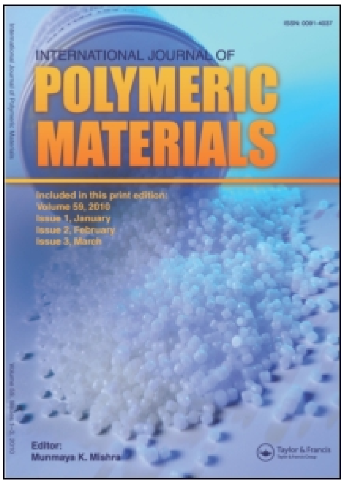

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Polyimides Based on Poly(2-Furanmethanol-Formaldehyde), Part 1

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Polyimides Based on Poly(2-Furanmethanol-Formaldehyde), Part 1

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Polyimides were prepared by Diels-Alder (DA) reaction of furan resin namely Poly[2-furanmethanol-formaldehyde] (PFF) with various bismaleimides. The DA reaction was carried out in tetrahydrofuran (THF) as solvent, as well as in bulk, followed by aromatization of tetrahydropthalimide intermediates in the presence of acetic anhydride. All the polyimides were characterized by elemental analysis, infrared (IR) spectral studies and thermogravimetry. The results show that polyimides based on FF resin exhibit good thermal stability. Preliminary test for glass reinforcement of the polyimides indicate that laminate with good mechanical strength can be prepared.

KEY WORDS Polyimides, poly(2-furanmethanol-formaldehyde).

1. INTRODUCTION

Recycling of agricultural waste is of importance in the ecological balance. Towards this end one of the author (HSP)[1-4] used 2-furaldehyde and 2-furanmethanol (i.e. agricultural waste organic liquids) based resins for the synthesis of Polyimides. In continuation of this work the present communication comprises the synthesis and characterization of polyimides based on Diels-Alder intermolecular reaction of poly[2-furanmethanol-formaldehyde] (FF)[5] and various bismaleimides. The research work is drawn schematically in Scheme I.

2. RESULTS AND DISCUSSION

The entire polyimide formation through DA reaction of FF resin I with bis(maleimides) IIa–d is shown in Scheme I. First the nonaromatized product IIIa–

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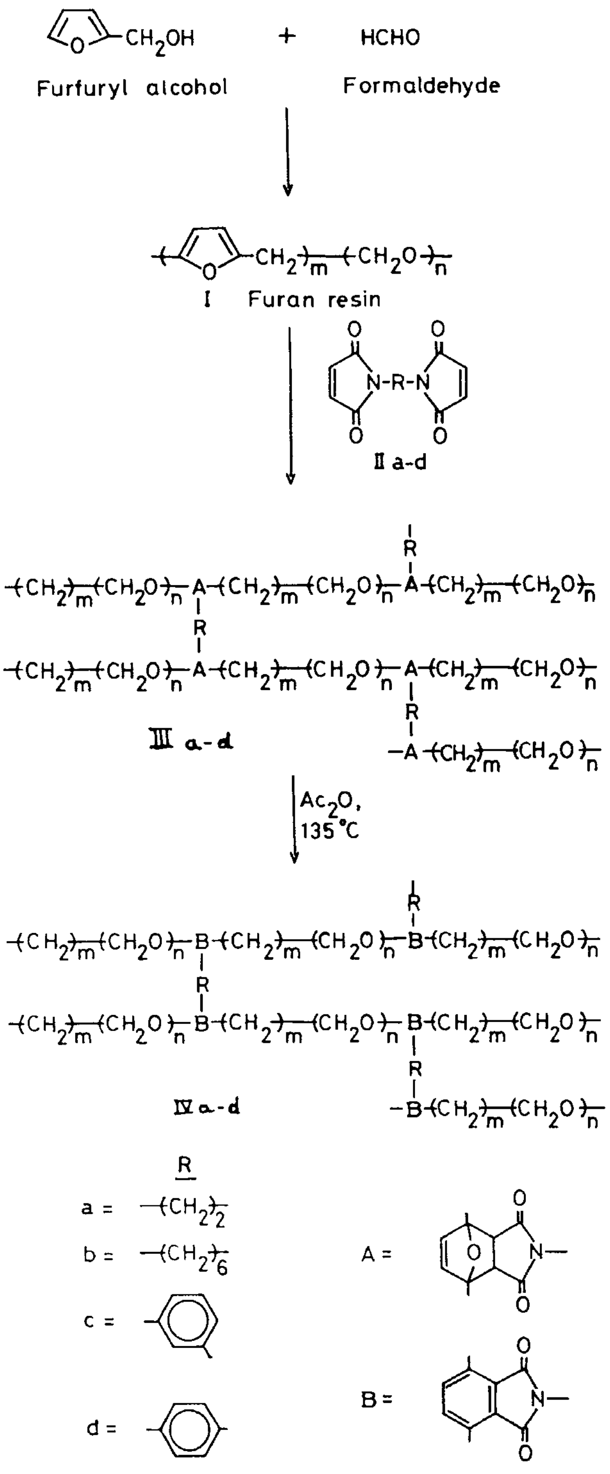
CH2OH
+
HCHO
Furfuryl alcohol
Formaldehyde
I Furan resin
II a-d
III a-d
Ac2O, 135°C
IV a-d
R
a =
b =
c =
d =
A =
B =

