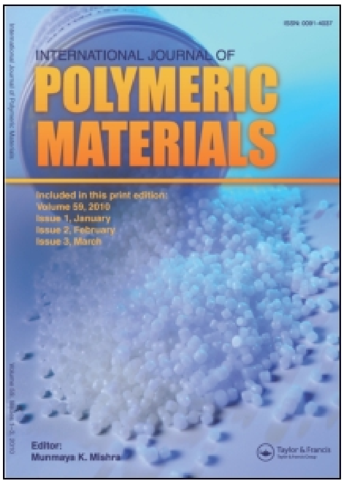

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Synthesis, Characterization and Glass-Reinforced Composites of Poly(Ether-imide)s Based on Epoxy Resin: II

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Synthesis, Characterization and Glass-Reinforced Composites of Poly(Ether-imide)s Based on Epoxy Resin: II

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Novel poly(ether-imide)s were prepared by Diels-Alder (DA) reaction of 1,1′-(1-methylethylidene)bis[4-{1-(2-furanyl-methoxy)-2-propanoloxy}] benzene with various bismaleimides. The DA reaction was carried out in solution using tetrahydrofuran (THF) as solvent, as well as in bulk. The post polymerization, involving aromatization of tetrahydrophthalimide intermediates was accomplished in the presence of acetic anhydride. All the poly(ether-imide)s were characterized by elemental analyses, infrared spectrometry and thermogravimetry. The glass reinforced composites of produced PEIs have also been prepared and characterized.

KEY WORDS Epoxy resin-diglycidyl ether of bisphenol-A (DGEBA), polyetherimides (PEIs), Diels-Alder reaction, thermogravimetry, glass fibre reinforced composites, mechanical properties.

INTRODUCTION

In an earlier communication[1] one of the authors (HSP) reported that the bisfuran (a diene) derivative of epoxy resin; diglycidyl ether of bisphenol-A (DGEBA) and bismaleimide (a dienophile) affords poly(ether-imide) through DA reaction. In continuation of this work[1] the present paper comprises synthesis, characterization and glass reinforcement of new PEIs based on epoxy resin-DGEBA (Scheme I).

RESULTS AND DISCUSSION

The entire work comprises the poly(ether-imide)s (PEIs) formation through the DA reaction of the bisfuran derivative III with bismaleimides IV(a–h) is shown in Scheme I.

First, the non-aromatized product V(a–h) is formed, which is then aromatized by treatment with acetic anhydride to yield VI(a–h). In the absence of IV(a–h), heating of III in THF at 70°C does not alter the properties of III. It was also observed that

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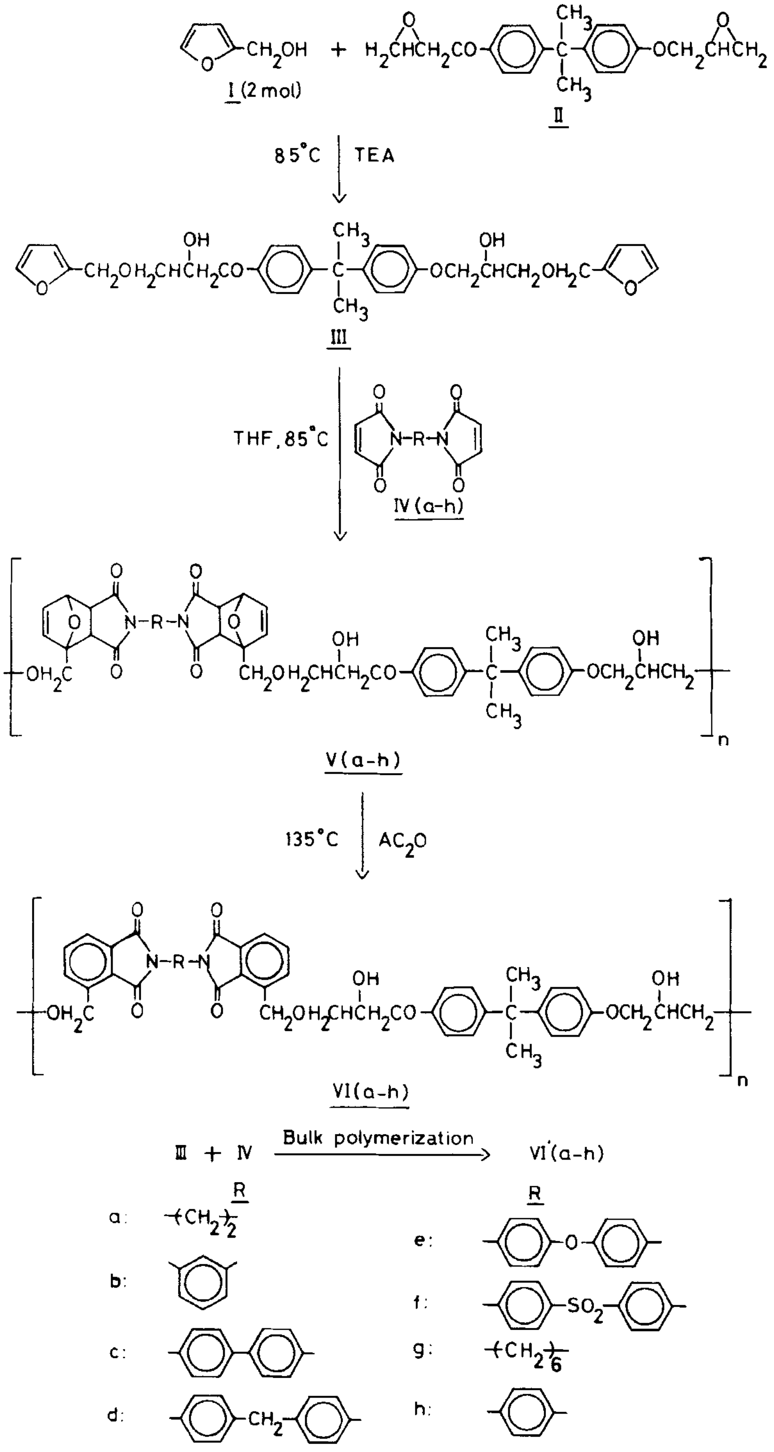
*To whom all correspondence should be addressed.


