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Synthesis of thermoplastic–thermosetting merged polyimides by use of the Diels–Alder reaction

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Abstract Novel thermoplastic–thermosetting merged polyimides (PIs) have been developed by Diels–Alder (DA) intermolecular reaction of the bisfuran 2,5-bis(furan-2-ylmethylcarbamoyl)terephthalic acid **A** with a series of bismaleimides, viz., *m*,*m*′-dimethyl *p*,*p*′-dimaleimidobiphenyl (**B_1**), *m*,*m*′-dimethoxy *p*,*p*′-dimaleimidobiphenyl (**B_2**), 1,1′-bis(4-maleimidophenyl)cyclohexane (**B_3**), and 2,2′-bis-[4-(4-maleimidephenoxy)phenyl]propane (**B_4**). The intermediate DA adducts obtained, **$C_{1–4}$**, were aromatized and imidized (i.e. cyclized) through the carboxyl and amide groups to afford thermoplastic–thermosetting merged PIs **$D_{1–4}$**. Bisfuran **A** was prepared by condensation of pyromellitic dianhydride with furan-2-ylmethanamine and duly characterized. Synthesized DA adducts and PIs were characterized by use of elemental analysis, spectral features, number average molecular weight, degree of polymerization, and thermal analysis. To facilitate the correct structure assignment and to verify the identities of the DA adducts and PIs, a model compound **4** was prepared in a similar way from phthalic anhydride and furan-2-ylmethanamine. FT-IR spectral features of PIs **$D_{1–4}$** were compared with those of model compound **4** and found to be identical. Glass fiber-reinforced composites **$GFRC_{1–4}$** were prepared from this system and characterized by chemical, mechanical, and electrical analysis. All the composites had good mechanical, electrical, and thermal properties and good resistance to organic solvents and mineral acids.

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Introduction

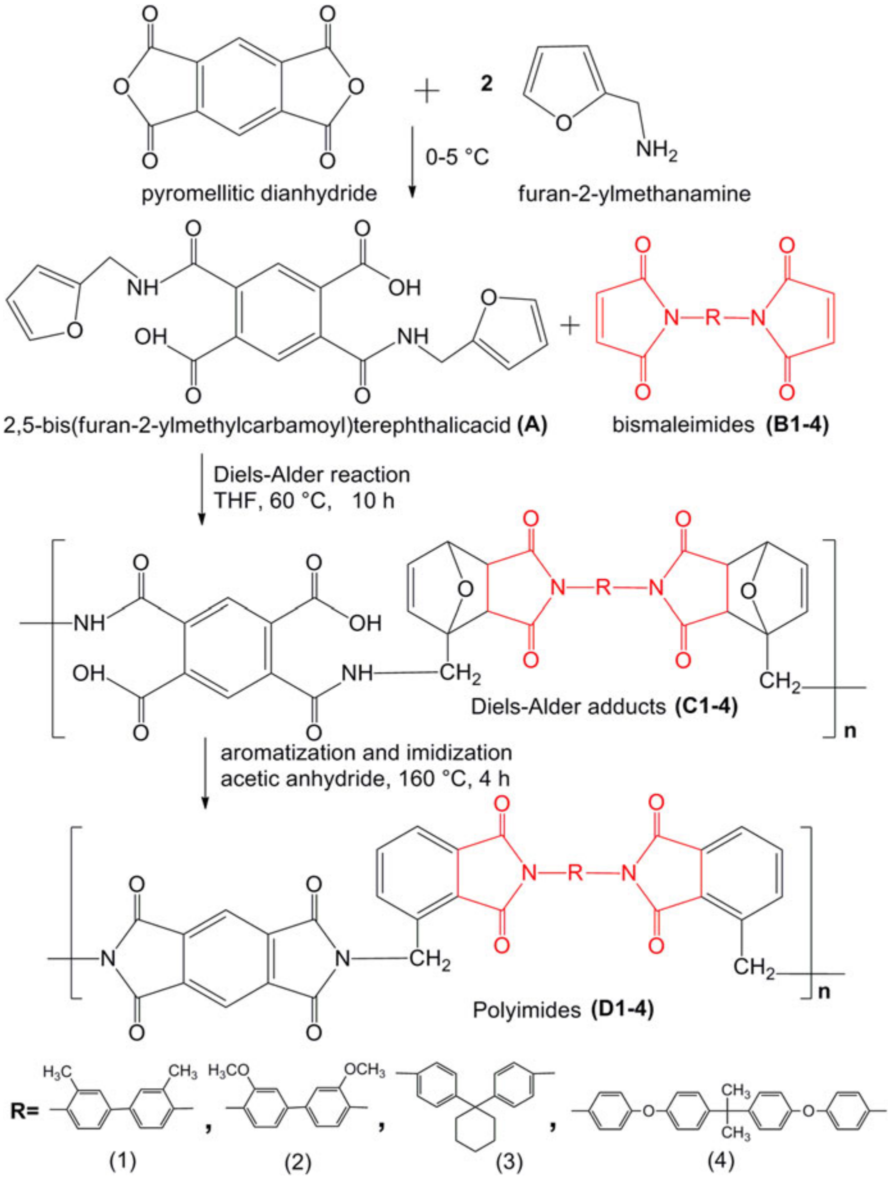
In the last few decades there has been a substantial increase in research in use of the Diels–Alder (DA) reaction in macromolecular chemistry, particularly in the field of polyimides (PIs). This reaction has been applied to the furan heterocycle with growing frequency, because its pronounced dienic character makes it particularly suitable for use as the diene in DA cycloaddition reactions. Use of bismaleimides as dienophiles is very useful because the double bond of maleimides is very reactive toward electron-rich dienes. The first investigation of a PI prepared from a bisfuran and bismaleimide was reported by Tesoro and Sastri [1]; this led to many publications on chemical modification of adduct by aromatization. Gaina et al. [2], Patel et al. [3], Sanyal [4], Peterson et al. [5], and Liu and Chen [6] used many strategies for synthesis or modification of polymer structures by exploiting the reactivity of this heterocycle with a variety of dienophiles. A systematic study of DA polymerization involving furan derivatives and a variety of bismaleimides had been performed by Gandini [7]. Owing to reported work on these topics and the long-standing interest of our laboratory in the study of PIs via the DA reaction, a more systematic investigation has been undertaken. Patel and co-workers have reported studies on such PIs as poly(epoxy–imide) [8], poly(s-triazine–imide) [9], poly(ether–imide) [10], poly(ester–amido–imide) [11], poly(amido–imide) [12], poly(ester–oxysilane–imide) [13], and poly(urethane–imide–ester) [14] with wide structural variation by DA polymerization of bisfurans and bismaleimides.

