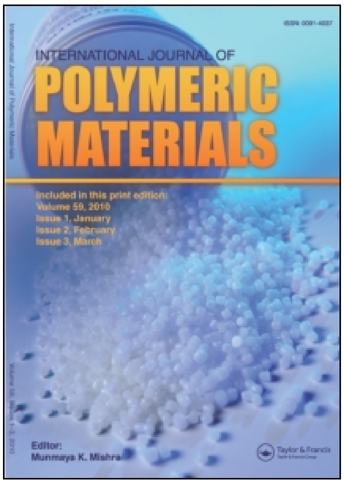


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Polyimides Containing S-Triazine Ring (Part-1)

H. S. Patel[a]; V. C. Patel[a]
[a] Department of Chemistry, Sardar Patel University, Gujarat, India

To cite this Article Patel, H. S. and Patel, V. C.(2000) 'Polyimides Containing S-Triazine Ring (Part-1)', International Journal of Polymeric Materials, 46: 3, 743 — 756
To link to this Article: DOI: 10.1080/00914030008033911
URL: http://dx.doi.org/10.1080/00914030008033911

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 743-756
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Polyimides Containing *S*-Triazine Ring (Part-1)

H. S. PATEL* and V. C. PATEL

Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar-388120, Gujarat, India

(Received 17 February 1999)

Novel polyimides containing *s*-triazine nucleus were prepared *via* Diels-Alder (DA) intermolecular polymerization of 2,4-bis(2-furanyl methyl imino)-4-methoxy-1,3,5-triazine (**1**) with different bis(maleimido) compounds (**2a-h**). The DA reaction was carried out in tetrahydrofuran as solvent, as well as in bulk followed by dehydration on aromatization of poly(tetrahydrophthalimido)-intermediates (**3a-h**) in the presence of acetic anhydride. All the poly(imino *s*-triazine imide)s (**4a-h**) were characterized by elemental analysis, IR spectral studies, and thermogravimetry. **1** and **2a-h** were polymerized (at 150 ± 10°C) by *in-situ* Diels-Alder intermolecular reaction into poly(imino *s*-triazine imide)s-glass fibre reinforced composites (*i.e.*, laminates) without evolution of bi-products. The prepared composites were characterized by chemical resistivity and mechanical properties.

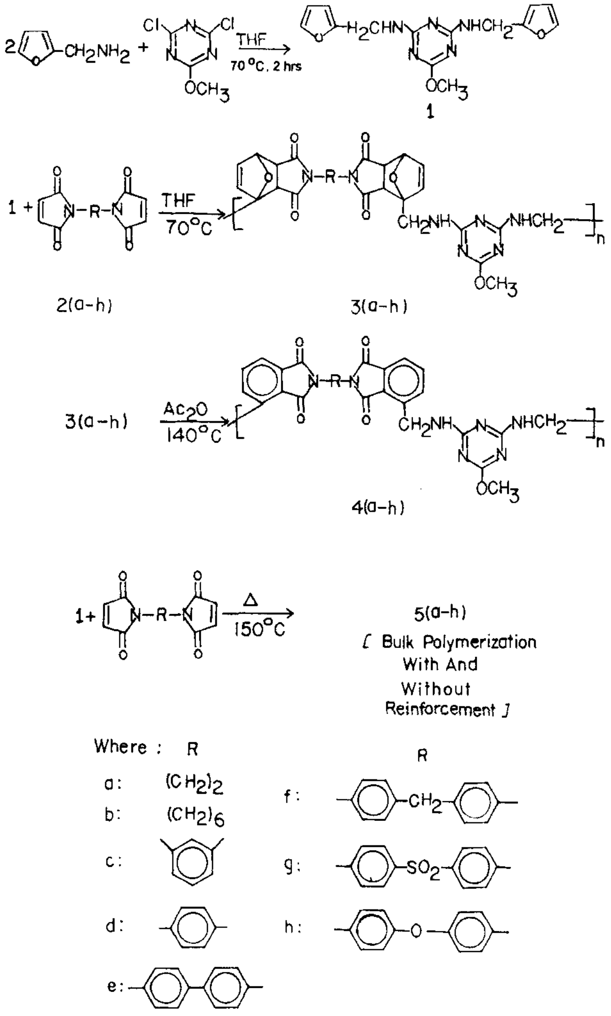
Keywords: Polyimides; triazine ring; composites; properties

INTRODUCTION

The high performance polymers, say polyimides have attained more importance for aerospace applications. The drawback of these polyimides is that they are difficult to process due to high thermal stability and insolubility. Several modifications [1-7] were made to modify the polyimides with a view to improve processing conditions but retaining the original properties. Such approaches were made successfully by introduction of functional groups [1-7]. One of the area in

---

*Corresponding author.



