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## ORIGINAL ARTICLE

# Thermoplastic-thermosetting merged polyimides via furan-maleimide Diels–Alder polymerization



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## KEYWORDS

Bisfuran;  
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Thermoplastic-thermosetting merged polyimide;  
Thermal analysis

**Abstract** Novel thermoplastic-thermosetting merged polyimide system has been developed via Diels–Alder intermolecular polymerization of bisfuran namely, 2,5-bis(furan-2-ylmethylcarbamoyl) terephthalic acid **A** with a series of bismaleimides **B**<sub>1–4</sub>. Thus obtained intermediate Diels–Alder adducts **C**<sub>1–4</sub> were aromatized and imidized (i.e. cyclized) through carboxylic and amide groups to afford thermoplastic-thermosetting merged polyimides **D**<sub>1–4</sub>. Bisfuran **A** was prepared by the condensation of pyromellitic dianhydride with furan-2-ylmethanamine and characterized by elemental, spectral, thermal and LCMS analyses. Synthesized Diels–Alder adducts **C**<sub>1–4</sub> and polyimides **D**<sub>1–4</sub> were characterized by elemental analysis, spectral features, number average molecular weight ( $\overline{M}_n$ ), degree of polymerization (DP) and thermal analysis. To facilitate the correct structural assessment and to be able to verify the occurrence of the DA adducts and PIs, a model compound **4** was prepared from phthalic anhydride and furan-2-ylmethanamine in a similar way. FTIR spectral features of polyimides **D**<sub>1–4</sub> were compared with model compound **4** and they were found to be quite identical. The ‘in situ’ void-free glass fiber reinforced composites GFRC<sub>1–4</sub> were prepared from the produced system and characterized by chemical, mechanical and electrical analyses. All the composites showed good mechanical, electrical and thermal properties and good resistance to organic solvents and mineral acids.

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## 1. Introduction

The last few decades have seen a flurry of activity in the synthesis and development of high performance polyimides (PIs)

through the Diels–Alder (DA) reaction. The pioneering work related to DA polymerization was done by **Stille and Plummer (1961)**. DA reaction has been applied to the furan heterocycle with growing frequency because of its pronounced dienic character, which makes it particularly suited to intervene in the DA cycloaddition reaction as the dienic partner. A more elaborate approach was applied to furan–maleimide Diels–Alder polymerization. The first investigation on PI involving a bisfuran and a bismaleimide monomer combination was reported by **Tesoro and Sastri (1986)**, who had also opened the way to a stream of publications by giving an idea of a chemical modification of adduct by aromatization. Various strategies can be envisaged to synthesize or modify polymer structures by