PIs are of two types. Thermoplastic PIs are usually synthesized from poly(amic acids) prepared by reaction of an aromatic dianhydride with an aromatic diamine followed by cyclodehydration to the PI. Because the final imide polymer is insoluble, infusible, and intractable, processing of the amic acid solution is frequently used for manufacture of articles. PIs synthesized from unsaturated monomers, e.g. bismaleimides, are known as thermosetting PIs. These PIs are processed in situ. Our main concern was to synthesize novel PIs with a combination of thermoplastic and thermosetting groups by introducing bisfuran and bismaleimide segments. The bisfuran (bisamic acid–pyromellitic part) segment is the thermoplastic portion and the bismaleimide segment is the thermosetting segment. This would alter the properties of PIs. Combinations of both types of segment in the PI chain has not received any attention. Hence, initial work on this topic was recently been reported by us [15]. This prompted us to extend our work by using other auxiliary bismaleimides.

In this study we synthesized PIs via the DA reaction with subsequent aromatization and imidization. Scheme 1 summarizes our synthetic approach to the various phases of this work, viz.:

1. preparation of bisfuran **A** from pyromellitic dianhydride and furan-2-ylmethanamine;
2. DA reaction between bisfuran **A** and bismaleimides $\mathbf{B_{1-4}}$; and
3. aromatization and imidization (i.e. cyclization) reaction to afford thermoplastic–thermosetting merged PIs $\mathbf{D_{1-4}}$.

Glass fiber-reinforced composites **$GFRC_{1–4}$** were prepared from this system and characterized by chemical, mechanical, and electrical analysis. To facilitate correct structure assignment and 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). The FT-IR spectral features of PIs **$D_{1–4}$** were compared



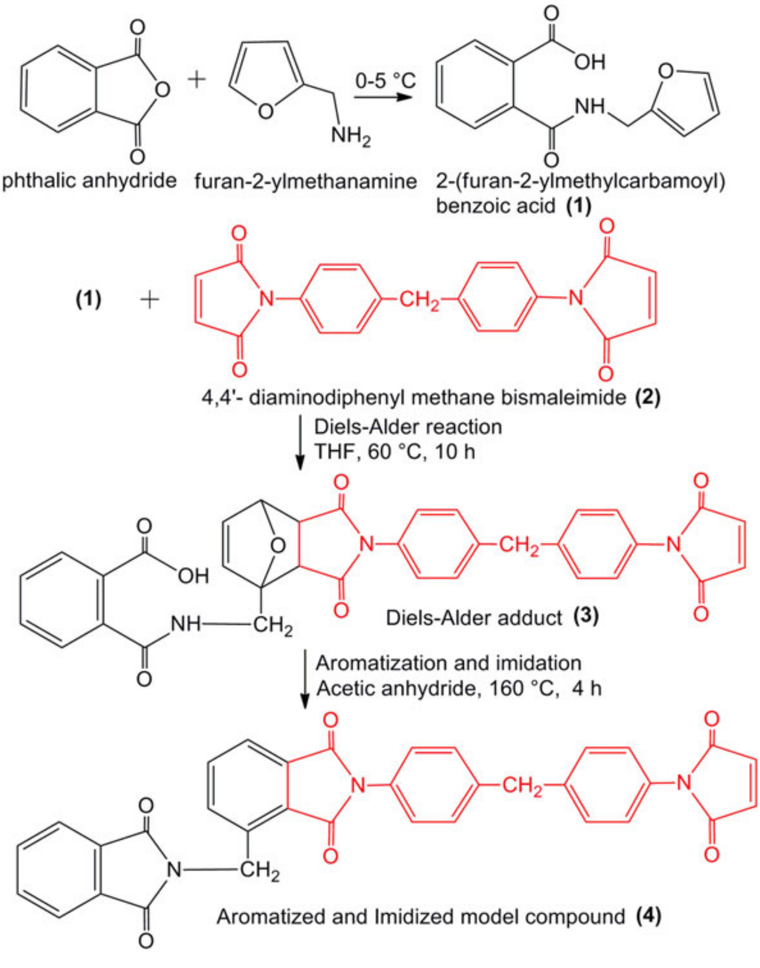
Scheme 1 Synthesis of thermoplastic–thermosetting merged PIs

with those of model compound **4** and found to be identical. The details of these procedures and the results obtained are discussed below.

