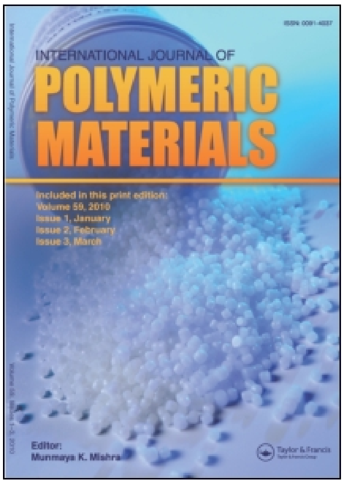

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Synthesis, Characterization and Material Application of Poly(Urea-Imide)s, Part 1

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Poly(urea-imide)s (PUIs) were prepared by Diels-Alder (DA) intermolecular polymerization of hexamethylenebis(2-furanmethylurea) (BFU) (1) with various bismaleimides (2a-f). The DA reaction was carried out using 1,4-dioxane as solvent, as well as in bulk, followed by aromatization (dehydration) of poly(tetrahydro phthalimide) intermediates (3a-f) in the presence of acetic anhydride. All the PUIs (3a-f, 4a-f and 5a-f) were characterized by elemental analysis, IR spectral studies and thermogravimetrically. BFU (1) and bismaleimides (2a-f) were polymerized (at 145 ± 10°C) by in situ DA intermolecular reaction into moderately thermally stable PUIs (5a-f), glass fiber and carbon fiber composites without evolution of any byproducts. The prepared composites were characterized by chemical resistance and mechanical properties.

Keywords bisfurans (BFU), carbon fiber-reinforced composite (CFRC), Diels-Alder (DA), glass fiber-reinforced composite (GFRC), poly(urea-imide)s (PUIS)

INTRODUCTION

The introduction of linkages such as ether, amide, oxysilane, and ester to improve the processability of polyimides without major sacrifice in thermo-oxidative stability has received great industrial attention [1–3]. The above properties make copolyimides suitable for interlaminary insulation, protective coatings in microelectronics and also for preparation of flexible composites [1–3]. The merging of urea linkage and imide linkage into the polymer chain

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may offer highly thermally stable polymers. With this view, the present author has published the initial work [4]. In continuation of this work the present communication refers to the synthesis and characterization of PUIs based on the Diels-Alder (DA) reaction of urea linkage containing bisfurans (BFU) (1), hexamethylenebis(2-furanmethylurea), and bismaleimides (2a-f). A novel approach was also conducted to prepare a matrix resin system for processible PUIs, glass and carbon-fiber composites based on in situ Diels-Alder (DA) intermolecular addition polymerization of BFU (1) and bismaleimides (2a-f). The prepared composites were characterized by their chemical and mechanical properties. Thus, the present article comprises synthesis, characterization, glass and carbon reinforcement of PUIs (5a-f).

EXPERIMENTAL

Materials

The diamines for bismaleimides used were:

