

ADVANCED COMPOSITES BASED ON NOVEL POLY (AMIDE-IMIDE)S

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ABSTRACT

Novel poly (amide-imide)s were prepared using polycondensation reaction of an amino terminated oligoimide with various aliphatic diesters. The resultants PAIs were characterized for preliminary tests and number average molecular weight estimation. PAI-epoxy resin was used as a matrix material for the preparation of carbon and glass fiber reinforced composites and they were characterized for mechanical and electrical properties and chemical resistances by ASTM methods.

Key words :- Advanced composites and Poly (Amide-imide)s.

Poly(amide-imide)s, non-aqueous conductometric titration, glass fiber reinforced composites, carbon fiber reinforced composites.

Abbreviations used:- BBM, benzidine bismaleimide; DDS, diamino diphenyl sulfone; GFRC, glass fiber reinforced composite; CFRC, carbon fiber reinforced composite.

INTRODUCTION

Polyimides with heteroatoms as links in the polymer chain have attained outstanding position in the field of polymeric materials¹. They offer outstanding stability, excellent mechanical properties and ability to be fabricated into useful articles. A typical polyimide synthesis involves the polycondensation reaction of a variety of dianhydrides containing heteroatoms and diamines^{2,3}. Bismaleimides are prime candidates for the synthesis of polyimides and can be prepared from an aromatic diamine with maleic anhydride as end capper⁴. Due to the presence of the two electron withdrawing carbonyl groups adjacent to the double bonds, the bismaleimide has better reactivity. The homo and copolymerization of bismaleimides with various vinyl monomers, allyl- and methallyl substituted phenols; triallyl cyanurates have

been reported⁵⁻⁹. Homopolymerization of bismaleimides has been shown to possible only either at elevated temperature or in the presence of an initiator^{10,11}. Patel *et al.* reported the synthesis of amino terminated oligoimides based on Michael addition reaction of bismaleimide with 4,4'-diamino diphenyl sulfone^{12,13}. Such oligoimides having terminal amino groups that make them suitable for further reactions such as amidation. The amidation of such amino terminated oligoimide with various diesters can afford novel poly(amide-imide)s possessing improved properties. The presence of the structural features of both amide and imide in the PAIs was expected to imbibe almost all the essentials and remove the shortcomings of neat polyimides. Much less, work is done in this field of PAIs and several anticipated applications prompted us to undertake the research work reported in the present research paper. The research

paper has been summarized in Scheme 1.

EXPERIMENTAL

Materials

4,4'-Diamino diphenyl sulfone; benzidine and various diesters (listed in Table 2) were obtained from SD fine Chemicals, Boisar, India. Benzidine bismaleimide (BBM) was prepared from 4,4'-Diamino diphenyl sulfone and benzidine using reported method¹⁴. A commercial epoxy resin (DGEBA) was obtained from Synpol Products Pvt. Ltd., Ahmedabad, India. The physical properties of the resin were: the epoxy equivalent weight, 190-210; viscosity at 25°C, 4-1 Op; density at 25°C, 1.16-1.17 g/cc. E-glass woven fabrics (Polyimide compatible) of 0.25 mm thick (Unnati Chemicals, Ahmedabad, India) of areal weight 270 g/m² was used for composite fabrication. Carbon fibers (12K) were obtained from Indian Petrochemicals Corporation Limited, Baroda, India.

Synthesis of oligoimide

A reported Michael addition reaction procedure^{12,13} has been modified for the synthesis of the amino terminated BBMDDS oligoimide as follows:

Benzidine bismaleimide (0.01 mole) was added gradually to a well-stirred solution of 4,4'-diamino diphenyl sulfone (0.02 mole DDS in 50 mL THF) with continuous stirring over a period of a half hour. The homogeneous viscous was obtained that was poured into ether (25 mL) and cooled by ice. The obtained powdered form of the oligoimide was filtered and washed with ether (10 mL) to remove unreacted DDS, followed by washing with warm DMF (10 mL) to remove unreacted bismaleimide. The resultant oligoimide was dried in vacuum oven. Preliminary characterisation of prepared oligoimide is presented in Table-1.

