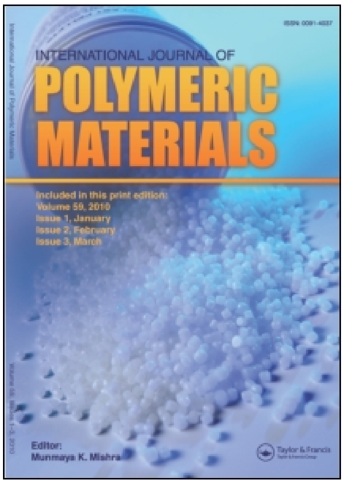

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Synthesis, Characterization and Glass Reinforcement of Poly(amido-imide)s

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Synthesis, Characterization and Glass Reinforcement of Poly(amido-imide)s

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Poly(amido-imide)s (PAI)s were prepared by the intermolecular Diels-Alder (DA) reaction of N-N′-1,4-phenylene bis[(2-furanyl methylamino)acetamide] (PBFA) with various bis(maleimide)s. The DA reaction was carried out in tetrahydrofuran as a solvent, as well as in bulk, followed by aromatization of sodium acetate intermediates in the presence of acetic anhydride. All the polymers were characterized by elemental analysis, IR spectral studies and thermogravimetry. The PAIs exhibit moderate thermal stability. PBFA and bismaleimides were polymerized (at 145 ± 10°C) by in situ *DA intermolecular reaction into moderately thermally stable PAIs(glass fiber composite laminates) and were characterized by their chemical resistance and mechanical properties.*

Keywords: bismaleimides, chloroacetylchloride, furfurylamine, polyamidoimides, p-phenylenediamine

INTRODUCTION

The polyimides are known as high-performance polymers [1]. Such polymers are synthesized by condensation or by addition polymerization [2]. One of the approaches to get the polyimides is via Diels-Alder reaction of dienes and bismaleimides [3]. H. S. Patel has created such polyimides from agriculture waste products such as furan derivatives [4]. He has made several different types of polyimides like polyetherimide, polysufoneimide, polyurethaneimide, and polysiloxaneimide

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through Diels-Alder polymerization of bisfurans with wide structural variation and bismaleimides [5,6]. Most of these polyimides have low processing temperature with good thermal stability in air. The polyimides with amide-imides linkages are reported commercially [7] and known as "Torlon". These poly(amido-imide)s (PAI)s are manufactured commercially by condensation polymerization of pyromaleic anhydride and diamines. Looking to the high-performance properties of these PAIs, it was thought to explore the field of PAIs. The present communication is an attempt to create the novel PAIs. The synthesis roots is shown in Scheme 1.