(1a) 1,3-phenylene diamine

(1b) 1,4-phenylene diamine

(1c) benzidine

(1d) 4,4′-diamino diphenyl methane

(1e) 4,4′-diamino diphenyl ether

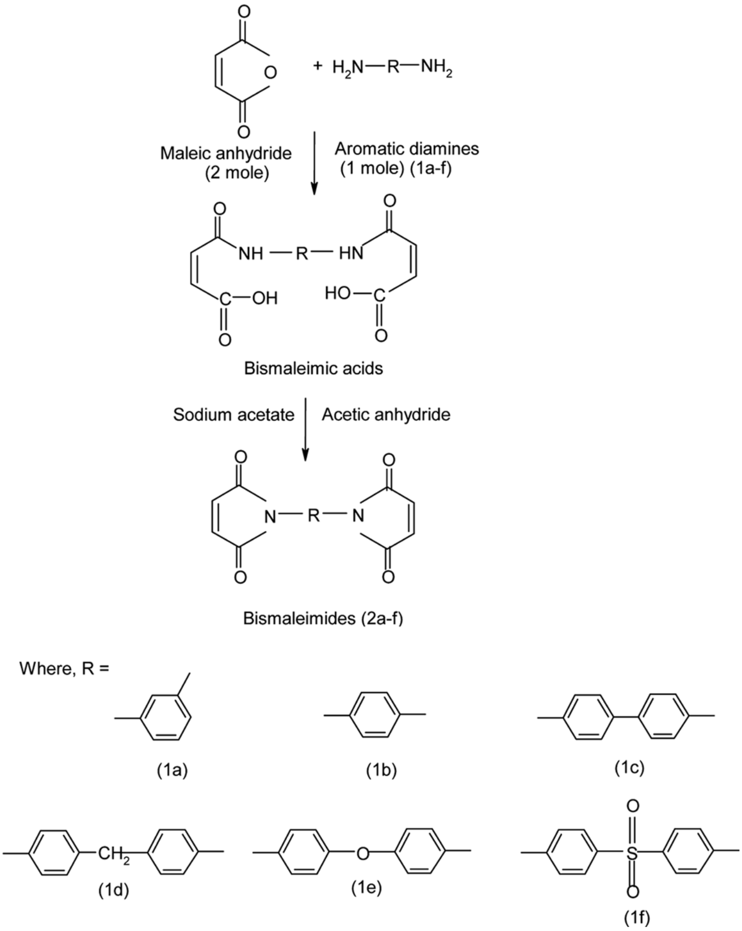
(1f) 4,4′-diamino diphenyl sulfone

E-type of glass woven fabric 0.25 mm thick used for glass reinforcement was obtained from Unnati Chemicals, India. Carbon fiber (12 K) used for carbon reinforcement was obtained from IPCL, Vadodara, India. All other chemicals were of pure grade.

Preparation of Bismaleimides (2a-f)

The bismaleimide monomers were prepared by slight modification of a method reported in the literature [5]. A typical procedure is as follows.

To a vigorously stirred solution of diamine (1a-f) (0.1 mole) in dry acetone, the maleic anhydride (0.22 mole) in dry acetone was added dropwise in a nitrogen atmosphere at 5°C in 30 min. The pale yellow or white precipitate of bismaleimic acid was obtained on the addition of maleic anhydride. The reaction mixture was vigorously stirred for 1 h after complete addition of maleic anhydride solution. The reaction mixture was kept for 1 h at room temperature. To this reaction mixture, fused sodium acetate (6 gm) and acetic



Scheme 1: Synthesis of Bismaleimides (2a-f).

anhydride (70 ml) were added with continuous stirring. Then reaction mixture was refluxed for about 3 h until the solution became clear. The clear solution was poured into crushed ice and repeatedly washed with water, and dried in air quickly. The resultant bismaleimides are designated as (2a-f). The synthetic route is shown in Scheme 1.

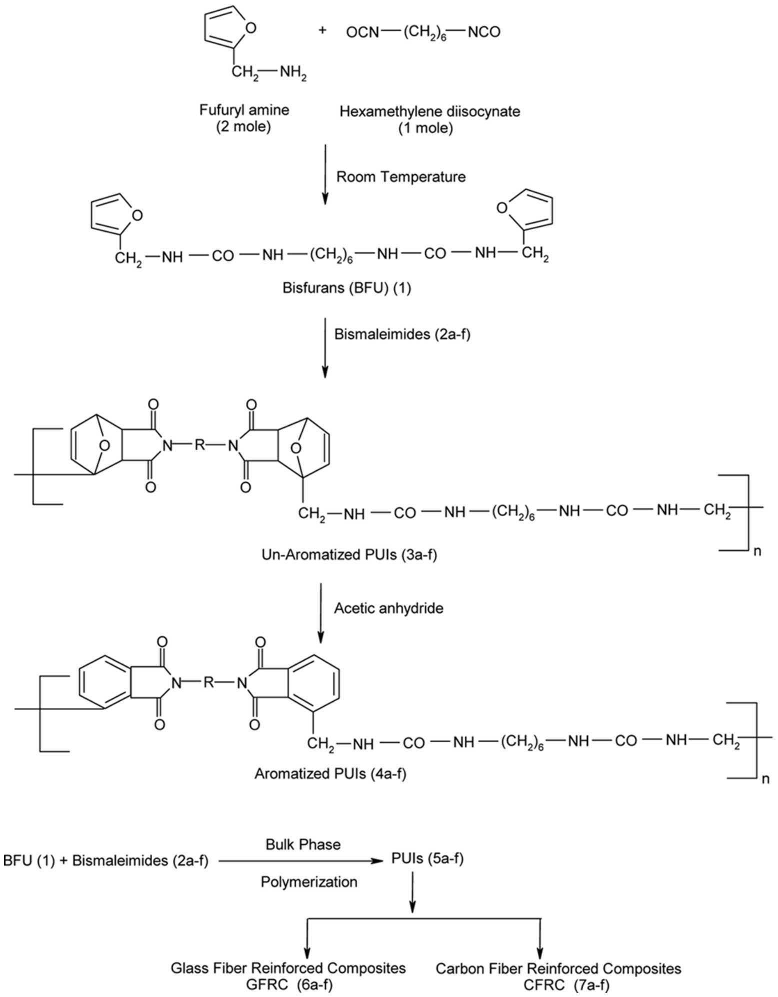
Preparation of Hexamethylenebis(2-furanmethylurea) (BFU) (1)