I (2 mol)
II
85°C
TEA
III
THF, 85°C
IV (a-h)
V (a-h)
135°C
AC2O
VI (a-h)
III + IV
Bulk polymerization
VI'(a-h)
R
a:
b:
c:
d:
e:
f:
g:
h:

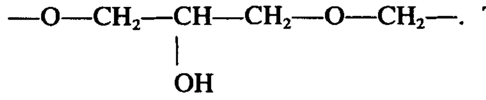
SCHEME I

TABLE I

Bismaleimide used

		Bis(maleimide)	m.p (°C)
IV	a	N,N′-ethylene bismaleimide	189–190
IV	b	N,N′-1,3-phenylene bismaleimide	202–203
IV	c	N,N′-(1,1′-biphenyl)-4,4′-diyl bismaleimide	>300
IV	d	1,1′-(methylene-di-4,4′-phenylene)-bismaleimide	156–158
IV	e	1,1′-(oxy-di-4,4′-phenylene)-bismaleimide	179–182
IV	f	1,1′-(sulfonyl-di-4,4′-phyenylene)-bismaleimide	253–255
IV	g	N,N′-hexamethylene bismaleimide	138–139
IV	h	N,N′-1,4-phenyle bismaleimide	>300

heating of IV(a–h) in THF at 70°C does not induce the addition polymerization of IV(a–h). This is possible only at elevated temperature or in the presence of an initiator.[4–6] However, to safeguard the reaction against unsaturation a little hydroquinone was added during the DA reaction of III and IV. All the PEI samples were obtained in good yields in the form of dark yellow to brown solid powders. They were insoluble in common organic solvents and were not affected by concentrated mineral acids and formic acid. The elemental analysis of all the PEI samples, shown in Tables II–IV are consistent with their predicted structure (Scheme I).

Examination of IR spectra (not shown) of all PEIs reveals that all the spectra comprise important characteristic bands of the imide group. The bands around 1700, 1650, 1050 and 730 cm^{-1} are contributions from imide groups. As the PEIs comprise bisphenol moieties, the IR spectra of all the PEIs comprise the bands 3030, 1600, 1580 and 830 cm^{-1} due to the aromatic system. However, no separate bands were observed from aromatization of the tetrahydrophthalimide V(a–h). All the spectra show the characteristic bands (mentioned earlier) of the aliphatic chains of the monomer bisfuran (III)  $—O—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—O—CH_2—$. The IR spectra (not shown) of polymers VI(a–h) also comprise all the characteristics of the imide group, indicating that the solid-phase polymerization also yields poly(ether-imide)s.

