Electronic Supporting Information (ESI)

Hybrid films of novel fluorinated polyimides and hyperbranched cyclotriphosphazene polymer for enhanced flame retardancy, thermomechanical properties, and reduced dielectric constant

Sivagangi Reddy Nagella and Chang-Sik Ha[*]

Department of Polymer Science and Engineering, School of Chemical Engineering, Pusan National University, Busan 46241, Korea. E-mail: csha@pnu.edu

Experimental details

Materials

4,4'-Oxydiphthalic anhydride (ODPA), 4-chloro-3-(trifluoromethyl) nitrobenzene (4-CTN), bisphenol-P (BP-P), and bisphenol-AF (BPAF) were procured from TCI (Osaka, Japan). Anhydrous potassium carbonate (K_2CO_3), Pd/C, hexachlorocyclotriphosphazene, N,N'-dimethylformamide (DMF), anhydrous N-methylpyrrolidone (NMP), acetic anhydride (Ac_2O), pyridine (Py) and triethylamine (TEA) were obtained from Sigma-Aldrich. Dichloromethane (DCM), ethyl acetate (EA), n-hexane, acetonitrile, and other solvents were sourced from Junsei Chemical (Tokyo, Japan). All chemicals were used as received without further purification.

CPAF synthesis

The soluble hyperbranched poly[cyclotriphosphazene-co-(4,4'-(perfluoropropane-2,2-diyl) diphenol)] (CPAF) polymer was synthesized by reacting HCP (0.348 g, 1.0 mmol) with BPAF (3.0 g, 9.0 mmol) in acetonitrile at room temperature under ultrasonic conditions. The reaction was facilitated by an excess of TEA, which acted as an acid scavenger, accelerating the nucleophilic substitution between the terminal hydroxyl groups and P-Cl bonds, leading to the formation of hyperbranched polymers in the presence of excess BPAF. After two h, the reaction mixture was transferred to a separating funnel and washed thoroughly with water to remove TEA salts and any unreacted TEA. The dichloromethane (DCM) layer was dried using anhydrous magnesium sulfate, followed by solvent evaporation to obtain the crude polymer. The crude product was further purified by repeated washing with n-hexane and acetone to remove residual HCP and BPAF. The final hyperbranched CPAF polymer was dried in a vacuum oven at 60°C. The resulting polymer was soluble in DMSO, NMP, and tetrahydrofuran (THF).

The TGA curves of HCP, BPAF, and CPAF shown in Fig. S1(d) indicate that thermal stability is significantly improved by the strengthening of the phosphazene ring, which is facilitated by the formation of P−O−Ph bonds. We can see this transformation in Fig. S7(e).[1]

BPAF Diol ^{1}H NMR: (400 MHz, d6-DMSO) δ 9.52 (s, 1H), 6.75 (d, J = 8.1 Hz, 2H), 6.45 (d, J = 8.3 Hz, 2H).

CPAF ^{1}H NMR: (400 MHz, d6-DMSO) δ 9.96 (s, 1H), 7.34 (s, 1H), 7.21 (s, 1H), 7.08 (d, J = 7.2 Hz, 3H), 6.80 (d, J = 8.0 Hz, 3H).

CPAF MALDI-TOF (dithranol+NaTFA): m/z: 7078.67 (DP=5) [C285H160F114N15O38P15+2Na], 7396.52 [C285H160F114N15O38P15+P3N3Cl5+2Na].

B2FDA monomer synthesis

The diamine monomer 4,4'-(1,4-phenyleneisopropylidene) diphenoxy bis(2-(trifluoromethyl)-4-aminobenzene) (B2FDA) was synthesized through a two-step process, starting with the nitration of BP-P followed by its reduction to yield the corresponding amine. The intermediate nitro compound (B2FDN) was prepared by reacting 4-CTN with BP-P. Specifically, 10.0 g of BP-P and 8.65 g of 4-CTN were dissolved in 80 mL of anhydrous DMF in a 250 mL round-bottom flask. Anhydrous potassium carbonate (K_2CO_3) was added as a base, and the reaction mixture was stirred at 120°C for 10 h under heating conditions. Once the reaction was complete, the mixture was cooled to room temperature and poured into excess water to precipitate the crude nitro compound. The precipitate was thoroughly washed with water and recrystallized using a 1:2 ethyl acetate:n-hexane (EA:n-hexane) mixture. The resulting pure nitro compound was dried at 80°C for 12 h. The yield of B2FDN was approximately 85%, with a melting point of 219.6°C.