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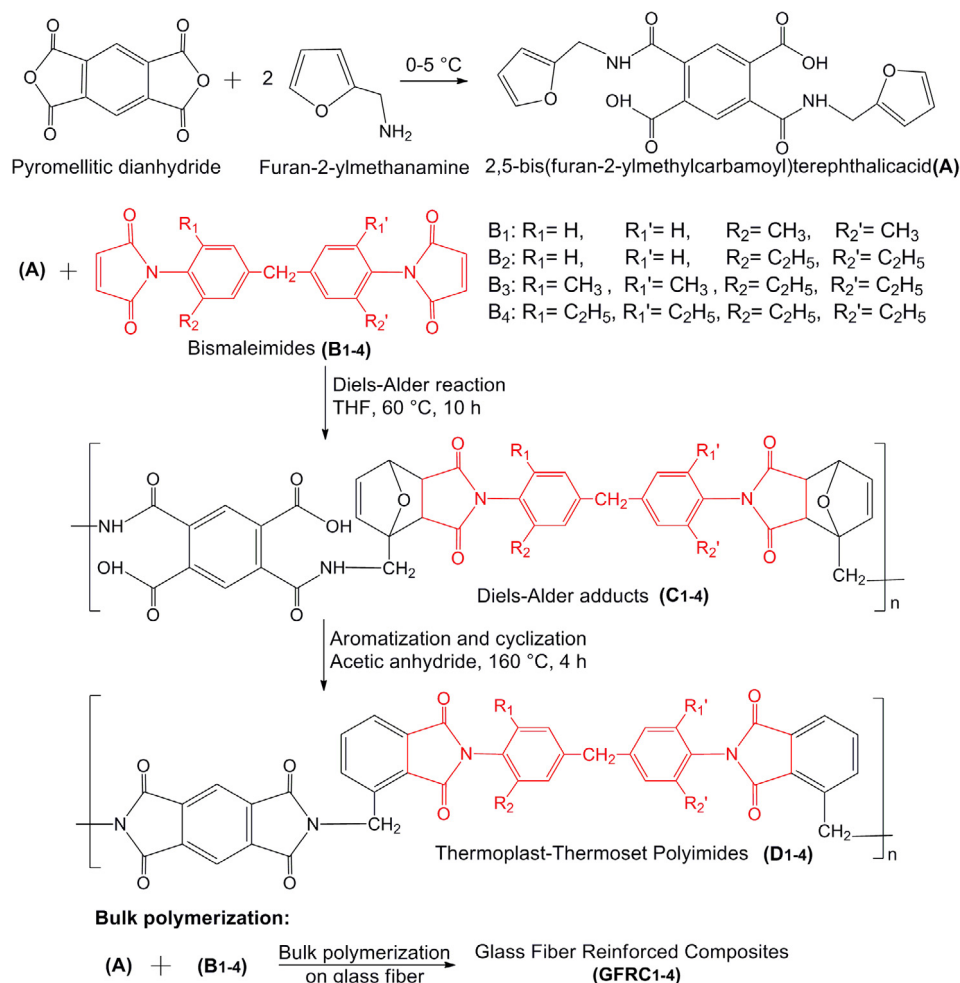
exploiting the reactivity of this heterocycle with various dienophiles by Gaina et al. (2012), Patel et al. (2012), Sanyal (2010), Peterson et al. (2011), Liu and Chen (2007). A systematic study of DA polymerization involving furan derivatives and various bismaleimides has been carried out by Gandini (2013). Owing to the published work on these topics and the long-standing interest of our laboratory in the study of PIs via DA reaction, a more systematic exploration has been undertaken with particular emphasis. One of the authors HSP and his co-workers have reported the studies on PIs like poly(epoxy-imide) (Prabhu and Patel, 2001), poly(s-triazine-imide) (Patel and Patel, 2001), poly(ether-imide) (Patel and Patel, 2001), poly(ester-amido-imide) (Patel et al., 2009), poly(amido-imide) (Patel and Patel, 2009), poly(ester-oxysilane-imide) (Patel et al., 2010), Poly(urethane-imide-ester) (Patel et al., 2011) through DA polymerization of bisfurans and bismaleimides with wide structural variation. Based on this concept, our main concern was to prepare PIs which possess the combination of thermoplastic and thermosetting properties by introducing bisfuran and bismaleimide segments. This would alter the properties of PIs. The present study concerns the synthesis of PIs via DA reaction and subsequent aromatization and imidization. Scheme 1 summarizes our synthetic approach to various phases of this work, viz., (i) Preparation of bisfuran **A** from pyromellitic dianhydride and furan-2-ylmethanamine (ii) DA

reaction between bisfuran **A** and bismaleimides **B1-4** (iii) Aromatization and imidization (i.e. cyclization) reaction to afford thermoplastic-thermosetting merged PIs **D1-4**. The 'in situ' void-free glass fiber reinforced composites GFRC<sub>1-4</sub> were prepared from the produced system and characterized by chemical, mechanical and electrical analyses. In order to facilitate the correct structural assessment and to be able to verify the occurrence of the DA adducts and PIs, a model compound **4** was synthesized from phthalic anhydride and furan-2-ylmethanamine (Scheme 2). FTIR spectral features of polyimides **D1-4** were compared with model compound **4** and it was found to be quite identical. The details of these procedures and the results obtained are discussed below.