Hexamethylenebis(2-furanmethylurea) (BFU) (1) was prepared by the following method.

To an ice-cold solution of 2-furfuryllamine (0.5 mole) in dry ether (0.25 mole) hexamethylene diisocynate in dry ether was added with stirring. The resulting product was filtered, washed with ether and air-dried. The product was white in color; m.p. is 112–113°C. The synthetic route is shown in Scheme 2.

Preparation of Poly(Urea-Imide) (PUIs)

The DA reactions of BFU (1) with bismaleimides (2a-f) were carried out by both solution phase and bulk phase polymerization.



Scheme 2: Synthesis of PUIs (5a-f).

Solution Phase Polymerization

Bisfuran (BFU) (0.01 mole) in 100 ml of dry 1,4-dioxane was mixed with bismaleimides (2a-f) (0.01 mole). The solution was stirred and refluxed at 100°C for 24 h. The resulting solution was cooled and poured into a large volume of dry ether. The precipitated polymer 3a-f was filtered off and dried. It was treated twice with hot dimethyl formamide to remove unreacted bisfurans (BFU) and bismaleimides (2a-f). Aromatization of polymer 3a-f was carried out by refluxing 2 gm of dried polymer in 2 ml of acetic anhydride for 4 h. The resulting mixture was poured into 1,4-dioxane-ether (50:50) mixture. The precipitates of aromatized polymer 4a-f were filtered off, and washed once each with water and methanol.

Bulk Phase Polymerization

A mixture of BFU (1) (0.005 mole) and bismaleimides (2a-f) (0.005 mole) was suspended in dry tetrahydrofuran, THF (25 ml), then spread in a petri dish and the THF allowed to evaporate at room temperature. 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 5a-f was filtered off, and washed once each with water and methanol. The details of all PUIs: 3a-f, 4a-f and 5a-f are given in Tables 1–3, respectively.

Composite Fabrication

Glass and carbon composites of PUIs (5a-f) were prepared by the same method. Preparation method of GFRC (6a-f) and CFRC (7a-f) for PUIs (5a-f) is given briefly below.

Table 1: Characterization of unaromatized poly(urea-imide)s (PUIs) (3a-f).

		Elemental analysis calc./(found)				Weight loss at various temperature (°C) from TGA				
PUIs	**(%) Yield**	**%C**	**%H**	**%N**	**%S**	**300**	**400**	**500**	**600**	**700**
3a	69	60.95 (60.62)	5.39 (5.10)	12.33 (12.13)	—	2	17	40	58	80
3b	72	60.95 (60.63)	5.39 (5.14)	12.33 (12.11)	—	2.2	17	37	57	82
3c	73	64.58 (64.43)	5.38 (5.15)	11.89 (11.60)	—	1.6	19	41	57	82
3d	69	65.0 (64.70)	5.55 (5.15)	11.66 (11.41)	—	1.5	15	39	60	81
3e	72	63.15 (62.82)	5.26 (5.06)	11.63 (11.46)	—	2	15	39	55	83
3f	73	59.22 (59.0)	4.93 (4.72)	10.9 (9.8)	4.15 (3.91)	2.1	16	42	54	80

Table 2: Characterization of aromatized poly(urea-imide)s (PUIs) (4a-f).