SCHEME 1

which the polyimides containing *s*-triazine nucleus have no attention academically and industrially inspite of the better properties of *s*-triazine polymers like melamine formaldehyde (MF) having excellent thermal and electrical properties [8]. The introduction of *s*-triazine ring into polyimide chain may alter the properties of polyimides upto greater extent. Hence it was thought interesting to explore the polyimides containing *s*-triazine.

The present paper comprises the synthesis and characterization of poly(imino-1,3,5-triazine imide)s. A novel approach was also conducted to prepare a matrix system for processable poly(imino 1,3,5-triazine imide)s-glass fibre reinforced composites based on *in-situ* DA intermolecular addition polymerization of **1** and **2a–h**. The whole research work is scanned in Scheme 1.

EXPERIMENTAL

Furfuryl amine was obtained from Chitichem, India and was redistilled before use. Cyanuric chloride was used as received from Ciba Atul, India. Tetrahydrofuran (THF) and diethyl ether were dried over sodium wire. Bis(maleimido) compounds (**2a–h**) were prepared by modification of the process reported previously [9]. 4-Methoxy-2,6-dichloro-1,3,5-triazine was prepared by method reported in literature [10]. Other chemicals used were of laboratory grade. Satin (2/2) weave (polyimide compatibe) fibre glass woven fabric, 0.25 mm thick, 'E' type, (Unnati chemicals India), 270 m/m^2, was used for laminate preparation.

Preparation of 2,6-bis(2-furanylmethyl imino)-4-methoxy-1,3,5-triazine (1)

This was prepared by method reported by us [11]. Though the report is under consideration, but the process is described below. This was prepared by mixing 2,4-dichloro-6-methoxy-1,3,5-triazine (0.05 mole) and sodium bicarbonate (10.6 gm, 0.1 mole) in dry 250 ml round bottom flask. THF was used as a solvent. To this content furfuryl amine (0.10 mole, d: 1.099) was added drop wise. The reaction mixture was then refluxed at 70°C in water bath for 2 hrs. The resultant mixture was then poured into crushed ice. The precipitates of 2,6-bis-(2-furanyl methyl imino)-4-methoxy-1,3,5-triazine (**1**) were filtered off, washed with ice water twice and water was sucked by vacuum. Light yellow crystalline products were obtained in about 60–70% yield. The bisfuran (**1**) was characterized by IR and NMR spectroscopy as well as by elemental analyses. The melting point of bisfuran (**1**) was 108–9°C (uncorrected). IR and NMR data and elemental analyses are furnished below.

Elemental Analysis

$C_{14}H_{15}N_5O_3$ (301) Calculated	C 55.81	H 4.98	N 23.25
Found	C 55.78	H 4.80	N 23.20

IR Spectra Features

s-triazine: 1260 cm^{-1}, 860 cm^{-1} furan ring: 1615 cm^{-1}, 1510 cm^{-1}, 1390 cm^{-1}
NH(sec): 3300 cm^{-1} —CH_2—: 2850 cm^{-1}, 2980 cm^{-1}
IR spectrum of sample-1 is traced in Figure 1.

NMR Signals

3.8 δ(s; —OCH_3, 3H), 4.5–4.6 δ (d;—NH—CH_2—, 4H), 5.8 δ (hump: —NH—, 2H), 6.2 δ(s; =CH—CH=, 4H), 7.3 δ(s; =CH —O—, 2H).

The NMR spectrum is traced in Figure 2.