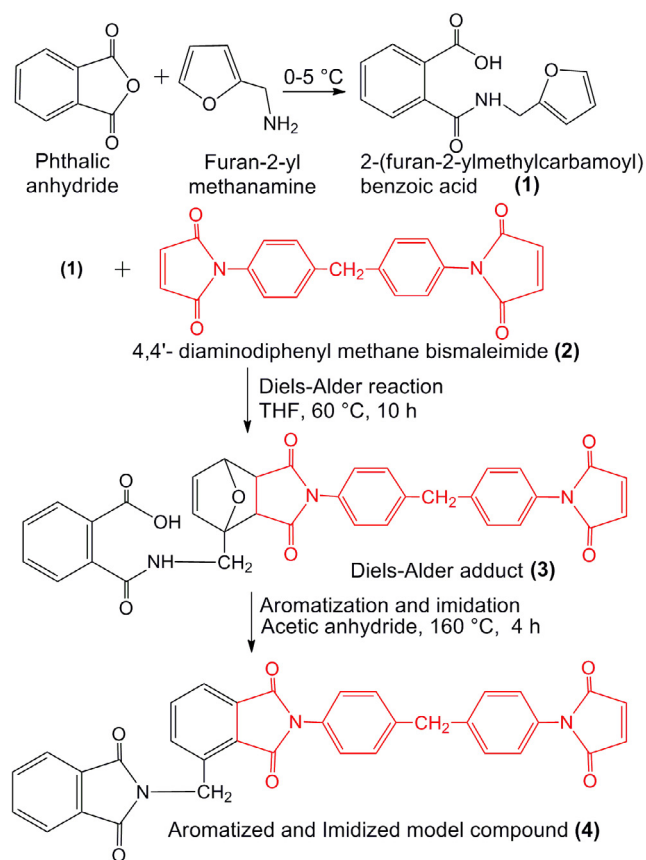
## 2. Experimental

### 2.1. Materials and measurements

All chemicals and solvents used were of laboratory grade. Pyromellitic dianhydride, phthalic anhydride and maleic anhydride were obtained from Fluka Analytical, Japan and Merck laboratory Ltd., Mumbai. Furan-2-ylmethanamine was obtained from the local market and redistilled before use. Various diamines used for the preparation of **B1**: N,N'-(methylenebis(2-methyl-4,1-phenylene))bismaleimide, **B2**: N,N'



Scheme 1 Synthesis of Thermoplastic-thermosetting merged polyimides.



Scheme 2 Synthesis of model compound.

(methylenebis(2-ethyl-4,1-phenylene))bis maleimide, **B3**: N,N'-(methylenebis(2-ethyl,6-methyl-4,1-phenylene))bismaleimide, **B4**: N,N'-(methylenebis(2,6-diethyl-4,1-phenylene))bismaleimide were obtained from the local market and used without purification. Solvents were dried and distilled before use according to standard procedures. Elemental analysis was carried out on a Thermofingan flash 1101EA (Italy). Infrared spectra were scanned on a Nicolet-760 FTIR spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on a Bruker spectrophotometer 400 MHz. Number average molecular weight ( $\overline{M}_n$ ) of PIs was determined by non-aqueous conductometric titration by a method reported earlier (Chatterji and Agrawal, 1971; Chatterji and Gupta, 1974; Patel and Patel, 1981). Pyridine was used as suspending solvent and tetra n-butyl ammonium hydroxide in 1,4-dioxane was used as a titrant. A digital conductivity meter of Tosaniwal (India) was used for the titration. The thermal behavior of A, **C1-4** and **D1-4** were investigated by thermogravimetric analysis on a Perkin Elmer TGA analyzer at a heating rate of  $10\text{ K min}^{-1}$  in the temperature range  $50\text{--}700\text{ }^\circ\text{C}$ . As the PIs are insoluble in common organic solvents, their viscometric properties have not been studied.

## 2.2. Synthesis of 2,5-bis(furan-2-ylmethylcarbamoyl) terephthalic acid A

Bisfuran A was synthesized by parity condensation of phthalic anhydride and furan-2-ylmethanamine (Patel and Hiran,

2011). Adding dropwise a solution of furan-2-ylmethanamine (0.2 mol) to a stirred solution of Pyromellitic dianhydride (0.1 mol) and keeping the temperature of the medium close to  $0\text{--}5\text{ }^\circ\text{C}$  for an hour (Scheme 1), thus the obtained ensuing solution was poured into ice water in which the reaction product precipitated. The final white precipitates were filtered, washed and purified by column chromatography. Yield was 65%; M. Wt. 412.35 g; Decomposition temp.:  $250\text{--}260\text{ }^\circ\text{C}$  (uncorrected); Elemental Analysis calculated for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_8$ : C 58.25, H 3.91, N 6.79% Found: C 57.87, H 3.75, N 6.58%;  $^1\text{H}$  NMR ( $\delta$  ppm): 10.9 (s, 2H,  $-\text{COOH}$ ), 8.9 (t,  $J = 5.2\text{ Hz}$ , 2H,  $-\text{NH}-\text{CO}-$ ), 8.1 (s, 2H, Ar.H), 7.50–7.93 (m, 6H, Ar.H), 4.32 (d,  $J = 5.2\text{ Hz}$ , 2H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR ( $\delta$  ppm): 42.24, 117.78, 119.24, 123.45, 126.10, 129.32, 132.67, 135.70, 167.12, 172.73; IR (KBr,  $\text{cm}^{-1}$ ): 3528 ( $-\text{COO}-\text{H}$  st.), 3254 ( $-\text{NH}-\text{C}=\text{O}$  st.), 3123 (C–H st. in furan rings), 3038 ( $-\text{CH}$  st. aromatic ring), 1711 (acid C=O st.), 1685 ( $\text{O}=\text{C}-\text{NH}$  free amide), 1500 (backbone st. aromatic ring), 1465 ( $\text{COO}^-$  sym. st.), 1039 (C–O st.), 730 (furan ring).

## 2.3. Synthesis of bismaleimides B1-4

Bismaleimides (Table 1) were prepared in two steps as per the method reported (Chandra and Rajabi, 1997; Dershem, 2012). The first step involved the addition of one equivalent of various diamines to two equivalents of maleic anhydride to form bisamic acid. The second step induced the cyclization of this amic acid end-group through the joint intervention of sodium acetate and acetic anhydride.