Experimental

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, Mumbai, India. Furan-2-ylmethanamine was obtained locally and redistilled before use. A variety of diamines were used for the preparation: m,m'-dimethyl p,p'-dimaleimidobiphenyl ($\mathbf{B_1}$), m,m'-dimethoxy p,p'-dimaleimidobiphenyl



Scheme 2 Synthesis of model compound

(**B$_2$**), 1,1′-bis(4-maleimidophenyl)cyclohexane (**B$_3$**), and 2,2′-bis-[4-(4-maleimidephenoxy)phenyl]propane (**B$_4$**) were obtained locally and used without purification. Solvents were dried and distilled before use according to standard procedures. Elemental analysis was performed with a Thermo Finnigan Flash 1101EA (Italy). Infrared spectra were acquired by use of a Nicolet-760 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded by use of a 400-MHz Bruker spectrophotometer. Number average molecular weight (M_n) of the PIs was determined by non-aqueous conductometric titration [16–18]. Pyridine was used as suspending solvent and tetra-*n*-butylammonium hydroxide in 1,4-dioxane was used as titrant. A digital conductivity meter from Toshniwal (India) was used for titration. Thermal behavior was investigated by thermogravimetric analysis by use of a Perkin–Elmer TGA analyzer at heating rate of 10 K/min in the temperature range 50–700 °C. Because the PIs were insoluble in common organic solvents, their viscometric properties were not studied.

Synthesis of 2,5-bis(furan-2-ylmethylcarbamoyl)terephthalicacid **A**

Bisfuran **A** was synthesized by condensation of of phthalic anhydride and furan-2-ylmethanamine [19]. A solution of furan-2-ylmethanamine (0.2 mol) was added dropwise over 1 h to a stirred solution of pyromellitic dianhydride (0.1 mol) at 0–5 °C (Scheme 1). The solution obtained was poured into ice water, in which the reaction product precipitated. The white precipitate was filtered, washed, and purified by column chromatography. Yield was 65 %; M.wt. 412.35 g; decomposition temp. 250–260 °C (uncorrected); elemental analysis calculated for $C_{20}H_{16}N_2O_8$: C 58.25, H 3.91, N 6.79 % found: C 57.87, H 3.75, N 6.58 %; ^{1}H NMR (δ ppm): 10.9 (s, 2H, –COOH), 8.9 (t, $J = 5.2$ Hz, 2H, –NH–CO–), 8.1 (s, 2H, Ar–H), 7.50–7.93 (m, 6H, Ar–H), 4.32 (d, $J = 5.2$ Hz, 2H, $-CH_2-$); ^{13}C NMR (δ ppm): 42.24, 117.78, 119.24, 123.45, 126.10, 129.32, 132.67, 135.70, 167.12, 172.73; IR (KBr, cm^{-1}): 3528 (–COO–H st.), 3254 (–NH–C=O st.), 3123 (C–H st. in furan rings), 3038 (–CH st. aromatic ring), 1711 (acid –C=O st.), 1685 (O=C–NH free amide), 1500 (backbone st. aromatic ring), 1465 (COO^- sym. st.), 1039 (C–O st.), 730 (furan ring).

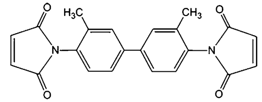
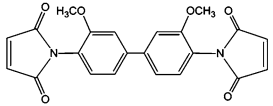
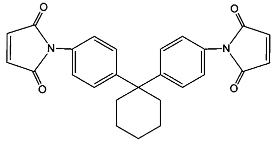
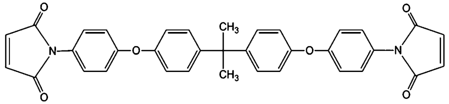
Synthesis of bismaleimides **B$_{1–4}$**

Bismaleimides (Table 1) were prepared in two steps as reported elsewhere [20–22]. The first step involved addition of one equivalent of diamine to two equivalents of maleic anhydride to form bisamic acid. In the second step cyclization of the amic acid end-group was induced by addition of sodium acetate and acetic anhydride.

DA reaction of A with **B$_{1–4}$** (formation of DA adducts **C$_{1–4}$**)

Equimolar amounts of bisfuran **A** and bismaleimide **B$_{1–4}$** were dissolved in 50 mL tetrahydrofuran. This solution was heated under reflux for 10 h at 60 °C (Scheme 1). The reaction mixture was then cooled, poured into a large volume of dry ether, and the precipitate formed was isolated by filtration, washed, and dried in

Table 1 Bismaleimides

No.	–R–	Name[a]	M.wt.	Ref.
B_1		*m*,*m*′-dimethyl *p*,*p*′-dimaleimidobiphenyl	372	[19]
B_2		*m*,*m*′-dimethoxy *p*,*p*′-dimaleimidobiphenyl	404	[20]
B_3		1,1′-bis(4-maleimidophenyl)cyclohexane	426	[21]
B_4		2,2′-bis-[4-(4-maleimidephenoxy)phenyl]propane	570	[21]

[a] Trivial names

air. The unaromatized and uncyclized products obtained were designated as DA adducts $\mathbf{C_{1–4}}$. These were purified and characterized by elemental analysis, degree of polymerization (D_p), M_n, FT-IR, and thermal analysis.

$\mathbf{C_1}$: Yield 45 %; color light brown; empirical wt. 784.72 g; IR (KBr, cm^{-1}): 3536 (–OH st. acid), 3250 (–NH st. amide), 3115 (–CH st. furan ring), 3027 (–CH st. aromatic ring), 2962, 2854 (–CH st. aliphatic), 1777 (–C=O st. asym. imide), 1730 (–C=O st. sym. imide), 1711 (–C=O st. acid), 1678 (–C=O st. amide), 1580 (–C=C– st. furan ring), 1461 ($-COO^-$ st. sym.), 1240, 1163, 1061 (furan –CH in-plane deformation), 1042 (–C–O st.), 913, 872, 731 (furan –CH out-of-plane deformation/–C=O bending); elemental analysis calculated for $C_{42}H_{32}N_4O_{12}$: C 64.28, H 4.11, N 7.14 %; found: C 64.20, H 4.04, N 7.09 %; D_p 7; M_n 5480 ± 60.

