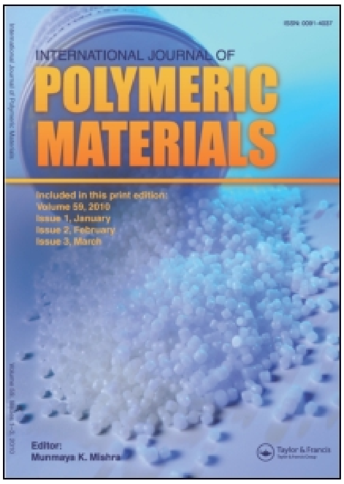

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Patel, H. S. , Patel, B. P. and Patel, D. B.(2009) 'Synthesis, Characterization and Glass Reinforcement of Poly(Ester Amido Imide)s', International Journal of Polymeric Materials, 58: 12, 625 — 635
To link to this Article: DOI: 10.1080/00914030903081547
URL: http://dx.doi.org/10.1080/00914030903081547

International Journal of Polymeric Materials, 58:625–635, 2009

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030903081547

Synthesis, Characterization and Glass Reinforcement of Poly(Ester Amido Imide)s

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Poly(ester amido imide)s (PEAI)s (IIIa–e) were prepared by the intermolecular Diels-Alder (DA) reaction of bismaleimide (II) having epoxy resin segment with various bisfurans (Ia–e) having amide bridge. The DA reaction was carried out with tetrahydrofuran as a solvent, as well as in bulk, followed by aromatization of DA polyadduct intermediates in the presence of acetic anhydride. All the resultant polymers, designated as poly(ester amido imide)s (PEAI)s, were characterized by elemental analysis, number average molecular weight, IR spectral studies and thermogravimetry. The PEAIs exhibit good thermal stability. Bismaleimide (II) and bisfurans (Ia–e) were polymerized (at $150 \pm 10°C$) by in situ *DA intermolecular reaction into moderately thermally stable PEAIs. The glass fiber-reinforced composites (i.e., laminates) of all PEAIs were prepared and characterized by their chemical resistance and mechanical properties.*

Keywords: bisfurans, bismaleimide, Diels-Alder reaction (DA), epoxy resin, glass fiber-reinforced composites (laminates), IR spectral study, poly(ester amido imides)s (PEAIs), polyimides (PI), thermogravimetric analysis

INTRODUCTION

The polyimides are known as high-performance polymers. Such polymers are synthesized by condensation or by additional polymerization [1]. One of the approaches to produce the polyimides is via Diels-Alder (DA) reaction of dienes and bismaleimides [2,3]. One of the authors (HSP) has created such polyimides via DA reaction using

