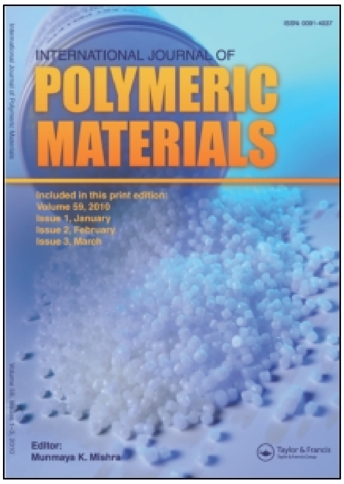

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Prabhu, Keshav G. and Patel, Hasmukh S.(2001) 'Modified Polyimides Based on Epoxy Resin (Part 2)', International Journal of Polymeric Materials, 50: 1, 93 — 107

To link to this Article: DOI: 10.1080/00914030108035093

URL: http://dx.doi.org/10.1080/00914030108035093

Intern. J. Polymeric Mater., 2001, Vol. 50, pp. 93–107
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Modified Polyimides Based on Epoxy Resin (Part 2)

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(Received 14 March 2000; In final form 25 March 2000)

A 2-furanyl oxy derivative of a novolac epoxy resin (FNE) was prepared using furfuryl alcohol (from agricultural waste) and characterised. The Diels–Alder polymerisation of FNE with various bismaleimides was carried out in solution as well as in bulk. The resultant novolac epoxy resin based polyimides were characterised by elemental analyses, IR spectral studies, and thermogravimetry. The '*in-situ*' glass reinforced composites of FNE-bismaleimides were prepared and characterised by chemical resistance and mechanical properties.

Keywords: Polyimides; Diels–Alder; Epoxy-resin; Composites

1. INTRODUCTION

Among high performance polymers, polyimides are prime candidates and find applications from microelectronics to aerospace applications. Their key drawback is that because of their insolubility and infusibility they are difficult to process at ambient temperatures. This has been achieved by introducing flexible functional group into the polymer chain. Several modifications have been made to improve the processing conditions without dilution of the properties [1]. Both addition and condensation polymerisation have been adopted. Addition polymerisation of bismaleimides yields brittle PIs with low performance. The objective of the present work was to modify the polymerisation

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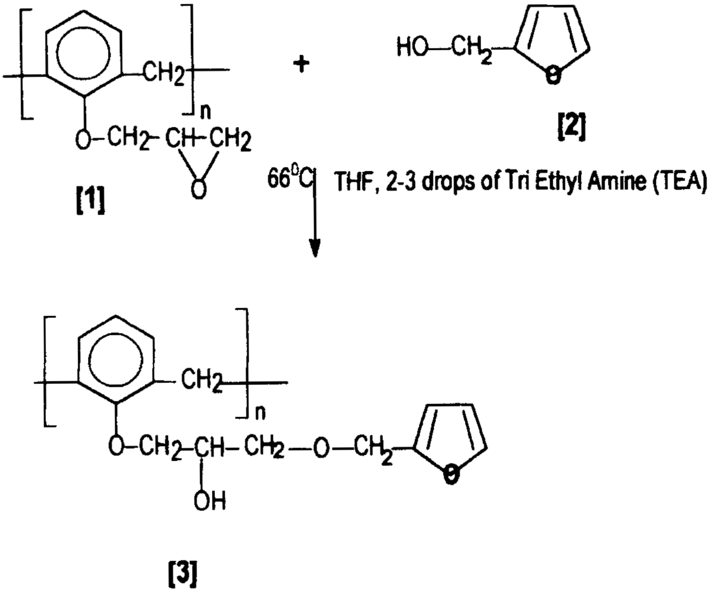