## 2.4. Synthesis of DA adducts C1-4

Bisfuran A and bismaleimides **B1-4** (1:1 by mole) in an equimolar ratio were dissolved in 50 mL of tetrahydrofuran. This was refluxed for 10 h at  $60\text{ }^\circ\text{C}$  (Scheme 1). The resultant reaction mixture was cooled and poured into a large volume of dry ether. The precipitate formed was filtered, washed and then air dried. The obtained unaromatized and uncyclized products were designated as DA adducts **C1-4** which were purified and characterized by elemental, IR and thermal analyses.

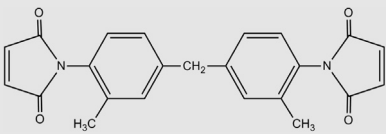
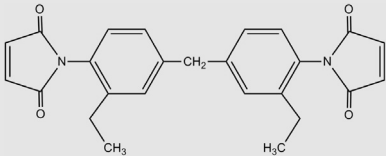
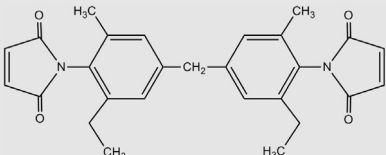
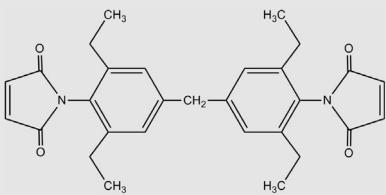
## 2.5. Synthesis of polyimides D1-4

Aromatization of the polymers was carried out by refluxing 1 g of the dried sample of DA adducts **C1-4** in 1 mL of acetic anhydride (Tesoro and Sastri, 1986) for 4 h at  $150\text{--}160\text{ }^\circ\text{C}$  (Scheme 1). Simultaneously, imidization reaction takes place. The resulting solution was cooled and poured into a large volume of water. The precipitates formed were filtered, washed and then air dried. Thus obtained brown colored precipitates of PIs **D1-4** were characterized by elemental analysis, IR analysis and by thermal analysis.

## 2.6. Bulk polymerization

A mixture of A (0.01 mol), **B1-4** (0.01 mol) and 2 ml acetic anhydride in THF was heated at  $150\text{--}160\text{ }^\circ\text{C}$  for 10 h with vigorous agitation. The resulting brown solid products were treated as describe above. The results were analogous with the synthesized polyimides **D1-4**.

**Table 1** List of bismaleimides **B1–4**.

No	–R–	Name of bismaleimides <sup>a</sup>	M.Wt.	M.P.
B1		N,N'-(methylenebis(2-methyl-4,1-phenylene)) bismaleimide	386	195 °C
B2		N,N'-(methylenebis(2-ethyl-4,1-phenylene)) bismaleimide	414	210 °C
B3		N,N'-(methylenebis(2-ethyl,6-methyl-4,1-phenylene)) bismaleimide	442	165 °C
B4		N,N'-(methylenebis(2,6-diethyl-4,1-phenylene)) bismaleimide	470	160 °C

<sup>a</sup> Trivial names are mentioned.

### 2.7. Synthesis of model compound

A suspension of 2-(furan-2-ylmethylcarbonyl) benzoic acid (0.01 mol) and 4, 4'-diaminodiphenyl methane bismaleimide (0.01 mol) in THF was refluxed for 10 h at 60 °C. The resultant unaromatized and unimidized product was designated as DA adduct **3**. It was refluxed at 150–160 °C for 4 h with 2 ml of acetic anhydride to afford aromatization and imidization. The resulting solution was cooled and poured into a large volume of water, washed, filtered and then air dried. Thus obtained brown colored precipitate of **4** was characterized by elemental analysis and IR analysis. Yield was 65%; M. Wt. 567.55 g; Elemental Analysis calculated for C<sub>34</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub>: C 71.95, H 3.73, N 7.40%; Found: C 71.86, H 3.67, N 7.31%; IR (KBr, cm<sup>-1</sup>): 3028, 2972, 2862, 1771, 1730, 1513, and 1379.

### 2.8. Preparation of glass fiber reinforced composites GFRC1–4

Glass fiber reinforced composites GFRC1–4 were prepared as follows: Suspensions of **A** and **B1–4** in THF were prepared on a weight basis and stirred well for 10 min. These resin suspensions were applied with a brush on to a PI compatible glass cloth. The solvent was allowed to evaporate for 10–20 min at room temperature. The dried ten prepregs so prepared were stacked one over another and placed between stainless steel plates and compressed under about 60–70 psi pressure at about

150 °C for 10 h in an air circulating oven. The composites were cooled to room temperature before pressure was released. The composites were then machined to desired final dimension for various mechanical and chemical tests.