$\mathbf{C_2}$: Yield 40 %; color light brown; empirical wt. 816.72 g; IR (KBr, cm^{-1}): 3532 (–OH st. acid), 3246 (–NH st. amide), 3112 (–CH st. furan ring), 3033 (–CH st. aromatic ring), 2950, 2849 (–CH st. aliphatic), 1783 (–C=O st. asym. imide), 1731 (–C=O st. sym. imide), 1715 (–C=O st. acid), 1674 (–C=O st. amide), 1583 (–C=C– st. furan ring), 1460 (–COO– st. sym.), 1240, 1161, 1060 (furan –CH in-plane deformation), 1039 (–C–O st.), 910, 875, 730 (furan –CH out-of-plane deformation/ C=O bending); elemental analysis calculated for $C_{42}H_{32}N_4O_{14}$: C 61.77, H 3.95, N 6.86 %; found: C 61.70, H 3.91, N 6.80 %; D_p 7; M_n 5703 ± 60.

$\mathbf{C_3}$: Yield 50 %; color light brown; empirical wt. 838.81 g; IR (KBr, cm^{-1}): 3533 (–OH st. acid), 3246 (–NH st. amide), 3117 (–CH st. furan ring), 3034 (–CH st. aromatic ring), 2956, 2846 (–CH st. aliphatic), 1787 (–C=O st. asym. imide), 1738 (–C=O st. sym. imide), 1710 (–C=O st. acid), 1670 (–C=O st. amide), 1585 (–C=C– st. furan ring), 1463 (–COO– st. sym.), 1245, 1167, 1063 (furan –CH in-plane deformation), 1040 (–C–O st.), 915, 877, 732 (furan –CH out-of-plane deformation/ C=O bending); elemental analysis calculated for $C_{46}H_{38}N_4O_{12}$: C 65.87, H 4.57, N 6.68 %; found: C 65.82, H 4.53, N 6.60 %; D_p 8; M_n 6710 ± 60.

$\mathbf{C_4}$: Yield 40 %; color light brown; empirical wt. 982.94 g; IR (KBr, cm^{-1}): 3527 (–OH st. acid), 3240 (–NH st. amide), 3122 (–CH st. furan ring), 3028 (–CH st. aromatic ring), 2957, 2838 (–CH st. aliphatic), 1775 (–C=O st. asym. imide), 1730 (–C=O st. sym. imide), 1716 (–C=O st. acid), 1679 (–C=O st. amide), 1587 (–C=C– st. furan ring), 1465 (–COO– st. sym.), 1246, 1163, 1065 (furan –CH in-plane deformation), 1037 (–C–O st.), 912, 875, 734 (furan –CH out-of-plane deformation/ C=O bending); elemental analysis calculated for $C_{55}H_{42}N_4O_{14}$: C 67.21, H 4.31, N 5.70 %; found: C 67.15, H 4.25, N 5.63 %; D_p 8; M_n 7860 ± 60.

Aromatization and imidization of DA adducts $\mathbf{C_{1–4}}$ (formation of PIs $\mathbf{D_{1–4}}$)

Aromatization of the polymers was performed by heating 1 g dried DA adduct $\mathbf{C_{1–4}}$ in 1 mL acetic anhydride [1] under reflux for 4 h at 150–160 °C (Scheme 1). Imidization occurs simultaneously. The resulting solution was cooled and poured into a large volume of water. The precipitate formed was isolated by filtration, washed, then dried in air. Thus brown precipitates of PIs $\mathbf{D_{1–4}}$ obtained were characterized by elemental, IR, and thermal analysis.

$\mathbf{D_1}$: Yield 45 %; color brown; empirical wt. 712.66 g; IR (KBr, cm^{-1}): 3034 (–CH st. aromatic ring), 2956, 2855 (–CH st. aliphatic), 1782 (–C=O st. asym.

imide), 1735 (–C=O st. sym. imide), 1500 (backbone st. aromatic ring), 1370 (imide, imide ring vibration, axial); elemental analysis calculated for $C_{42}H_{24}N_4O_8$: C 70.78 H 3.39 N 7.86 %; found: C 70.71 H 3.32 N 7.80 %.

D_2: Yield 45 %; color brown; empirical wt. 744.66 g; IR (KBr, cm^{-1}): 3040 (–CH st. aromatic ring), 2960, 2853 (–CH st. aliphatic), 1780 (–C=O st. asym. imide), 1732 (–C=O st. sym. imide), 1502 (backbone st. aromatic ring), 1373 (imide, imide ring vibration, axial); elemental analysis calculated for $C_{42}H_{24}N_4O_{10}$: C 67.74, H 3.25, N 7.52 %; found: C 67.68, H 3.18, N 7.46 %.

D_3: Yield 40 %; color brown; empirical wt. 766.75 g; IR (KBr, cm^{-1}): 3041 (–CH st. aromatic ring), 2964, 2858 (–CH st. aliphatic), 1781 (–C=O st. asym. imide), 1733 (–C=O st. sym. imide), 1504 (backbone st. aromatic ring), 1376 (imide, imide ring vibration, axial); elemental analysis calculated for $C_{46}H_{30}N_4O_8$: C 72.06, H 3.94, N 7.31 %; found: C 72.00, H 3.89, N 7.26 %.