EXPERIMENTAL DETAILS

Materials

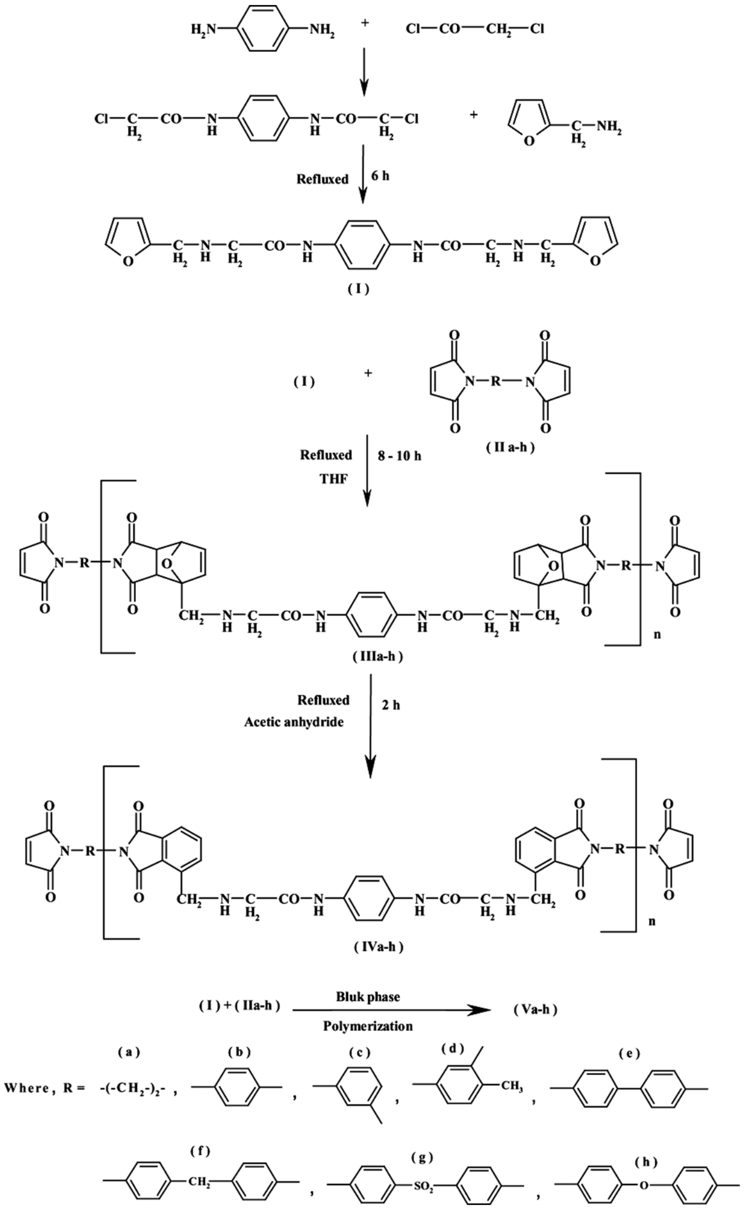
Ethylenediamine, 1,4-phenylenediamine, 1,3-phenylenediamine, benzidine, diaminodiphenyl methane, diaminodiphenyl ether, diaminodiphenyl sulfone, and 2,4-toluenediamine were obtained from SDS Chemicals, Boisar, India. Furfural amine was redistilled before use. Chloroacetylchloride was used as received from Merck. All other chemicals used were of laboratory grade. Sation (2/2) weave (polyimide compatible) fiber glass woven fabric 0.25 mm thick of 'E' type glass (Unnati Chemicals, India) 270 gm^{-2} was used for laminate preparation.

Preparation of Monomers

Preparation of N-N′-1,4-Phenylene bis[(2-furanyl methylamino)acetamide] (I)

To a solution of 0.1 mol 1,4-benzenediamine in acetone (20 ml) chloroacetylchloride (0.2 mol) dissolved in acetone (20 ml) was added slowly with vigorous stirring. $NaHCO_3$ (0.2 mol) was added as an acid acceptor. The resulting mixture was stirred for 6 h at room temperature. The so called precipitate was poured into ice-cooled water. The resultant product was filtered, dried in air and used without further purification. The process is already reported in the literature [8].

This bischloroacetyl-1,4-benzenediamine derivative was then dissolved in THF (30–40 ml). To this solution furfuryl amine (0.2 mol) was added with stirring. $NaHCO_3$ (0.2 mol) was added as an acid acceptor. Then the reaction mixture was refluxed for 6 h. The product was filtered, washed with acetone and air dried. M.P 280–282°C (uncorrected), yield was quantitative.



SCHEME 1 Synthetic route.

Elemental analysis:

$C_{20}H_{22}N_4O_4$ (382)
Calculated (%) C 62.82 H 5.75 N 14.65
Found (%) C 62.7 H 5.7 N 14.6

IR spectral features:

IR (KBr), cm^{-1}:
1520, 1530(Amide); 1620, 1380(Furan ring)
3380(NH (sec.); 2840, 2950($-CH_2-$); 830(Aromatic)

NMR signals:

^{1}HNMR ($CDCl_3$):
4.5–4.6δ(d;$-NH-CH_2-$,4H); 5.8δ(hump: $-NH-$,2H); 6.2δ(s;$=CH-CH=$,4H); 7.2δ(s;$=CH-O-$,2H); 7.6δ(d;$-CH=CH-$,4H); 3.4δ(d; $-CH_2-$,4H).

