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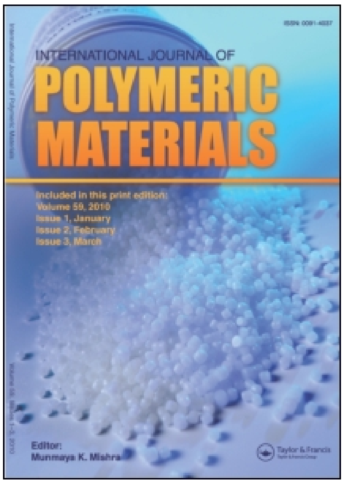

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Novel Polyimide System Based on Nitro Displacement/Diels-Alder Reactions

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Novel Polyimide System Based on Nitro Displacement/ Diels-Alder Reactions

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Poly(ether-imides) were prepared by two simultaneous reactions, that is, Diels-Alder reaction and nitro displacement reaction. Thus 3-nitrophthalic anhydride was reacted with furfuryl amine and the resultant amic acid was then reacted with three bismaleimides (2a–c) and disodium salt of bisphenol–A. The obtained polymers were treated with acetic anhydride to form cyclic imide, as well as aromatization of Diels-Alder adduct. The poly(ether-imide)s were characterized by IR spectral studies and theromgravimetry. A "in situ" polymerization on glass fibers was also carried out and the laminates were characterized by physical, mechanical, and chemical properties.

Keywords: amic acid, bismaleimides, Diels-Alder reaction, glass fiber reinforced composite, melting point, nitrodisplacement, poly(ether imides)

INTRODUCTION

One of the authors (HSP) and his co-workers have reported the preparation of polyimides through Diels-Alder (DA) reaction of bisfuran derivatives/furan resins and bismaleimides [1–6]. The reports indicate that thermally stable polyimides can be created in situ at lower temperature than conventional polyimide [1–6]. To avail the processable polyimide, several modifications [7] of polyimides has also been made without the dilution of properties of polyimides. One such area

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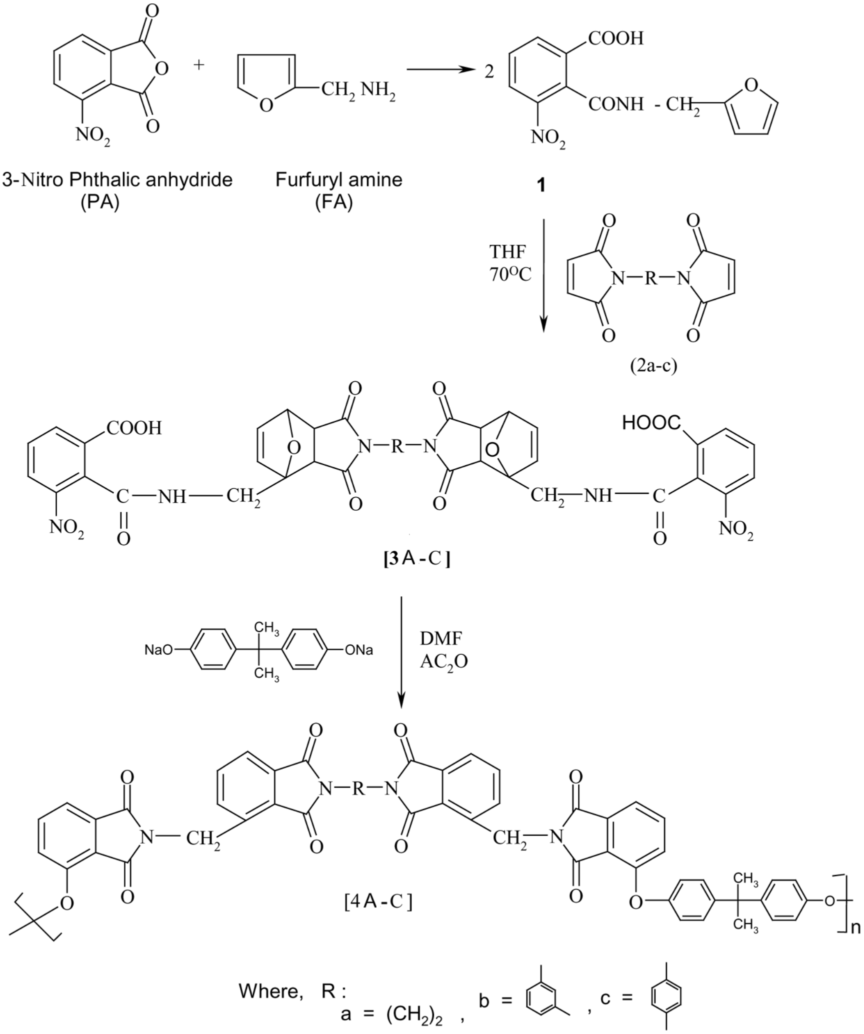
in which the poly(ether-imide)s formation by nitrodisplacement (ND) reaction has been well documented [8–11]. The formation of poly(ether-imide)s through simultaneous DA and ND reactions has not been reported. Hence it was thought to undertake such type of work. Hence the work presented in this communications was carried out regarding the novel poly(etherimide)s formation shown in Scheme 1.