D_4: Yield 40 %; color brown; empirical wt. 910.88 g; IR (KBr, cm^{-1}): 3046 (–CH st. aromatic ring), 2963, 2850 (–CH st. aliphatic), 1785 (–C=O st. asym. imide), 1731 (–C=O st. sym. imide), 1503 (backbone st. aromatic ring), 1375 (imide, imide ring vibration, axial); elemental analysis calculated for $C_{55}H_{34}N_4O_{10}$: C 72.52, H 3.76, N 6.15 %; found: C 72.45, H 3.69, N 6.10 %.

Bulk polymerization

A mixture of **A** (0.01 mol), **$B_{1–4}$** (0.01 mol), and 2 ml acetic anhydride was heated at approximately 150 °C for 10 h with vigorous agitation. The resulting brown solid products were cooled and poured into a large volume of water. The precipitates formed were isolated by filtration, washed, then dried in air. The results obtained by bulk polymerization were analogous with those for the synthesized PIs.

Synthesis of model compound

A suspension of 2-(furan-2-ylmethylcarbamoyl)benzoic acid (0.01 mol) and 4,4′-diaminodiphenylmethane bismaleimide (0.01 mol) in THF was heated under reflux for 10 h at 60 °C. The resulting unaromatized and unimidized product was designated as DA adducts **3**. It was heated under reflux at 150–160 °C for 4 h with 2 ml acetic anhydride to afford aromatization and imidization (Scheme 2). The resulting solution was cooled and poured into a large volume of water, washed, filtered, then dried in air. The brown precipitate of **4** thus obtained was characterized by elemental and IR analysis. Yield was 65 %; M.wt. 567.55 g; elemental analysis calculated for $C_{34}H_{21}N_3O_6$: C 71.95, H 3.73, N 7.40 %; found: C 71.86, H 3.67, N 7.31 %; IR (KBr, cm^{-1}): 3028, 2972, 2862, 1771, 1730, 1513, and 1379; ^1H NMR (δ ppm): 2.49 (s, 2H, Ph–CH_2–Ph), 4.40 (s, 2H, N–CH_2–Ph), 7.28–8.06 (m, 15H, Ar–H), 8.41 (d, $J = 8.8$, 2H, maleimide) (Supplementary Fig. 1).

Preparation of glass fiber-reinforced composites **$GFRC_{1–4}$**

To prepare glass fiber-reinforced composites **$GFRC_{1–4}$**, suspensions of **A** and **$B_{1–4}$** in THF were prepared on a weight basis and stirred well for 10 min. These resin

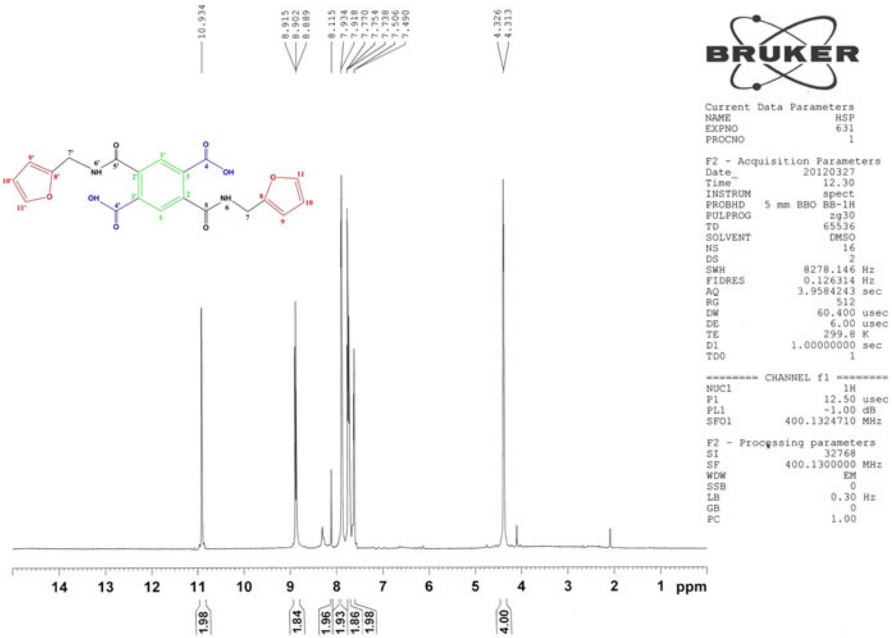


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Fig. 1 ^{1}H NMR of bisfuran **A**

suspensions were used to vanish PI-compatible glass cloth. The suspensions were applied with a brush and the solvent was left to evaporate for 10–20 min at room temperature. The ten dried prepregs so prepared were stacked one over another and placed between stainless steel plates and compressed under approximately 60–70 psi pressure at 150 °C for 10 h in air circulating oven. The composites were cooled to room temperature before the pressure was released. The composites were then machined to desire final dimension for mechanical and chemical tests.

Chemical resistance test

The chemical resistance test for all the composite samples was performed according to ASTMD 543–67. The composite sample dimensions were 25 × 25 × 3 mm^3. The samples were immersed in 25 % *v*/*v* H_2SO_4, 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 removed from the reagents and analyzed for the percentage change in their thickness and weight.

Mechanical and electrical tests

All mechanical tests were performed using three specimens.

- The compressive strength was measured on a Universal Instron testing machine model no. A-74-37, at room temperature according to ASTM D 695.

- The notched Izod impact strength of the composites was measured on a Zwick model no. 8900 impact machine at room temperature according to ASTM D256.
- Rockwell hardness was measured at room temperature by use of a model RAS (Saro Engineering, India) Rockwell hardness tester according to ASTM D 785.
- Measurement of flexural strength was performed with a Universal Instron Testing Machine, model no. A-74-37, at room temperature according to ASTM method D790.