Synthesis of bismaleimides

Bismaleimides compounds (2a-h) were prepared by a modification of the process reported previously [9–11]. They are listed in Table 1.

Preparation of Poly(amido-imide)s

The Diels-Alder reaction of (I) with various bis(maleimide)s (IIa-h) was carried out both in solution and in the bulk. General procedure for the preparation of poly(amido-imides)s is given below.

Solution Phase Polymerization

(I) (0.01 mol) in 100 ml of dry THF was mixed with (II) (0.01 mol). The solution was stirred and refluxed at 100°C for 8–10 h.

TABLE 1 List of Bis(maleimide)s Compounds

No.	Bismaleimides	Molecular weight	Melting point (°C)
2a	Ethylene bismaleimide	220	189–190
2b	1,4-phenylene bismaleimide	268	300
2c	1,3-phenylene bismaleimide	268	202–203
2d	2,3-toluene bismaleimide	282	100–101
2e	4,4′-biphenylene bismaleimide	344	300
2f	4,4′-diaminodiphenylene methane bismaleimide	385	156–158
2g	4,4′-diaminodiphenyl sulfone-bismaleimide	408	254–255
2h	4,4′-diaminodiphenyl ether-bismaleimide	360	179–181

The resulting solution was cooled and poured into a large volume of dry ether. The precipitated polymer (III) (0.01 mol) was filtered off and dried. Aromatization of polymer (III) was carried out by refluxing 2 g of the dried polymer in 2 ml of acetic anhydride for 2 h [12]. The resulting mixture was poured into 1,4-dioxane-ether (50:50) mixture. The precipitate of aromatized polymer (IV) was filtered off the washed once with water.

Bulk Polymerization

A mixture of (I) (0.0005 mol) and (II) (0.0005 mol) was suspended in dry THF (25 ml), then spread in a Petri dish. The THF was evaporated at room temp. The dried mixture was heated at 110°C for 4 h and then heated with acetic anhydride (1 ml) at 130 ± 5°C for 4 h with vigorous agitation. The resulting solid product (V) was treated as (V).

Composite Fabrication

A typical method of fabrication for composites is given below. A suspension of PBFA (I) and bis(maleimide)s ($II_{a\text{-}h}$) in tetrahydrofuran was prepared and was stirred well for 2 min. The suspension mixture was applied with a brush to a 25 mm × 25 mm glass fiber cloth and the solvent was allowed to evaporate. The 10 dried prepegs so prepared were stacked one on top of another and pressed between steel plates with Teflon film release sheet and compressed in a flat platen press under about 70 psi pressure. The prepegs were cured by heating the press to 145°C for 10 h in an air-circulated oven. The composite so obtained was cooled to 50°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions.

Measurements

The C, H and N contents of all the PAIs were estimated by means of a Carlo Erba elemental analyzer (Italy). The IR spectra were taken in KBr using a Perkin-Elmer 983 spectrophotometer. All polymer samples were subjected to thermogravimetric analysis (TGA) (Du Pont 950 thermogravimetric analyzer) in air at a heating rate of 10 K min^{-1}.

Chemical Resistance

The chemical resistance of the composite was measured according to ASTM D543. The sample size was approximately 20 mm × 20 mm. The data are included in Table 2.

