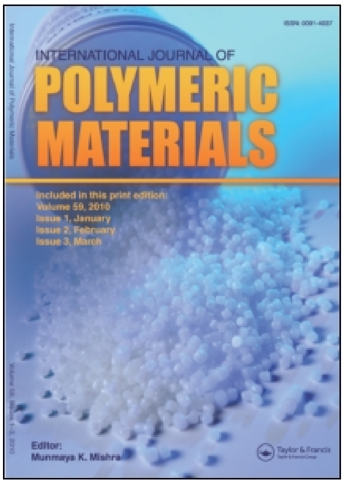

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Synthesis, Characterization and Material Application of Glass-reinforced Poly[urethane-imide]s

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Synthesis, Characterization and Material Application of Glass-reinforced Poly[urethane-imide]s

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Poly(urethane-imide)s (PUIs) were prepared by the intermolecular Diels-Alder (DA) reaction of 4-methyl-1,3-phenylene bis(2-furanylmethyloxyethyl-carbamate) (MPFC) with various bismaleimides. The DA reaction was carried out in 1, 4-dioxane as a solvent as well as in bulk, followed by aromatization of tetrahydrophthalimide intermediates in the presence of acetic anhydride. All the polymers were characterized by elemental analysis, IR spectral studies and thermogravimetry (TGA). The PUIs exhibit moderate thermal stability. MPFC and bismaleimides were polymerized (at 140 ± 10°C) by an "in situ" DA intermolecular reaction into moderately thermally stable PUIs glass-fiber, composite (i.e. laminates) and were characterized by their chemical resistance and mechanical properties.

Keywords: Poly(urethane-imide)s (PUIs); Bismaleimides; IR spectroscopy; TGA; Glass-fiber reinforced composites

INTRODUCTION

Syntheses of polyimides based on Diels-Alder (DA) reaction of bis-dienes, e.g., bis(furans) with bismaleimides, are well documented in literature [1, 2]. The Poly-(urethane-imide)s in which the urethane and imide groups are separated by arylene or alkylene have no more

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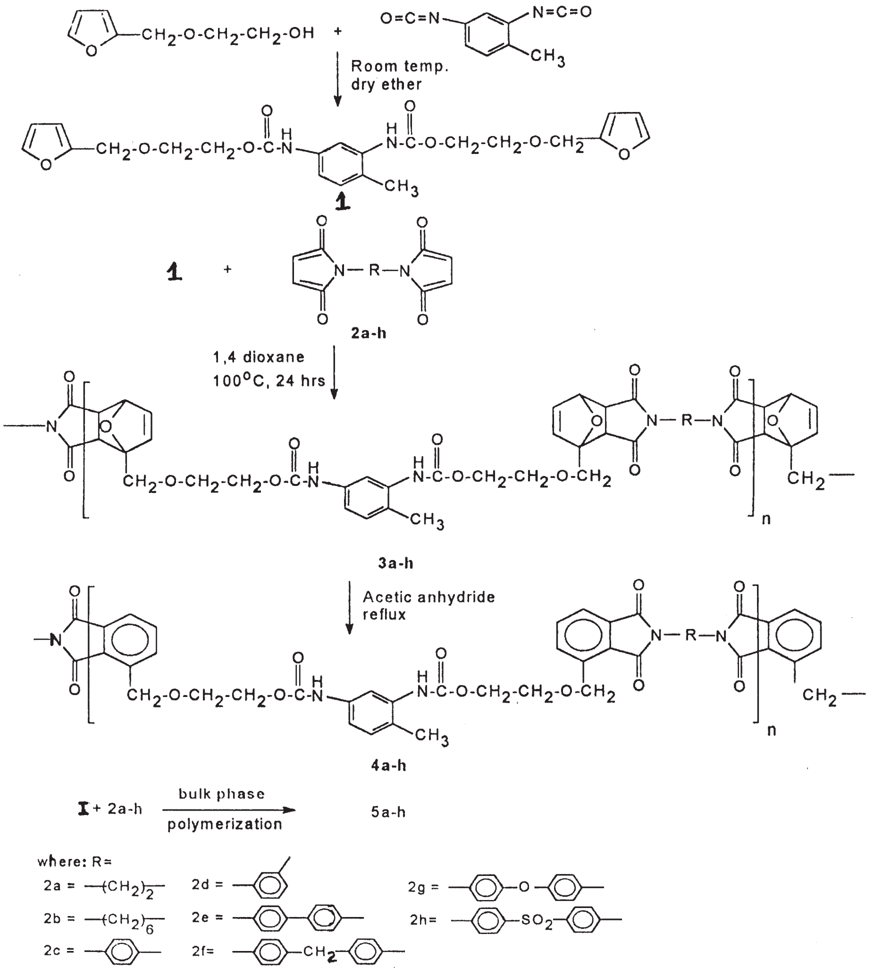
attention, in spite of well-defined applications of polyurethanes [3] and polyimide [4]. Only one instance indicated the synthesis of poly (urethane-imide) based on DA reaction of bisbutadiene derivatives with bis(maleimides) [5]. There are, however, the synthesis of poly (urethane-imide)s containing urethane and imide group linked to each other [6, 7]. The blends of polyurethane, polyimide and polyester, etc., are found to be heat-resistant and electric insulators and are reported in the literature [8–10]. The presence of both urethane and imide linkages in the polymer chain may alter the properties of