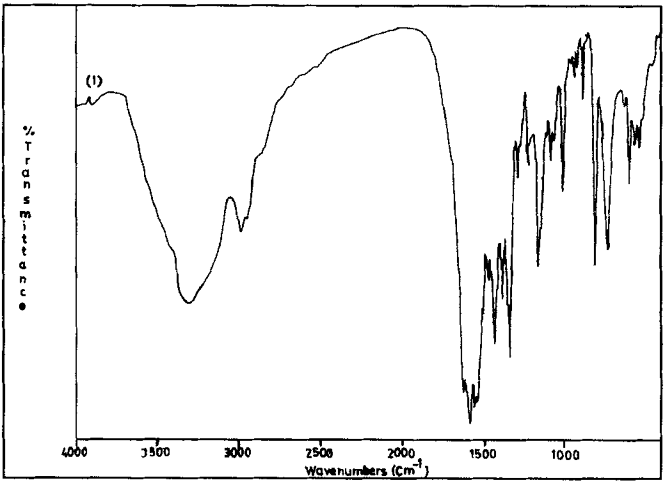


FIGURE 1 IR spectrum of bisfuran-triazine (1).

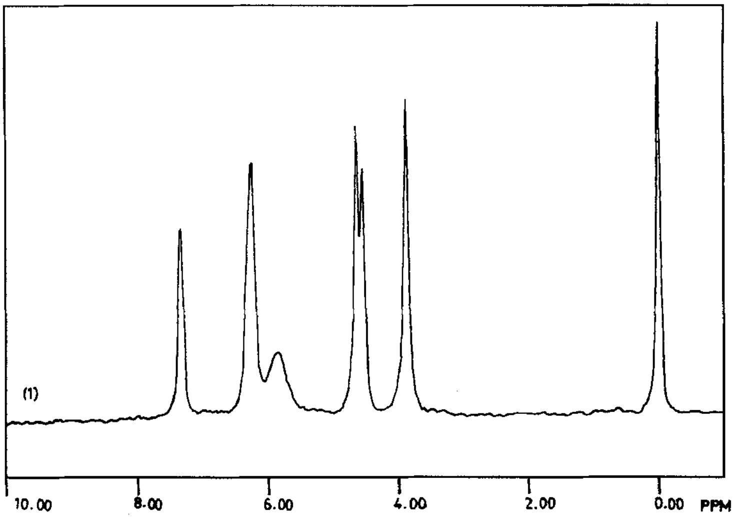


FIGURE 2 NMR spectrum of bisfuran-triazine (1).

Preparation of Poly(imino-1,3,5-triazine imide) (PITI)

The Diels-Alder reaction of 2,4-bis(2-furanyl methyl imino)-4-methoxy-1,3,5-triazine (**1**) with various bis(maleimido)-compounds (**2a**–**h**) was carried out both in solution and bulk phase system. Typical syntheses are given here.

[a] Solution Polymerization

In 100 ml of dry THF **1** (3.01 gm; 0.01 mole) was mixed with **2a** (2.2 gm; 0.01 mole) and the mixture was refluxed at 70°C for 8 hrs. The resulting mixture was then cooled and poured into a large volume of water. The precipitate of PITI (**3a**) was filtered off and dried. It was treated twice with hot DMF (15 ml) to remove unreacted (**1 and 2a**). Aromatization of PITI (**3a**) was carried out by refluxing 1 gm of the dried sample in 1 ml of acetic anhydride for four hrs. The resulting mixture was poured into water. The precipitates of aromatized PITI (**4a**) was filtered off, washed once with water and then with methanol.

[b] Bulk Polymerization

A mixture of **1** (1.502 gm; 0.005 mole) and **2a** (1.1 gm; 0.005 mole) was heated with acetic anhydride (2 ml) at 125 to 135°C for 10 hrs. with vigorous agitation. The resulting solid product (**5a**) was treated as described above. Other PITIs (**3b – h, 4b – h, 5b – h**) were also obtained in a similar way. The yields of prepared PITIs are included in Tables I – III.

COMPOSITE FABRICATION

A suspension of 2,6-bis(2-furanyl methyl imino)-4-methoxy-1,3,5-triazine (**1**) and various bis(maleimido)-compounds (**2a – h**) in tetrahydrofuran was prepared on the weight bases and was stirred well for 2 min. To a 254 mm × 254 mm-fibre glass cloth, the suspension