SCHEME 1 Synthesis of poly(ether imide)s.

TABLE 1 List of Bis(maleimide) Compounds

No.	Bis(maleimides)	Molecular weight	Melting point (°C)
2a	Ethylene bismaleimide	220	189–190
2b	1,3-phenylene bismaleimide	268	202–203
2c	1,4-phenylene bismaleimide	268	300

EXPERIMENTAL

Materials

3-Nitrophthalic acid and furfuryl amine obtained form Chitti Chem., Baroda. Bismaleimides (shown in Table 1) have been prepared according to a method reported in the literature [12]. All other chemicals used were of laboratory grade.

Synthesis of Amic Acid of Furfuryl Amine and 3-Nitrophathalic Anhydride. Formation of 1 (i.e., (2-Furanylmethyl aminocarbonyl)-3-nitro benzoic acid)

Amic acid was prepared by a simple condensation reaction between 3-nitrophthalic anhydride (prepared from 3-nitrophthalic acid) and furfuryl amine, following the method reported in the literature for phthamic acid [13].

The procedure is: To an ice cooled (0–5°C) solution of 3-Nitrophthalic anhydride (0.01 mole) in ethanol (30 ml) a solution of furfuryl amine (FA) (0.01mole) in ethanol was added gradually with vigrous stirring. The precipitate of furfuryl amic acid of 3-nitrophthatlic anhydride were obtained. It was filtered, washed with ethanol, and air dried. It was a pale yellow powder. The melting point was 103–4°C (uncorrected).

Elemental Analysis

$$\text{MF}: C_{13}H_{10}N_2O_6 (266)$$

Calculated (%) C 53.79 H 3.44 N 9.65

Found (%) C 53.74 H 3.39 N 9.64

Number of COOH groups 1.1 (estimated by non-aqueous conductometric titration).

FTIR Spectral Features

IR (KBr) cm^{-1}

3030, 1500, 1600	(aromatic),	3600, 1680	OH of COOH
3320, 1700, 1550	(amide),	2920, 2850	CH_2 of $NHCH_2$
1570, 1370,	(Nitro),		

NMR Signals

1HNMR (DMSO): δ 4.5 ppm (s CH_2), δ 7.5–8.5 ppm (m, aromatic phenyl), δ 6.3 ppm (s furan) δ 8.8 ppm (s, COOH).

Diels-Alder Reaction of Amic Acid and Various Bismaleimide (BM) (2a–c). Formation of DA adduct (3a–c)

A suspension of amic acid [1] (0.02 mole) and BM (2a–c) (0.01 mole) in tetrahydrofuran (50 ml) was refluxed for 8 h at 70°C. The resultant reaction mixture was filtered and washed with water and air dried. The obtained product was DA adduct (unaromatized and uncyclized) of amic acid and BM. It was a yellow to brownish powder, the yield was quantitative. M.P. was in the range of 173–198°C (uncorrected) [14–16].

IR and NMR spectral features are presented in Table 2.

Polymerization of DA Adduct and Disodium Salt of Bisphenol-A(BA). Formation of Poly Ether Imides (PEIs)

A suspension of DA adduct (0.01 ml) in DMF with disodium salt of bisphenol-A (0.02 mole) in DMF was refluxed at 70°C for 4 h [17]. The product obtained was filtered and washed with DMF. Such polymer contains the uncyclized polyamic acid and unaromatized segments. Thus, these polymers are treated with acetic anhydride to afford aromatization and cyclization reactions simultaneously.

Thus, the intermediate unaromatized uncyclized products (1.0 g) were refluxed with acetic anhydride (2 ml) for 4 h. The resultant products were poured into water and filtered off and then air dried.