SCHEME 1

polymers to some extent. The initial work in this direction was carried out by Patel et al. [11]. They synthesized PUIs and formed glass laminates. Hence, it was thought interesting to extend their work.

An approach was also made to prepare processable PUIs glass-fiber reinforced composites based on "in situ" DA intermolecular addition polymerization of MPFC and bismaleimide. The prepared composites were characterized by their chemical and mechanical properties. The research work is shown in Scheme 1.

EXPERIMENTAL DETAILS

Materials

Diamines, viz. ethylenediamine, hexamethylenediamine, 1,4-phenylene-diamine, 1,3-Phenylenediamine, benzidine, 4,4,′-diaminodiphenylmethane, 4,4′-diaminodiphenyl-ether, 4,4′- diaminodiphenylsulphone, were obtained from SDS Chemicals (Boiser, India). 2-furanylmethyloxyethanol was prepared by a method reported in the literature [12]. Tolylene-2,4-diisocyanate was used as received from Merck, Germany. All other chemicals used were of laboratory grade. Stain (2/2) weave (polyimide compatible) fiber glass woven fabric 0.25 mm thich of "E" type glass (Unnati Chemicals, India) of areal weight 270 gm^{-2} was used for laminate preparation.

Preparation of Monomers

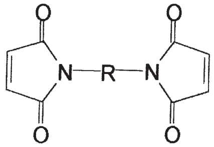
All the bismaleimides (2a–h) listed in Table 1 were prepared by reported methods [13, 14]. The bisfuran derivative 4-methyl-1,3-phenylenebis(2-furanylmethyloxy-ethylcarbamate) (MPFC) was prepared following the method reported for urethane containing bisfuran [15]. In a typical synthesis, 2(2-furanylmethyloxy) ethanol (0.01 mol) in 35 ml dry ether was added by toluene- 2,4-diisocyanate (0.005 mol) in 35 ml dry ether at 10°C. The resulting reaction mixture was kept at room temperature for 3 hrs. The product was filtered and air dried. It was white amorphous powder f.p. 147°C (uncorrected).

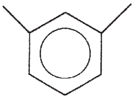
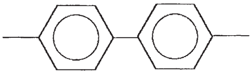
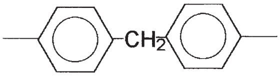
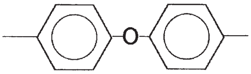
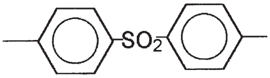
Analysis:

$C_{23}H_{26}O_8N_2$ (458): C (calcd.%) 60.26 and (found %) 60.15; H (calcd.%) 5.67 and (found %) 5.54 and N (calcd.%) 6.11 and (found %) 6.02.