Received 28 April 2009; in final form 13 May 2009.
The authors thank Udyog Bhavan, Gujarat Government, Gandhinagar, Gujarat, India for providing financial assistance. We are grateful to Dr. (Miss) R. G. Patel, Head of the Department for providing research facilities.
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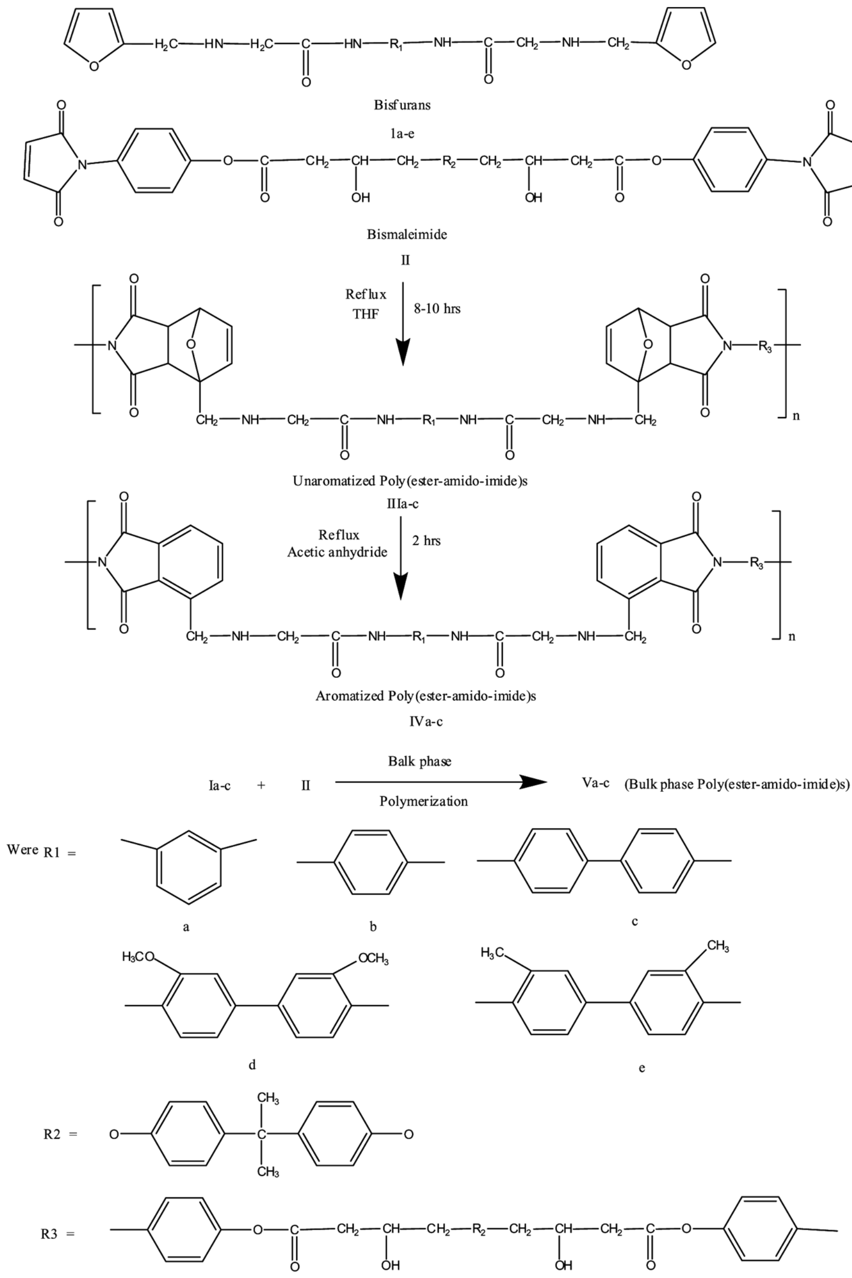

SCHEME 1 Synthetic steps.

agricultural waste products such as furan derivatives [4–10]. He established the different types of polyimides like poly(ether imide), poly(sulfone imide), poly(urethane imide), poly(s-triazine imide)s and poly(siloxane imide) through Diels-Alder polymerization of bisfurans and bismaleimides with wide structural variation. The key focus of these polyimides [4–15] is that they have low processing temperature with good thermal stability in air. One commercial co-polyimide, such as poly(amido imide)s known as “Torlon”, has excellent serviceable properties. It is manufactured industrially by condensation polymerization of trimelitic anhydride and diamines [16–22]. Patel and his coworkers also reported the epoxy modified polyimides and poly (amido imide)s [23,24]. Thus looking to the properties of poly (amido imide) and polyesters [1,25], it was thought to merge all three segments into one polymer chain. So the present communication comprises synthesis, characterization and glass reinforcement of the poly(ester amido imide)s shown in Scheme 1.

EXPERIMENTAL

Materials

Bisfurans (Table 1) were prepared by a method reported in our earlier communications [26,27]. The bismaleimides were prepared by condensation of diglycidyl ether of bisphenol-A and N-4-carboxy phenyl maleimide following the method reported [28,29].

Commercial epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), was obtained from Synpol Products Ltd., Ahemdabad, Gujarat, India.

The specification of DGEBA is 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.