Examination of TGA data (Tables II–IV) (figure is not shown) show that the produced PEI samples start their decomposition between 225 to 250°C depending upon the nature of the polyimides. The rate of weight loss is high around 450°C and it complete at 600°C. The unaromatized PEIs V(a–h) start their degradation at around 225°C, whereas the aromatized PEIs VI(a–h) start to degrade at a slightly higher temperature 230°C. On the other hand PEIs VI(a–h) obtained in the solid phase start degradation at around 250°C. The lower thermal stability of the PEIs sample produced compared to that of well known commercial PEIs may be due to presence of

TABLE II

Characterization of non-aromatic poly(ether-imide)s V(a–f)

Poly (ether-imide)s	Yield (%)	Elemental analysis						% weight loss at °C from TGA				
		C(%)		H(%)		N(%)						
		calc.	found	calc.	found	calc.	found	250	300	400	500	600
Va	65	65.07	65.00	5.82	6.00	3.70	3.80	2.2	9.8	34.8	54.2	90.1
Vb	70	67.16	67.06	5.47	5.50	3.48	3.50	2.2	9.9	35.0	54.9	90.0
Vc	72	69.79	69.81	5.59	5.60	3.13	3.03	2.2	10.0	35.0	55.0	90.2
Vd	70	69.54	69.44	5.45	5.40	3.18	3.20	2.5	10.0	35.2	55.0	90.0
Ve	67	68.30	68.19	5.35	5.24	3.12	3.10	2.2	10.0	35.0	54.2	90.0
Vf	71	64.83	64.80	5.08	5.00	2.96	3.00	2.0	10.0	35.0	55.0	90.0

TABLE III

Characterization of aromatic poly(ether-imide)s VI(a–f)

Poly (ether-imide)s	Yield (%)	Elemental analysis						% weight loss at °C from TGA				
		C(%)		H(%)		N(%)						
		calc.	found	calc.	found	calc.	found	250	300	400	500	600
VI a	65	68.33	68.30	5.55	5.60	3.88	3.90	1.0	8.2	33.0	53.0	92.0
VI b	63	70.30	70.00	5.20	5.22	3.64	3.68	1.0	9.0	33.2	53.1	91.0
VI c	69	72.51	72.50	5.01	5.10	3.31	3.38	1.0	9.0	32.0	53.5	91.0
VI d	60	72.72	72.80	5.36	5.40	3.26	3.30	1.0	8.0	32.0	52.4	90.0
VI e	59	71.16	71.00	5.11	5.10	3.25	3.30	1.0	8.0	30.0	50.0	92.0
VI f	59	67.40	67.50	4.84	4.90	3.08	3.00	1.0	8.5	30.0	48.1	90.0

TABLE IV

Characterization of bulk-phase poly(ether-imide)s VI'(a–f)

Poly (ether-imide)s	Yield (%)	Elemental analysis						% weight loss at °C from TGA				
		C(%)		H(%)		N(%)						
		calc.	found	calc.	found	calc.	found	300	350	400	500	600
VI'a	65.0	68.33	68.30	5.55	5.60	3.88	3.90	1.0	9.0	31.0	50.0	92.0
VI'b	69.0	70.3	70.0	5.20	5.22	3.64	3.68	1.1	9.5	31.2	50.0	92.0
VI'c	69.9	72.51	72.50	5.01	5.10	3.31	3.38	1.0	9.5	30.6	50.0	92.3
VI'd	65.0	72.72	72.8	5.36	5.40	3.26	3.30	1.0	9.0	31.0	50.1	94.0
VI'e	62.0	71.16	71.0	5.11	5.10	3.25	3.30	1.0	9.2	32.0	50.6	90.0
VI'f	63.0	67.4	67.5	4.84	4.90	3.08	3.00	1.2	9.0	31.2	49.6	91.0

the aliphatic moiety in the polymer chain. The well known PEIs are mainly aromatic and symmetrical.[7]

All the composites prepared at 140°C are in the form of dark brown sheets. The specific gravity of all composites are in the range of 1.20–1.27 (Table V). The results of the chemical resistance of all the PEIs composites (Table V) to organic solvents, acids and alkali reveal that the organic solvents and concentrated acids did not affect the composites which have remarkable resistance to them.

The mechanical properties of all the PEIs composites are shown in Table V. Examination of the results reveals that all the composites have good mechanical properties. The overall trends of the mechanical properties of the prepared PEIs composite decrease as follows:

$$C_g > C_b > C_a > C_c > C_e > C_f > C_d > C_h.$$

This may be attributed to a certain increase in the rigidity of the bismaleimide component. The electrical strengths of all the composites are in the range 19.0–27.2 kV mm^{-1}.

