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SYNTHESIS AND CHARACTERIZATION OF MODIFIED POLYIMIDES: POLY(URETHANE-IMIDE)

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Key Words: Polyimides; Poly(urethane-imide)s; Glass fiber reinforced composites

ABSTRACT

Poly(urethane-imide)s (PUIs) were prepared by the Diels–Alder (DA) reaction of 5-(2-furanylmethylcarbamato)-1-[1-(2-furanylmethylcarbamatomethyl)]-1,3,3,-trimethylcyclohexane (FFCH) with various bismaleimides. The DA reaction was carried out in 1,4-dioxane as the solvent as well as in bulk. This was followed by aromatization of the polytetrahydrophthalimide intermediate in the presence of acetic anhydride. All polymers were characterized by elemental analysis, IR spectral studies, and thermogravimetry. The PUIs exhibited moderate thermal stability. FFCH and bismaleimide were polymerized (at 145 ± 10°C) by an in-situ DA reaction into thermally stable PUIs–glass fiber composites (i.e., laminates) and were characterized by their chemical resistance and mechanical properties.

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INTRODUCTION

5-(Isocyanato)-1-(1-isocyanatomethyl)-1,3,3′-trimethylcyclohexane (IICH), recognized by its trivial name isophorone diisocyanate, has received much attention recently for many industrial polymeric products [1]. If such a cyclohexane moiety is introduced into a polyimide chain, it may alter the properties of the polyimide. With this in view and as an extension of previous work [2, 3], the present paper reports on modified polyimides i.e., poly(urethane-imide)s.

In this study the bisfuran derivative containing the urethane linkage was prepared from furfuryl alcohol and IICH. Poly(urethane-imide)s (PUIs) were prepared by the Diels–Alder reaction of the bisfuran derivative 5-(2-furanylmethylcarbamoto)-1-[1-(2-furanylmethylcarbamatomethyl)]-1,3,3-trimethycyclohexane (FFCH) (1) and bismaleimides (2a–h) (Scheme 1). The PUIs were characterized for their molecular composition, IR spectroscopy, and thermogravimetry. An attempt has also been made to prepare their composites with glass fiber.

EXPERIMENTAL

Materials

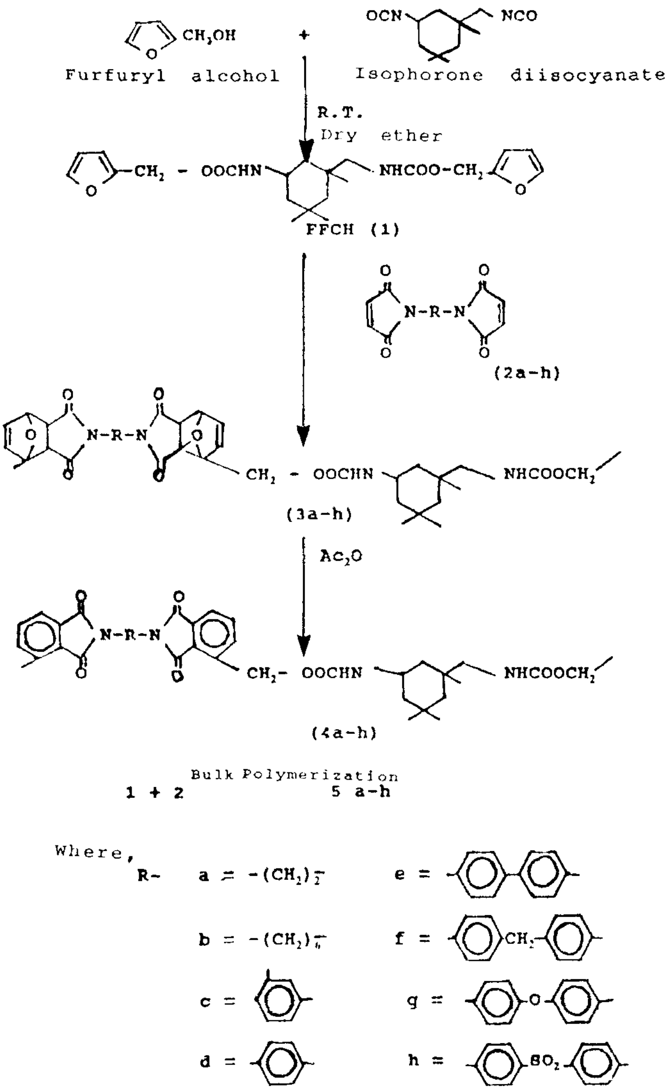
Ethylenediamine, hexamethylenediamine, 1,3-phenylene-diamine, 1,4-phenylene-diamine, benzidine, 4,4′-diamino diphenyl methane, 4,4′-diaminodiphenylether, and 4,4′-diaminodiphenylsulfone were obtained from SDS Chemicals (Boiser, India). Furfuryl alcohol was redistilled before use. Isophorone diisocyanate (IICH) was used as received from Merck, Germany. All other chemicals used were of laboratory grade. Satin (2/2) weave (polyimide compatible) glass fiber in the form of woven fabric (0.25 mm thick of E-type glass) of Unnati Chemicals, India, was used for laminate preparation.

