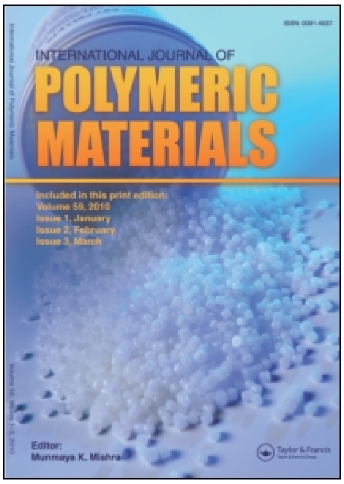

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Synthesis, characterization, and glass fiber reinforced composites of poly(urethane-imide)s

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SYNTHESIS, CHARACTERIZATION, AND GLASS FIBER REINFORCED COMPOSITES OF POLY(URETHANE-IMIDE)S

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Poly(urethane-imide)s (PUI)s were prepared by the intermolecular Diels-Alder (DA) reaction of 4-methyl-1,3-phenylene-bis(2-furanylmethylthioethylcarbamate) (MPFTC) 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. The PUIs exhibit moderate thermal stability. MPFTC and bismaleimides were polymerized (at 145 ± 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

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INTRODUCTION

Synthesis of polyimides based on Diels-Alder (DA) reaction of bisdienes *e.g.*, bis(furans) with bis(maleimides) are well documented in the literature [1, 2]. The Poly(urethane-imide)s in which the urethane and imide groups are separated by arylene or alkylene enjoyed no attention despite the 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] and of blends of polyurethane, polyimide and polyester *etc.* [8–10]. Polyurethane, polyimide, polyester blends are found also in heat resistant electric insulators [8–10]. The presence of both urethane and imide linkages in the polymer chain may alter the properties of polymer to a great extent.

Patel *et al.*, has done the initial work in this direction [11]. They have prepared poly(urethane-imide)s by DA reaction of urethane containing bisfurans with various bismaleimides. Hence it was thought interesting especially in view of processing to synthesize and characterize novel PUIs by the DA reaction of a new bisfuran derivative, namely (MPFTC) and various bismaleimides (Scheme 1).

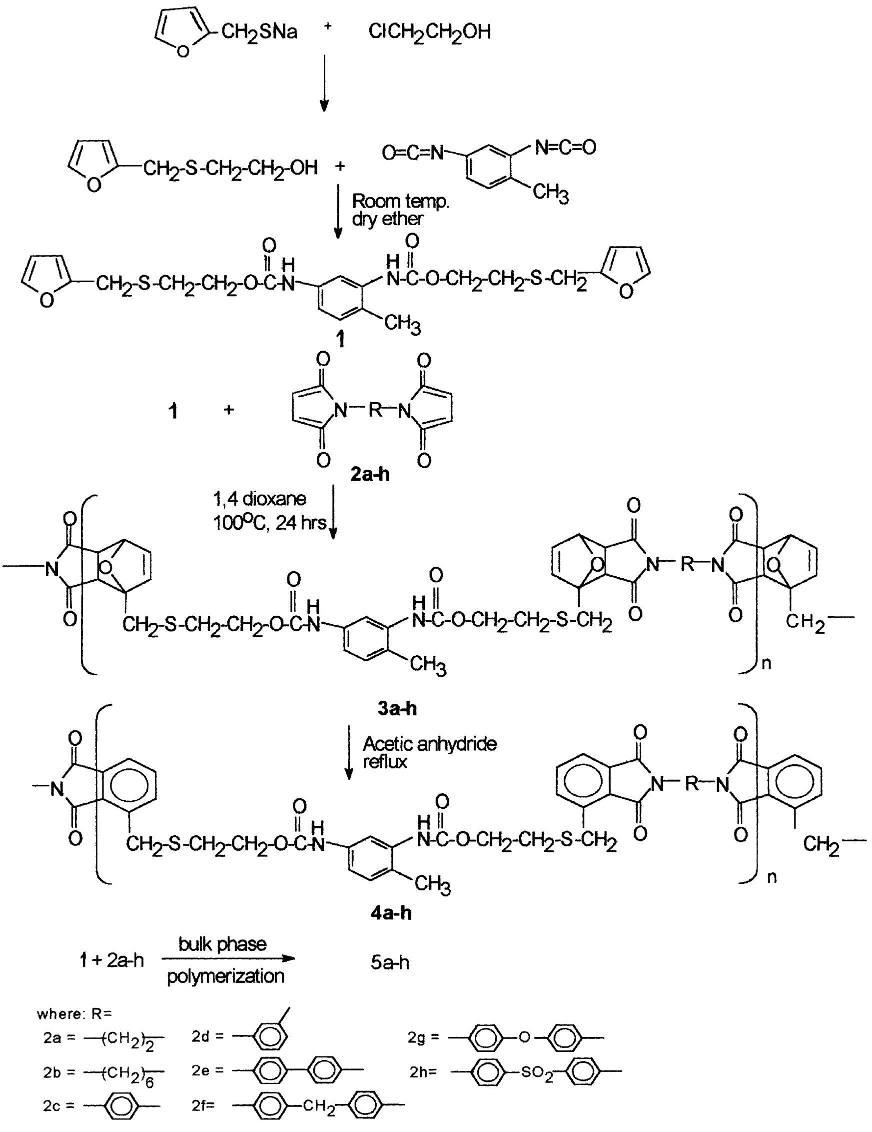
An approach was also made to prepare matrix bismaleimides processable PUI glass-fiber reinforced composites based on "*in situ*" DA intermolecular addition polymerization of MPFTC and bismaleimide. The prepared composites were characterized by their chemical resistance and mechanical properties.