TABLE 1 List of Bisfuran Compounds (Ia–e)

No	Bisfurans
Ia	N–N′-1,3-phenylene bis[(2-furanyl methylamino) – acetamide] (Ia)
Ib	N–N′-1,4-phenylene bis[(2-furanyl methylamino) – acetamide] (Ib)
Ic	N–N′-(biphenyl-4-4′diyl)bis(2-furan-2-yl methyl amino) – acetamide(Ic)
Id	N–N′-(3,3′-dimethoxy biphenyl-4-4′diyl)bis(2-furan-2-yl methyl amino) – acetamide (Id)
Ie	N–N′-(3,3′-dimethyl biphenyl-4-4′diyl)bis(2-furan-2-yl methyl amino) – acetamide (Ie)

The following dimines were used for preparation of bisfurans:

(a) 1,3-Phenylene diamine
(b) 1,4-Phenylene diamine
(c) Benzidine
(d) 3,3′-Dimethyl biphenyl-4,4′-diamine
(e) 3,3′-Dimethoxy biphenyl-4,4′-diamine

All other chemicals used were of pure grade.

Sation (212) weave (polyimide-compatible) fiberglass woven fabric 0.25 mm thick of "E" type glass (Unnati Chemicals, India) 270 gm^{-2} was used for laminate preparation.

Preparation of Poly (Ester Amido Imide)s (PEAI)s

The unaromatized PEAIs ($III_{a–e}$) and aromatized PEAIs ($IV_{a–e}$, $V_{a–e}$) (Scheme 1) were prepared through the DA reaction of different bisfurans (Ia–e) (Table 1) with bismaleimide (II) in solution as well as in the bulk phase system (Scheme 1) following the methods given in our earlier communications [26,27].

Composite Fabrication

A typical method of fabrication for composites is given below.

Suspension of bisfurans and bismaleimide in tetrahydrofuran was prepared and stirred well for 2 min. The suspension mixture was applied with a brush to a 250 mm $\times$ 250 mm fiberglass cloth and the solvent was allowed to evaporate. The 10 dried prepregs so prepared were stacked one on top of another and pressed between steel plates with Teflon release sheets and compressed in a flat platen press under about 70 psi pressure. The prepregs were cured by heating at $150 \pm 10°C$ for 10 h 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 dimensions.

MEASUREMENTS

The C, H, and N contents of all the PEAIs were determined by means of a Themofingman flash elemental analyzer 1101EA (Italy). The IR spectra were taken in KBr using a Perkin-Elmer 760 spectrophotometer. All polymer samples were subjected to thermogravimetric analysis (TGA) (Du Pont 950 thermogravimetric analyzer) in air at a heating rate of 10°C min^{-1}.

The number average molecular weight ($\overline{Mn}$) of the PEAIs were determined by nonaqueous conductometric titration method reported in the literature [30,31]. Laboratory-grade formic acid to which an appropriate amount of acetic anhydride was added was used as a nonaqueous solvent, and standard perchloric acid in acetic acid was used as titrant.

Characterization of Composite Samples

Chemical Resistance

The chemical resistance of the composite was measured according to ASTM D543. The sample size was approximately 20 mm $\times$ 20 mm. The data are included in Table 2 below.

Mechanical and Electrical Properties

All the mechanical and electrical properties were measured according to ASTM standards.

1. The flexural strength was measured according to ASTM D 790.
2. The compressive strength was measured according to ASTM D 695.
3. The impact strength was measured according to ASTM D 256.
4. The Rockwell hardness was measured according to ASTM D 785.
5. The electrical strength was measured according to ASTM D 149.

All mechanical and electrical tests were performed using three specimens and their average results are summarized in Table 2.

RESULTS AND DISCUSSION

The formation of all the PEAIs (IIIa–e, IVa–e, and Va–e) from bisfurans (Ia–e) and bismaleimide (II) is shown in Scheme 1.

The nonaromatized product III_{a-e} is first formed and then aromatized by treatment with acetic anhydride to yield IV_{a-e}. In the absence of bismaleimide, heating of (I) in tetrahydrofuran and refluxing for 8–10 h does not alter its properties. It was also observed that heating each of II_{a-e} in tetrahydrofuran and refluxing for 8–10 h does not induce the additional polymerization of II_{a-e}. This has been shown to be possible only in elevated temperatures or in the presence of an initiator [32–34].