In the second step, 10.0 g of B2FDN and 0.5 g of palladium on carbon (Pd/C) were added to a 500 mL round-bottom flask. Subsequently, 250 mL of a 1:1 mixture of THF and ethanol was added. The reaction mixture was heated to reflux under a nitrogen atmosphere to maintain an inert environment. Once the solid B2FDN was completely dissolved, hydrazine monohydrate was carefully added dropwise over 30 min. The reaction was maintained under reflux for 7–8 h, with progress monitored using thin-layer chromatography. After the reaction was complete, the mixture was cooled to room temperature and allowed to stand overnight to promote crystallization of the diamine product (B2FDA). The crystallized product was filtered, and the remaining solid was dried under vacuum at 80°C for 15 h. The resulting B2FDA monomer was obtained with an 80% yield (M.P. 202.8°C).

B2FDN ^{1}H NMR: (400 MHz, d6-DMSO) δ 8.48 (s, 1H), 8.45 (d, J = 9.4 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.19–7.09 (m, 3H), .06 (d, J = 9.2Hz, 1H).

B2FDA ^{1}H NMR: (400 MHz, d6-DMSO) δ 7.12 (d, J = 8.4 Hz, 1H), 7.08 (s, 1H), 6.87 (s, 1H), 6.82 (d, J = 8.8 Hz, 1H), 6.75 (t, J = 9.9 Hz, 1H), 5.41 (s, 1H).

Preparation of PI and PI-CPAF Hybrid Films

Eight different formulations of PI/CPAF hybrids were prepared using an Experimental Matrix for a One-Factor Full Factorial Design, with 8 levels of additive concentration ranging from 0 % to 10 % (0 %, 0.5%, 1 %, 2 %, 3 %, 4 %, 5 %, and 10 %). The B2FO is pure PI film, while the corresponding hybrid films were labeled as B2FO-CPAF-1, B2FO-CPAF-2, B2FO-CPAF-3, B2FO-CPAF-4, B2FO-CPAF-5, B2FO-CPAF-6, and B2FO-CPAF-7, respectively, and each formulation was individually tested to evaluate the impact of CPAF on different properties of the PI.

In this study, B2FO polyimide (PI) was synthesized using a two-step imidization method. Initially, poly (amic acid) (PAA) was prepared via a condensation reaction between B2FDA (1.37 g, 2 mmol) and ODPA (0.64 g, 2.05 mmol) in 7.5 mL of anhydrous NMP at room temperature under a nitrogen (N_2) atmosphere. Subsequently, the resulting viscous PAA was imidized using Ac_2O and Py at 60°C for approximately 6 h. The PI resin solution was then precipitated by pouring it into a methanol solution, resulting in the formation of white fibrous resins, which was washed several times and dried at 110 °C under vacuum. The dried PI was dissolved in NMP to prepare a 10 wt.% solution, which was applied to a glass plate and allowed to evaporate under a nitrogen atmosphere for 10 hours at 80°C, followed by 1 hour at 180°C. The resulting films were removed from the glass plates using warm deionized water and kept in water for about 5 h, subsequently dried in a vacuum oven at 100°C.

Although the complete removal of NMP was not confirmed from any technique, it should be noted that we employed post-curing solvent elimination process with water, a solvent with high NMP affinity. Particularly, after curing the films in the oven, we placed them in water for approximately five hours to aid the removal of residual NMP.

The preparation of PI/CPAF hybrids was demonstrated with the example B2FO-CPAF-7. A solution of B2FDA (1.37 g, 2 mmol), ODPA (0.67 g, 2.1 mmol), and 7.5 mL (20% w/w solid content) of anhydrous NMP was stirred under nitrogen conditions for about 6 h and was chemically imidized to PI as discussed above. A 10 wt% PI solution in NMP (1 g of dried PI) was prepared, to which 0.104 g of CPAF in 2 mL of NMP was added and stirred at room temperature for an additional 2 hours. The homogeneous solution obtained was then cast onto a glass substrate and thermally treated as described above.