TABLE 2 Mechanical and Electrical Properties of Glass-Reinforced PAIs[a]

Composite	% Change on exposure to 25% (w/v) NaOH[b]		Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness	Electrical strength (in air) (kV mm^{-1})
	Thickness	Weight					
Ca	1.9	1.7	328	292	305	104	17.4
Cb	1.7	1.8	280	270	287	101	16.7
Cc	1.7	1.9	284	272	286	100	16.2
Cd	1.6	1.6	265	205	166	120	18.9
Ce	1.5	1.2	215	181	185	111	20.2
Cf	1.3	1.1	235	215	212	108	21.9
Cg	1.3	1.3	228	191	197	103	18.0
Ch	1.4	1.1	245	188	200	100	19.1

[a] Conditions: Reinforcement: E glass cloth; plain weave; 10 mm; 10 layers. Resin content, 40 ± 2%; mole ratio (bismaleimide:PBFA), 1:1; curing temperature, 145 ± 10°C; time, 10 h; pressure, 60–70 psi.

[b] Composite size: 25 mm × 25 mm, 3.0–3.5 mm thick.

Mechanical Properties

All the mechanical properties were measured on three individual specimens and the average results have been documented.

Flexural Strength Test

The measurements of flexural strength of composites were carried out on a Universal Instron Testing Machine model number A-74-37 at room temperature according to the testing method of ASTM D770. The crosshead speed was 100 mm/min^{-1}.

Compressive Strength Test

The compressive strength was measured according to an IS method. The sample size was 12.5 mm × 12.5 mm.

Impact Strength Test

According to the testing method of ASTM D256, the measurements were made through an Izod-type impact tester at room temperature.

Hardness Test

The Rockwell hardness strength was measured according to ASTM D785. The sample size was 25 mm × 25 mm.

Electrical Testing

Dielectric strength measurements were carried out on a high-voltage tester machine oil test set.

RESULTS AND DISCUSSION

The formation of all the PAIs (III, IV, and V) from (I) and bismaleimides ($II_{a\text{-}h}$) is shown in Scheme 1. The formation of the monomer is also shown in the Scheme. Based on the reactive sites of reagents the structure of (I) is predicted. It was confirmed by elemental analysis and spectral studies. The IR spectral comprises the bands due to amide and amine groups and the NMR spectral show the signal of protons. As mentioned in the Experimental section.

The nonaromatized product $III_{a\text{-}h}$ is first formed and then aromatized by treatment with acetic anhydride to yield $IV_{a\text{-}h.}$ In the absence of bismaleimide, heating of (I) in THF and refluxed for 8–10 h does not alter the properties of (I). It was also observed that heating each of $II_{a\text{-}h}$ in THF and refluxed for 8–10 h does not induce the additional polymerization of $II_{a\text{-}h}$. This has been shown to be possible only at elevated temperature or in the presence of an initiator [13–15].

TABLE 3 Characterization of Unaromatized PAIs

		Elemental analysis (%)			IR spectral features wave number (cm^{-1})					Weight loss (%) at various temperatures				
Polymer	M. F. [M. W.]		Calc.	Found	$-CH_2-$	Aromatic	NH (Sec.)	Imide	Amide	200°C	300°C	400°C	500°C	600°C
	$C_{30}H_{30}N_6O_8$	C	59.80	59.70	2860	3020	3380	1715,1770	1520					
IIIa		H	4.98	4.80	2940	830		1120	1530	1.4	29	38	66	95
	[602]	N	13.98	13.80				735						
	$C_{34}H_{30}N_6O_8$	C	62.76	62.70	2870	3020	3400	1715,1780	1525					
IIIb		H	4.61	4.60	2990	830		1100	1530	1.5	30	47	65	91
	[650]	N	12.92	12.89				730						
	$C_{30}H_{30}N_6O_8$	C	62.76	62.70	2820	3020	3370	1715,1780	1525					
IIIc		H	4.61	4.60	2990	820		1120	1530	1.5	30	42	63	90
	[650]	N	12.92	12.89				740						
	$C_{35}H_{32}N_6O_8$	C	63.25	63.10	2830	3030	3380	1720,1770	1530					
IIId		H	4.81	4.79	2950	830		1130	1530	1.6	29	44	67	92
	[664]	N	12.65	12.62				730						
	$C_{40}H_{34}N_6O_8$	C	66.11	66.00	2860	3040	3350	1710,1770	1540					
IIIe		H	4.68	4.64	2930	830		1120	1520	1.2	24	32	62	94
	[726]	N	11.57	11.54				740						
	$C_{41}H_{36}N_6O_8$	C	66.48	66.40	2860	3040	3370	1710,1780	1530					
IIIf		H	4.68	4.83	2920	820		1100	1520	1.4	25	36	66	95
	[740]	N	11.35	11.34				730						
	$C_{40}H_{34}N_6O_{10}S$	C	60.75	62.72	2860	3040	3360	1720,1990	1520					
IIIg		H	4.30	4.28	2920	820		1130	1530	1.2	23	34	66	96
	[790]	N	10.63	10.60				730						
	$C_{40}H_{34}N_6O_9$	C	64.69	64.66	2870	3040	3380	1710,1780	1530					
IIIh		H	4.58	4.54	2940	820		1130	1540	1.4	25	36	66	97
	[742]	N	11.32	11.30				750						