**Chemical Resistance Test** for all the composite samples was performed according to ASTM D 543–67. The composite sample dimension was 25 mm × 25 mm × 3 mm. The samples were immersed in 25% v/v H<sub>2</sub>SO<sub>4</sub>, 25% v/v HCl, 25% w/v NaOH, ethanol, acetone, DMF, and THF for 7 days at room temperature. After 7 days the samples were taken out from the reagents and were analyzed for the percentage change in their weight.

**Mechanical Test** was performed using three specimens.

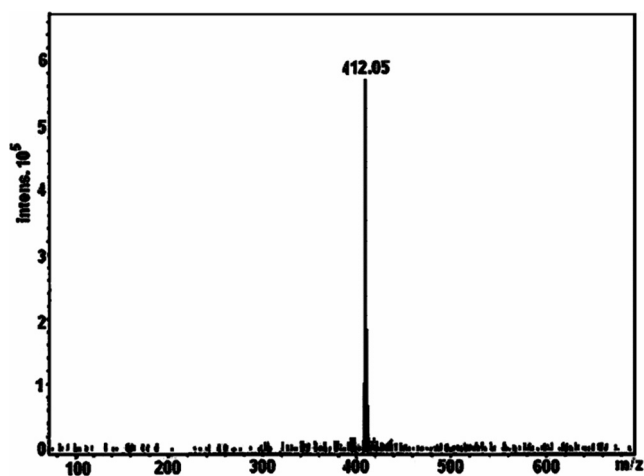
- The measurement of Flexural strength was carried out with a Universal Instron Testing Machine model No. A-74-37, at room temperature according to the ASTM D790 method.
- The compressive strength was measured on a Universal Instron testing machine model No. A-74-37, at room temperature according to the ASTM D 695 method.
- The notched Izod impact strength of the composites was measured on a Zwick Model No. 8900 Impact machine at room temperature according to the ASTM D256 method.
- Rockwell hardness was measured on a Rockwell hardness tester model No. RAS/Saro Engg. Pvt. Ltd. India according to the ASTM D785 method at room temperature.

*Electrical strength measurement Test* was carried out on a high voltage tester machine at room temperature according to the ASTM D 149 method using a Hewlett–Packard 4329-A high resistance meter.

### 3. Results and discussion

#### 3.1. Monomer synthesis

To the best of our knowledge, product **A** has not been reported previously. The characterization of the reaction product provided the first unambiguous proof of the successful synthesis of 2,5-bis(furan-2-ylmethylcarbamoyl)terephthalic acid **A**. The FTIR spectrum of **A** showed the most relevant peaks of the furan ring and 1,2,4,5-tetra substituted benzene ring, other than the typical absorptions arising from the carboxylic acid and amide group (Silverstein and Webster, 2004). In the  $^1\text{H}$  NMR spectrum, signals obtained were ascribed to the protons of the aromatic rings, carboxylic acid group and amide group which were further confirmed by  $^{13}\text{C}$  NMR values. The expected structure was thus clearly verified by the spectroscopic analysis which indicated moreover the absence of any detectable impurity, particularly of the two reagents used to prepare **A**. This was additionally confirmed by LCMS data (Fig. 1) and elemental analysis.



**Figure 1** LCMS of 2,5-bis(furan-2-ylmethylcarbamoyl)terephthalic acid **A**.

#### 3.2. Polymer synthesis

The thermoplastic-thermosetting merged polyimide system has been performed by the Diels–Alder intermolecular reaction followed by aromatization of DA adduct and imidization simultaneously. The elemental analyses (Table 2) of the DA adducts indicated that the reactions had reached good yields of cycloaddition of the furan rings and were consistent with their predicted structures (Scheme 1). The Degree of polymerization (DP) for the polymers **C1–4** was estimated by non-aqueous titration. It was found in the range of 8–9.

While comparing the IR spectra of DA adducts **C1** and Polyimides **D1** (Fig. 2) significant differences should be observed. The IR spectra of the adducts showed important changes with respect to those of the initial monomers, which clearly confirmed that the Diels–Alder reaction had taken place with good yields with all the bismaleimides. The IR spectra of DA adducts **C1–4** have prominent characteristic bands of furan, amide and carboxylic acid groups. The bands near  $3120$  and  $1585\text{ cm}^{-1}$  were attributed to furan. The bands around  $3225$ ,  $1675\text{ cm}^{-1}$  were attributed to amide groups, while the bands around  $3535$  and  $1715\text{ cm}^{-1}$  were corresponding to  $-\text{OH}$  and  $\text{C}=\text{O}$  groups of carboxylic acid respectively. Comparison of the IR spectra of non aromatized and non cyclized **C1–4** with aromatized and imidized (cyclized) **D1–4** revealed discernible differences. The bands due to carboxylic acid and amide groups in the spectra of **C1–4** almost disappeared in the spectra of **D1–4**, indicating that imidization reaction had taken place very smoothly and the disappearance of the bands due to furan ring confirmed the aromatization reaction has been completed simultaneously. For the sake of convenience, the IR spectra of PIs **D1–4** were compared with model compound. IR spectral features of PIs **D1–4** were quite identical with the model compound. These features confirmed the predicted structure of aromatized-imidized PIs **D1–4**.