IR data: $^{\nu}$Urethane: 3340 cm^{-1}, 1740 cm^{-1}
$^{\nu}$Furanyl: 3030 cm^{-1}, 830 cm^{-1}

TABLE 1 Bismaleimide (2a–h) [4, 5] Used



Nos.	Name	R
2a	N, N′-ethylene bismaleimide	$-CH_2\ CH_2-$
2b	N, N′-hexamethylene bismaleimide	$-(CH_2)_6-$
2c	N, N′-1,4-phenylene bismaleimide	
2d	N, N′-1,3-phenylene bismaleimide	
2e	N, N′-(1,1′-biphenyl)-4,4′-bismaleimide	
2f	N, N′-1,1′-(methylene-di-4,4′-phenylene)bismaleimide	
2g	N, N′-1,1′-(oxy-di-4,4′-phenylene) bismaleimide	
2h	N, N′-1,1′-(sulphonyl-di-4,4′-phenylene) bismaleimide	

NMR data: Singlet: 6H δ 7.1 ppm furanyl
Singlet: 4H δ 1.6 ppm $-CH_2$
Triplet: 4H δ 1.9 ppm $-CH_2$
Triplet: 4H δ 2.1 ppm $-CH_2$
Singlet: 3H δ 1.8 ppm $-CH_3$

Preparation of PUIs 3a–h

The non-aromatized (3a–h) and aromatized PUIs (4a–h, 5a–h) were prepared by Diels-Alder intermolecular reaction of MPFC [1] with different bismaleimides (2a–h) in solution as well as in the bulk phase system (Scheme 1). The details about the preparation are given in the literature [11, 15].

Composite Fabrication

A typical method of composite fabrication is given below. A suspension of MPFC [1] and of bismaleimides (2a–h) in THF was prepared and stirred well for 2 min. The resulting mixture was applied with a brush to a 25 mm × 25 mm fiber glass cloth and the solvent was allowed to evaporate. The 10 dried prepregs so prepared were stacked one on top of another and pressed between steel plates with a Teflon cloth as a release sheet and compressed in a flat platen press under about 70 psi pressure. The prepregs were cured by heating the press to 145°C for 10 hrs in an air-circulated oven. The composite so obtained was cooled at 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 PUIs were estimated by means of a Carlo-Erba elemental analyzer (Italy). The IR spectra of all the samples were scanned in KBr pellets on a NICOLET 400D FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Du Pont 950 thermal analyser. All the chemical, mechanical and electrical tests of the prepared composites were conducted according to ASTM or IS methods [16].

RESULTS AND DISCUSSION

The synthesis of new bisfuran derivatives such as MPFC was performed by simple reaction. The characterization of MPFC is mentioned in the experimental part. The spectral features of this compound were found to be consistent with the predicted structure. The formation of all the PUIs (3, 4, 5) from 1 (i.e. MPFC) and bismaleimides (2a–h) is shown in Scheme 1. The non-aromatized product 3a–h is first formed and then aromatized by treatment with acetic anhydride to yield compounds (4a–h). In the absence of bismaleimide, heating of compound 1 in 1,4-dioxane at 100°C does not alter the properties of compound 1. It was also observed that heating each of 2a–h in 1,4-dioxane at 100°C does not induce the addition polymerization of 2a–h. This has been shown to be possible only at elevated temperature in the presence of an initiator [17–19].

All the polymer samples were obtained at about 70% yields 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 PUI samples are consistent with their predicted structures (Scheme 1) and the results of these analyses are shown in Tables 1–3.

The important IR spectral features of PUIs are summarized in Tables 1–3. Examination of IR spectra of all the PUIs reveals that all the spectra a contain prominent characteristic band of the imide and urethane groups. The bands around 1780, 1710 and 720 cm^{-1} are contributions from the imide group, while bands around 3340 and 1740 cm^{-1} (shoulder) correspond to the urethane group. The IR spectra of PUI 3a and 3b do not show distinct bands around 3030 cm^{-1} because of the aromatic moiety of monomer 1 but show a band at 830 cm^{-1} due to C–H bending vibration of two adjacent hydrogen atoms. The IR spectra of aromatized PUI (i.e. 4b, 4d) show the distinct aromatic band at 3030 cm^{-1} as well as multiple absorption bands in the region 800–1200 cm^{-1}. This may be assigned to the C–H inplane and out of plane bending vibration character of aromatic system. The band at 780 cm^{-1} may be due to C–H bending vibrations of three adjacent hydrogen atoms of a phthalimide moiety arising from the aromatization of poly(tetrahydro-phthalimide) intermediate (3a). This indicates the aromatization of the poly(tetrahydrophthalimide) (3a). These bands could not be observed in the monomer and the aromatic system in poly(tetrahydrophthalimide) (non-aromatized PUIs, 3b–h) in spectra of PUIs 4b–h. Bands around 2875 and 2920 cm^{-1} in the spectra of the PUIs 3, 4 and 5 are attributed to $-CH_2$ of monomer 1. The IR spectra of polymers 5a–h also show all the characteristics of imide and urethane groups (Table 3), indicating that solid phase polymerization occurs, too.