TABLE I

Characterization of non-aromatized poly(imino-1,3,5-triazineimide)s

Polymer sample	*Molecular formula (formula weight)*	*Elemental analysis (wt%)*			*Yield (%)*	*Weight loss (%) at different temperatures (°C)*					
			Calc.	*Found*		300	400	500	600	700	750
3a	$(C_{24}H_{23}N_7O_7)_n$	C	55.27	55.20							
	521	H	4.41	4.40	81	3	26	48	59	79	92
		N	18.80	18.80							
3b	$(C_{28}H_{31}N_7O_7)_n$	C	58.23	58.20							
	577	H	5.37	5.40	82	3	26	50	61	80	95
		N	16.90	17.00							
3c	$(C_{28}H_{23}N_7O_7)_n$	C	59.05	59.10							
	569	H	4.04	4.10	84	2	24	48	60	74	92
		N	17.22	17.20							
3d	$(C_{28}H_{23}N_7O_7)_n$	C	59.05	59.10							
	569	H	4.04	4.10	80	2	22	42	62	71	90
		N	17.22	17.20							
3e	$(C_{34}H_{27}N_7O_7)_n$	C	63.25	63.30							
	645	H	4.18	4.20	82	2	23	46	64	85	92
		N	15.19	15.20							
3f	$(C_{35}H_{29}N_7O_7)_n$	C	63.73	63.70							
	659	H	4.40	4.40	83	2.5	25	46	59	75	90
		N	14.87	14.90							
3g	$(C_{34}H_{27}N_7O_9S)_n$	C	57.54	57.50							
	709	H	4.08	4.10	81	2.5	23	45	60	74	92
		N	14.82	14.90							
3h	$(C_{34}H_{27}N_7O_8)_n$	C	61.72	61.70							
	661	H	4.08	4.10	84	3	24	47	60	75	91
		N	14.82	14.90							

TABLE II

Characterization of aromatized poly(imino-1,3,5-triazineimide)s

Polymer sample	*Molecular formula (formula weight)*	*Elemental analysis (wt%)*			*Yield (%)*	*Weight loss (%) at different temperatures (°C)*					
			Calc.	*Found*		300	400	500	600	700	750
4a	$(C_{24}H_{19}N_7O_5)_n$	C	59.38	59.30							
	485	H	3.91	3.90	85	2.5	18	35	59	75	92
		N	20.20	20.10							
4b	$(C_{28}H_{27}N_7O_5)_n$	C	62.1	62.10							
	541	H	4.99	5.00	87	2.5	20	36	60	72	92
		N	18.11	18.10							
4c	$(C_{28}H_{19}N_7O_5)_n$	C	63.0	63.10							
	533	H	3.56	3.57	89	2	18	32	59	70	91
		N	18.38	18.30							
4d	$(C_{28}H_{19}N_7O_5)_n$	C	63.0	63.10							
	533	H	3.56	3.58	88	1.0	15	39	55	75	90
		N	18.38	18.50							
4e	$(C_{34}H_{23}N_7O_5)_n$	C	67.0	67.10							
	609	H	3.77	3.75	84	1.0	18	41	62	80	91
		N	16.09	16.00							
4f	$(C_{35}H_{25}N_7O_5)_n$	C	67.41	67.40							
	623	H	4.01	4.00	90	1.5	17	31	58	70	92
		N	15.73	15.60							
4g	$(C_{34}H_{23}N_7O_7S)_n$	C	60.62	60.50							
	673	H	3.41	3.40	86	2.0	16	30	59	72	95
		N	14.56	14.50							
4h	$(C_{34}H_{23}N_7O_6)_n$	C	65.28	65.30							
	625	H	3.68	3.69	84	2.0	17	35	60	73	92
		N	15.68	15.60							

mixture 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 released sheet and compressed in flat platen under pressure. The prepregs were cured by heating the press to 150°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 composites and machining them to final dimensions.

MEASUREMENTS

The C, H, N contents of all the PITIs were estimated by the means of a Carlo Erba Elemental Analyzer (Italy). IR spectral analysis