PI ^{1}H NMR: (400 MHz, d6-DMSO) δ 8.05 (s, 1H), 7.87 (s, 1H), 7.62 (d, J = 26.8 Hz, 1H), 7.26 (s, 1H), 7.07 (d, J = 40.5 Hz, 1H), 1.59 (s, 1H).

Characterization

The proton nuclear magnetic resonance (1H NMR) spectra were recorded on a Varian-400 (400 MHz) instrument using deuterated dimethyl sulfoxide (d6-DMSO) as the solvent. The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded using a Cary 630 (Agilent) spectrometer, equipped with an internal reflection accessory. The films were scanned from 400 to 4000 cm^{-1}, using 32 scans at a resolution of 4 cm^{-1}. The experiment was conducted with careful attention to maintaining a clean crystal surface to obtain an optimal sample spectrum. Each sample spectrum was obtained after subtraction of the background air spectrum. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analysis was performed using a Bruker Autoflex maX (Germany) equipped with a nitrogen laser emitting at 337 nm, operating in linear mode. The mass spectrum was acquired with dithranol as the matrix, utilizing 30–50 laser shots. The molecular weights of B2FO PI were measured using gel permeation chromatography (Waters GPC, 1515 isocratic pump, 2414 RI detector, USA). Approximately 5 mg of the sample was dissolved in 1 mL of DMF and eluted at a flow rate of 1.0 mL/min using DMF as the mobile phase. The molecular weights of the PI were determined by comparison with a polystyrene (PS) external standard, and the results are presented in Table 1.

The melting points of the monomers and the Tg of the PI/PI hybrids were measured using a differential scanning calorimeter (DSC-25, TA Instruments, USA) in a nitrogen atmosphere at heating rates of 20°C/min and 10°C/min, respectively. The dynamic mechanical analysis (DMA) studies (Tg and loss modulus) were performed using a temperature sweeping method (at 2°C/min, 3 Hz frequency, and 20 μm amplitude) on a DMA Q800 (TA Instruments, USA). Thermogravimetric measurements were conducted on a Discovery series thermal analyzer (TA Instruments, USA) at a heating rate of 10°C/min with a 40 mL/min nitrogen flow rate. Mechanical properties were measured using an RB301 universal testing machine (Instron 5969 UTM, USA). Tensile strength (Ts), tensile modulus (Tm), and elongation at break (Eb) were calculated as the average of three samples, with a crosshead speed of 2 mm/min (ISO 527-3:2018). The water contact angle was measured (average of three samples) using a Phoenix-300 contact angle measurement device (Surface Electro Optics, South Korea) at room temperature.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) of the hybrids were performed on an ultra-high analytical field emission scanning electron microscope (GEMINI500) to observe the surface of the films and the dispersion of CPAF in the PI matrix. Before measurement, the sample surfaces were coated with a 180 nm layer of platinum (for SEM) or chromium (for EDS) to enhance conductivity. Imaging was performed using an accelerating voltage of 15 kV. The ultraviolet-visible (UV-vis) spectra of the B2FO PI and B2FO-CPAF hybrid films were recorded on a spectrophotometer (Hitachi U-2010, Japan) over a wavelength range of 200 to 800 nm, with a resolution of 0.5 nm and a scanning speed of 300 nm/min. The WAXD patterns of films were obtained from PANalytical Xpert-3 Powder X-ray diffractometer, employing Cu Kα radiation (λ=1.54Å). The samples were scanned over a range of 5 to 90 at a scan rate of 12°/min. The dielectric properties of the B2FO PI and B2FO-CPAF hybrids were measured using an impedance analyzer (HIOKI IM-3570, Japan) within a frequency range of 100 kHz to 3 MHz under ambient conditions. A two-parallel-plate configuration was employed, with a layer of copper and necessary electrical connections prepared in advance to facilitate parallel capacitance (C_P) measurements.