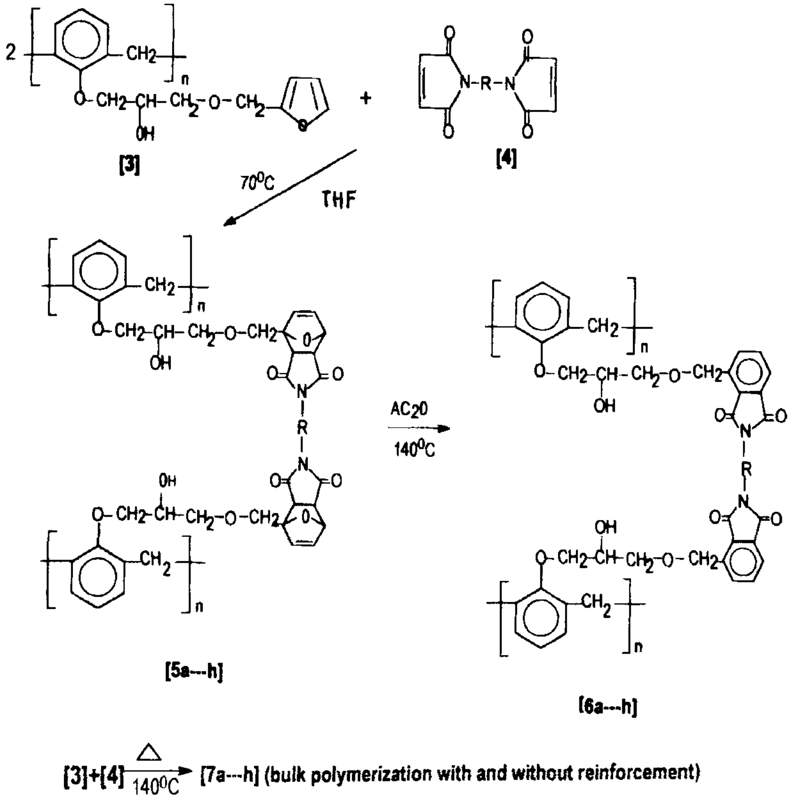
SCHEME 1

method, improve the properties of polyimides and ease of processing for polyimides. One of the authors and his co-workers adopted these views and succeeded in forming processable polyimides [2–6]. In these reports, the Diels Alder (DA) reaction of furan derivatives and bismaleimides has been carried out and '*in-situ*' glass reinforced composites were processed at lower temperatures. The merging of a flexible segment epoxy group and hard segments phenolics and polyimide into a polymer chain may alter the properties of polyimides to some extent. With this view and the above mentioned objective the authors reported [15] the initial work entitled "Modified polyimides based on novolac epoxy resin 1". The present continuation of the work comprises in Schemes 1 and 2.

2. EXPERIMENTAL DETAILS

2.1. Materials

Furfuryl alchol was purchased from Chitti Chem. (Baroda, India), and redistilled before use. Tetrahydrofuran and diethyl ether were dried



SCHEME 2

before use. A commercial novolak epoxy resin was procured from Synpol Products Pvt. Ltd. (India).

The specifications of the epoxy resin were as follows:

(1) Epoxy equivalent weight: 180–190
(2) Viscosity: 5–15 poises at 25°C
(3) Density at 25°C: 1.22–1.24 g/cm^3

All other chemicals used were of laboratory grade. Satin (2/2) weave (polyimide compatible) fibre glass woven fabric, 0.25 mm thick, *E*-type (Unnati Chemicals, India), 270 m/m^2 was used for composite preparation. Bis(maleimido) compounds were prepared by a modification of the process reported earlier and are listed [7, 8].