The thermal stability of **C1–4** and **D1–4** was evaluated from their TG curves. The **C1–4** (Fig. 3) underwent two stages of mass loss. The first major stage corresponded to the decarboxylation of the polymer in the temperature range of  $180$ – $280\text{ }^\circ\text{C}$ . The values of wt. loss observed in **C1–4** samples were quite consistent with the calculated values obtained from the proposed structures. The process of the second stage above  $280\text{ }^\circ\text{C}$  was due to polymer pyrolysis. The char residue left at  $700\text{ }^\circ\text{C}$  was in the range of 4–6% for **C1–4**. A very rapid rate of weight loss was observed between  $400\text{ }^\circ\text{C}$  and  $600\text{ }^\circ\text{C}$ . Whereas in the case of **D1–4** (Fig. 4) their decomposition

**Table 2** Physico chemical analysis of DA adducts **C1–4** and polyimides **D1–4**.

Sample	Empirical formula	Empi. Wt. g.	Color	Yield	Elemental analysis Calc./(Found)			$(\overline{M}_n \pm 60)$	DP
					C	H	N		
<b>C1</b>	$\text{C}_{43}\text{H}_{34}\text{N}_4\text{O}_{12}$	798.7	Light brown	55	64.66 (64.54)	4.29 (4.18)	7.01 (6.89)	$7188 \pm 60$	9
<b>C2</b>	$\text{C}_{45}\text{H}_{38}\text{N}_4\text{O}_{12}$	826.8	Light brown	50	65.37 (65.24)	4.63 (4.56)	6.78 (6.63)	$6620 \pm 60$	8
<b>C3</b>	$\text{C}_{47}\text{H}_{42}\text{N}_4\text{O}_{12}$	854.9	Light brown	55	66.03 (65.92)	4.95 (4.86)	6.55 (6.48)	$6831 \pm 60$	8
<b>C4</b>	$\text{C}_{49}\text{H}_{46}\text{N}_4\text{O}_{12}$	882.9	Light brown	45	66.66 (66.51)	5.25 (5.21)	6.35 (6.30)	$7069 \pm 60$	8
<b>D1</b>	$\text{C}_{43}\text{H}_{26}\text{N}_4\text{O}_8$	726.7	Brown	45	71.07 (70.94)	3.61 (3.54)	7.71 (7.64)	–	–
<b>D2</b>	$\text{C}_{45}\text{H}_{30}\text{N}_4\text{O}_8$	754.7	Brown	45	71.61 (71.53)	4.01 (3.90)	7.42 (7.35)	–	–
<b>D3</b>	$\text{C}_{47}\text{H}_{34}\text{N}_4\text{O}_8$	782.8	Brown	40	72.11 (72.03)	4.38 (4.32)	7.16 (7.07)	–	–
<b>D4</b>	$\text{C}_{49}\text{H}_{38}\text{N}_4\text{O}_8$	810.8	Brown	40	72.58 (72.51)	4.72 (4.65)	6.91 (6.84)	–	–