Measurements

The C, H, N contents of all the samples were estimated by means of a Thermofinningan flash EA. The data are included in Tables 2 and 3. Number of COOH group for amic acid of DA adducts were estimated by nonaqueous conductometric titration [18–21].

The IR spectra were taken using a Nicolet 760D spectrophotometer. The ^{1}HNMR spectra were made in CDC_{13}/DMSO on a Hitachi R-1500,

TABLE 2 Characterization of DA Adduct

Polymer sample	Molecular formula [formula weight]	Elemental analysis (wt%)			Yield %	IR spectral feature (cm^{-1})			PMR signals δ ppm	M.P.° C	Number of COOH group	% weight loss at various temperatures				
			calc.	found		Imide	CH_2	NH				200	300	400	500	600
3a	$C_{36}H_{28}N_6O_{16}$	C	545.00	53.96	82	1715, 1780			3.4–3.7	173	2.1	3	5	40	70	80
	[800]	H	3.50	3.90		400	2860	3350	(s,CH_2)							
		N	10.50	10.10		735	2950		6.3 (s, furan)							
3b	$C_{40}H_{28}N_6O_{16}$	C	56.60	56.40	85	1715,1770			7.6–8.5	194	2.2	4	7	42	72	82
	[848]	H	3.30	3.20		1100	2820	3360	(m,aromatic)							
		N	9.90	9.80		730	2970		8.7 (s, COOH)							
3c	$C_{40}H_{28}N_6O_{16}$	C	56.60	56.44	80	1715,1780				198	2.0	4	8	43	68	85
	[848]	H	3.30	3.28		1120	2870	3390								
		N	9.90	9.86		740	2990									
		H	3.95	3.92												
		N	7.91	7.80												

TABLE 3 Characterization of PEIs

Polymer sample	Molecular formula [formula weight]	Elemental analysis (wt%)			Yield %	IR spectral feature (v cm^{-1})				% weight loss at various temperatures				
			calc.	found		Imide	CH_2	NH	Ar-O-Ar	200	300	400	500	600
4a	$C_{36}H_{28}N_4O_9$ [660]	C	65.45	65.40		1730,1790			1241	4	6	41	75	86
		H	4.24	4.20	83	1120	2840	3380						
		N	8.48	8.40		740	2960							
4b	$C_{40}H_{28}N_4O_9$ [708]	C	67.80	67.70		1720,1780			1242	5	8	43	74	88
		H	3.95	3.90	84	1100	2830	3350						
		N	7.91	7.86		730	2930							
4c	$C_{40}H_{28}N_4O_9$ [708]	C	67.80	67.72		1710,1780			1240	6	8	42	72	89
		H	3.95	3.92	81	1130	2860	3360						
		N	7.91	7.80		750	2930							

60 MHz spectrophotometer using TMS as an internal standard. The thermogravimetric (TG) of all the polymer samples were carried out on a Dupont 950 thermogravimetric analyzer in air at a heating rate of 10 K/min. Their results are furnished in Tables 2 and 3.

Composite Fabrication

A suspension of poly(ether-imide) of various bis(maleimide), compounds (4a–c) in THF was prepared on a weight basis and stirred well for 2 min. To a 254 mm × 254 mm polyimide compatible glass cloth, the suspension was applied with a brush and the solvent was allowed to evaporate. The dried ten prepregs so prepared were stacked one over another and pressed between iron plates with Teflon® Film release sheet and compressed between platens under pressure.

The prepregs were cured by heating the platens to 150°C for 10 h in air circulating oven. The composite so obtained was cooled to 50°C before the pressure was released. The composites were then machined to final dimension for various physical, mechanical, and chemical tests.

COMPOSITE CHARACTERIZATION

Chemical Resistance Test

The chemical resistance test for all the composite samples were performed according to ASTM D 543–67.The composite sample dimension were 25 mm × 25 mm × 3 mm. The samples were immersed in 25% v/v H_2SO_4, 25% v/v HCI 25% w/v NaOH, Ethanol, Acetone, DMF, and THF for 7 days at room temperature. After 7 days the samples were taken out from the reagents and were analyzed for the percentage