TABLE I Bis(maleimido) compounds used

No.	*Bismaleimides*	*Mol. wt.*	*M.P. (°C)*
[a]	Ethylene bismaleimide (EBM)	220	189–190
[b]	1,4- Phenylene bismaleimide (MBM)	268	300
[c]	4,4- Diaminodiphenyl methane bismaleimide (DDMBM)	358	156–158
[d]	4,4-Biphenylene bismaleimide(BBM)	344	300
[e]	Hexamethylene bismaleimide(HMBM)	276	138–140
[f]	1,3-Phenylene bismaleimide(PBM)	268	202–203
[g]	4,4-Diaminophenyl sulfone bismaleimide (DDSBM)	408	254–255
[h]	4,4-Diaminodiphenyl ether bismaleimide(DDEBM)	360	179–181

TABLE II Analysis of furan derivative

($C_{15}H_{16}O_4$) (260)	C(%)	H(%)	O(%)
Calculated	60.82	6.10	24.61
Found	59.98	5.88	23.50

2.2. Preparation of Furan Derivative of Novolak Epoxy Resin

A mixture of 2-furanmethane alcohol (10 millimole), novolak epoxy resin (10 millimole) and 3 to 4 drops of triethylamine(TEA) was heated at 65 ± 2°C for 4 h. The resultant mixture was poured into 250 ml of dry ether and the unreacted reactants removed by decantation. The resultant reddish brown viscous liquid was vacuum distilled to remove any remaining solvent. Analyses of the resultant furan derivative, designated as **3** (Scheme 1), are as follows:

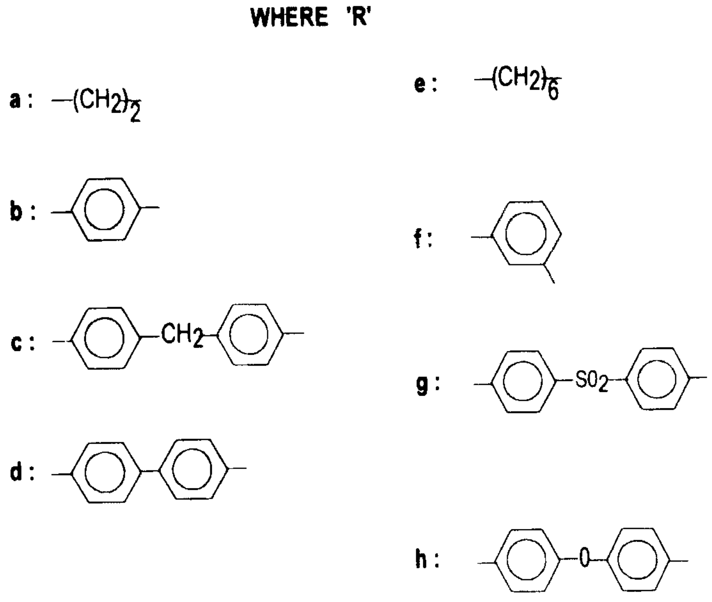
IR spectral features were as follows (in KBr):

2-furanyl (3 H)	~762 cm^{-1}(m)
Furan ring -	~1125 cm^{-1}(v)
$-CH_2-O-CH_2-$	~1100 cm^{-1}(s)
HC—OH (secondary) -	~1360 cm^{-1}(m)
$Ar-O-CH_2-$	~1246 cm^{-1}(m)

2.3. Preparation of Poly(ether-imide) (PEI)

The Diels Alder reaction of **3** with various bis(maleimido)-compounds (**4a-h**) was carried out both in solution and in bulk.

Typical Syntheses



SCHEME 3

2.3.1. Solution Polymerization

3 (20 g, 0.077 mole) in 100 ml of dry THF was mixed with **4c** (13 g, 0.037 mole) and the mixture was refluxed at 70°C for 4 to 5 h. The resulting mixture was cooled and poured into water. The precipitate of poly(ether-imide)s was filtered and dried. It was treated twice with hot DMF (15 ml) to remove unreacted **3** and **4c**. Aromatization of poly (ether-imide) **5c** was carried out by refluxing 2 g of dried sample **5c** in 2 ml of acetic anhydride for 4 h [9]. The resulting mixture was poured into water. The precipitate of aromatized poly(ether-imide) **6c** was filtered and washed with water. The yields of unaromatized and aromatized polyimides are summarised in Tables III and IV respectively.