Preparation of Monomers

FFCH (1) was prepared by reaction between furfuryl alcohol (0.02 mol in 20 mL dry ether) and IICH (0.01 mol in 20 mL dry ether) at room temperature. The melting point of FFCH was found to be ~165.6°C. The preparative method was adopted from earlier communications [2, 3]. The bismaleimides used in the poly(urethane-imide) synthesis are listed in Table 1, and they were prepared according to methods reporfed in the literature [4–9].

Preparation of PUIs

The unaromatized PUIs (3a–h) and aromatized PUIs (4a–h, 5a–h) were prepared through the DA reaction of FFCH (1) with different bismaleimides (2a–h) in solution as well as in bulk phase (Scheme 1). Details about the preparation are given in earlier communications [2, 3].



SCHEME 1.

Composite Fabrication

A typical method of composite fabrication is as follows. A suspension of FFCH (1) and bismaleimides (2a-h) in THF was prepared and stirred well for 2 minutes. The resulting mixture was applied with a brush to a 25 mm × 25 mm fiberglass cloth, and the solvent was allowed to evaporate. Ten dried prepregs so prepared were stacked and placed between steel plates with a Teflon film release sheet and compressed in a press under about 70 psi pressure. The prepregs were cured by heating the press to 145°C for 10 hours in an air circulating oven. The

TABLE 1. Synthesized Bismaleimides and Their Melting Points

Bis(maleimide) (2)		mp, °C
a.	*N*,*N*′-Ethylene bismaleimide	189–190
b.	*N*,*N*′-Hexamethylene bismaleimide	138–139
c.	*N*,*N*′-1,3-Phenylene bismaleimide	202–203
d.	*N*,*N*′-1,4-Phenylene bismaleimide	>300
e.	*N*,*N*′-(1,1′-Biphenyl)-4,4′-diyl bismaleimide	>300
f.	1,1′-(Methylene-di-4,4′-phenylene)-bismaleimide	156–158
g.	1,1′-(Oxy-di-4,4′-phenylene)-bismaleimide	179–182
h.	1,1′-(Sulfonyl-di-4,4′-phenylene)-bismaleimide	253–255

composite so obtained was cooled to 50°C before the pressure was released. Test specimens were prepared by cutting and machining the sheet to the desired final shape.

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 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.

All chemical, mechanical, and electrical tests of the prepared composites were conducted according to ASTM or IS methods.

RESULTS AND DISCUSSION

The formation of all the PUIs (4, 5) from FFCH (1) and bismaleimides (2a–h) is shown in Scheme 1. The unaromatized product (3a–h) was first formed and then aromatized at 135°C by treatment with acetic anhydride to yield polymers (4a–h). Heating of Compound 1 or 2 alone in solution/bulk polymerization conditions did not alter its properties. Polymerization of Compound 2 was found to be possible only at elevated temperature in the presence of an initiator [10–12].

All the polymer samples were obtained with about 65% yield as dark brown solid powders. They did not melt up to 300°C, were found to be insoluble in common organic solvents, and were not affected by concentrated mineral acids or formic acid. The elemental analysis 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.

Typical IR spectra of PUIs are shown in Fig. 1. Examination of IR spectra of all the PUIs has been found to 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 does not show a

TABLE 2. Characterization of Unaromatized PUIs 3a–h (solution polymerization)

PUIs	Yield, %	Elemental analysis, % C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	TG analysis, % weight loss at various temperatures, °C 200	300	400	500	600	700
3a	65	61.34	60.87	4.15	4.00	8.94	8.83	4	22	38	48	72	98
3b	65	64.10	63.90	3.85	3.71	8.30	8.10	4	24	43	56	84	99
3c	65	64.10	63.76	3.85	3.70	8.30	8.13	3	20	28	48	85	99
3d	70	64.10	63.81	3.85	3.70	8.30	8.15	3	14	25	38	58	98
3e	75	67.20	66.34	4.00	3.67	7.46	7.30	3	14	26	37	69	99
3f	75	67.50	66.30	4.18	4.00	7.33	7.22	3	18	35	44	89	98
3g	75	65.80	64.70	3.91	3.82	7.31	7.18	3	16	36	55	82	97
3h	75	61.91	61.10	3.68	3.58	6.87	6.77	3	15	32	47	75	99

