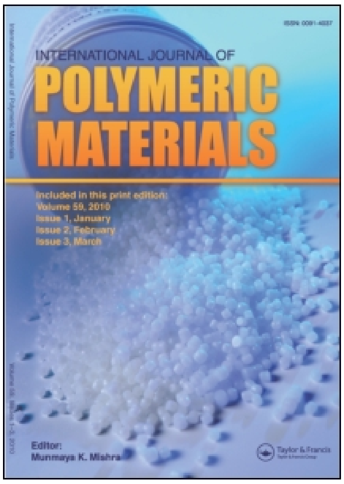

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Synthesis, Characterization and Glass Reinforcement of Poly(Urea-imide)s, Part-1

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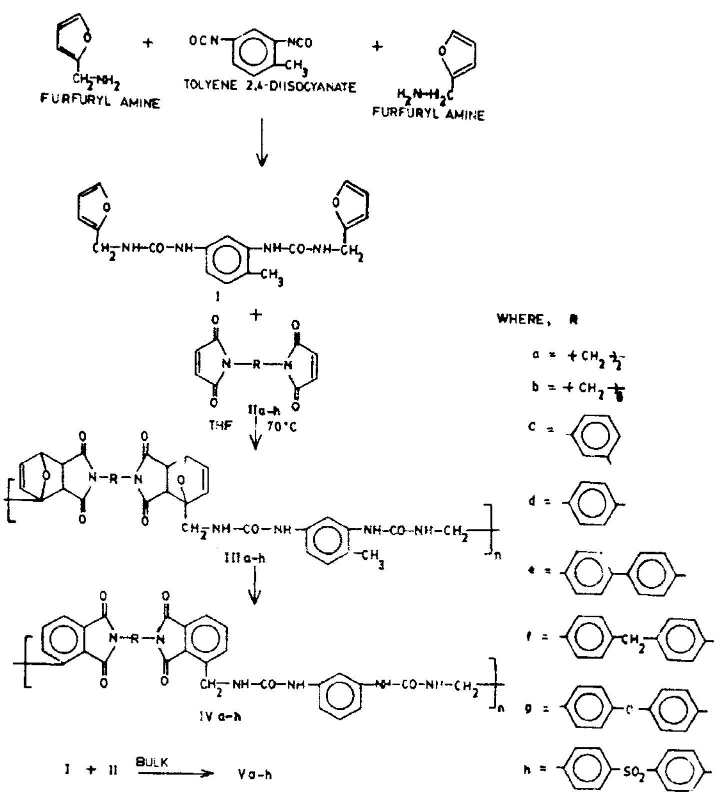
Poly(urea-imide)s (PUIs) were prepared by Diels-Alder(DA) intermolecular polymerization of 4-methyl-1,3-phenylene bis(2-furanyl methyl urea) (BFU) I, with various bis-(maleimido) compounds (II_{a-h}). The DA reaction was carried out in 1,4-dioxane as solvent as well as in bulk followed by aromatization (dehydration) of poly(tetrahydro phthalimide) intermediates (III_{a-h}) in the presence of acetic anhydride. All the PUI (IV_{a-h}) samples were characterized by elemental analysis , IR spectral studies and thermogravimetry. The PUIs exhibit good thermal stability. BUF and bismaleimides were polymerized (at 145±10°C) by in situ DA intermolecular reaction into moderately thermally stable PUIs glass fibre composites (i.e. laminates) without evolution of by-products. The prepared composites were characterized by chemical resistivity and mechanical properties.