2.3.2. Bulk Polymerization

A mixture of **3** (13 g, 0.05 mole) and **4c** (8.5 g, 0.025 mole) was suspended in 25 ml of dry THF, then spread into a petri dish, and the

TABLE III Characterization of non-aromatic poly(ether-imide)s 5a-h

Polymer	*Elemental analysis (Wt. %)*				*Weight loss (%) at various temperatures (°C)*			
sample		**Calc.*	*Found*	*Yield (%)*	300	400	500	700
5a	C	62.42	61.52	72	3.6	20.5	42.0	86.4
	H	5.78	5.5					
	N	4.03	3.74					
5b	C	64.86	63.96	70	3.7	26.0	51.5	87.6
	H	5.40	5.12					
	N	3.78	3.47					
5c	C	67.95	67.05	73	3.5	28.0	48.0	93.5
	H	5.54	4.87					
	N	3.37	3.06					
5d	C	67.64	63.27	76	3.6	30.0	53.0	92.6
	H	5.14	4.87					
	N	3.43	3.12					
5e	C	64.17	63.27	71	3.7	23.0	54.0	93.7
	H	6.41	6.12					
	N	3.74	3.43					
5f	C	64.86	63.92	70	3.7	25.0	55.0	96.4
	H	5.40	5.29					
	N	3.78	3.42					
5g	C	62.72	61.82	72	3.6	27.0	58.0	98.5
	H	5.00	4.72					
	N	3.18	2.87					
5h	C	66.34	65.44	75	3.6	28.0	60.0	98.8
	H	5.28	5.01					
	N	3.36	3.05					

*Calculated values are based on approximate repeat units.

TABLE IV Characterization of aromatic poly(ether-imide)s 6a-h

Polymer	*Elemental analysis* (*Wt.* %)				*Weight loss* (%) *at various temperatures* (°*C*)			
sample		**Calc.*	*Found*	*Yield* (%)	300	400	500	700
6a	C	64.09	63.19	79	3.4	18.5	40.5	82.2
	H	5.63	5.35					
	N	4.15	3.84					
6b	C	66.48	65.58	82	3.5	24.0	49.5	85.8
	H	5.26	4.98					
	N	3.87	3.56					
6c	C	69.45	68.55	80	3.3	26.0	47.0	91.5
	H	5.41	5.13					
	N	3.44	2.83					
6d	C	69.17	68.27	81	3.4	26.2	51.2	91.4
	H	5.26	4.98					
	N	3.50	3.19					
6e	C	65.75	64.85	80	3.5	21.1	52.5	91.7
	H	6.30	6.02					
	N	3.83	3.52					
6f	C	66.48	65.52	81	3.5	23.0	53.2	95.4
	H	5.26	4.92					
	N	3.87	3.54					
6g	C	64.03	63.13	81	3.4	25.2	56.1	96.8
	H	4.87	4.54					
	N	3.24	2.93					
6h	C	67.81	66.91	79	3.4	26.3	58.0	97.1
	H	5.15	4.87					
	N	3.43	3.12					

*Calculated values are based on approximate repeat units.