TABLE 3. Characterization of Aromatized PUIs 4a-h (solution polymerization)

		Elemental analysis, %						TG analysis, % weight loss at various temperatures, °C					
		C		H		N							
PUIs	Yield, %	Calcd.	Found	Calcd.	Found	Calcd.	Found	200	300	400	500	600	700
4a	65	65.08	64.00	3.72	3.58	9.50	9.10	2	18	28	44	70	95
4b	70	67.71	66.50	3.44	3.30	8.77	8.37	2	20	40	50	78	95
4c	70	67.71	66.30	3.44	3.30	8.77	8.27	1	16	24	42	75	95
4d	75	67.71	66.40	3.44	3.35	8.77	8.30	1	11	21	35	53	95
4e	80	67.20	66.30	4.00	3.50	7.46	7.16	1	10	22	32	60	95
4f	75	70.87	70.01	3.84	3.63	7.70	7.30	1.5	12	28	40	80	93
4g	80	69.64	68.02	3.56	3.30	7.67	7.10	1.5	11	32	50	78	95
4h	80	64.78	63.10	3.34	3.10	7.20	6.50	1	10	25	42	70	95

TABLE 4. Characterization of Aromatized PUIs 5a-h (bulk polymerization)

		Elemental analysis, %						TG analysis, % weight loss at various temperatures, °C					
		C		H		N							
PUIs	Yield, %	Calcd.	Found	Calcd.	Found	Calcd.	Found	200	300	400	500	600	700
5a	70	65.08	64.00	3.72	3.22	9.50	9.10	2	17	26	43	67	93
5b	75	67.71	66.10	3.44	3.00	8.77	8.28	2	18	36	48	75	95
5c	78	67.71	66.30	3.44	3.10	8.77	8.31	1	14	23	40	75	95
5d	80	67.71	66.32	3.44	3.00	8.77	8.32	1	10	20	35	54	95
5e	75	67.20	66.10	4.00	3.60	7.46	7.16	1	10	23	30	61	95
5f	80	70.87	69.30	3.84	3.44	7.70	7.14	1.5	10	28	37	75	95
5g	80	69.04	68.20	3.56	3.17	7.67	7.30	1	10	30	48	75	95
5h	80	64.78	63.10	3.34	3.10	7.20	6.70	1	10	23	40	68	91

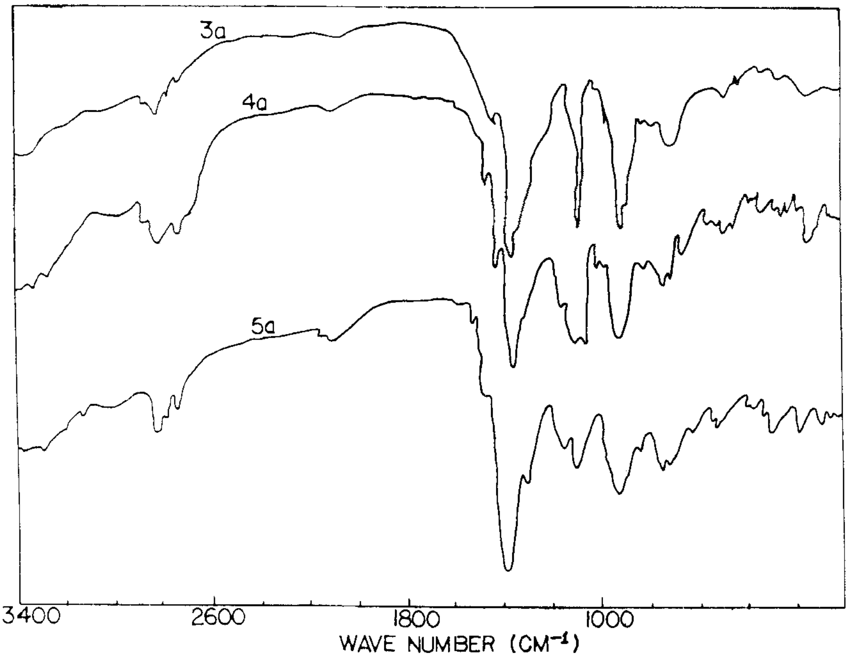


FIG. 1. I.R. spectra of PUIs.