EXPERIMENTAL

Materials

2-Furanmethanol was obtained from SDS chemicals, Boisar, India. Various bismaleimides IV(a–h) listed in Table I were prepared by modification of the process reported previously.[2,3] Commercial epoxy resin; diglycidyl ether of bisphenol-A (DGEBA) was obtained from Synpol Products Pvt. Ltd., Ahmedabad, India. The specifications of DGEBA are as follows:

1. epoxy equivalent weight, 190;
2. viscosity, 40–100 Poise at 25°C;
3. density at 25°C, 1.16–1.17 g cm^{-3}.

All other chemicals used were of laboratory grade.

Preparation of Bisfuran Derivatives Based on Epoxy Resin; Diglycidyl Ether of Bisphenol-A (DGEBA)

Formation of 1,1'-(1-methylethylidene) bis[4-{1-(2-furanylmethoxy)-2-propanolyl-oxy}] benzene III. This was prepared by the reaction of 2-furanmethanol and DGEBA epoxy resin following the method reported in an earlier communication.[1]

Synthesis of PEIs from Bisfuran Derivatives of Epoxy Resin and Bismaleimides

Various PEIs formation through the DA reaction of bisfuran derivative-III with different bismaleimides IV(a–h) listed in Table I was carried out both in solution and in the bulk phase system following the methods reported in an earlier communication.[1]

TABLE V

Mechanical and electrical properties of glass-reinforced PEIs

Composite[a]	% Change on exposure to 25% (W/V) NaOH[b]		Specific gravity	Flexural strength	Compressive strength	Impact strength	Rockwell hardness (in air)	Electrical strength
	Thickness	Weight		(mPa)	(mPa)	(mPa)		(kV mm^{-1})
C a	1.7	1.5	1.21	315	291	273	110	20.4
C b	1.6	1.5	1.20	331	301	297	109	19.0
C c	1.7	1.5	1.25	302	281	260	106	22.1
C d	1.6	1.5	1.22	280	253	223	103	23.0
C e	1.8	1.6	1.27	287	260	271	102	24.2
C f	1.7	1.6	1.26	280	255	224	121	27.2
C g	1.9	1.7	1.20	335	302	301	105	19.2
C h	1.6	1.4	1.20	273	242	219	101	19.2

[a] Conditions. Reinforcement: E glass cloth; Plain wave, 10 mm; 10 layers. Resin content, 50 ± 2%; mole ratio (bismaleimide: Bisfuran DGEABA), 1:1, curing temperature, 140 ± 10°C; time 10 h; pressure, 60–70 Psi. Composite size: 25 mm × 25 mm, 3.0–3.5 mm thick.

[b] Unaffected by organic solvents and concentrated mineral acids (25% V/V).

Composite Fabrication

A typical method of fabrication for composites is given below.

A suspension of bisfuran derivative (III) and bismaleimide IV(a–h) in tetrahydrofuran was prepared and was stirred well for 2 min. The suspension mixture was applied with a brush to a 150 mm × 150 mm fibre glass cloth and the solvent was allowed to evaporate. The 10 dried prepregs were stacked one on top of 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 140 ± 10°C for 10 hrs in an air circulated oven. The composite so obtained was cooled to 50°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimension.

MEASUREMENTS

The C, H and N contents of all the PEIs 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 (Du Pont 950 thermogravimetric analyzer) in air at a heating rate of 10°K min^{-1}.

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

CONCLUSION

The overall advantage of the present Bisfuran derivative and Bismaleimides composites systems are as follows:

—the intermolecular DA reaction of bisfuran derivative of DGEBA with bismaleimides formed PEIs with good resistance to mineral acids, alkali, organic solvents and whethers.
—the 'insitu' produced PEIs show good adhesion to glass fibres.
—void free composites prepared with good mechanical and electrical properties.

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References

1. H. S. Patel and N. R. Patel, *High Perform. Polym.*, **6**, 13–19 (1994).
2. N. E. Searle and H. W. Arnold, US patent 2467835, 1949; *Chem. Abstr.*, **43**, 4421b (1941).

3. J. V. Crivello, *J. Polym. Sci.*, (1976); *Polym. Chem. Edn.*, **14**, 159 (1976).
4. D. Edelmonn and H. Rutler, *Makromol. Chem.*, **194**, 1183 (1993).
5. D. D. Hummel, K. U. Heimen, H. Stenzenberger and H. Sieter, *J. Appl. Polym. Sci.*, **18**, 2015 (1974).
6. T. T. Serafini, P. Delvigs and G. R. Lightsey, *J. Appl. Polym. Sci.*, **16**, 905 (1972).
7. M. A. Androva, M. I. Bessonv, L. A. Louic and A. P. Rudakov, "Polyimides" (Jerusalem:Israel Program for Scientific Translation) 1969.