TABLE V Characterization of bulk phase poly(ether-imide)s 7a-h

Polymer	*Elemental analysis (Wt. %)*				*Weight loss (%) at various temperatures (°C)*			
sample		** Calc.*	*Found*	*Yield (%)*	300	400	500	700
7a	C	64.09	63.17	80	3.3	16.3	39.1	81.1
	H	5.63	5.30					
	N	4.15	3.81					
7b	C	66.48	65.56	83	3.4	21	48.2	83.4
	H	5.26	4.92					
	N	3.87	3.52					
7c	C	69.45	68.53	81	3.3	24.4	45.0	90.5
	H	5.41	5.08					
	N	3.44	2.93					
7d	C	69.17	68.25	82	3.3	24.9	49.2	90.9
	H	5.26	4.91					
	N	3.50	3.14					
7e	C	65.75	64.82	81	3.4	19.5	50.1	90.9
	H	6.30	5.95					
	N	3.83	3.49					
7f	C	66.48	65.66	82	3.4	22.0	52.1	93.9
	H	5.26	4.91					
	N	3.87	3.50					
7g	C	64.03	63.11	82	3.3	23.2	54.9	94.9
	H	4.87	4.52					
	N	3.24	2.92					
7h	C	67.81	66.8	80	3.3	24.1	55.5	95.1
	H	5.15	4.83					
	N	3.43	3.06					

*Calculated values are based on approximate repeat units.

THF evaporated at room temperature. The dried mixture was then heated with acetic anhydride (2 ml) at 125–130°C for 10 h with vigorous stirring. The resulting solid product **7c** was obtained in a similar way. The yields of the aromatized poly(ether-imide)s **7a-h** are included in Table V.

3. COMPOSITE FABRICATION

Suspensions of the furan derivative and various bis(maleimido) compounds in THF were prepared on a weight basis and stirred well for 2 min. To 254 mm × 254 mm fibreglass cloth, the suspension was applied with a brush, and the solvent was allowed to evaporate. The dried prepregs so prepared were stacked one over another and pressed between iron plates with Teflon® film release sheet and compressed in flat platens under 0.48 Mpa pressure. The prepregs were cured by heating to 160°C (± 2°C) for 10 h in an air circulated oven. The composite so obtained was cooled to 50°C before the pressure was released. The composites were then machined to final dimensions for various physical and mechanical tests.

4. ANALYSIS

The C, H and N contents of all the poly(ether-imide)s samples were estimated by means of a Carlo Erba elemental analyser (Italy). The IR spectra were taken in potassium bromide using a Nicolet Impact 400 D spectrophotometer. The thermogravimetry (TG) of all the polymer samples was carried out on a Du-Pont 950-thermogravimetric analyser in air, at a heating rate of 10 K/min.

5. CHEMICAL RESISTANCE TEST

The resistance against chemicals of the composite samples having dimension of 25 mm × 25 mm was measured according to ASTM D543. The data are included in Table VI.

TABLE VI Mechanical and electrical properties of glass – reinforced poly(ether-imide)s ($C_{4a\text{-}d}$)

	** Chemical resistance percent change in*		*Density*	*Flexural strength*	*Compressive strength*	*$Impact strength*	*# Hardness*	*Electrical strength (in air)*
@Composites	*Thickness*	*Weight*	*(g/cm³)*	*(MPa)*	*(MPa)*	*(MPa)*	*(R)*	*(kv/min)*
C_{4a}	1.4	1.3	1.31	327	314	298	128	20.3
C_{4b}	1.5	1.2	1.30	354	325	319	126	19.2
C_{4c}	1.3	1.3	1.35	322	304	285	124	22.4
C_{4d}	1.4	1.1	1.32	302	278	229	120	23.5
C_{4e}	1.5	1.4	1.37	309	283	294	121	24.4
C_{4f}	1.3	1.0	1.36	304	278	246	139	27.3
C_{4g}	1.6	1.3	1.30	357	325	322	122	20.6
C_{4h}	1.4	1.2	1.31	395	267	241	118	19.8

@Reinforcement: E' type glass cloth, plain weave, 0.254 mm (tenmil), ten layers: Resin content: 40 ± 2 wt. % molar ratio 1 : 2a-h, curing temp: 140 ± 10°C, time: 10H, Pressure: (~)0.50 MPa, Composite size: 254 mm × 254 mm × 3.0 – 3.5 mm thick.

*Chemical resistance to 6.2 Molar NaOH; Composites are unaffected by organic solvents and 1.51 M HCl.