Table S1. Molecular weights, optical, thermal properties of PI and PI hybrid films

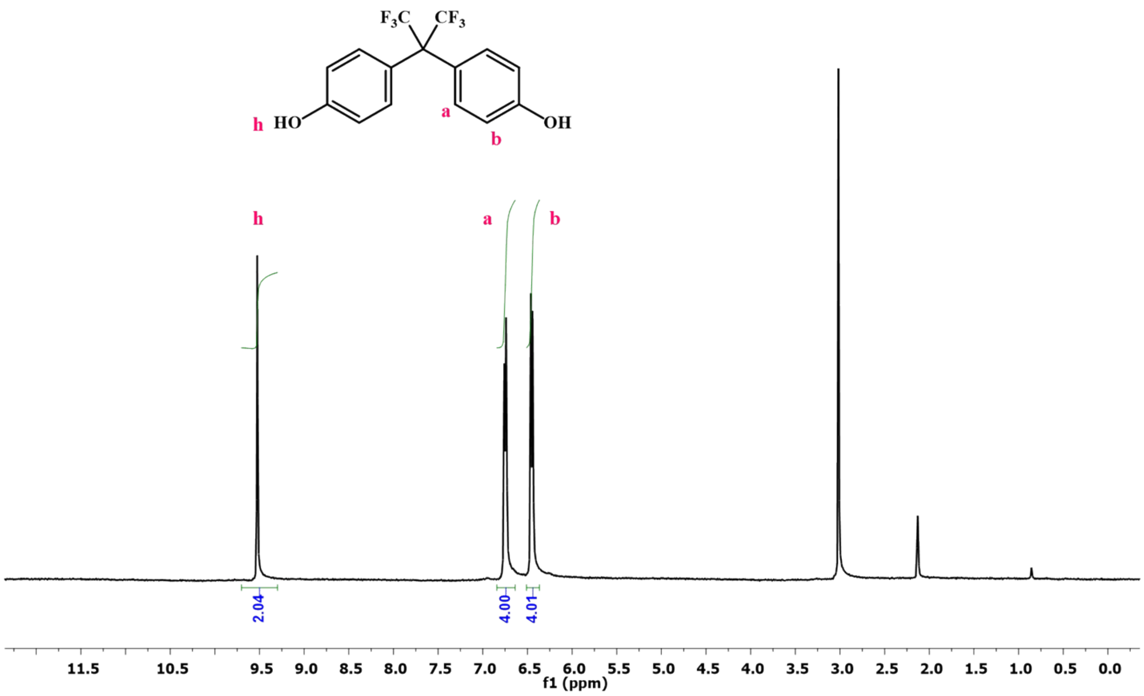
Name of the PI film	Mn	PDI	Transmittance (a.u.)		Glass transition temperature Tg		$T_d^{10\%}$ (°C)	R_w^{700} (%)
			T^{450}	T^{500}	DSC	DMA		
B2FO	22900	1.18	82.7	86.2	208	202	474	51.1
B2FO-CPAF-1	24080	1.21	81.7	85.9	209	206	492	52.8
B2FO-CPAF-2	27010	1.12	80.3	85.1	207	206	494	53.1
B2FO-CPAF-3	23460	1.37	78.1	83.3	207	205	496	54.4
B2FO-CPAF-4	25020	1.17	71.6	78.3	211	205	500	55.0
B2FO-CPAF-5	23620	1.19	58.2	67.0	212	204	482	55.6
B2FO-CPAF-6	23050	1.35	47.7	57.7	215	201	500	55.7
B2FO-CPAF-7	24780	1.29	43.9	52.0	217	203	482	56.5

Notes: Mn: number-average molecular weight by GPC (only the PIs was analyzed with GPC not the PI-CPAF hybrids. Because, after precipitation and drying, the PI-CPAF hybrids became insoluble in DMF and other solvents.); PDI: polydispersity index (Mw/Mn, where Mw is the weight-average molecular weight); T^{450} and T^{500}: UV-vis transmittance at wavelengths of 450 nm and 500 nm, respectively; $T_d^{10\%}$: temperature at which 10% weight loss was observed in TGA measurements; R_w^{700}: weight residue at 700°C from TGA measurements.