TABLE 4 Chemical Resistance Test of Poly(ether-imide)s

SEMI IPN Polyimide sample	4a C % Change		4b C % Change		4c C % Change	
	Thickness	wt.	Thickness	wt.	Thickness	wt.
25% H_2SO_4	1.24	1.90	1.21	1.97	1.19	1.84
25% HCl	1.19	7.80	1.19	1.76	1.16	1.77
25%NaOH	.075	1.11	0.76	1.14	0.79	1.20
Ethanol	0.51	1.1	0.52	1.11	0.51	1.08
Acetone	0.45	0.92	0.40	0.80	0.38	0.74
DMF	1.11	1.82	1.04	1.77	1.05	1.75
THF	1.0	1.70	0.87	0.87	0.86	1.70

TABLE 5 Mechanical and Electrical Properties of Poly(ether-imide)s

Poly(ether-imide)s composites (C)	Flexural strength (MPa)	Compressive strength (MPa)	Notched impact strength (MPa)	Rockwell hardness (MPa)	Electrical strength in air (kv/mm)
4a	311	285	279	68	20.5
4b	295	291	280	95	23.0
4c	290	288	282	90	24.0

change in their thickness and weight. The results are summarized in Table 4.

Mechanical Tests

All the mechanical tests were performed using three specimens and their average results are summarized in Table 5.

The compressive strength was measured on a Universal Instron testing machine model no. A-74-37, at room temperature according to ASTM D 695.

The notched izod impact strength of the composites was measured on a Zwick Model no. 8900 Impact machine at room temperature according to ASTM D256.

Rockwell hardness was measured on a Rockwell hardness tester model no. RAS/Saro Engg. Pvt. Ltd. India according to ASTM D 785 at room temperature.

The measurement of Flexural strength was carried out with Universal Instron Testing Machine model no. A-74-37, at room temperature according to ASTM method D790.

RESULTS AND DISCUSSION

The synthesis of amic acid (1) based on 3-nitrophthalic anhydride and furfuryl amine was performed by a reported method [13]. The amic acid was an amorphous powder. Its C, H, N contents (Table 2) are consistent with those of the predicted structure (Scheme 1). The number of carboxyl groups determined by non-aqueous conductometric titration was found to be one carboxyl group. The IR spetrum of (1) comprises the band at 1680 cm^{-1} due to bonded COOH group. The bands at 1320, 1700, 1550 are from amide group. The bands at 2920, 2850 cm^{-1} are mainly due to νCH_2 group. The NMR data of 1 also support the structure. On this basis and reaction of phthalic anhydride and amine [13] the proposed structure of amic acid is shown in Scheme 1. The amic acid containing the furan ring and thus a Diels-Alder reaction with three bismaleides (Table 1) was carried out. The elemental analysis of all three adducts is consistent with the predicted structures. The IR spectra of DA adducts comprises the spectral features of the parent compound. Although the only discernible differences appeared at the band due to olefinic double bond at 1610 cm^{-1} and the band at 1680 cyclic carboxyl group, which is consistent with molecular structure. NMR spectral data of DA adducts 3a–c (Table 2) also confirm the structures of 3a–c.

The entire synthesis of poly(ether-imide)s through Diels Alder reaction of amic acid and various bis(maleimide)-compounds (2a–c) is shown in Scheme 1. Thus, the non-aromatized Diels-Alder product 3a–c contain the NO_2 group. Hence, the cyclization-aromatization of polyetherimides is carried out through nitro displacement. Thus 3a–c afford poly(ether imide)s 4a–c. In absence of (2a–c), heating of 1 in THF at 70°C does not alter the properties of 1. It was also observed that heating of 2a–c in THF at 70°C does not induce an addition polymerization of 2a–c. This reaction occurs either at elevated temperature or in the presence of an initiator [22–25]. All the polymer samples were obtained in good yields and were in the form of yellow to dark brown solid powders. They were insoluble in common organic solvents and were not affected by concentrated mineral acids. The elemental analysis of all the poly(ether-imide)s samples is shown in Table 3 and is consistent with their predicted structure (Scheme 1).

Important IR spectral features of the poly(ether-imide)s are summarized in Table 2. Examination of the IR spectra of all the poly (ether-imide) reveals that all the spectra contain characteristic bands of the imide group. The bands around 1780–1720, 1380, 1100, and 730 cm^{-1} are contributions from poly(ether-imide)s. The band around 3300–3400 cm^{-1} shows the stretching vibrations of -NH- of CH_2NH-group. Bands around 2870 and 2930 cm^{-1} appearing in the spectra of poly(ether-imide)s are attributed to the –CH_2-group. The band around 1240 cm^{-1} is attributed to diaryl ether. The IR spectra of PEI_S (4a–c) also show all the characteristics of imide groups, -NH- and ether linkages via nitro displacement, indicating that the bulk polymerization yields poly(ether-imide)s as well.