TABLE III

Characterization of bulk poly(imino-1,3,5-triazineimide)s

Polymer sample	*Molecular formula (formula weight)*	*Elemental analysis (wt%)*			*Yield (%)*	*Weight loss (%) at different temperatures (°C)*					
			Calc.	*Found*		300	400	500	600	700	750
5a	$(C_{24}H_{19}N_7O_5)_n$	C	59.38	59.50							
	485	H	3.91	3.92	83	2	15	38	58	74	91
		N	20.20	20.20							
5b	$(C_{28}H_{27}N_7O_5)_n$	C	62.1	62.20							
	541	H	4.99	5.00	84	2	15	32	57	70	92
		N	18.11	18.10							
5c	$(C_{28}H_{19}N_7O_5)_n$	C	63.0	63.10							
	533	H	3.56	3.50	85	1.5	15	30	59	73	90
		N	18.38	18.50							
5d	$(C_{28}H_{19}N_7O_5)_n$	C	63.0	63.10							
	533	H	3.56	3.50	82	1	11	35	56	73	90
		N	18.38	18.30							
5e	$(C_{34}H_{23}N_7O_5)_n$	C	67.0	67.10							
	609	H	3.77	3.70	83	1	13	35	57	76	91
		N	16.09	16.20							
5f	$(C_{35}H_{25}N_7O_5)_n$	C	67.41	67.30							
	623	H	4.01	4.10	86	1.1	14	30	60	78	92
		N	15.73	15.60							
5g	$(C_{34}H_{23}N_7O_7S)_n$	C	60.62	60.50							
	673	H	3.41	3.40	85	1.1	13	30	58	72	92
		N	14.56	14.50							
5h	$(C_{34}H_{23}N_7O_6)_n$	C	65.28	65.20							
	625	H	3.68	3.70	81	1.5	14	36	58	73	91
		N	15.68	15.60							

was carried on Nicolet Impact 400 D with KBr as a reference and the NMR spectral analysis was carried out on HITACHI R-1500, 60 MHz instrument. All the polymer samples were subjected to thermogravimetry (TG) (Du pont 950 thermogravimetric analyzer) in air at a heating rate of 10°K/min.

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 IV.

TABLE IV

Mechanical and electrical properties of glass-reinforced poly(imino-1,3,5-triazine imides)s

Composites$^{@}$	*Chemical resistance** *Percentage change in*		*Density (gm/cm)*	*Flexural strength (M Pa)*	*Compressive strength (M Pa)*	*Impact strength (M Pa)*	*Hardness*$^{\#}$ *(R)*	*Electrical strength in air (kV/mm)*
	Thickness	*Weight*						
C2a	1.1	1.4	1.43	476	462	461	85	20.5
C2b	1.3	1.3	1.50	516	498	490	80	21.5
C2c	1.1	1.3	1.46	497	451	459	90	27.0
C2d	1.3	1.2	1.55	353	329	310	90	30.0
C2e	1.2	1.0	1.59	375	345	328	85	28.6
C2f	1.0	1.1	1.53	417	399	378	90	26.8
C2g	1.0	1.0	1.61	388	378	352	75	23.3
C2h	1.2	1.1	1.67	395	380	365	70	22.6

[@] Reinforcement: 'E' type glass cloth, plain weave, 0.254 mm (ten mil), ten layers; resin content: 40 ± 2 wt.%; molar ratio: 1 : 2a – h = 1 : 1 (mol/mol); curing temperature: 150 ± 10°C; curing time 10 hrs; curing pressure 0.48 M Pa; Composite size: 254 mm × 254 mm × 3.0 – 3.5 mm.

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

[#] Hardness in rockwell (R).

Mechanical Testing

(1) 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.
(2) The compressive strength was measured according to ASTM 0695 having 12.5 mm × 12.5 mm × 12.5 mm cube.
(3) Impact strength measurements were done according to the testing method of ASTM D256 with Izode type impact tester at room temperature.
(4) The hardness strength (Rockwell) was measured according to ASTM D785, having dimension of 25 mm width and 25 mm long specimen.
(5) 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 IV.

RESULTS AND DISCUSSION

The entire synthesis of Poly(imino-1,3,5-triazine-imide)s (PITIs) through DA reaction of 2,6-bis(2-furanylmethyl imide)-4-methoxy-1,3,5-triazine (**1**) with different bis(maleimido)-compounds (**2a–h**) is shown in Scheme 1. First the non-aromatized DA product **3** is formed which is then aromatized by the treatment of acetic anhydride to yield **4**. In absence of **2**, heating of **1** in THF at 70°C does not alter the properties of **1**. It was also observed that heating of **2a–h** in THF at 70°C does not induce the addition polymerization of **2a–h**. This reaction occurs either at elevated temperature or in the presence of an initiator [12–14]. All the polymer samples were obtained in better yields and were in the form of yellowish white to dark brown 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 the PITIs samples are shown in Tables I–III are consistent with their predicted structure (Scheme 1).