Electrical strength measurements were conducted on a high voltage tester machine oil test set.

Results and discussion

Monomer synthesis

To the best of our knowledge, product **A** has not been reported previously. 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 FT-IR spectrum of **A** showed the most relevant peaks of the furan ring and the 1,2,4,5-tetra-substituted benzene ring, and typical absorption of carboxylic acid at 3528 and 1711 cm^{-1} and of the O=C–NH group at 3254 and 1680 cm^{-1} [23]. In ^1H NMR spectroscopy, signals in the range 7.5–8.1 ppm were ascribed to the protons of the aromatic rings. The singlet at 10.9 ppm was ascribed to the protons of carboxyl –OH group and a triplet at 8.9 ppm was attributed to the –NH proton of the amide group (Fig. 1), which was further confirmed by ^{13}C NMR. Monomer **A** lost weight during thermal degradation. TGA data for **A** indicated that degradation occurred into two steps. The first stage was from 180 to 300 °C and might be attributed to decarboxylation of **A**. The weight loss of 20.91 % is consistent with the theoretical value, 21.34 %. The second major stage at approximately 300–700 °C was attributed to decomposition and/or pyrolysis of the monomer. Three to four percent of charred residue remained at 700 °C. The expected structure was thus clearly verified by this spectroscopic and thermal analysis which indicated, moreover, the absence of any detectable impurity, particularly of the two reagents used to prepare **A**. This was also confirmed by elemental analysis.

Polymer synthesis

The thermoplastic–thermosetting merged PI system was prepared by DA intermolecular reaction followed by aromatization of the DA adduct and simultaneous imidization via cyclization. Results from elemental analysis of the DA adducts indicated that the reactions led to good yields in cycloaddition of the furan rings, and were consistent with their predicted structures (Scheme 1). D_p for polymers $\mathbf{C}_{1\text{–}4}$ was estimated by non-aqueous titration and was in the range 8–9. The IR spectra of the adducts revealed important changes compared with the initial monomers; these clearly confirmed the DA reaction had occurred with good yields