EXPERIMENTAL

Materials

Diamines as Ethylenediamine, hexamethylenediamine, 1,4-phenylenediamine, 1,3-phenylenediamine, benzidine, 4,4′-diamino-diphenylmethane , 4,4′-diamino-diphenyl ether, and 4,4′-diaminodiphenyl sulphone were obtained from SDS Chemicals (Boiser, India). 2-furanyl methyl thioethanol (FTE) was prepared by condensation reaction of Na-salt of furfuryl thiol and chloroethanol. The resultant liquid was vaccum distilled.

Analysis: $C_7H_{10}O_2S$ (158): C% Calcd. 53.16, Found 53.25; H% Calcd. 6.33, Found 6.32 and S% Calcd. 20.25, Found 20.12; B.P. 176°C (20 ml) uncorrected.


CH2SNa
+
ClCH2CH2OH
CH2-S-CH2-CH2-OH
O=C=N
N=C=O
CH3
Room temp.
dry ether
1
2a-h
1,4 dioxane
100°C, 24 hrs
3a-h
Acetic anhydride
reflux
4a-h
1 + 2a-h
bulk phase
polymerization
5a-h
where: R=
2a = —(CH2)2—
2b = —(CH2)6—
2c =
2d =
2e =
2f=
2g =
2h=
n

SCHEME 1

IR:	ν CH_2 of CH_2-S-CH_2:	2925, 2855 cm^{-1}	
	ν furanyl:	1615, 1510 cm^{-1}	
	δ C-S of CH_2:	640 cm^{-1}	
NMR:	Multiplet:	δ 7.00 ppm (3H)	Furanyl
	Singlet:	δ 1.90 ppm (2H)	-CH_2-
	Singlet:	δ 2.9 ppm (1H)	-OH
	Triplet:	δ 2.1 ppm (2H)	-CH_2-CH_2-
	Triplet:	δ 2.3 ppm (2H)	-CH_2-CH_2-

Tolylene-2,4-diisocyanate (TDI) 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 thick of "E" type glass (Unnati Chemicals, India) of areal weight 270 gm^{-2} was used for laminate preparation.

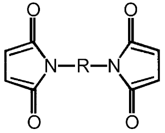
Preparation of Monomers

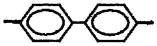
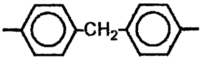
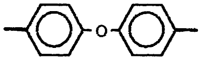
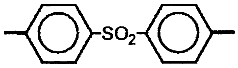
4-methyl-1,3-phenylene-bis(2-furanyl methyl thioethyl carbamate) (MPFTC) was prepared by the method reported for urethane synthesis [12]. This was prepared simply by gradually adding a TDI solution (0.1 mol) in (100 ml) THF to a solution of FTE (0.2 mol) in 100 ml THF at 20°C. The mixture was then stirred for 6 hrs at room temperature. The resulting solid product was washed by THF and air dried. It's m.p. was 107–9°C (uncorrected). Analysis: $C_{23}H_{26}O_6N_2S_2$ (490): C% Calcd. 56.32, Found 56.27; H% Calcd. 5.30, Found 5.18, N% Calcd. 5.71, Found 5.65 and S% Calcd. 13.06, Found 13.19.