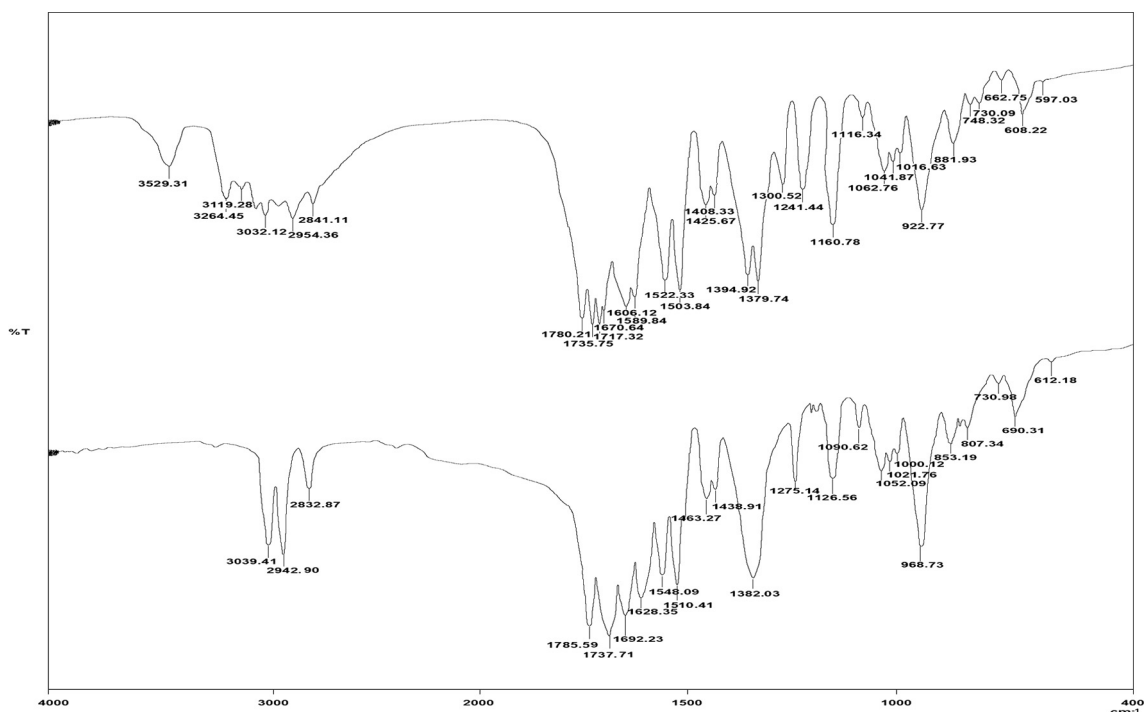


Figure 2 FTIR frequency of DA adducts C1 and Polyimides D1.

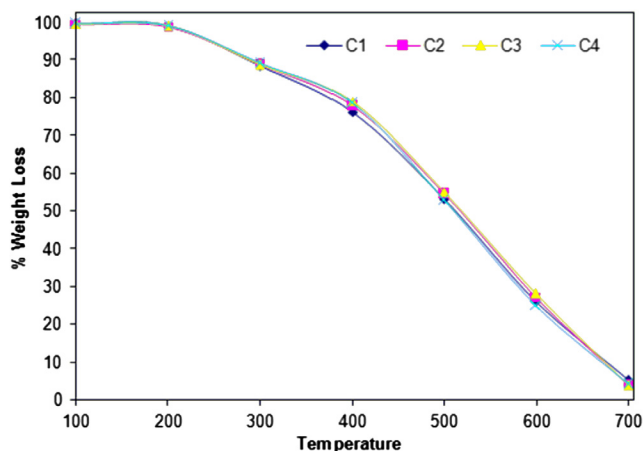


Figure 3 Thermogram of Diels Alder adducts C1-4.

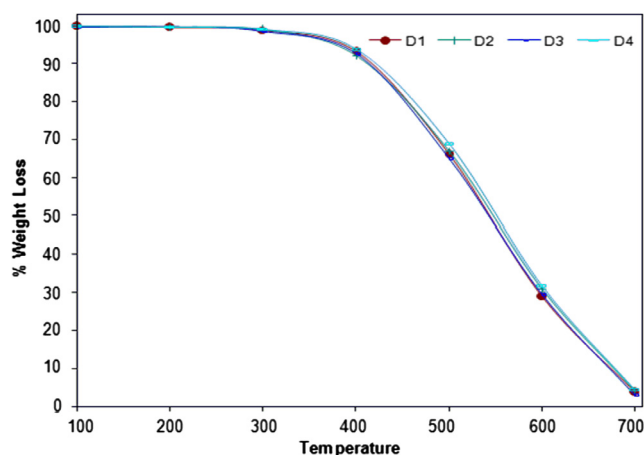


Figure 4 Thermogram of Polyimides D1-4.

started at about 350 °C depending upon the nature of PIs. Almost all polymer samples showed 50% weight loss in the range of 500–600 °C. Complete weight loss (around 95–97%) was observed at about

700 °C. The aromatized samples D1-4 were more thermally stable as their pre polymers have a nature of decarboxylation. Thus D1-4 started their degradation at slightly higher temperature as compared to non-aromatized samples C1-4. Comparison of thermal stability of all PIs revealed the following order of stability: B1 > B2 > B3 > B4. The reported thermal data of most of commercial PIs were determined in N<sub>2</sub>. The present study was carried out in air. So it was worthwhile to compare, but it could be concluded that the produced PIs were quite thermally stable and competent to commercial PIs.

### 3.3. Composite characterization

Void-free glass fiber reinforced dark brown colored composites were prepared from the produced system and characterized by chemical resistance tests, mechanical tests and electrical tests.

The results of the chemical resistance (Table 3) of all the PIs composite to organic solvents, acids and alkali revealed that the negligible weight loss was observed in ethanol, acetone, THF and in HCl. The weight loss of about 1.46–1.64% was observed in 25% H<sub>2</sub>SO<sub>4</sub>. The concentrated alkali causes changes of about 1.90–2.07% in their weight while in DMF about 1.96–2.08% weight change was observed. The results indicated that the composites have remarkable resistance to organic solvents, acids and alkali.