Synthesis of poly (amide-imide)s

PAIs were prepared by polyconden-

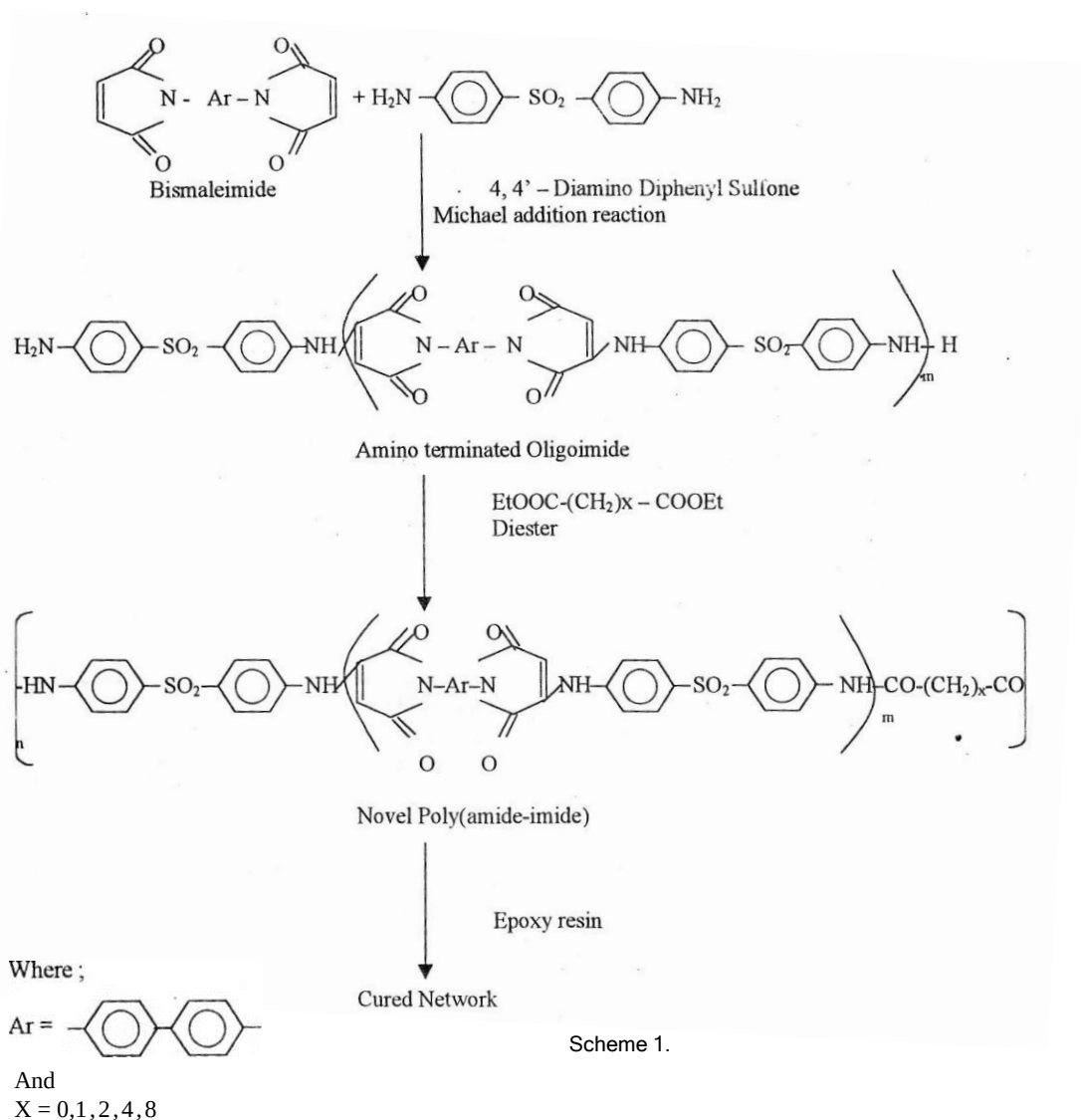
sation reaction using an equimolar ratio of prepared oligoimide with various aliphatic diesters (listed in Table 2) by following method:

The amino terminated BBMDDS oligoimide (0.01 mole), an aliphatic diester (0.01 mole) and potassium hydroxide (catalytic amount) in 70:30 (v/v) THF-ethanol mixture (50 mL) was mixed in three necked round bottom flask equipped with mechanical stirrer and water condenser and reaction mixture was refluxed for 4-5 h on a water bath at 70-80°C. The obtained product was then cooled at room temperature and poured into 75:25 (v/v) water-methanol mixture (80 mL) and filtered off. The resultant product was washed with THF (10 mL) and then with DMF (10 mL) to remove unreacted reactants and dried in vacuum oven. Thus, poly (amide-imide)s were obtained in the form of yellow to dark brown amorphous powder. The details of all PAIs prepared in a similar method are furnished in Table 2.