Keywords: Poly(urea-imide)s; synthesis; structure; properties; composites

INTRODUCTION

The introduction of linkages such as ether, amide, oxysilane, ester etc. to improve processability of polyimides without major sacrifice in thermo oxidative stability has received great industrial attention [1–5]. The above properties make copolyimides suitable for interlaminary insulation, protective coating in microelectronics and also for preparation of flexible composites [1–5]. The amino resins containing urea linkages have potential applications due to infusible insoluble properties of their cured end products [6]. The merging of urea linkage and imide linkage into polymer chain may offer high thermally stable polymers. With this view the present communication refers to the synthesis and characterization of PUIs based on DA reaction of urea linkage containing bis(furnas), 4-methyl 1, 3-phenylenebis(2-furanyl methyl urea) (BFU) (I) and bis(maleimides) (II a–h). A novel approach was also conducted to prepare a matrix resin system for processible PUI-glass fibre composites based on 'in situ' DA intermolecular addition polymerization of BFU and bismaleimides. The prepared composites were characterized by their chemical resistance, and mechanical properties. The whole research work in outlined scanned in the Scheme I.



SCHEME I

EXPERIMENTAL DETAILS

Materials

Furfuryl amine and all the diamines used for synthesize bismaleimides were obtained from SDS Chemicals, Boisar, India. Furfuryl amine was redistilled before use. Tolylene 2, 4-diisocyanate (TDI) was used as received from Merk, FRG. All other chemicals used were of laboratory grade. Satin (2/2) weave (polyimide compatible) fibre glass fabric 0.25 mm thick of 'E' type glass (Unnati Chemicals, India) 270 gm^{-2} was used for laminate preparation.

Preparation of Monomers

4-methyl 1, 3-phenylene bis (2-furanylmethyl urea) (BFU) (1) was prepared by the following method:

To a ice cooled solution of 2-furfuryulamine (0.03 mol) in dry ether (50 ml) the solution of 4-methyl 1, 3-phenylene diisocyanate (0.01 mol) in 50 ml dry ether was added with stirring. The resulting product was filtered, washed with dry ether and air dried. It was white powder. m.p. 141° - 2°C (uncorrected).

Analysis : $C_{19}H_{20}O_4N_4$(368)

%Elemental Analysis:		C	H	N
	Cacl.	61.95	5.43	15.21
	Found	61.7	5.38	15.1
IR Features [10,11]: Urea				
	ν_{NH}	3450 cm^{-1}		ν_{NH} (sec)
	$\nu_{C=O}$	1695 cm^{-1}		
	—NH—	1540 cm^{-1}		
	NC—N	1480, 1010 cm^{-1}		
	CH_2	2920 cm^{-1}, 2875 cm^{-1}		
	Furanring	1615 cm^{-1}, 1510 cm^{-1}, 1390 cm^{-1}		

Bismaleimides (2a - h) listed in Table I were prepared by the method reported previously [9].

TABLE I Synthesized Bismaleimides [7–9]

	Bismaleimide : II	*m.p. °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′-Bisphenyl)-4, 4′-diylbismaleimide	> 300°
f)	N, N′-[1,1-(Methylene-bis-4, 4′-phenylene)-bismaleimide]	156° – 158°
g)	N, N′-[1,1-(Oxy-bis-4, 4′-phenylene)-bismaleimide]	179° – 182°
h)	N, N′-[1,1-(Sulfonyl-bis-4, 4′ -phenylene)-bismaleimide]	253° – 255°

Formation of Poly (Urea-Imide) III, IV, V

The DA reactions of I with bismaleimides (l_{a-h}) were carried out both I solutions and in bulk phase system.

Solution Phase Polymerization

I (0.01 mol) in 100 ml. of dry 1, 4-dioxane was mixed with II (0.01 mol). The solution was stirred and refluxed at 100°C for 24 hrs. The resulting solution was cooled and poured into a large volume of dry other. The precipitated polymer III was filtered off and dried. It was treated twice with hot DMF to remove unreacted I and II. Aromatization of polymer III was carried out by refluxing 2 g of the dried Polymer in 2 ml of acetic anhydride for 4 hrs. The resulting mixture was poured into 1,4-dioxane-ether (50:50) mixture. The precipitates of aromatized polymer IV was filtered off, washed once each with water and methanol.