All the PEAIs samples were obtained in 60% yield as dark brown solid powders. They were insoluble in common organic solvents and are not affected by concentrated mineral acids or formic acid. All samples were sparingly soluble in dimethylformamide. The elemental analyses (Tables 3–5) of all the PEAIs samples are consistent with their predicted structures (Scheme 1).

TABLE 2 Mechanical and Electrical Properties of Glass–Reinforced PEAIs

[a]Composite	% Change on exposure to 25% (w/v) NaOH[b]		Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (m air) (Kv mm^{-1})
	Thickness	Weight					
Ca	1.6	1.8	290	280	292	104	18.1
Cb	1.8	1.7	285	275	294	103	17.9
Cc	1.7	1.9	270	207	172	115	19.4
Cd	1.8	2.0	268	190	189	117	19.2
Ce	1.6	1.5	265	193	194	119	18.5

[a]Conditions: −Reinforcement: E glass cloth; plain weave; 10 mm; 10 layers. Resin content, $40 \pm 2\%$; mole ratio (bismaleimide:PBFA), 1:1; curing temperature, $145 \pm 10°C$; time, 10 h; pressure, 60–70 psi.

[b]Composite size: 25 mm × 25 mm, 3.0–3.5 mm thick.

TABLE 3 Characterization of Unaromatized PEAIs (IIIa–e)*

Polymer	M. F. [M. W.]	Elemental analysis (%) (wt%) Calc./Found % C	% H	% N	Number average molecular weight	Weight loss (%) at various temperatures 300°C	400°C	500°C	600°C	700°C
IIIa	$C_{63}H_{59}N_6O_{16}$ [1155]	65.45/65.24	5.10/4.94	7.27/7.04	4578	2.0	35	51	73	96
IIIb	$C_{63}H_{59}N_6O_{16}$ [1155]	65.45/65.12	5.10/4.97	7.27/7.03	4567	2.1	36	53	66	95
IIIc	$C_{69}H_{63}N_6O_{16}$ [1231]	67.26/67.02	5.11/4.95	6.82/6.45	6155	2.4	34	49	64	93
IIId	$C_{71}H_{67}N_6O_{18}$ [1291]	65.99/65.67	5.18/4.99	6.18/5.87	5106	2.2	31	48	63	91
IIIe	$C_{71}H_{67}N_6O_{16}$ [1259]	67.67/67.24	5.29/5.13	6.67/6.43	4989	1.9	33	50	65	93

*IR bands observed around 2860 and 2940 cm^{-1} $-CH_2-$; 3020 and 830 cm^{-1} Aromatic; 3380 cm^{-1} NH (Sec.); 3300–2600 and 1100 cm^{-1} –OH group, respectively. 1780, 1720, 1050, and 720 cm^{-1} are contributions from the imides groups, 1530 cm^{-1} shows the presence of amide and 1680 shows the presence of ester group.

TABLE 4 Characterization of Aromatized PEAIs (IVa–e)*

		Elemental analysis (%)				Weight loss (%) at various temperatures				
		(wt%) Calc./Found								
Polymer	M. F. [M. W.]	% C	% H	% N	Number average molecular weight	300°C	400°C	500°C	600°C	700°C
IVa	$C_{63}H_{55}N_6O_{14}$ [1119]	67.56/67.24	4.91/4.76	7.50/7.04	4435	1.3	34	49	71	94
IVb	$C_{63}H_{55}N_6O_{14}$ [1119]	67.56/67.12	4.91/4.45	7.50/7.26	4424	1.2	35	51	65	93
IVc	$C_{69}H_{59}N_6O_{14}$ [1195]	69.28/69.02	4.93/4.56	7.02/6.45	5916	1.1	33	47	63	92
IVd	$C_{71}H_{63}N_6O_{16}$ [1255]	67.88/67.67	5.01/4.78	6.69/6.35	4979	1.1	30	46	62	92
IVe	$C_{71}H_{63}N_6O_{14}$ [1223]	69.66/69.24	5.15/4.98	6.86/6.43	4816	1.0	32	48	64	93

*IR bands observed around 2860 and 2940 cm^{-1} $-CH_2-$; 3020 and 830 cm^{-1} Aromatic; 3380 cm^{-1} NH (Sec.); 3300–2600 and 1100 cm^{-1} –OH group, respectively. 1780, 1720, 1050, and 720 cm^{-1} are contributions from the imides groups, 1530 cm^{-1} shows the presence of amide and 1680 shows the presence of ester group.