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Composite fabrication

The glass and carbon fiber reinforced composites based on PAI-epoxy system were prepared by the reported procedure¹². A mixture of equimolar proportion of PAI and epoxy resin (40% weight 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 150mm x 150mm polyimide compatible fiberglass cloth, and the solvent was allowed to evaporate. Once dried, the ten prepregs were stacked one on top of another, pressed between steel plates coated with a Teflon film, released and compressed in flat platten under 80-90 psi pressure. Heating them at 180-185°C for an hour in an air-circulated oven cured the prepregs. The composite so obtained was cooled to 25°C before the pressure was released. Cutting the composites and machining them to final dimension made test specimens. The carbon fiber composites were prepared by using 30 tows of (30 cm each) carbon fiber



Scheme 1.

(12K), where in the fibers were allowed to pass through the suspension (mentioned above) and were then compression molded under similar molding conditions to those used for glass fiber composites. The composites have 40% (w/w) PAI-epoxy resin content.

Measurements

Non-aqueous conductometric titration

method reported by Patel *et al*¹⁵ was used to estimate the number average molecular weights of all PAIs. Non-aqueous conductometric titration was carried out by a digital conductivity meter (Toshniwal, India) using 85:15(v/v) formic acid-acetic acid mixture as a solvent and standard (0.1M) perchloric acid as a titrant.

All the mechanical and electrical properties and chemical resistances were deter-

Table-1. Preliminary characterisation of amino terminated BBMDDS oligoimide

No.	Test / Details	Observation / Result
1.	State	Amorphous powder.
2.	Yield (%)	82 %.
3.	Colour	Brown.
4.	Melting point	298-300°C.
5.	Solubility	Insoluble in almost all common organic solvents (except formic acid)
6.	Azo-dye test	Positive
7.	Average molecular weight	2165

Table-2. Characterisation of PAIs based on BBMDDS oligoimide and various diesters

PAI	Diester	Colour	Yield	#M _n
	<u>Used*</u>			
PAI - I	DEO	Dark Brown	83	7040
PAI-2	DEM	Yellow	88	7065
PAI-3	DES	Brown	79	7195
PAI- 4	DEA	Dark Brown	75	7240
<u>PAI- 5</u>	<u>DESb</u>	<u>Dark Brown</u>	<u>84</u>	<u>7310</u>

*Diesters: Diethyl oxalate (DEO), Diethyl malonate (DEM), Diethyl succinate (DES), Diethyl adipate (DEA), Diethyl sebacate (DESb)

Number average molecular weights of PAIs were estimated by non-aqueous conductometric titration method.

mined according to ASTM methods.

RESULTS AND DISCUSSION

Preliminary characterisation of amino terminated oligoimide (Table 1) indicates that it is brown coloured amorphous powder and is insoluble in almost all the common organic solvents (except formic acid). A positive red azo dye test confirms the presence of the terminal aryl amino groups in the oligoimide. Its average molecular weight reveals that it has 3-4 repeating units in the polymer chain.

All the PAIs presented in Table 2 are yellow to dark brown coloured amorphous powder. They show the qualitative amide and imide tests to be positive. They are insoluble in almost all common organic solvents (except formic acid) and therefore the study of colligative properties could not be

possible for the average molecular weight estimation.

The average molecular weights of all PAIs (Table 2) reveal that average molecular weight of PAI increases with increasing molecular weight of an aliphatic diester.