A mixture of I (0.005 mol) and II (0.005 mol) was suspended in dry tetrahydrofuran (25 ml) then spread into a petri-dish and tetrahydrofuran was evaporated at room temperature. The dried mixture was heated at 110°C for 4 hrs and then heated with acetic anhydride (1 ml) at 130±5°C for 4 hrs with vigorous agitation. The resulting solid product V was treated as described above.

The details about all PUIs: III, IV and V are given in Tables II–IV.

Composite Fabrication

A typical method of fabrication for composites is given below.

As suspension of BFU (I) and bismaleimide (2a–h) in tetrahydrofuran was prepared and stirred well for 2 min. The suspension mixture

TABLE II Characterization of Non-Aromatized Poly (Urea-Imide)s, PUIs, IIIa – h

PUIs	*Yield*	*Elemental Analysis (%)*						*%age wt. loss at temperature °C*				
Sample	*%*	*C*		*H*		*N*						
		Cal	*Found*	*Cal*	*Found*	*Cal*	*Found*	*300*	*400*	*500*	*600*	*700*
III_a	75	59.2	58.7	4.76	4.46	14.3	14.0	2.5	17	44	65	82
III_b	77	61.5	61.1	5.6	5.4	13.04	12.8	2.3	18	45	67	83
III_c	80	62.26	61.8	4.4	4.1	13.2	12.9	2.0	15	38	57	79
III_d	84	62.26	61.7	4.4	4.2	13.2	12.9	2.0	15	35	55	80
III_e	76	65.73	65.2	4.5	4.3	11.8	11.5	1.6	18	40	55	80
III_f	78	66.11	65.7	4.68	4.4	11.57	11.3	1.8	16	38	58	82
III_g	82	64.86	64.3	4.32	4.03	11.35	11.0	2.0	16	38	56	83
III_h^*	85	66.91	66.4	4.06	3.7	10.66	10.3	1.9	15	40	57	81

*% S Calc. 4.46; Found 4.5.

TABLE III Characterization of Aromatized Poly (Urea-Imide)s, PUIs, IVa–h

PUIs	*Yield*	*Elemental Analysis (%)*						*%age wt. loss at temperature deg °C*				
Sample	*%*	*C*		*H*		*N*						
		Cal	*Found*	*Cal*	*Found*	*Cal*	*Found*	*300*	*400*	*500*	*600*	*700*
IV_a	80	63.5	63.1	3.65	3.35	15.32	15.02	2.0	15	42	63	80
IV_b	75	66.0	65.5	4.0	3.7	14.0	13.7	2.0	16	44	65	81
IV_c	84	64.44	66.0	3.35	3.1	14.1	13.8	1.5	12	36	56	78
IV_d	77	66.44	66.1	3.35	3.05	14.1	13.7	1.2	12	36	54	77
IV_e	82	69.64	69.1	3.57	3.3	12.5	12.2	1.4	14	38	54	78
IV_f	85	69.97	69.5	3.8	3.4	12.24	12.0	1.0	13	35	56	80
IV_g	76	70.17	69.7	3.5	3.2	12.28	11.8	1.2	12	36	54	82
IV_h^*	79	67.03	66.7	3.35	3.1	11.73	11.4	1.0	14	38	55	80

*% S Calc. 4.46; Found 4.4.

TABLE IV Characterization of Bulk phase, PUIs,Va–h

PUIs	*Yield*	*Elemental Analysis (%)*						*%age wt. loss at temperature °C*				
Sample	*%*	*C*		*H*		*N*						
		Cal	*Found*	*Cal*	*Found*	*Cal*	*Found*	*300*	*400*	*500*	*600*	*700*
V_a	76	63.5	63.0	3.65	3.2	15.32	15.0	1.5	14	41	62	79
V_b	79	66.0	65.3	4.0	3.6	14.0	13.6	1.5	15	41	64	79
V_c	82	66.44	66.0	3.35	3.0	14.1	13.6	1.0	11	35	55	77
V_d	85	66.44	66.0	3.35	2.9	14.1	13.5	1.0	11	35	53	76
V_e	75	69.64	68.8	3.57	3.1	12.5	12.1	1.1	13	37	53	77
V_f	80	69.97	69.4	3.8	3.2	12.24	11.8	–	12	34	55	79
V_g	78	70.17	69.5	3.5	3.0	12.28	11.7	1.2	11	35	53	80
V_h^*	83	67.03	66.6	3.35	3.2	11.73	11.3	–	13	37	54	79