#Hardness in Rockwell(R).

$Impact strength measured by Izod type impact tester.

6. MECHANICAL TESTING

All the mechanical testing were conducted using three test specimens.

- The measurements of flexural strength of composites were done on universal Instron testing machine model number A-74-37 at room temperature according to the testing method of ASTM D770. The crosshead speed was kept at 100 mm/min with 0.5 cm/min of chart speed.
- The compressive strength was measured according to ASTM D695 having 12.5 mm cube.
- Impact strength measurements were done according the testing method of ASTM D256 with an Izod type impact tester at room temperature.
- The hardness strength (Rockwell) was measured according to ASTM D785, having dimension of 25 mm width and 25 mm long specimens.
- Dielectric strength measurements were done on a high voltage tester machine-oil test set.

All the mechanical and electrical properties of composites are furnished in Table VI.

7. RESULTS AND DISCUSSIONS

The reaction of epoxy resin novolac (**1**) in the presence of excess 2-furanmethane alcohol (**2**) was performed according to a previously reported method [10]. The resulting furan derivative from the epoxy resin was isolated as a reddish brown thick viscous liquid. The yield was around 80%. The C, H and N contents of **3** were in good agreement with the structure proposed in Scheme 1.

Examination of the IR spectra of all polyimides reveals that all the spectra comprise important characteristic bands of the imide group. The bands around 1716 cm^{-1}, 1770 cm^{-1}, 1140 cm^{-1} and 780 cm^{-1}, are believed to be contributions from imides. Polyimide comprises of the bands around 3039, 1602, 1570 and 829 cm^{-1} due to aromatic system. A sharp and well-resolved medium band at around 1290 cm^{-1} may be assigned to the $-Ar-O-CH_2-$ linkage. The strong and sharp bands around 1350 and 1180 cm^{-1} may be assigned to the secondary —OH groups formed from the epoxy group. The discernible difference between the IR spectrum of the novolac epoxy and that of the 2-furan methyl alcohol derivative of the epoxy resin is that in the IR spectrum of the furan derivative there is no band at 910 cm^{-1} related to the epoxy ring.

The absence of an epoxy ring in the furan sample was further confirmed by the epoxy equivalent determination method. The effect of TEA on the novolac epoxy resin was found to negligible, as there was no significant change in the properties of the epoxy resin when heated at 85°C for 3 to 4 h under the same experimental conditions. However, the properties are altered at elevated temperature or by the addition of a Lewis acid [11]. The furan derivative (**3**) was obtained as a viscous liquid, which remained in that form even after 6 to 7 months, by storage in a vacuum desiccator. The efflux viscosity time at room temperature (32°C) for the flow of furan derivative (**3**) remains constant during the storage period.

The entire synthesis of poly(ether-imide)s (PEIs) through the DA reaction of furan derivative **3** with different bismaleimides **4a-h** is shown in Scheme 2. First, the non-aromatized product **5a-h** is formed, which is then aromatized by treatment with acetic anhydride to yield 6a-h. In the absence of **4a-h**, heating of **3** in THF at 70°C does not alter the properties of **3**. It was also noted that heating of **4a-h** in THF at 70°C does not induce the addition polymerisation of **4a-h**. This is possible only at an elevated temperature or in the presence of an initiator [12–14]. However, to safeguard the reaction against unsaturation a little hydroquinone was added during the DA reaction of **3** and **4**. The entire PI samples were obtained in good yields in the form of dark brown to pink solid powders. They were insoluble in common organic solvents and were not affected by concentrated mineral acids or formic acid. The elemental analyses of all polyimides samples, shown in Tables III to V are consistent with their predicted structure (Schemes 1 and 2). The typical thermograms are shown in Figure 1.