The TGA data show that the synthesized PUI samples exhibited less than 4.0% weight loss at 200°C, probably corresponding to residual solvents. The polyimide samples undergo decomposition between 250°C to 350°C depending upon the nature of the PUI. Polymer samples suffer complete degradation in the range of 250°C to 700°C. A very rapid rate of weight loss is observed around 350°C to 450°C. In almost all cases the polymer samples showed 50% weight loss in the range of 450°C to 500°C. Complete weight loss, i.e. around 95–99%, was observed at about 700°C. The non-aromatized PUI 3a–h undergoes initial degradation at around 200°C whereas the aromatized PUI 4a–h started to degrade at slightly higher temperature 220°C. On the other hand, PUIs 5a–h obtained in the bulk phase start degrading at around 250°C. Comparison of thermal stability of all PUI

TABLE 2 Characterization of Non-aromatized PUIs 3a–h

		Elemental analysis											
		C (%)		H (%)		N (%)		% Wt. loss at °C from TGA					
Polymer sample	Yield (%)	Calcd.	Found	Calcd.	Found	Calcd.	Found	200	300	400	500	600	700
3a	68	58.41	58.32	5.01	5.05	8.26	8.18	2	20	35	50	84	96
3b	65	60.49	60.38	5.72	5.65	7.62	7.59	3.5	19	36	58	88	98
3c	72	61.16	61.12	4.68	7.59	7.71	7.65	2.5	18	28	52	89	99
3d	66	61.16	61.08	4.68	4.62	7.71	7.75	3	22	35	58	86	98
3e	74	64.34	64.26	4.74	4.67	6.98	6.94	2	19	33	53	87	98
3f	72	64.70	64.59	4.90	4.82	6.86	8.78	2.5	21	40	62	90	99
3g	73	63.08	63.18	4.65	4.42	6.85	6.75	3.5	24	38	59	85	96
3h*	70	59.58	59.50	4.39	4.28	6.46	6.36	3	21	34	52	84	99

*S(%): Calcd., (3.69); Found, (3.61).

→ IR spectra (figures are not shown) of all the PUI samples comprising the bands at 1780, 1715, 1130, 725 cm^{-1} due to imide group, the bands at 3300, 1680, 1255, 1120 cm^{-1} from urethane linkage and bands due to aromatic groups. The other bands due to slight structural change appeared at their respective positions.

TABLE 3 Characterization of Non-aromatized PUIs 4a–h

		Elemental analysis													
		C (%)		H (%)		N (%)		S (%)		% Wt. loss at °C from TGA					
Polymer sample	Yield (%)	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	200	300	400	500	600	700
4a	69	61.11	61.08	5.55	5.48	8.64	8.72	–	–	2	22	35	52	85	96
4b	66	63.07	63.15	6.25	6.16	7.95	7.86	–	–	2.5	17	40	59	83	99
4c	72	63.79	63.62	5.17	5.10	8.05	8.13	–	–	2	18	27	54	88	99
4d	75	63.79	63.72	5.17	5.19	8.05	8.12	–	–	3	24	32	55	87	99
4e	70	66.84	66.76	5.18	5.05	7.25	7.18	–	–	2.5	20	34	50	89	99
4f	69	67.17	67.11	5.34	5.27	7.12	7.09	–	–	2	22	38	60	88	98
4g	74	65.48	65.41	5.07	5.16	7.11	7.02	–	–	2.5	19	36	57	84	95
4h	75	60.56	60.41	4.69	5.56	6.57	6.48	3.75	3.66	2	18	32	64	75	98

IR spectra (figures are not shown) of all the PUI samples comprising the bands at 1780, 1715, 1130, 725 cm^{-1} due to imide group, the bands at 3300, 1680, 1255, 1120 cm^{-1} from urethane linkage and bands due to aromatic groups. The other bands due to slight structural change appeared at their respective positions.