Examination of IR spectra of all the PITIs reveals that all the spectra comprise important characteristic bands of the imide group. The bands around 1780, 1700, 1100 and 730 cm^{-1} are contributions from imide II, III, IV, and I respectively. There are also bands around 1250 cm^{-1} and 850 cm^{-1} shows the presence of 1,3,5-triazine ring. The band around 3300–3400 cm^{-1} shows the stretching vibrations of —NH—. There are also bands around 1590–1690 cm^{-1} indicating the stretching vibration for —C=N— of *s*-triazine ring. Bands around 2870 and 2930 cm^{-1} appearing in the spectra of PITIs are attributed to the —CH_2— bridge. The IR spectra of polymers **5a–h** also show all the characteristics of imide groups *s*-triazine ring and —NH— linkages, indicating that the bulk phase polymerization yields PITIs as well. The IR spectra of samples 5e, 4e and 3e are traced in Figure 3.

Typical TG curves are shown in Figure 4. The TG data of all the PITIs are listed in Tables I–III. The TG data shows that the produced PITI samples exhibit less than 3% weight loss at 300°C probably corresponding to residual solvent; they decompose in one step. PITI samples start their decomposition above 300°C depending upon the nature of polymer. The rate of weight loss is high around 500°C, and completed at ~750°C. The non aromatized PITIs **3a–h** start their

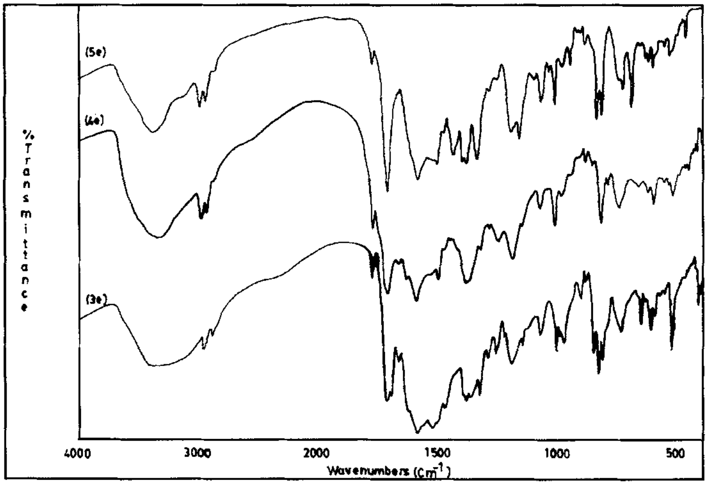


FIGURE 3 IR spectra of samples 5e, 4e, and 3e.

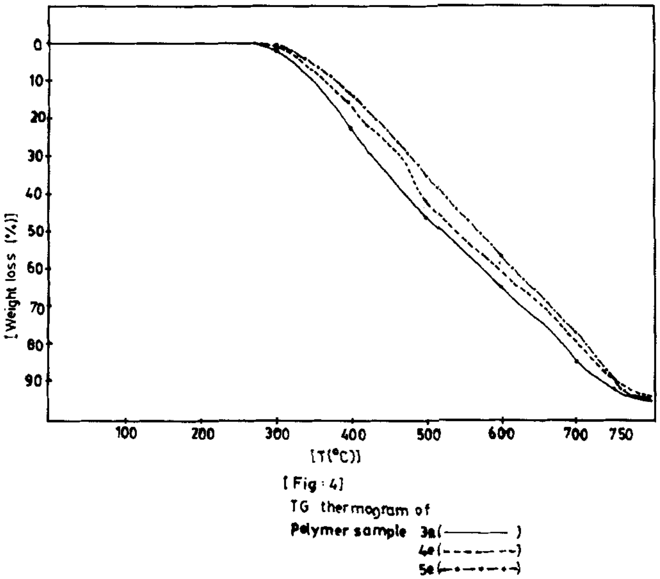


FIGURE 4 TG curves of samples 3e, 4e, and 5e.

degradation at around 310°C, where as the aromatized PITIs **4a–h** start to degrade at slightly higher temperature (325°C). On the other hand PITIs **5a–h** were obtained in the solid phase, start degradation around 350°C. A comparison of the thermal stability of all PITIs reveals the order of thermal stability based on bis(maleimido)-components **2a–h** (Scheme 1) as follows

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

The present PITIs are found to be good thermally stable and they retain acid, solvent and weather resistance. Though the thermal degradation is done in air, it may be certainly more stable in nitrogen atmosphere. In brief as expected the produced polyimides have comparable stability with that of commercial PIAs. It is also noted that the produced PIAs have better thermal stability then those reported by us [1–6]. Because of non-processibility of the present insoluble PITIs, a novel approach was also conducted to develop a matrix system for processable (150 ± 10°C) PITI-glass fibre composites.