TABLE 5 Characterization of Bulk Phase PEAIs (Va–c)*

Polymer	M. F. [M. W.]	Elemental analysis (%) (wt%) Calc./Found			Number average molecular weight	Weight loss (%) at various temperatures				
		% C	% H	% N		300°C	400°C	500°C	600°C	700°C
Va	$C_{63}H_{55}N_6O_{14}$ [1119]	67.56/67.15	4.91/4.56	7.50/7.35	4420	1.3	34	49	71	94
Vb	$C_{63}H_{55}N_6O_{14}$ [1119]	67.56/67.47	4.91/4.46	7.50/7.35	4413	1.2	35	51	65	93
Vc	$C_{69}H_{59}N_6O_{14}$ [1195]	69.28/69.09	4.93/4.47	7.02/6.78	5975	1.1	33	47	63	92
Vd	$C_{71}H_{63}N_6O_{16}$ [1255]	67.88/67.68	5.01/4.79	6.69/6.46	4997	1.1	30	46	62	92
Ve	$C_{71}H_{63}N_6O_{14}$ [1223]	69.66/69.56	5.15/4.89	6.86/6.56	4834	1.0	32	48	64	93

*IR bands observed around 2860 and 2940 cm^{-1} $-CH_2-$; 3020 and 830 cm^{-1} Aromatic; 3380 cm^{-1} NH (Sec.); 3300–2600 and 1100 cm^{-1} –OH group respectively. 1780, 1720, 1050, and 720 cm^{-1} are contributions from the imides groups, 1530 cm^{-1} shows the presence of amide and 1680 shows the presence of ester group.

The IR spectra of all the polymers were found to be consistent with their predicated structures. As the polymer samples are insoluble in common organic solvents the NMR spectra has not been attempted. The D_p value (degree of polymerization) for all PEAIs samples were estimated by nonaqueous conductometric titration to be in the range 4–6. The values of number average molecular weight based on this method are mentioned in Tables 3–5.

The TGA data of all PEAIs, shown in Tables 4 and 5, reveal that aromatized and bulk PEAIs samples degrade in a single step. Their decomposition starts around 290°C, depending on the nature of the polymers. The rate of decomposition increases by increasing the temperature and it is fastest between 400 and 550°C. It was observed that the weight loss is completed beyond 760°C. The unaromatized PEAIs (Table 3) start degrading at a slightly lower temperature (275°C) than that of aromatized and bulk PEAIs.

The present PEAIs are thermally stable and resist acid, solvent, and weather exposure. Because of the nonprocessability of the present polyimides, a novel approach was taken to develop matrix systems for processable (150 ± 10°C) polyimide glass fiber composites. The addition a polymerization by the DA reaction of bisfurans (Ia–e) with bismaleimide (II) starts from the surfaces of the composites from which the polymerization continues towards the inner part of the composite without evolution of any reaction by-product or solvent molecules.

The mechanical properties of all the PEAIs composites are shown in Table 2. Examination of the results reveals that all the composites have good mechanical properties. The decreasing order according to their mechanical properties is shown below:

$$Ca > Cb > Cc > Cd > Ce$$

This may be attributed to increases in the rigidity of the bismaleimide component. The electrical strength of all the composites are in the range 18–19.5 kV/mm.

As the produced PEAIs were insoluble in almost all common organic solvents, their molecular. weight determination has not been attempted by osmometric method.

CONCLUSIONS

The overall advantages of the produced PEAIs formation are as follows:

- The intermolecular DA reaction with bismaleimides formed PEAIs with good chemical resistivity and moderate thermal stability.

- The glass fiber-reinforced composites of all the PEAIs have been laminated and showed excellent resistance properties against chemicals and good mechanical and electrical properties.

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