TABLE 4 Characterization of Bulk Phase PUIs 5a–h

		Elemental analysis								% Wt. loss at °C from TGA					
		C (%)		H (%)		N (%)		S (%)							
Polymer sample	Yield (%)	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	200	300	400	500	600	700
5a	75	61.11	61.22	5.55	5.42	8.64	8.56	–	–	2	17	32	52	88	96
5b	75	63.07	63.19	6.25	6.08	7.95	7.88	–	–	2	18	39	58	84	99
5c	84	63.79	63.65	5.17	5.02	8.05	8.19	–	–	2	12	25	60	84	98
5d	88	63.79	63.84	5.17	5.04	8.05	8.12	–	–	3.5	15	38	60	86	99
5e	82	66.84	66.72	5.18	5.23	7.25	7.12	–	–	2.5	17	32	58	89	99
5f	80	67.17	67.02	5.34	5.24	7.12	7.18	–	–	2.5	16	37	84	86	98
5g	85	65.48	65.36	5.07	5.15	7.11	7.22	–	–	2.5	18	36	56	88	99
5h	75	60.56	60.48	4.69	5.49	6.57	6.44	3.75	3.65	2.5	16	30	52	70	96

IR spectra (figures are not shown) of all the PUI samples comprising the bands at 1780, 1715, 1130, 725 cm^{-1} due to imide group, the bands at 3300, 1680, 1255, 1120 cm^{-1} from urethane linkage and bands due to aromatic groups. The other bands due to slight structural change appeared at their respective position.

TABLE 5 Mechanical and Electrical Properties of Glass-reinforced PUIs

Composites	% change on exposure to 25% (w/v) NaOH		Specific gravity	Flexural strength (Mpa)(ASTM D-790) S.D. 1.5	Compressive strength (Mpa) (ISO method) S.D. 2.8	Impact strength (Mpa) (ASTM D-256) S.D. 1.8	Rockwell hardness (R) (ASTM D-785) S.D.2	Electrical Strength (in air) (kV mm^{-1})
	Thickness	Weight						
C_{2a}	2.0	2.1	1.25	302	285	265	102	13.5
C_{2b}	1.3	1.1	1.34	250	216	243	106	18.5
C_{2c}	1.3	1.2	1.30	240	190	208	125	19.1
C_{2d}	1.9	2.1	1.29	301	295	298	98	13.9
C_{2e}	1.2	1.2	1.32	252	211	249	112	12.5
C_{2f}	1.7	1.6	1.31	242	218	215	116	15.2
C_{2g}	1.9	1.7	1.28	306	265	312	114	15.7
C_{2h}	1.2	1.1	1.29	236	198	196	140	17.5

Conditions reinforcement: E-glass; plain weave; 10 mm, 10 layers, Resin content, 40 ± 2%, mole ratio (bismaleimides: MPFTC), 1:1 Curing temperature, 145 ± 10°C, Time, 10 hrs, pressure, 60–70 psi, Composite size: 25.4 mm × 25.4 mm, 3.0–3.5 mm thick.

reveals the following order of stability based on the bismaleimides component as follows:

$$2c > 2e > 2d > 2f > 2h > 2g > 2a > 2b$$

All the composites prepared at 145°C are in the form of dark-brown sheets. The specific gravity of all composites is in the range 1.25 to 1.34 (Table 4). The result of the chemical resistance of all the PUI composite to organic solvents, acids and alkali (Table 4) reveals that the organic solvents and concentrated acid (25% v/v) did not affect the composite, which has remarkable resistance to them. However, the concentrated alkali causes changes of about 1.1–2.1% in their thickness and weight (Table 4).

The mechanical properties of all the PUI composites are shown in Table 5. Examination of the results reveals that all the composites have good mechanical properties. The overall trend of the mechanical properties of the prepared PUI composites decreases as follows:

$$C_{2b} > C_{2d} > C_{2a} > C_{2f} > C_{2g} > C_{2h} > C_{2e} > C_{2c}$$

This may be attributed to a certain increase in the rigidity of the bismaleimide component. The electric strength of all the composites is in the range of 12.3–19.1 kV/mm.

CONCLUSIONS

The overall advantages of the present MPFC and bismaleimide systems are as follows:

The intermolecular DA reaction of MPFC with bismaleimides produces PUIs with good resistance to organic solvents and mineral acid and moderate resistance to heat.

The in situ produced PUIs show good adhesion to glass fibers.

Void–free composites could be prepared with good mechanical and electrical properties.

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