IR:	ν furanyl:	1615, 1510 cm^{-1}	
	νCH_2 of CH_2-S-CH_2:	2925, 2855 cm^{-1}	
	δC-S of CH_2-S-CH_2:	640 cm^{-1}	
	νNHCOO:	3300, 1640, 1250, 1120 cm^{-1}	
NMR:	Singlet:	δ 7.1 ppm (6H)	Furanyl
	Singlet:	δ 7.2 ppm (3H)	-CH_2
	Singlet:	δ 1.91 ppm (4H)	-CH_2
	Triplet:	δ 2.3 ppm (4H)	-CH_2-CH_2-
	Triplet:	δ 2.4 ppm (4H)	-CH_2-CH_2-
	Singlet:	δ 7.2 ppm (3H)	Phenyl ring
	Singlet:	δ 3.2 ppm (2H)	-NH
	Singlet:	δ 1.9 ppm (3H)	-CH_3

Bismaleimides listed in Table 1 were prepared by method reported previously [13, 14].

TABLE 1 Bismaleimides (2a–h) [4, 5] used



Nos.	Name	R
2a	N,N′-ethylenebismaleimide	$—CH_2CH_2—$
2b	N,N′-hexamethylene bismaleimide	$—(CH_2CH_2)_6—$
2c	N,N′-1,4-phenylene bismaleimide	
2d	N,N′-1,3-phenylene bismaleimide	
2e	N,N′-(1,1′-biphenyl)-4,4′-diylbismaleimide	
2f	1,1′-(methylene-di-4,4′-phenylene)bismaleimide	
2g	1,1′-(oxy-di-4,4′-phenylene)bismaleimide	
2h	1,1′-(sulphonyl-di-4,4′-phenylene)bismaleimide	

Preparation of PUIs 3a–h

The non-aromatized (3a–h) and aromatized PUIs (4a–h, 5a–h) were prepared by intermolecular Diels-Alder reaction of bisfuran (MPFTC) [1] with different bismaleimides (2a–h) listed in Table 1 in solution as well as in the bulk phase system (Scheme 1). The preparation details are given in the literature [15, 16].

Composite Fabrication

A typical method of composite fabrication is given below.

A suspension of MPFTC (1) and 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 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, N and S content of all the PUIs were estimated by means of Carlo-Erba elemental analyser (Italy). The IR spectra of all the samples were scanned in KBr pellets on NICOLET 400D FTIR Spectrophotometer. Thermogravimetric analysis (TGA) were 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 [17].

RESULTS AND DISCUSSION

The synthesis of new bisfuran derivatives such as (MPFTC) was performed by a simple reaction. The characterizations of both 2-furanylmethylthioethanol and MPFTC are mentioned in the experimental part. The spectral features of these two compounds are also shown and are consistent with the predicted structure.

The formation of all the PUIs (3,4,5) from 1 (*i.e.*, MPFTC) 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 its properties. 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 [18–20].

All the polymer samples were obtained in about 70% 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 PUI samples are consistent with their predicted structures (Scheme 1) and the results of these analyses are shown in Tables 2–4. The important IR spectral features of PUIs are summarized in Tables 2–4. Examination of IR spectra of all the PUIs reveals that all the spectra contain prominent characteristic bands of the imide and urethane groups. The bands around 1780, 1710, 1050 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 spectrum of PUI 3a and 3b do not show distinct band around 3030 cm^{-1} because of the aromatic moiety of monomer 1 but show a band at 830 cm^{-1} due to CH bending vibration of two adjacent hydrogen atoms. The IR spectrum of aromatized PUI (*i.e.*, 4e, 4b) show the distinct aromatic band at 3030 cm^{-1} as well as multiple absorption bands in the 800–1200 cm^{-1} region. They may be assigned to the CH in plane and out of plane bending vibration character of aromatic system. The band at 780 cm^{-1} may be due to CH bending vibrations of three adjacent hydrogen atoms of a phthalimide moiety arising from the aromatization of poly(tetrahydrophthalimide) intermediate (3a). This indicates the aromatization of the poly(tetrahydrophthalimide) (3a). Bands around 2855 and 2925 cm^{-1} appear in the spectra of the PUIs 3,4 and 5 and are attributed to CH_2 of monomer 1. The band at 640 cm^{-1} is attributed to thioether [21]. The IR spectra of polymers 5a–h also show all the characteristics of imide and urethane groups (Table 4) indicating that solid phase polymerization occurs also.

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 and 350°C, depending upon the nature of the PUI.

The 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 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 1.22 to 1.32 (Table 5). The result of the chemical resistance of all the PUI composite to organic solvents, acids and alkali (Table 5) reveals that the organic solvents and concentrated acid (25% v/v) did not affect the composites which have remarkable resistance to them. However, the concentrated alkali causes changes of about 1.1–2.1% in their thickness and weight (Table 5).