TABLE 4 Characterization of Aromatized PAIs

		Elemental analysis (%)			IR spectral features wave number (cm^{-1})					Weight loss (%) at various temperatures				
Polymer	M. F. [M. W.]		Calc.	Found	$-CH_2-$	Aromatic	NH (Sec.)	Imide	Amide	200°C	300°C	400°C	500°C	600°C
	$C_{30}H_{26}N_6O_6$	C	63.60	63.58	2860	3030	3380	1715,1770	1520					
IVa		H	4.59	4.56	2940	830		1120	1530	1.5	29	33	51	94
	[566]	N	14.84	14.80				735						
	$C_{34}H_{26}N_6O_6$	C	66.44	66.40	2850	3030	3400	1715,1790	1525					
IVb		H	4.23	4.20	2990	830		1100	1530	1.4	25	31	56	93
	[614]	N	13.68	13.65				730						
	$C_{34}H_{26}N_6O_6$	C	66.44	66.40	2820	3030	3360	1715,1780	1525					
IVc		H	4.23	4.19	2940	820		1120	1530	1.3	24	30	55	93
	[614]	N	13.68	13.64				740						
	$C_{35}H_{28}N_6O_6$	C	66.87	66.85	2830	3020	3370	1720,1770	1525					
IVd		H	4.45	4.42	2970	830		1120	1530	1.3	28	33	57	92
	[628]	N	13.37	13.34				740						
	$C_{40}H_{30}N_6O_6$	C	69.54	69.55	2850	3040	3350	1720,1770	1540					
IVe		H	4.34	4.30	2920	830		1120	1530	1.2	26	28	54	91
	[690]	N	12.12	12.10		780		740						
	$C_{41}H_{32}N_6O_6$	C	69.88	69.84	2860	3040	3370	1710,1780	1530					
IVf		H	4.54	4.50	2920	820		1100	1520	1.1	23	37	68	94
	[704]	N	11.93	11.90				730						
	$C_{40}H_{30}N_6O_8S$	C	63.66	63.62	2860	3040	3360	1720,1790	1530					
IVg		H	3.97	3.90	2920	820		1120	1520	1.1	22	35	61	93
	[754]	N	11.14	11.10		770		730						
	$C_{40}H_{30}N_6O_7$	C	67.98	67.93	2870	3040	3390	1710,1780	1540					
IVh		H	4.24	4.20	2940	830		1130	1530	1.3	26	36	64	93
	[706]	N	11.89	11.84		780		750						