SCHEME I

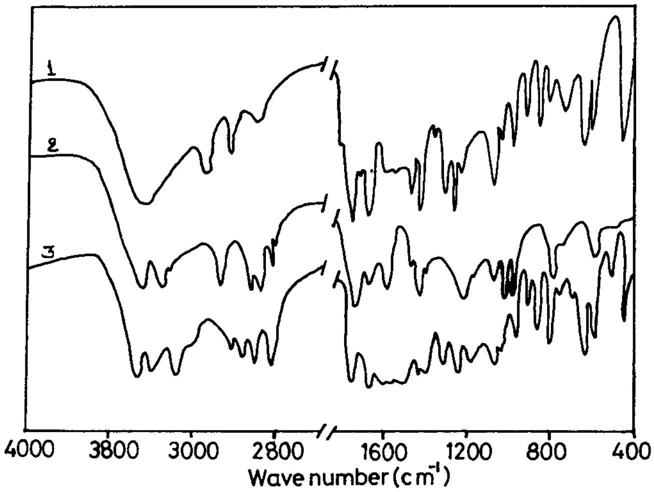

FIGURE 1 Infra red spectra of polyimides: 1) IIIa, 2) IVa, and 3) Va.

d is formed which is then aromatized by treatment of acetic anhydride to yield IVa–d. In the absence of IIa–d heating of I in the THF at 75°C does not alter the properties of (I). It was also observed that heating of IIa–d in THF at 75°C does not induce the addition polymerization of IIa–d. This has been only possible either at elevated temperature or in the presence of an inhibitor.[1,8,9] All the polymer samples were obtained in high yields in form of dark brown to yellow solid powders. They are insoluble in common organic solvents and are not affected by concentrated mineral acids and formic acid. The elemental analysis of all polyimides samples shown in Tables II–IV are consistent with their predicted structure (Scheme I). Some slight deviations in elemental analysis may be due to the presence of unreacted furan rings.

Typical IR Spectra of polyimides are shown in Figure 1. Important IR spectral features of the polyimides revealed that all the spectra comprise important characteristic bands of the imide group. The bands around 1700 cm^{-1}, 1675 cm^{-1}, 1050 cm^{-1} and 730 cm^{-1} are contributions from imide. The spectra of aliphatic polyimide IIIa–d do not show a band around 3030 cm^{-1}, due to absence of aromatic moieties in the polymeric chain. The spectra of IVa and IVb show multiple absorption bands in the region 800–1200 cm^{-1}, which may be assigned to the C—H in plane and out of plane bending vibration characteristics of the aromatic system. This indicates the aromatization of the tetrahydropolyimides IIIa and IIIb to IVa, IVb. Bands pertaining to aliphatic chains of FF resin are also observed in the spectra of all unaromatic and aromatic polyimides. This suggest that the aliphatic chains of FF resin remains intact throughout the DA reaction. The IR spectra of Va–d exhibit also the characteristics of imide group (Figure 1); indicating that solid phase polymerization also takes place.

TG data of all polyimide samples furnished in Tables II–IV reveals that the produced polyimide samples start their decomposition between 275°C to 325°C depending upon the nature of polyimide. The rate of weight loss is high around 500–600°C. It was observed that more than 50% losses weight at 500–600°C and at 775°C the weight is about 75–80% depending upon the nature of polyimide.

The unaromatized polyimides IIIa–d start their degradation at 275°C whereas the

TABLE I

Bismaleimides used

a	N,N'-Ethylenebismaleimide
b	N,N'-Hexamethylenebismaledimide
c	N,N'-1,3'-Phenylenebismaleimide
d	N,N'-1,4'-Phenylenebismaleimide

aromatized polyimides IVa–d start to degrade at 325°C. On the other hand polyimides Va–d obtained in the solid phase start degrading at 350°C. The lower thermal stability of the produced polyimides samples compared to that of well known commercial polyimides may be due to their asymmetrical molecular structures. The well known polyimides are mainly linear and symmetrical. However, the produced polyimides are based on linear FF resin I and bismaleimides IIa–d. Hence the DA reaction lead to cross linking (see Scheme I). The major advantages of the produced polyimides consists in their solvent, weather, acid and alkali resistivity. Comparison of the thermal stability of the produced polyimides based in FF resin with the polyimides based on FA resin [Poly(2,5-furandiyl-methylene)] prepared by us[1,2] reveals that the produced polyimide have somewhat higher thermal stability (ca. ~350°C) than FA based polyimides.