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:

$$C2b > C2d > C2a > C2f > C2g > C2h > C2d > C2c$$

TABLE 2 Characterization of Nonaromatized PUIs 3a–h

		Elemental analysis (%)			IR spectral features wave number(cm^{-1})					%wt loss at °C from TGA					
Polymer sample	Yield (%)		Calcd.	Found	-CH_2-	Aromatic	-C=C-	Imide group	Urethane group	200	300	400	500	600	700
3a	65	C	55.77	55.68	2940	–	1610	1780	3300	2	18	37	46	80	99
		H	4.79	4.65	2870			1720	1640						
		N	7.89	7.94	1420			1120	1250						
		S	9.01	9.12				725	1120						
3b	68	C	57.96	57.88	2940	3070	1610	1780	3300	2.5	17	34	56	85	96
		H	5.48	5.32	2870	850		1720	1650						
		N	7.31	7.24	1420	830		1120	1250						
		S	8.35	8.27				720	1120						
3c	70	C	58.57	58.49	2940	3070	1600	1780	3300	3	16	25	50	85	98
		H	4.48	4.36	2870	850		1720	1640						
		N	7.39	7.45	1420	830		1380	1260						
		S	8.44	8.56				1170	1120						
								720							
3d	69	C	58.57	58.46	2940	3070	1600	1770	3300	2	20	33	55	82	95
		H	4.48	4.52	2870	850		1720	1640						
		N	7.39	7.48	1410	830		1380	1250						
		S	8.44	8.55				1120	1120						
								720							

		C	61.87	61.69	2950	3070		1780	3300						
		H	4.55	4.58	2870	840	1610	1720	1640	2.5	18	30	51	84	99
3e	75	N	6.71	6.64	1420	830		1360	1250						
		S	7.67	7.58				1120	1120						
								720							
		C	62.26	62.17	2940	3060		1770	3300						
		H	4.72	4.85	2880	850	1600	1720	1650	2	19	42	59	89	99
3f	70	N	6.60	6.49	1420	830		1380	1250						
		S	7.55	7.59				1130	1130						
								720							
		C	60.70	60.62	2940	3070		1770	3300						
		H	4.47	4.38	2870	850	1600	1720	1650	3	21	35	55	83	99
3g	75	N	6.59	6.47	1420	830		1370	1260						
		S	7.53	7.45				720	1130						
		C	57.46	57.38	2940	3060		1780	3300						
		H	4.23	4.13	2870	850	1600	1720	1650	2	18	31	50	86	98
3h	78	N	6.24	6.15	1420	830		1370	1250						
		S	10.69	10.88				720	1120						

TABLE 3 Characterization of Nonaromatized PUIs (4a–h)

		Elemental analysis			IR spectral features wave number(cm^{-1})					%wt loss at °C from TGA					
Polymer sample	Yield (%)		Calcd.	Found	-CH_2-	Aromatic	-C=C-	Imide group	Urethane group	200	300	400	500	600	700
4a	68	C	58.23	58.15	2950	3080	1610	1770	3300	2	20	32	50	84	95
		H	5.29	5.21	2860	1170		1720	1650						
		N	8.23	8.16	1410	780		1120	1250						
		S	9.41	9.35				720	1120						
4b	69	C	60.33	60.27	2940	3080	1610	1770	3300	2	14	42	60	80	99
		H	5.98	5.86	2860	1120		1720	1640						
		N	7.61	7.46	1420	780		1120	1250						
		S	8.69	8.55				720	1120						
4c	75	C	60.99	60.87	2950	3070	1610	1770	3300	2.5	15	24	56	86	98
		H	4.94	4.89	2860	850		1720	1640						
		N	7.69	7.54	1420	760		1380	1240						
		S	8.79	8.66				1120	1150						
								720							
4d	80	C	60.99	60.90	2940	3080	1610	1770	3300	3.5	21	30	52	82	98
		H	4.94	4.88	2870	820		1720	1640						
		N	7.69	7.72	1420	760		1370	1250						
		S	8.79	8.84				1120	1150						
								720							