PAI-epoxy contents of the prepared composites are found in the range of 35-40%w/w. Bismaleimide produce a highly cross-linked and brittle product⁷, they can not be applied for preparing advanced composites. Modifications to the bismaleimide system by addition of diamines are examined to improve the toughness and mechanical properties¹. Addition of the epoxy resin to PAI having -CO-NH- and -CO-NH-CO- groups increases the toughness of the final products. The mechanical properties of the produced composites (Table 3 & 4) are quite

Table-3. Mechanical and Electrical properties and Chemical resistances of Glass fiber reinforced composites based on PAI- epoxy system (PAI based on BBMDDS oligoimide)

@	Specific	PAI-	% Change on		Flexural	Compressive	Impact	Rockwell	Dielectric	
Reinforcement	gravity	epoxy	exposure to 25%		strength	strength	strength	hardness	Strength	
	D-792	content	w/v NaOH		MPa	MPa	Jm ¹	(R)	(In air)	
		%w/w	Thickness	Weight	ASTM	ASTM	ASTM	ASTM	(KV/mm)	
					D-790	D-695	D-256	D-785	ASTM D-149	
	PAI-1	1.7	40	1.2	1.3	250	240	215	130	12
	PAI-2	1.8	39	1.1	1.0	260	245	220	140	12
	PAI-3	2.0	38	1.3	1.1	260	230	220	115	14
	PAI-4	2.1	38	1.0	1.2	265	210	210	130	13
*	PAI-5	2.0	39	1.0	1.0	250	220	220	120	14

Unaffected by organic solvents and by (25% w/v) concentrated mineral acid [ASTM D-543 method]

@ Reinforcement: E' type glass cloth, plain weave, 10 mm, 10 layers, PAI-resin content: 38 + 3 weight %, Curing temperature:

140 ± 2°C, Curing time: an hour. Curing pressure: 80 - 90 psi, Composite size: 150 mm X 150 mm X 3 mm.

Table-4. Mechanical and Electrical properties and Chemical resistances of Carbon fiber reinforced composites based on PAI- epoxy system (PAI based on BBMDDS oligoimide)

Reinforcement	Specific gravity D-792	PAI-epoxy content %w/w	% Change on exposure to 25% * w/v NaOH		Flexural strength MPa ASTM D-790	Compressive strength MPa ASTM D-695	Impact strength Jnr ¹ ASTM D-256	Rockwell hardness (R) ASTM D-785	Dielectric Strength (In air) (KV/mm) ASTM D-149
			Thickness	Weight					
PAI-1	1.2	40	1.7	1.7	175	180	180	130	13
PAI-2	1.2	39	1.6	1.7	188	185	185	132	12
PAI-3	1.3	38	1.8	1.4	192	185	194	135	13
PAI-4	1.4	38	1.6	1.6	195	190	196	125	14
PAI-5	1.3	39	1.4	2.0	185	198	196	138	12

* Unaffected by organic solvents and by (25% w/v) concentrated mineral acid [ASTM D-543 method]

@ Reinforcement: Carbon fiber (12K) of 30 tow (of 12" each) 10 layers, PAI-resin content: 38 + 3 weight %, Curing temperature:

140 ± 2°C, Curing time: an hour. Curing pressure: 80 - 90 psi. Composite size: 150 mm X 150 mm X 3 mm.

The specific gravities of the composites (Tables 3 & 4) suggest that CFRCs are lighter in weight than GFRCs. The mechanical properties of GFRCs are better than that of CFRCs, due to its texture structure.

The lower values of electric breakdown potential of composites (Tables 3 & 4) could imply the presence of a charred path, over which subsequent discharge could take place more rapidly. Additionally, minute leakage of current may arise from surface contamination. The lower values of dielectric break-down strength for the present composites indicate that the composites are insulated.

The high chemical resistances of both types of composites (Tables 3 & 4) indicate that the imide moiety might contribute to a high level of cross-linking of epoxy resin with PAI during composite fabrication. However,

the concentrated alkali (25% w/v NaOH) affects the composites in weight and thickness.

CONCLUSION

The presence of terminal amide (-CO-NH-) and imide (-CO-NH-CO-) groups in the chain, novel PAIs possess the anticipated properties of polyamides and polyimides. The extraordinary thermal stability arises out of the resonance stabilisation due to aromatic rings near sulfone (SO₂) group. The PAI- epoxy system shows good adhesion to glass and carbon fibers. Prepared void free sheets are insulated and have good mechanical properties. GFRCs have better chemical resistances and mechanical properties, but they are heavier than

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