*% S Calc. 4.66; Found 4.4.

was applied with a brush to a 25 mm×25 mm fibre glass cloth and the solvent was allowed to evaporate. The 10 dried prepregs so prepared were stacked one on top for another and pressed between steel plates with a Teflon film 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 air circulated oven. The composite so obtained was cooled 50°C before the pressure was released. Test specimens were made by cutting the composite and machining then to final dimensions.

Measurements

The C, H, N contents of monomer I and 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 thermogravimetry (TG) on Du pont 950 thermogravimetric Analyzer in air at a heating rate 10 K/min. The chemical resistance and mechanical strengths were evaluated according to ASTM or ISO methods.

RESULTS AND DISCUSSION

The synthesis of 4-methyl-1,3-phenylene-bis(2-furanyl-methylurea) (BFU) (I) and formation of all the poly (urea-imide)s (PUIs) (III, IV, V) from (I) and bis(maleimides) II_{a-h} is shown in Scheme I. First the non-aromatized DA product III is formed which is then aromatized by treatment of acetic anhydride to yield IV. In the absence of II, heating of I in 1, 4-dioxane at 100°C does not alter the properties of I. It was also observed that heating of II a–h in 1, 4-dioxane at 100°C does not induce the addition polymerization of II a–h. This has been shown to be possible only at elevated temperature or in the presence of an initiator [7–9]. 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 effected by concentrated mineral acids and formic acid. The elemental analysis of all the PUIs samples shown in Tables II to Table IV are consistent with their predicted structure (Scheme I). Typical IR spectra of PUIs are shown in Figure 1. Examination of IR spectra of all PUIs reveals that all the spectra comprise prominent characteristic bands of the imide and urea groups [10]. The bands around 1700 cm^{-1}, 1620 cm^{-1}, 1050 cm^{-1} and 720 cm^{-1}, are contributions from imides I, II and III and IV respectively. Bands around 1700 cm^{-1}, 3450 cm^{-1} and 1695 cm^{-1} (shoulder) correspond to the urea group. The IR spectra of PUIs, III a,b does not show distinct band at 3030 cm^{-1} because of the aromatic of monomer I 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, IIIa (i.e. IV a) shows the distinct aromatic band at 3030 cm^{-1} as well as multiple absorption bands in the region 800–1200 cm^{-1}. They may be assigned to the C—H in plane and out of plane bending vibration character of 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 poly(tetrahydrophthalimide) III a,b. These bands could not be