**Table 3** Chemical resistance of glass fiber reinforced composites **GFRC1-4**.

Composite <sup>b</sup>	GFRC <sub>1</sub> % Change in weight	GFRC <sub>2</sub> % Change in weight	GFRC <sub>3</sub> % Change in weight	GFRC <sub>4</sub> % Change in weight
25% H <sub>2</sub> SO <sub>4</sub>	1.46	1.53	1.56	1.64
25% HCl	1.23	1.27	1.29	1.39
25% NaOH	1.90	1.94	2.04	2.07
Ethanol	1.00	1.13	1.19	1.27
Acetone	1.22	1.17	1.28	1.30
DMF	1.96	1.99	2.06	2.08
THF	1.16	1.57	1.64	1.71

<sup>b</sup> Condition: Reinforcement – E type glass cloth, Plain weave, 10 mm, 10 layers, Resin Content: 40 ± 2%, Weight % molar ratio: - A: B1-4 = 1:1(mol/mol), Curing temperature = 150 ± 10 °C, Curing time = 10 h, Curing pressure = 60–70 psi, Composite size: 25 mm × 25 mm × 3 mm.

**Table 4** Mechanical and electrical properties of glass fiber reinforced composites **GFRC1-4**.

Composite	Flexural strength (MPa)	Compressive strength (MPa)	Notched Impact strength (MPa)	Rockwell hardness (MPa)	Electrical strength in air (kv/mm)
GFRC <sub>1</sub>	275	225	250	107	22.0
GFRC <sub>2</sub>	270	220	240	105	20.9
GFRC <sub>3</sub>	270	215	230	103	19.6
GFRC <sub>4</sub>	265	210	230	100	19.0

Mechanical tests were performed using their specimens. Results (Table 4) obtained were compared with the reported data of various polyimides e.g. poly(ester-amide) (Patel and Patel, 2013), poly(ester-oxysilane-imide) (Patel et al., 2010), semi IPN based on acryl end capped oligoimides (Patel and Patel, 2007) and poly(urethane-imide) (Patel et al., 2003).

The flexural strength of a material is defined as its ability to resist deformation under load. The results of flexural strength of the composites found between 265 and 275 Mpa were quite low as compared to poly(ester-amide) and found almost equal to poly(ester-oxysilane-imide), semi IPN based on acryl end capped oligoimides and poly(urethane-imide).

Compressive properties describe the behavior of a material when it is subjected to a compressive load. The results of compressive strength of the composites were observed between 210 and 225 Mpa, which were low as compared to poly(ester-amide) and semi IPN based on acryl end capped oligoimides and found nearly equal to poly(ester-oxysilane-imide) and poly(urethane-imide).

Notched Izod Impact is a single point test that measures a material's resistance to impact from a swinging pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. Impact strength of the composites observed between 230 and 250 Mpa is quite low as compared to poly(ester-amide) and found nearly equal to poly(ester-oxysilane-imide), semi IPN based on acryl end capped oligoimides and poly(urethane-imide).

Rockwell hardness is a measure of the indentation resistance of a material. Testing is performed by first forcing a steel ball indenter into the surface of a material using a specified minor load. The load is then increased to a specified major load and then decreased back to the original minor load. Rockwell hardness is a measure of the net increase in depth of the indenter. Rockwell hardness found between 100 and

107 Mpa is almost equal to poly(ester-amide), poly(ester-oxysilane-imide), semi IPN based on acryl end capped oligoimides and poly(urethane-imide).

The results of Mechanical test revealed that all the composites have good mechanical properties especially due to the presence of bismaleimides. The overall trend of the mechanical properties of the prepared PI glass fiber reinforced composites decreases as follows: GFRC<sub>1</sub> > GFRC<sub>2</sub> > GFRC<sub>3</sub> > GFRC<sub>4</sub>. This may be attributed to a certain increase in the rigidity of the bismaleimide component.

The dielectric strength of an insulating material is defined as the maximum voltage required for producing a dielectric breakdown. The sample was kept between the two electrodes and the applied voltage method was used to measure the voltage. According to this method, the voltage was raised from zero at a uniform rate of 500 V/s such that breakdown occurs on an average between 10 and 20 s. Five measurements of breakdown voltage were taken and the electric strength was calculated in kV/mm. The electric strength of all the composites was in the range of 19.0–22.0 kV/mm. As there is no wide change in electrical strength, no attempt was made to interpret these data.

#### 4. Conclusion

A novel PIs having both thermoplastic and thermosetting in a merged segment system have been successfully developed through the Diels–Alder reaction of 2,5-bis(furan-2-ylmethyl carbamoyl)terephthalic acid with different bismaleimides, followed by aromatization and imidization reaction. The 'in situ' produced PIs show good adhesion to glass fibers. All the void-free glass fiber reinforced composites have good mechanical, electrical and thermal properties and good resistance to organic solvents and mineral acid.

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