TABLE 5 Characterization of Bulk Phase PAIs

		Elemental analysis (%)			IR spectral features wave number (cm^{-1})					Weight loss (%) at various temperatures				
Polymer	M. F. [M. W.]		Calc.	Found	$-CH_2-$	Aromatic	NH (Sec.)	Imide	Amide	200°C	300°C	400°C	500°C	600°C
Va	$C_{30}H_{26}N_6O_6$	C	63.60	63.57	2860	3030	3370	1715,1770	1520	1.5	29	34	53	94
		H	4.59	4.55	2940	830		1120	1530					
	[566]	N	14.84	14.80		780		735						
Vb	$C_{34}H_{26}N_6O_6$	C	66.44	66.40	2850	3030	3400	1715,1790	1530	1.4	25	33	58	93
		H	4.23	4.20	2990	830		1100	1520					
	[614]	N	13.68	13.61		770		730						
Vc	$C_{34}H_{26}N_6O_6$	C	66.44	66.40	2820	3030	3350	1715,1780	1530	1.3	24	31	59	93
		H	4.23	4.19	2940	830		1120	1520					
	[614]	N	13.68	13.60		780		740						
Vd	$C_{35}H_{28}N_6O_6$	C	66.87	66.80	2830	3020	3370	1720,1770	1530	1.3	22	35	56	92
		H	4.45	4.40	2970	830		1120	1530					
	[628]	N	13.37	13.31		760		740						
Ve	$C_{40}H_{30}N_6O_6$	C	69.56	69.50	2850	3030	3360	1720,1770	1520	1.2	26	29	55	91
		H	4.34	4.30	2920	830		1120	1525					
	[690]	N	12.17	12.11		780		740						
Vf	$C_{41}H_{32}N_6O_6$	C	69.88	69.80	2860	3040	3370	1710,1780	1520	1.1	23	33	69	94
		H	4.54	4.50	2920	830		1100	1530					
	[704]	N	11.93	11.90		770		730						
Vg	$C_{40}H_{30}N_6O_8S$	C	63.66	63.61	2860	3030	3360	1720,1790	1530	1.1	24	37	60	93
		H	3.97	3.91	2920	830		1120	1525					
	[754]	N	11.14	11.11		780		730						
Vh	$C_{40}H_{30}N_6O_7$	C	67.98	67.92	2870	3040	3380	1710,1780	1525	1.3	26	36	64	93
		H	4.24	4.21	2940	820		1130	1530					
	[742]	N	11.89	11.82		780		750						

All the polymer samples were obtained at about 65% yield as dark brown solid powders. They are insoluble in common organic solvents and are not affected by concentrated mineral acids or formic acid. The elemental analyses of all the PAIs samples are consistent with their predicted structures (scheme) and the results of this analysis are shown in Tables 3–5.

Examination of IR spectra contain prominent characteristic bands of the amide and imides. The bands around $1780\,\mathrm{cm}^{-1}$, $1720\,\mathrm{cm}^{-1}$, $1050\,\mathrm{cm}^{-1}$ and $720\,\mathrm{cm}^{-1}$ are contributions from the imides groups, while bands around $1530\,\mathrm{cm}^{-1}$ show the presence of amide. The band around $3300–3400\,\mathrm{cm}^{-1}$ shows the stretching vibrations of –NH–. The other IR spectral features of PAIs are summarized in Tables 3–5.

The TGA data of all PAIs shown in Tables 3–5 reveal that all PAIs samples degrade in a single step. Their decomposition starts around 190°C depending on the nature of the polymers. The rate of decomposition increases by increasing the temperature and it is high between 220°C and 550°C. It was observed that around 630°C, almost all the PAIs are lost.

The present PAIs are thermally stable and retain acid, solvent, and weather resistance. Because of non-processability of cross-linked polyimides, a novel approach was also searched to develop matrices for processable (145 ± 10°C) polyimide glass fiber composites. The addition polymerization by the DA reaction of (I) and with (II) starts from the surfaces of the composites from which the polymerization continues towards the inner part of the composite without evolution of any reaction by-product or solvent molecules.

CONCLUSION

The overall advantages of the present PBFA and bis(maleimide)s matrix systems are as follows:

- The intermolecular DA reaction of PBFA with bismaleimides created PAIs with good resistance to organic solvents and mineral acids, and moderate resistance to heat;
- The in situ produced PAIs show good adhesion to glass fibers;
- Void-free composites could be prepared with good mechanical and electrical properties.

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