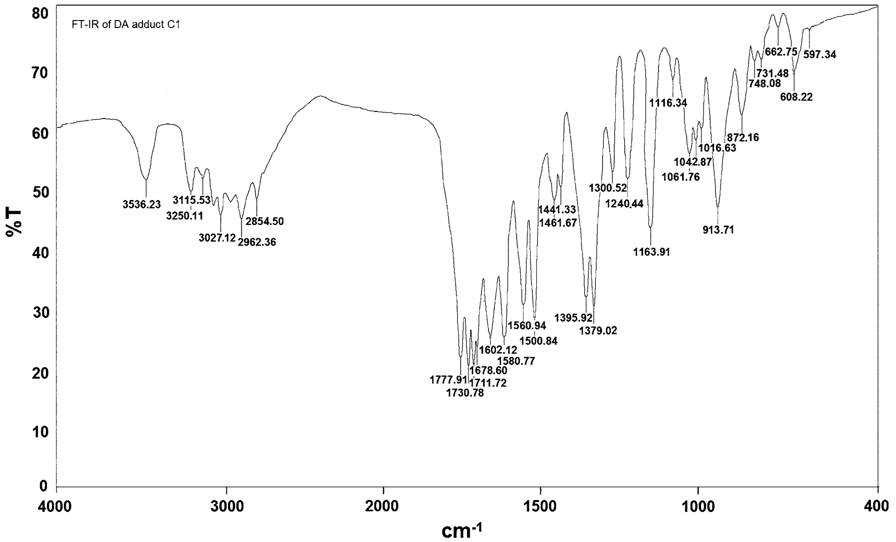

Fig. 2 FT-IR of DA adduct $\mathbf{C_1}$

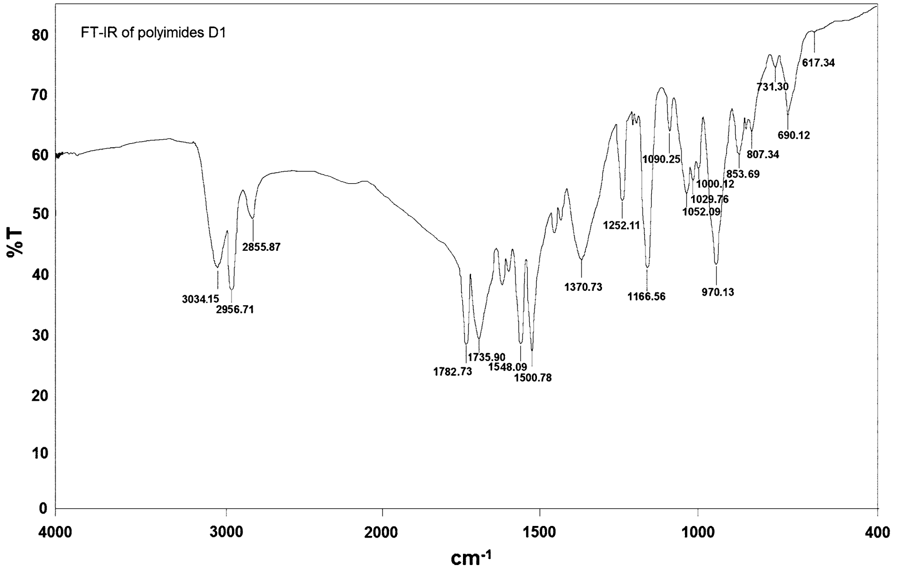

Fig. 3 FT-IR of PI $\mathbf{D_1}$

with all the bismaleimides. The IR spectra of DA adducts $\mathbf{C_{1–4}}$ had prominent characteristic bands of furan, amide, and carboxylic acid groups (Fig. 2). The bands near 3125 and 1585 cm^{-1} were attributed to furan. The bands at approximately 3225 and 1675 cm^{-1} were attributed to amide groups and the bands at approximately 3530 and 1710 cm^{-1} were attributed to –OH and –C=O groups, respectively, of the carboxylic acid. Comparison of the IR spectra of non-aromatized and-non cyclized $\mathbf{C_{1-4}}$ with aromatized and imidized (cyclized) $\mathbf{D_{1-4}}$ revealed discernible differences. The bands of the carboxylic acid and amide groups in the spectra of $\mathbf{C_{1-4}}$ were almost absent from the spectra of $\mathbf{D_{1-4}}$, indicating that imidization had occurred very smoothly, and the disappearance of the bands of the furan ring confirmed aromatization reaction had been completed simultaneously.

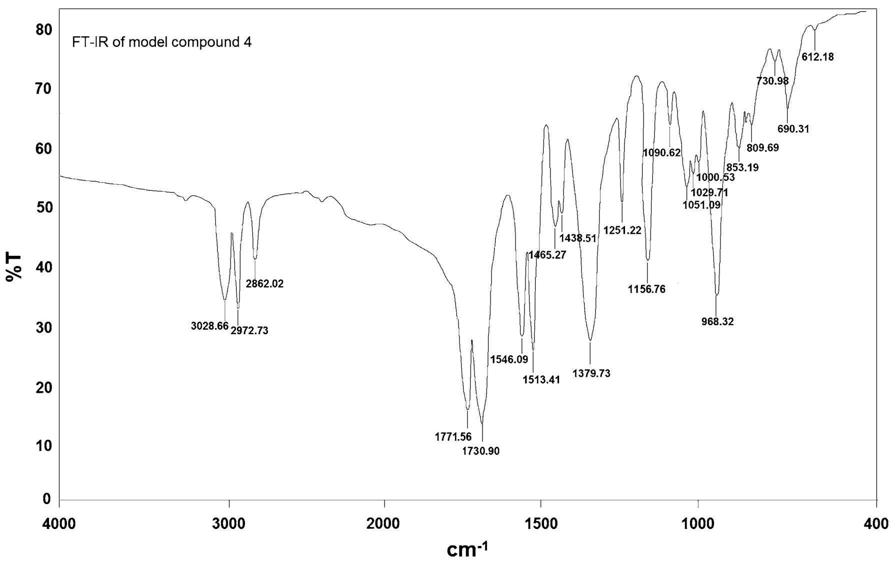

Fig. 4 FT-IR of model compound **4**

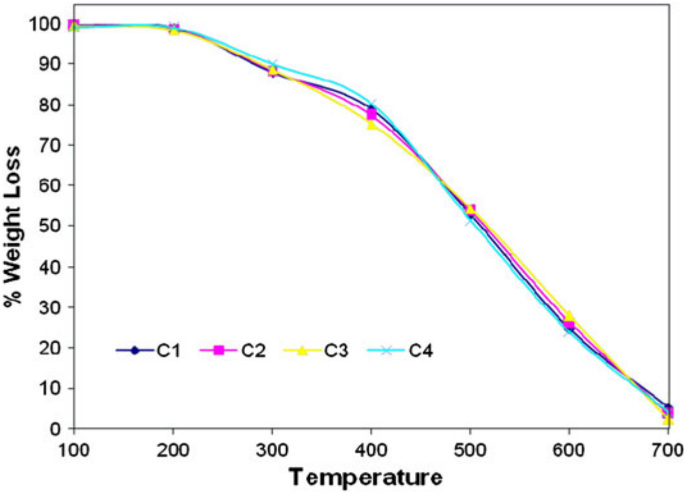

Fig. 5 Thermogram of the DA adducts ($\mathbf{C_{1-4}}$)

For the sake of convenience, the IR spectra of PIs $\mathbf{D_{1-4}}$ (Fig. 3) were compared with that of the model compound (Fig. 4). IR spectral features of PIs $\mathbf{D_{1-4}}$ were identical with those of the model compound. These features confirmed the predicted structure of aromatized–imidized PIs $\mathbf{D_{1-4}}$.

The thermal stability of $\mathbf{C_{1-4}}$ (Fig. 5) and $\mathbf{D_{1-4}}$ (Fig. 6) were evaluated from their TG curves. $\mathbf{C_{1-4}}$ underwent two stages of mass loss. The first, major, stage, in the temperature range 180–280 °C, corresponded to decarboxylation of the polymer. The weight loss observed for $\mathbf{C_{1-4}}$ was consistent with the theoretical value. The second stage of mass loss, above 280 °C, was because of polymer pyrolysis. Approximately 4–6 % charred residue of $\mathbf{C_{1-4}}$ was left at 700 °C. Very rapid weight loss was observed between 400 and 600 °C.

Decomposition of $\mathbf{D_{1-4}}$ started at 350 °C, depending upon the nature of PIs. For almost all the polymer samples weight loss was 50 % in the range 500–600 °C. Complete weight loss (approx. 95–97 %) was observed at approximately 700 °C. Aromatized samples $\mathbf{D_{1-4}}$ were more thermally stable that their prepolymers because of the decarboxylation of the former. Thus degradation of $\mathbf{D_{1-4}}$ started at slightly higher temperatures than that of the non-aromatized samples $\mathbf{C_{1-4}}$. Comparison of the thermal stability of all PIs revealed the following order of stability: $\mathbf{B_4} > \mathbf{B_1} > \mathbf{B_2} > \mathbf{B_3}$. Thermal data reported for most commercial PIs were determined in N_2. This study was conducted in air, so it is worth mentioning that these PIs were quite thermally stable compared with commercial PIs.