distinct band at 3030 cm^{-1} because of the aromatic moiety of Monomer 1, but shows a band at 830 cm^{-1} due to C—H bending vibrations of two adjacent hydrogen atoms. The IR spectrum of aromatized PUI (i.e., 4a) shows 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 C—H in-plane and out-of-plane bending vibration character of the aromatic system. The band at 780 cm^{-1} might be due to C—H bending vibrations of three adjacent hydrogen atoms of a phthalimide moiety arising from the aromatization of a poly(tetrahydrophthalimide) intermediate (3a). Bands around 2875 and 2920 cm^{-1} in the spectra of PUIs 3, 4, and 5 are attributed to —CH— of Monomer 1. The IR spectra of Polymers 5a-h also show all the characteristics of imide and urethane groups (Fig. 1), indicating that solid-phase polymerization also occurs.

The TGA data show that the synthesized PUI samples exhibited less than 3.5% weight loss at 200°C, probably corresponding to residual solvents (Tables 2-4).

The polyimide samples undergo decomposition between 200 to 300°C (the temperature depending upon the nature of the PUI) and suffer complete degradation in the 200 to 700°C range (Fig. 2). A rapid rate of weight loss is observed around 450 to 550°C. In almost all cases the polymer sample showed a 50% weight loss in the 490 to 520°C range. Complete weight loss, i.e., around 91-98%, was observed at about 700°C. The unaromatized PUIs (3a-h) undergo initial degradation at around 200°C whereas the aromatized PUIs (4a-h) started degrading at a slightly higher temperature (220°C). On the other hand, PUIs 5a-h, obtained in the bulk phase, start degrading at around 250°C.

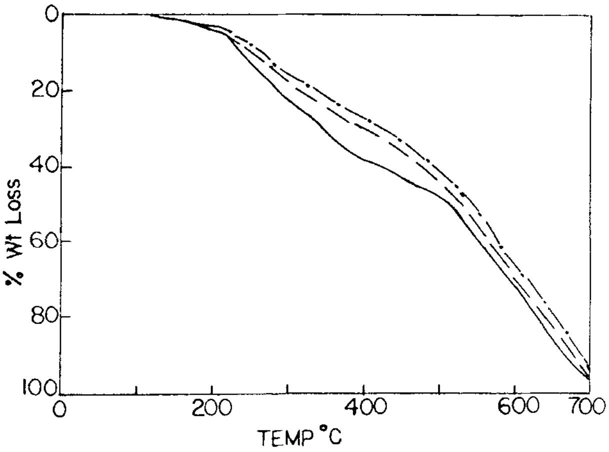


FIG. 2. TG thermograms of PUIs: 3a (——), 3b (--), 3c (-·-·).

Comparison of the thermal stability of all PUIs reveals the following order of stability based on the bismaleimide component:

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

All the composites prepared at 145°C are in the form of dark brown sheets. The specific gravities of the composites have been found to be in the 1.25–1.39 range. The results of chemical resistance tests of all the PUI composites to organic solvents, acids, and alkalies reveal that the organic solvents and concentrated acid (25% v/v) do not affect the composites. However, concentrated alkali causes a change of about 0.90–1.25% in their thickness and weight (Table 5).

The composites have been found to have good mechanical properties. The overall trend of the mechanical properties of the prepared PUI composites decreases as follows:

TABLE 5. Mechanical and Electrical Properties of Glass-Reinforced PUIs

	Percent change on exposure to 25% (w/v) NaOH						
Composite	Thickness	Weight	Flexural strength, MPa	Compressive strength, MPa	Impact strength, MPa	Rockwell hardness, R	Electrical strength (in air), kV/mm
C4a	1.1	1.0	298	280	280	120	17.4
C4b	1.25	1.0	312	321	330	115	19.0
C4c	0.9	1.1	340	290	300	105	24.1
C4d	0.78	1.2	222	201	216	133	25.7
C4e	1.2	0.88	216	211	210	130	20.4
C4f	1.0	0.9	258	231	270	111	24.4
C4g	0.8	0.9	265	237	272	118	24.4
C4h	1.1	1.1	228	215	220	120	24.8

C2c > C2b > C2a > C2g > C2f > C2h > C2e > C2d

This may be attributed to an increase in the rigidity of the bismaleimide component.

The electrical strength of all the composites was in the 18.0–25.8 kV/mm range.

CONCLUSIONS

The overall advantages of the FFCH and bismaleimides system produced are as follows:

The DA reaction of FFCH with bismaleimides produces PUIs with good resistance to organic solvents and mineral acids.
The in-situ produced PUIs show good adhesion to glass fiber.
Void-free sheets could be prepared with good mechanical and electrical properties.

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