The thermogravimetric data of all polyimides are listed in Tables III to V. The thermogravimetric data on examination reveals that the polyimide samples start their decomposition between ~350–500°C, depending upon the polyimide formation. The rate of weight loss is

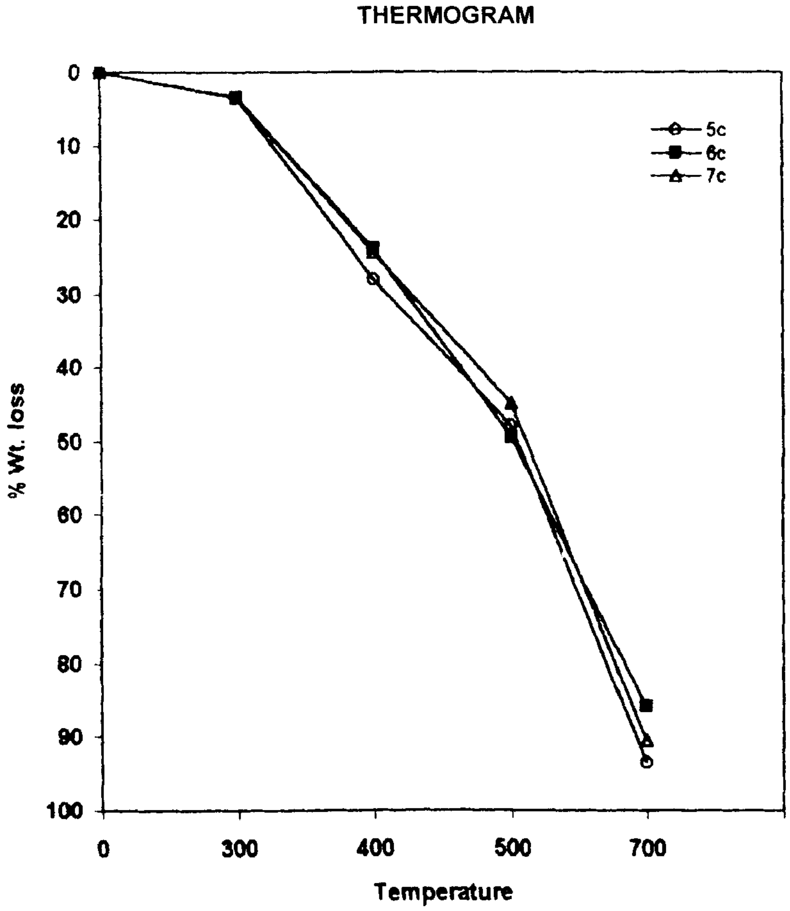


FIGURE 1 Thermograms of polyimide samples 5c, 6c and 7c.

high around 500°C and completed at ~700°C. The non aromatized polyimides **5a-h** start their degradation at around 500°C whereas aromatized polyimides **6a-h** start to degrade at a slightly higher temperature (~550°C). On the other hand, polyimides **7a-h** obtained in solid phase, start degrading at around ~600°C.

The present polyimides are thermally stable and they retain acid, solvent, and weather resistance. Because of non-processability of the present polyimides, a novel approach was also conducted to develop matrices system for processable (160 ± 10°C) polyimide glass fibre composites. The addition polymerisation by the DA reaction of **3** with **4** starts from the surface of the composite, from which the polymerisation continues towards the inner part of the composite without evaporation of any reaction by-products or solvent molecules.

8. CONCLUSIONS

The advantages of furan derivatives and bismaleimide composite systems are as follows:

- The inter molecular DA reaction of furan derivatives of novolak epoxy resin with bismaleimides resulted in polyimides with good resistance to mineral acids, alkali and organic solvents, heat resistance.
- Composites could be prepared with good mechanical properties.
- The '*in-situ*' produced Poly(ether-imide)s show good adhesion to glass fibres.

Acknowledgements

The authors are grateful to UGC, New Delhi for providing a research grant. The authors are also grateful to Prof. H. C. Trivedi, Head, Department of Chemistry for providing the necessary facilities.

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