Because of non-processability of the present insoluble polyimides, quantitative observation were made on "in situ" glass reinforcement using a mixture of FF resin (I) and bismaleimides (II) in an organic solvent. It was noted that laminate sheets could be made at lower temperature. The synthesis of polyimides based on various bismaleimides (II) on a wide range of structure, optimization of fabrication conditions and evaluation of properties of composites are in progress.

3. EXPERIMENTAL PROCEDURES

Material

2-Furanmethanol and formaldehyde were obtained from SD fine chemical limited, Boisar, India and were purified by method reported in literature. Diamines used were obtained from SDS Chemical, Boisar, India. All other chemical used were of laboratory grade.

Bis(maleimide) Synthesis

Bis(maleimide) IIa–d listed in Table I were prepared by methods reported in literature.[9,10]

TABLE II

Characterization of unaromatized polyimides (IIIa–d)

P.I.	ELEMENTAL ANALYSIS												
Poly-imide	YIELD %	% C		% H		% N		WEIGHT LOSS AT VARIOUS TEMP. (%					
		CALC	FOUND	CALC	FOUND	CALC	FOUND	300	400	500	600	700	750
3a	77	56.97	55.8	5.63	5.4	4.15	4.0	8	36	50	64	73	80
3b	78	59.83	57.8	5.26	5.0	3.82	3.6	6	42	52	67	77	81
3c	80	59.83	57.8	5.26	5.0	3.82	3.6	7	38	46	62	72	73
3d	79	57.00	55.9	5.20	5.0	3.50	3.3	5	10	3	56	62	75

TABLE III

Characterization of aromatic polyimides (IVa–d)

Poly-imides	YIELD %	% C		% H		% N		WEIGHT LOSS AT VARIOUS TEMP. (%)					
		CALC	FOUND	CALC	FOUND	CALC	FOUND	300	400	500	600	700	750
4a	76	55.46	54.0	5.04	4.7	5.88	5.7	8	26	44	57	66	81
4b	77	59.54	58.1	4.58	4.3	5.34	5.2	7	27	47	54	70	77
4c	79	59.54	58.1	4.58	4.3	5.34	5.2	8	30	45	60	68	80
4d	78	64.00	62.8	4.66	4.4	4.66	4.6	6	28	50	58	66	77

TABLE IV

Characterization of bulk-phase polyimides (Va–d)

	ELEMENTAL ANALYSIS												
Poly-imides	YIELD %	% C		% H		% N		WEIGHT LOSS AT VARIOUS TEMP. (%)					
		CALC	FOUND	CALC	FOUND	CALC	FOUND	300	400	500	600	700	750
5a	74	55.46	54.0	5.04	4.7	5.88	5.7	4	22	40	53	62	77
5b	79	59.54	58.1	4.58	4.3	5.34	5.2	3	23	96	50	66	73
5c	77	59.34	58.1	4.58	4.3	5.34	5.2	2	24	46	54	62	73
5d	75	64.00	62.9	4.66	4.4	4.66	4.6	4	26	32	56	64	76

Preparation of 2-Furanmethanol-Formaldehyde (FF) I Resin

Polymerization of 2-furanmethanol with formaldehyde in presence of aq. acid was carried out by method reported in literature.[5] 15 gms. of FA and 7.5 gms of formaldehyde (37%) were heated in the presence of 0.12 ml of dil. phosphoric acid for 90 min. The resultant resin was then neutralized to pH 4–5 with NaOH (aq.), cooled to 70°C and dehydrated by vacuum. The dark viscous liquid was 17 gm.

Solution Polymerization

To a solution of I (i.e. PFF) (0.02 mol) in 50 ml THF, bismaleimide (IIa–d) was added gradually at room temperature. The mixture was heated on a water bath (~90°C) for 6 hr. The resulting mixture was cooled and poured into 75:25 (v/v) water/methanol. The precipitate of polyimide IIIa was filtered off and dried. It was treated twice with hot DMF (15 ml) to remove unreacted I and IIa. Aromatization of IIIa was carried out by refluxing 2 g of the dried sample IIIa in 2 ml of acetic anhydried for 4 hr. Then the resulting mixture was poured in to water. The precipitate of aromatized polymer IVa was filtered off, washed are with water and methanol. The yield of all unaromatized (IIIa–d) and aromatized polyimides (IVa–d) are included in Tables II and III.

Bulk Polymerization

A mixture of I (0.01 mole) and IIa–d (0.05 mole) was suspended in dry THF (25 ml) then spread into a petri dish and THF was evaporated at room temperature. The dried mixture was heated at 105°C for six hours and then heated with acetic anhydride (2 ml) at 128 + 5°C for six hours with vigorous agitation. The resulting solid product Va was treated as described above. Polymers Va–d were obtained similarly and are included in Table IV.

4. MEASUREMENTS

The C, H, N contents of the all polyimides 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) (AMB 10-800). DuPont 9900 thermogravimetric analyzer in air at heating rate 10 K/min air purge 100 ml/min.

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