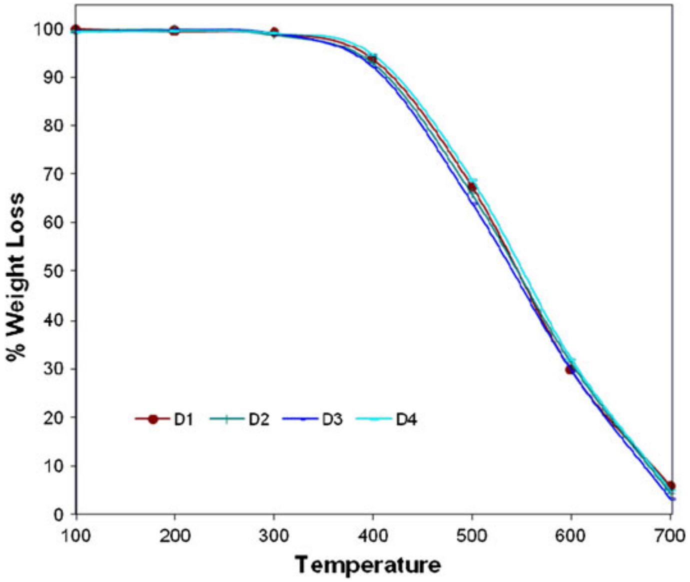

Fig. 6 Thermogram of the PIs ($\mathbf{D_{1-4}}$)

Composite characterization

Glass fiber-reinforced dark brown composites were prepared and characterized. Results from testing of the chemical resistance of the PI composites to organic solvents, acids, and alkalis (Table 2) revealed that weight loss was negligible in ethanol, acetone, THF, and HCl. Weight loss of approximately 1.40–1.56 % was observed in 25 % H_2SO_4. Concentrated alkali resulted in weight changes of approximately 1.70–2.04 %; in DMF approximately 1.88–2.06 % weight change was observed. The results indicated that the composites had remarkable resistance to organic solvents, acids, and alkali.

Mechanical tests were performed on the specimens and the results obtained (Table 3) were compared with reported data [15]. The flexural strength of a material is defined as its ability to resist deformation under load. The flexural strength of the composites was between 272 and 287 Mpa. Compressive properties describe the behavior of a material when it is subjected to a compressive load. The compressive strength of the composites was between 220 and 239 Mpa. The notched Izod impact test 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. The impact strength of the composites was between 232 and 256 Mpa. 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 by use of a specified minor load. The load is then increased to a specified major load, then reduced to the original minor load. Rockwell hardness is a measure of the net increase in depth of the indenter. Rockwell hardness was between 106 and 110 Mpa. The results of mechanical testing (Table 3) revealed that all the composites have good mechanical properties compared with our previously reported data. This may be attributed to increased rigidity because of the aromatic backbone in the bismaleimides. The overall trend of the mechanical properties of the prepared PI glass fiber-reinforced composites decreases as follows: $\mathbf{GFRC_4 > GFRC_1 > GFRC_2 > GFRC_3}$. The dielectric

Table 2 Chemical resistance of glass fiber-reinforced composites[a]

Composite[b]	**GFRC$_1$** % change		**GFRC$_2$** % change		**GFRC$_3$** % change		**GFRC$_4$** % change	
	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.
	1.1	1.46	1.2	1.53	1.2	1.56	1.1	1.40
25 % HCl	1.0	1.23	1.1	1.27	1.2	1.29	1.0	1.19
25 % NaOH	1.3	1.90	1.4	1.94	1.4	2.04	1.2	1.70
Ethanol	1.0	1.11	1.0	1.13	1.2	1.19	0.8	0.87
Acetone	1.0	1.12	1.2	1.17	1.2	1.28	0.9	1.10
DMF	1.3	1.96	1.4	1.99	1.5	2.06	1.3	1.88
THF	1.3	1.41	1.4	1.57	1.4	1.64	1.1	1.21

[a] *Condition*: reinforcement—E type glass cloth, plain weave, 10 mm, 10 layers, resin content 40 ± 2 %, weight % molar ratio: $A{:}B_{1\text{–}5} = 1{:}1$ (mol/mol). Curing temperature = 150 ± 10 °C, curing time = 10 h, curing pressure = 60–70 psi. Composite size: $25 \times 25 \times 3\ \text{mm}^3$

Table 3 Mechanical and electrical properties of glass fiber-reinforced composites

Composite	Flexural strength (MPa)	Compressive strength (MPa)	Notched impact strength (MPa)	Rockwell hardness (MPa)	Electrical strength in air (kV/mm)
GFRC$_1$	281	231	250	109	17.2
GFRC$_2$	275	224	238	107	18.6
GFRC$_3$	272	220	232	106	19.8
GFRC$_4$	287	239	256	110	21.9

strength of an insulating material is defined as the maximum voltage required to cause dielectric breakdown. The electric strength of all the composites was in the range of 17.2–21.9 kV/mm. This was high compared with previous data.

Conclusion

Novel PIs with a merged segment system and both thermoplastic and thermosetting properties have been successfully prepared by DA reaction of 2,5-bis(furan-2-ylmethylcarbamoyl)terephthalic acid with different bismaleimides, followed by aromatization and imidization. The in-situ-produced PIs adhere well to glass fiber. All the glass fiber-reinforced composites had good mechanical, electrical, and thermal properties and good resistance to organic solvents and mineral acid.

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