All the composites prepared are dark brown sheets. The addition polymerization by DA reaction of **1** with **2a–h** of compressed composites starts from the surface of the composites, from which the polymerization continues towards the inner part of the composite without evaporation of any reaction bi-products or solvent molecule. Characteristics of prepared glassreinforced PITI composites are summarized in Table IV. The density of all composites is in the range of 1.43 – 1.67 g/cm^3 and indicates that there is no appreciable change in their specific gravity with respect to the nature of bis(maleimido)-compounds. Examination of chemical resistance test reveals that all composites have remarkable resistance to organic solvents and concentrated 1.51 M HCl. However treatment with concentrated 6.2 M NaOH changes their thickness in small amount and weight by about 1.4%. Results of mechanical properties of PITI composites reveal that all the composites have good mechanical properties. The overall trends for the mechanical properties of prepared Poly(imino-1,3,5-triazine imide)-composites $\mathbf{C_{2a-h}}$ decreases as follows, which may be attributed to a certain increase in the rigidity of 2,6-bis(maleimido)-components.

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

The electrical strength of all the composites is in the range of 20.5 to 30.0 kV/mm. As there is no wide change in electrical strength, no attempt was made to interpret these data.

CONCLUSIONS

- The ease of synthesis of 2,6-bis(2-furanyl methyl imino)-4-methoxy-1,3,5-triazine from agricultural waste (*e.g.*, furfuryl amine).
- The intermolecular DA reaction of 2,6-bis(2-furanylmethyl imino)-4-methoxy-1,3,5-triazine with different bis(maleimido)-compounds formed poly(imino-1,3,5-triazine imide)s having good organic solvents, mineral acids, and heat resistance.
- The *in-situ* produced poly(imino-1,3,5-triazine imide)s adhere well to glass fiber.

- The processing temperature (150°C) for composites prepared is lower than for conventional co-polyimide composites.
- Void free composites could be prepared with good mechanical properties and electrical properties.

Acknowledgement

The authors wish to thank Dr. H. C. Trivedi, Head of Department for providing laboratory facilities. One of the authors (V. C. Patel) thanks Government of Gujarat for granting Gujarat Government Research Fellowship.

References

[1] Patel, H. S. and Lad, B. D. (1989). *Makro Chemie.* (*Ger*), **190**, 2055–2061.
[2] Patel, H. S., Vyas, H. S. and Lad, B. D. (1990). *High Performance Polymers* (*UK*), **2**, 113–120.
[3] Patel, H. S., Vyas, H. S. and Lad, B. D. (1990). *High Performance Polymers* (*UK*), **2**(4), 245–249.
[4] Patel, H. S. and Patel, H. D. (1991). *High Performance Polymers* (*UK*), **4**, 19–34.
[5] Patel, H. S. and Patel, H. D. (1992). *High Performance Polymers* (*UK*), **4**, 35–40.
[6] Patel, H. S. and Patel, H. D. (1992). *High Performance Polymers* (*UK*), **4**, 237–246.
[7] Wilson, D., Stenzenberger, H. D. and Hergenrother, P. M. (Eds.) (1990). *Polyimides*, Blackie, Chapman and Hall publisher, New York.
[8] *Encyclo. of Poly. Sci. and Tech.*, Vol. 2., *Amino Resins*, Interscience Publishers, New York.
[9] Crivello, J. V. (1976). *J. Poly. Sci., Polym. Chem.*, Ed., **14**, 159.
[10] Dudley, J., Thurston, J., Schaefer, F., Dagfrid, Holm-Hansen, Hull, C. and Pierrepont, Adams (1951). *J. Am. Chem. Soc.*, **73**, 2986.
[11] Patel, H. S. and Patel, V. C., *Designed Monomers and Polymers*, USA (communicated).
[12] Hummel, D. O., Heinen, K. U., Stenzenberge, H. and Siesler, H. (1974). *J. Appl. Polym. Sci.*, **18**, 2015.
[13] Seratini, T. T., Delvigs, P. and Lightsey, G. R. (1972). *J. Appl. Polym. Sci.*, **16**, 905.
[14] Galanti, A. V. (1984). *J. Appl. Polym. Sci.*, **29**, 1611.