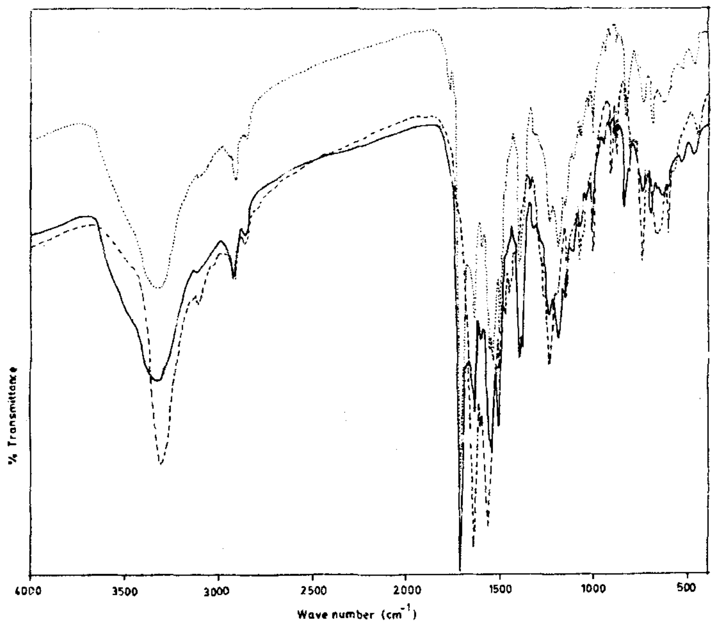


FIGURE 1 IR Spectra of IIIa (·····), IVa (----) and Va (—).

observed discernibly for the aromatic system already present in monomer and the aromatic system in poly(tetrahydrophthalimide) unaromatized PUIs, III_{c-h}). Bands around 2875 cm^{-1} and 2920 cm^{-1} appear in the spectra of all PUIs, III, IV, V are attributed to CH_2 of monomer-I. The IR spectra of PUI samples V (bulk Polymer) also show all the characteristics of imide and urea groups (Fig. 1) indicating that bulk phase polymerization fields PUI, as well. Typical TG curves are shown in Figure 1. The TG data of all PUIs are listed in Tables II–IV. The TG data show that the produced PUIs samples exhibit less than 3% weight loss at 300°C probably corresponding to residual solvent, they decompose in one step. PUIs samples start their decomposition above 320°C depending upon the nature of polymer. The rate of weight loss is high around 425°C. aand complete at 700°C. The non-aromatized PUIs 4a–h start to degrade at slightly higher temperature (~350°C) on the other hand, PUIs 5a–h obtained in the bulk phase, start degradation at around 360°C. A comparison of the thermal stability of all PUIs reveals the order of stability based on bis-(maleimide) components 2a–h as follows (of Scheme I).

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

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) PUI-glass fiber composites. All the composites prepared are dark brown sheets. The addition polymerization by DA reaction of I with II a–h of composite, from which the polymerization continues towards the inner part of the composite without evolution of any reaction by products or solvent molecules. Characteristics of prepared glass reinforced PUI composites are summarized in Table V. The density of all composites is in the range of 1.3 to 1.0 g/cm^3 and indicates that there is no appreciable change in their specific gravity with respect to the nature of bis-(maleimide) compounds. Examination of chemical resistance test reveals that all composites have remarkable resistance to organic solvents and concentrated 1.5 M HCl. However, treatment with concentrated 2M NaOH changes their thickness and weight by about 1.1 to 1.6%.

TABLE V Mechanical and electrical properties of galss-reinforced poly(urea-imide)s Va – j

PUIs Sample	*Chemical Resistance percent change in*		*Density*	*Flexural strength*	*compressive strength*	*Impact strength*	*Hardness*	*Electrical Strength*
	Thickness	*Weight*	(g/cm^3)	(*MPa*)	(*MPa*)	(*MPa*)	(*R*)	(*in air*) (*kV/mm*)
V_a	1.1	1.5	1.31	445	392	401	76	22.4
V_b	1.2	1.2	1.46	359	470	467	71	21.3
V_c	1.4	1.4	1.51	452	464	469	76	24.6
V_d	1.3	1.1	1.55	375	336	341	90	26.0
V_e	1.0	1.2	1.40	382	312	319	64	25.2
V_f	1.2	1.3	1.59	425	373	362	69	23.8
V_g	1.1	1.6	1.44	398	387	365	54	20.2
V_h	1.3	1.1	1.38	406	392	370	55	19.8

Results of mechanical properties of PUI composites reveal that all the composites have good mechanical properties. The overall trends for all mechanical properties of poly (urea-imide) – composites C_{a-h} decrease as follows, which may be attributed to a certain increase in the rigidity of bis-(maleimide) components:

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

The electrical strength of all the composites is in the range of 22.0 to 30.0 kv/mm. As there is no wide change in electrical strength no attempt was made to interpret these data.

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