4e	75	C	64.18	64.25	2940	3080	1600	1770	3300	2.5	18	33	48	87	99
		H	4.97	4.91	2870	850		1720	1640						
		N	6.96	6.85	1430	830		1360	1250						
		S	7.96	7.81		780		1170	1120						
								720							
4f	70	C	64.55	64.39	2950	3090	1600	1770	3300	2.5	20	35	56	85	96
		H	5.13	5.08	2870	850		1710	1640						
		N	6.84	6.92	1420	830		1370	1120						
		S	7.82	7.96		780		1120							
								720							
4g	72	C	62.93	62.85	2940	3070	1600	1770	3300	2.5	18	38	52	88	98
		H	4.88	4.80	2870	830		1720	1650						
		N	6.83	6.72	1410	760		1370	1250						
		S	7.80	7.68				1120	1130						
								720							
4h	78	C	58.37	58.32	2940	3070	1610	1770	3300	2	24	34	60	72	98
		H	4.52	4.43	2880	850		1720	1640						
		N	6.33	6.25	1420	830		1370	1250						
		S	10.86	10.76		760		1120	1150						
								720							

TABLE 4 Characterization of Bulk Phase PUIs (5a–h)

		Elemental analysis			IR spectral features wave number(cm^{-1})					%wt loss at °C from TGA					
Polymer sample	Yield (%)		Calcd.	Found	-CH_2-	Aromatic	-C=C-	Imide group	Urethane group	200	300	400	500	600	700
5a	78	C	58.23	58.17	2940	3080	1600	1770	3300	2.0	19	30	54	82	98
		H	5.29	5.32	2870	1170		1710	1650						
		N	8.23	8.29	1410	780		1370	1250						
		S	9.41	9.36				720	1120						
5b	78	C	60.33	60.38	2940	3070	1610	1770	3300	3.0	18	40	55	80	95
		H	5.98	5.85	2870	1170		1710	1650						
		N	7.61	7.52	1420	780		1120	1250						
		S	8.69	8.55				720	1120						
5c	82	C	60.99	60.84	2950	3080	1600	1700	3300	2.5	17	28	68	78	98
		H	4.94	4.82	2870	850		1710	1640						
		N	7.69	7.54	1440	780		1370	1250						
		S	8.79	8.64				1120	1120						
								720							
5d	85	C	60.99	60.82	2950	3070	1600	1770	3300	3.0	14	38	64	83	96
		H	4.94	4.85	2870	820		1720	1640						
		N	7.69	7.77	1420	780		1380	1250						
		S	8.79	8.66				1120	1120						
								720							

		C	64.18	64.25	2950	3070		1780	3300						
5e	80	H	4.97	4.86	2880	840	1610	1720	1640	2.5	15	34	59	87	99
		N	6.96	6.84	1420	830		1370	1240						
		S	7.96	7.83		780		1120	1120						
								720							
		C	64.55	64.43	2940	3080		1765	3300						
5f	84	H	5.13	5.28	2870	860	1610	1710	1650	2.5	18	38	67	84	98
		N	6.84	6.96	1440	830		1370	1250						
		S	7.82	7.78		780		720	1120						
		C	62.93	62.86	2950	3070		1775	3300						
5g	82	H	4.88	4.74	2860	840	1600	1720	1640	2.0	16	35	58	85	99
		N	6.83	6.73	1420	830		1320	1250						
		S	7.80	7.71		780		1120	1120						
								720							
		C	58.37	58.29	2950	3070		1770	3300						
5h	88	H	4.52	4.45	2870	850	1610	1710	1640	2.5	19	36	54	79	97
		N	6.33	6.24	1430	830		1365	1240						
		S	10.86	10.78		780		1120	1120						
								720							

TABLE 5 Mechanical and Electrical Properties of Glass-Reinforced PUIs

	% change on exposure to 25% (w/v NaOH)							
Composites	Thickness	Weight	Specific gravity	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV mm^{-1})
C2a	2.1	2.0	1.22	310	273	278	111	12.8
C2b	1.3	1.2	1.32	240	226	234	100	17.8
C2c	1.2	1.2	1.26	250	182	205	116	18.4
C2d	1.8	2.0	1.27	304	285	287	102	13.5
C2e	1.2	1.1	1.30	250	217	236	105	12.4
C2f	1.8	1.9	1.29	232	212	208	110	14.8
C2g	1.7	1.9	1.25	316	255	305	106	16.7
C2h	1.3	1.1	1.26	226	189	186	135	17.9

Conditions Reinforcement: E − glass cloth; 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 min, 3.0−3.5 mm thick.

This may be attributed to a increase in the rigidity of the bismaleimide component. The electric strength of all the composites is in the range of 12.4–18.4 kV/mm.

CONCLUSIONS

The overall advantages of the present MPFTC and bismaleimides systems are as follows:

- The intermolecular DA reaction of MPFTC 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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