		Elemental analysis calc./(found)				**Weight loss at various temperature (°C) from TGA**				
PUIs	**(%) Yield**	**%C**	**%H**	**%N**	**%S**	**300**	**400**	**500**	**600**	**700**
4a	71	64.64 (64.40)	5.5 (4.80)	14.14 (13.90)	—	1.2	13	37	54	79
4b	74	64.64 (64.38)	5.5 (4.83)	14.14 (13.91)	—	1.2	13	37	53	78
4c	71	67.16 (67.01)	5.07 (4.90)	12.53 (12.20)	—	1.3	16	40	53	76
4d	71	68.42 (68.21)	5.26 (5.0)	12.28 (12.02)	—	1.0	13	36	57	79
4e	76	66.41 (66.28)	4.95 (4.70)	12.24 (11.99)	—	1.1	14	38	55	83
4f	75	62.12 (61.93)	4.63 (4.41)	11.44 (11.24)	4.35 (4.16)	0.9	15	40	54	80

A suspension of BFU (1) and bismaleimides (2a-f) in THF was prepared and stirred well for 5 min. The suspension mixture was applied with a brush to a 200 mm × 200 mm glass cloth and the solvent was allowed to evaporate. The ten dried fiber plies prepared in this way were then stacked one on top of another and pressed between steel plates coated with a Teflon release sheet and compressed under 70 psi pressure. The fiber plies stacks were cured by heating in an autoclave oven at $145 \pm 10°C$ for about ~10 h. The composites so obtained were cooled to 45–50°C before the pressure was released. The composites were then machined to final dimensions.

Carbon fiber-reinforced composites (CFRC) were prepared by using 30 tows (12 K) of carbon fiber. Then by following a similar method and molding

Table 3: Characterization of bulk phase poly(urea-imide)s (PUIs) (5a-f).

		Elemental analysis calc./(found)				**Weight loss at various temperature (°C) from TGA**				
PUIs	**(%) Yield**	**%C**	**%H**	**%N**	**%S**	**300**	**400**	**500**	**600**	**700**
5a	81	64.64 (64.45)	5.05 (4.91)	14.14 (13.90)	—	2	16	38	59	81
5b	86	64.64 (64.43)	5.05 (4.90)	14.14 (13.91)	—	2	15	37	58	80
5c	84	67.16 (66.98)	5.07 (4.94)	12.53 (12.21)	—	1.6	17	41	55	81
5d	83	68.42 (68.21)	5.26 (5.11)	12.26 (12.03)	—	1.5	16	39	58	83
5e	87	66.47 (61.11)	4.95 (4.80)	12.24 (12.11)	—	2	16	38	57	83
5f	88	62.12 (61.90)	4.63 (4.43)	11.44 (11.21)	4.35 (4.19)	1.8	17	42	59	80

conditions used in the case of glass reinforcement, as indicated above, CFRC were laminated.

ANALYSIS

The C, H, N and S contents of monomer BFU (1) and all PUIs (3a-f, 4a-f and 5a-f) were estimated by means of Carlo Earba Elemental Analyzer (Italy). The IR spectra of all the samples were taken in KBr pellets on a NICOLET 760 D spectrophotometer. All polymer samples were subjected to thermogravimetric analysis (TGA) on Du Pont 950 thermogravimetric analyzer in air at a heating rate of 10°C/min. The sample weight for this investigation was in the range of 4–5 mg.

COMPOSITE CHARACTERIZATION

All the chemical, mechanical and electrical tests on composites were conducted according to ASTM methods (as listed below) using three specimens for each test.

Chemical Resistance Test

The resistances against chemicals of the composite samples were measured according to ASTM D 543.

Mechanical and Electrical Testing

(1) The flexural strength was measured according to ASTM D 790.

(2) The compressive strength was measured according to ASTM D 695.

(3) The impact strength was measured according to ASTM D 256.

(4) The Rockwell hardness was measured according to ASTM D 785.

(5) The electrical strength was measured according to ASTM D 149.

All the results are furnished in Tables 4 and 5.

RESULTS AND DISCUSSION

The synthesis of bismaleimides (2a-f) is shown in Scheme 1. The synthesis of hexamethylenebis(2-furanmethylurea) (BFU) (1) and formation of all

Table 4: Chemical and mechanical properties of glass fiber-reinforced composites (6a-f) of PUIs (5a-f).