The TG thermogram (Figure 1) shows that the poly(ether-imide)s samples exhibit initial weight loss of about 3% at –300°C, probably due to residual solvent, and decompose in one step. It was observed that preheated (at 200°C) samples of poly(ether-imide) start their

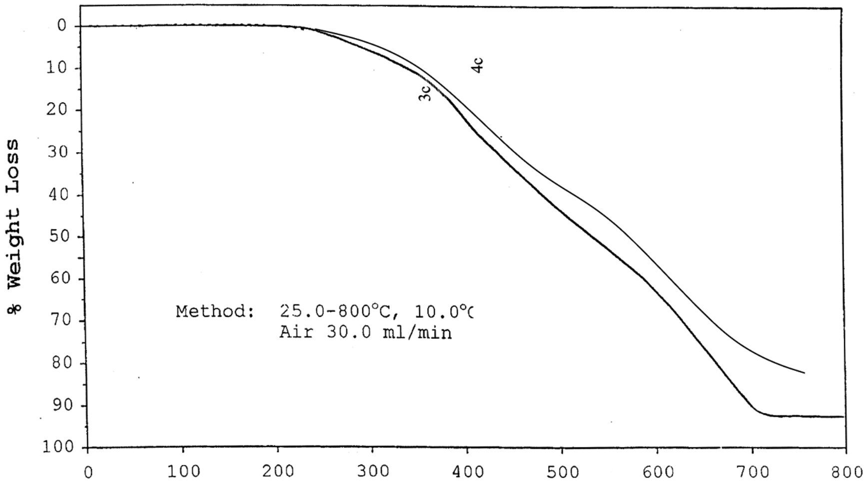


FIGURE 1 TG thermogram of 3c, 4c.

decomposition above 300°C depending on the nature of the polymer. The rate of weight loss is high around 500°C, and completed at −750°C. Comparison of thermal stability of the three types of poly(ether-imide) reveals that the nonaromatized poly(ether-imide) 3a–c start their degradation at 305°C, whereas the aromatized poly(ether-imide) 4a–c start to degrade at a slightly higher temperature (315°C).

The produced polyimides were found to be thermally stable and they showed short-term acid, solvent, and weather resistance. Though the thermal degradation is done in air, they are certainly more stable in a nitrogen atmosphere. In brief, as expected, the polyimides produced have comparable stability with that of commercial polyimides prepared from bismaleimides [7]. Other polyimides are mostly made from condensation of tetracarboxylic acid and diamines and are more thermally stable than polyimides made from bismaleimides. It is also noted that the produced poly(ether-imide)s have better thermal stability then those reported earlier by the present authors [1–6]. Because of the non-processability of the present insoluble poly(ether-imide), a novel approach was also conducted to develop a matrix system for poly(ether-imide)-glass-fiber composites. All the composites prepared were dark brown sheets. The addition polymerization by Diels-Alder reaction of 1 with (2a–c) of compressed composites starts from the surface of the composites, from which the polymerization continues toward the inner part of the composite without evaporation of any reaction by-products or solvent molecules. Characteristics of the glass reinforced poly(ether-imide) composites are summarized in Tables 4 and 5. Chemical resistance tests reveal that all the composites have remarkable resistance to organic solvents (mentioned in Table 3) and concentrated 1.51 M HCl. However, treatment with concentrated 6.2 M NaOH changes their thickness a little and the weight by about 1.3%. Examination of the results of mechanical properties of poly (ether-imide) composites reveals that all the composites have good mechanical strength.

The electrical strength of all the composites is in the range of 20.5 to 28.6 kV/mm. As there was not much change in electrical strength, no attempt was made to interpret these data.

CONCLUSIONS

The present work indicates that synthesis of poly(ether imides) from agricultural waste product (e.g., furfuryl amine) is easy. The intermolecular Diels-Alder reaction with different bismelimides and nitro displacement reaction of this adduct formed poly(ether-imide) having good organic solvent, mineral acid, and heat resistance as shown in Table 5. The processing temperature (150°C) for composite preparation is lower than for conventional polyimide composites. Composites produced from PEIs could be prepared with good mechanical strength.

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