IR spectra of all oligoimides and their epxoy-cured products were scanned in KBr pellets on a Nicolet 400 D Spectrophotometer. The number-average molecular weight, ($\bar{M}n$) of PAI samples was determined by a non-aqueous conductometric titration method reported earlier [19]. A formic acid-acetic acid mixture was used as the solvent, and standard perchloric acid in acetic acid was used as a titrant. A digital conductivity meter (Toshniwal India.) was used for the titration.

Curing of DGEBA epoxy resin with PAI was montiored by differential scanning calorimetry using DuPont 900 DSC. this study. The instrument was calibrated using standard materials with known heats of fusion. Curing was carried out using a single heating rate (10 K/min). The sample weight for this investigation was in the 4 to 5 mg range and an empty cell was used as a reference.

Thermogravimetric Analysis (TGA) of all PAI and their cure products was carried out on a DuPont thermobalance in air at a heating rate of 10 K/min.

CONCLUSIONS

The overall advantage of poly(amido-imide)s systems produced are as follows:

- The PAIs having some —NH— groups and —NH—CO— groups, can act as curing agents for epoxy resins.
- Poly(amido-imide)s have good resistance to organic solvents and mineral acids.
- The PAIs-epoxy system shows good adhesion to glass fibre and carbon fibre.
- Void free sheets could be prepared with good mechanical and electrical properties.

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References

[1] Wilson, D. (in Polyimides), Wilson, D. Stenzenberger, H. D. and Hergenrother (1990). Eds. Champman and Hall, N.Y.

[2] Partridge, I. K. (in advanced composites) and Partridge, I. K. (1989). Ed. Elsevier, London.

[3] Patel, H. S. and Vyas, H. S. (1992). *Angew Macro. Chem.*, **195**, 1.

[4] Patel, H. S. and Patel, H. D. (1992). *High Perform. Polym.*, **4**, 19.

[5] Tesoro, G. C., Sastri, V. R. and Narang, S. C. (1987). U.S. Pat. 4276344.

[6] Varma, I. K. Fohlen, G. M. and Parker, J. A. (1987). U.S. Pat. 4276344.

[7] Varma, I. K. and Sharma, S. (1984). *Eur. Polym. J.*, **20**, 1101.

[8] Varma, I. K., Sangita and Varma, D. S. (1984). *J. Appl. Polym. Sci.*, **29**, 2807.

[9] Crivello, J. V. (1973). *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **14**, 293.

[10] Gannett, T. P., Gibbs, H. H. and Kassal, R. J. (1984). U.S. Pat. **4**, 485, 140.

[11] Gannett, T. P. and Gibbs (1986). U.S. Pat. **4**, 576, 857.

[12] Gannett, T. P., Kassal, R. J. and Ro, R. S. (1988). U.S. Pat. **4**, 725, 642.

[13] Patel, H. S. and Shah, V. J. (1993). *High Perform. Polym.*, **5**, 145.

[14] Patel, H. S. and Shah, V. J. (1994). *Macromol. Reports*, **31**, 545.

[15] Patel, H. S. and Shah, V. J. (1994). *Macromole Sci. Pure and Appl. Chem.*, **32**, 405.

[16] Patel, H. S. and Shah, V. J. (1994). *Intern J. Polymeric Mater.*, **26**, 79.

[17] Crivello, J. V. (1979). *J. Polym. Sci. Polym. Chem. Edd.*, **14**, 150.

[18] Patel, R. N. and Patel, S. R. (1981). *Die Angew. Makromol. Chem.*, **96** 85.

[19] Roff, W. J. and Scott, J. R. (1971). Fibres Films, Plast, Rubbers, pp. 265–266.