GFRC (6a-f)	% Loss on exposure to 25% (W/V) NaOH		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight						
6a	1.5	1.3	1.49	456	328	354	80	25.1
6b	1.4	1.2	1.50	460	332	350	86	25.8
6c	1.3	1.4	1.42	390	325	323	72	25.6
6d	1.4	1.5	1.60	432	382	369	75	24.1
6e	1.4	1.6	1.43	400	390	372	59	21.1
6f	1.5	1.2	1.40	412	401	376	58	20.1

Table 5: Chemical and mechanical properties of carbon fiber-reinforced composites (7a-f) of PUIs (5a-f).

GFRC (7a-f)	% Loss on exposure to 25% (W/V) NaOH		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight						
7a	1.4	1.2	1.50	455	331	356	82	25.3
7b	1.4	1.2	1.51	462	333	352	87	25.9
7c	1.2	1.3	1.46	393	327	324	74	25.7
7d	1.3	1.4	1.67	435	383	371	77	24.2
7e	1.4	1.4	1.46	403	392	374	62	21.3
7f	1.4	1.0	1.45	414	404	378	62	20.3

poly(urea-imide)s (PUIs) (3a-f, 4a-f and 5a-f) is shown in Scheme 2. First, the nonaromatized DA product 3a-f is formed which is then aromatized by treatment of acetic anhydride to yield 4a-f. In the absence of bismaleimides (2a-f), heating of BFU (1) in 1,4-dioxane at 100°C does not alter the properties of BFU (1). It was also observed that heating of bismaleimides (2a-f) in 1,4-dioxane at 100°C does not induce the addition polymerization of bismaleimides (2a-f). This has been shown to be possible only at elevated temperature or in the presence of an initiator [6, 7]. All the polymer samples were obtained in high yields in the form of dark brown, solid powders. They are insoluble in common organic solvents and are not affected by concentrated mineral acids and formic acid. The elemental analyses of all PUIs samples (3a-f, 4a-f and 5a-f) are shown in Tables 1, 2 and 3, respectively, and are found to be consistent with their predicted structures. Typical IR spectra of PUIs (3a-f, 4a-f and 5a-f) were also found to be consistent with their predicted structures. The TG data of all PUIs (3a-f, 4a-f and 5a-f) are listed in Tables 1, 2 and 3, respectively. The data shows that the produced PUIs samples exhibit less than 2% weight loss around 300°C; they decompose in a single step. The rate of decomposition of the polymers increases rapidly beyond 400°C. The samples were lost completely beyond 700°C.

The present PUIs are found to be moderately thermally stable, and they retain acid, solvent and weather resistance. Because of non-processability of the present insoluble PUIs, a novel approach was also conducted to develop a matrix system for processable (145 ± 10°C) PUIs (5a-f) glass and carbon fiber composites. All the composites prepared are dark brown sheets. The addition polymerization by DA reaction of BFU (1) with bismaleimides (2a-f) starts at the surface of the composite, from which the polymerization continues towards the inner part of the composite without evolution of any reaction by-products or solvent molecules. Characterizations of prepared glass and carbon fiber-reinforced composites are given in Tables 4 and 5, respectively. The density of all the glass fiber-reinforced composites (6a-f) was in the range of 1.4 to 1.6 g/cm^3 and shows that there is not appreciable change in their specific gravity related to the nature of bismaleimides (2a-f). Also, the density of all the carbon fiber-reinforced composites (7a-f) was in the range of 1.45 to 1.67 g/cm^3 and shows that there is not appreciable change in their specific gravity related to the nature of bismaleimides (2a-f). Examination of chemical resistance test reveals that all GFRC (6a-f) have remarkable resistance to organic solvents and concentrated acids. However, the treatment with concentrated 2 M NaOH changes their thickness, and weight loss of about 1.2 to 1.6 was found. For CFRC (7a-f) weight loss of about 1.0 to 1.4 was found. Results of mechanical properties of PUIs (5a-f) GFRC (6a-f) reveal that all the composites have good mechanical properties. The electrical strength of all the GFRC (6a-f) was found to be in the range of 20.1 to 25.8 kV/mm. Also, CFRC (7a-f) reveal that all the composites have good mechanical properties compared to GFRC (6a-f). The electrical strength of all the CFRC (7a-f) was found to be in the range of 20.3 to 25.9 kV/mm.

CONCLUSION

From the above results we can say that composites prepared from PUIs had remarkable chemical and mechanical properties and these PUIs may be competitive with other resins. Also, CFRC (7a-f) shows improvement in all the properties compared to GFRC (6a-f).

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