Table S2. Mechanical, dielectric, and water resistance properties of PI and PI hybrid films

	CPAF (wt%)	Tensile strength (MPa, std)	Tensile modulus (GPa, std)	Elongation at break (% std)	WAP (wt %)	WCA (°)	ε (3 MHz)	D_f (3 MHz)
B2FO	0	52.13 ± 1.85	2.393 ± 2.40	4.77 ± 030	0.39	89.5	1.83	0.0315
B2FO-CPAF-1	0.5	52.91 ± 4.22	2.683 ± 4.89	1.98 ± 0.09	0.35	92.5	1.79	0.0310
B2FO-CPAF-2	1	53.98 ±7.85	2.789 ± 8.12	1.74 ± 0.21	0.33	94.7	1.73	0.0307
B2FO-CPAF-3	2	56.15 ± 14.84	2.793 ± 9.86	0.69 ± 0.11	0.21	96.1	1.71	0.0296
B2FO-CPAF-4	3	58.98 ± 3.99	2.880 ± 4.65	0.87 ± 0.06	0.18	97.0	1.69	0.0285
B2FO-CPAF-5	4	59.63 ± 0.92	2.883 ± 1.91	0.97 ±0.20	0.17	99.0	1.66	0.0272
B2FO-CPAF-6	5	60.25 ± 4.68	2.970 ± 5.26	1.04 ± 0.20	0.15	100.6	1.63	0.0258
B2FO-CPAF-7	10	71.92 ± 0.77	3.315 ± 1.98	0.89 ± 0.40	0.11	103.7	1.58	0.0245

(a)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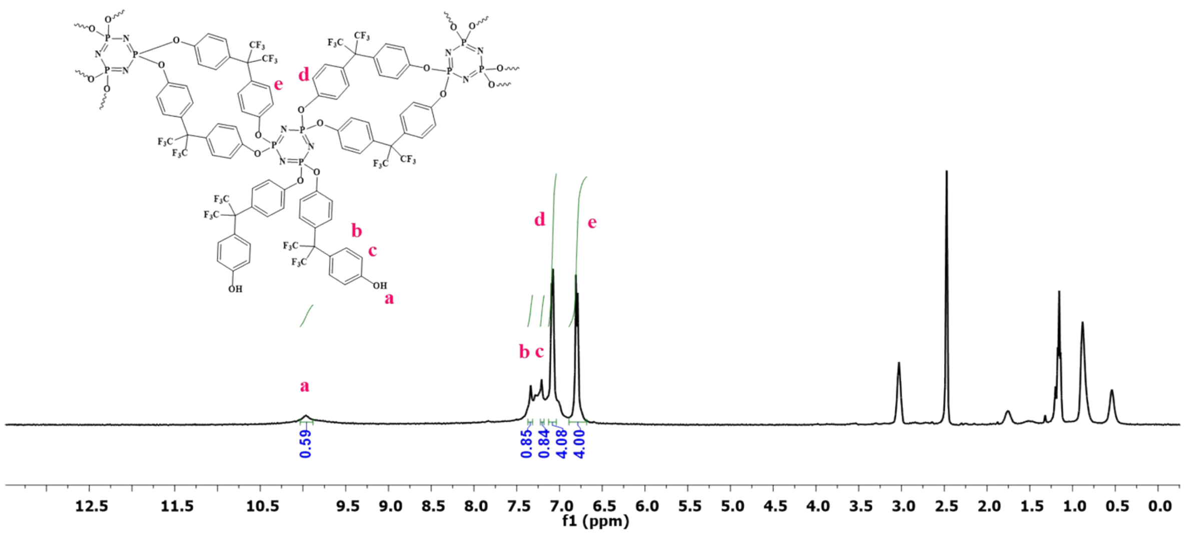
f1 (ppm)

(b)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O
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CF$_3$
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d
e
b
c
a
d
e
b c
a
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0.84
4.08
4.00
12.5
11.5
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f1 (ppm)

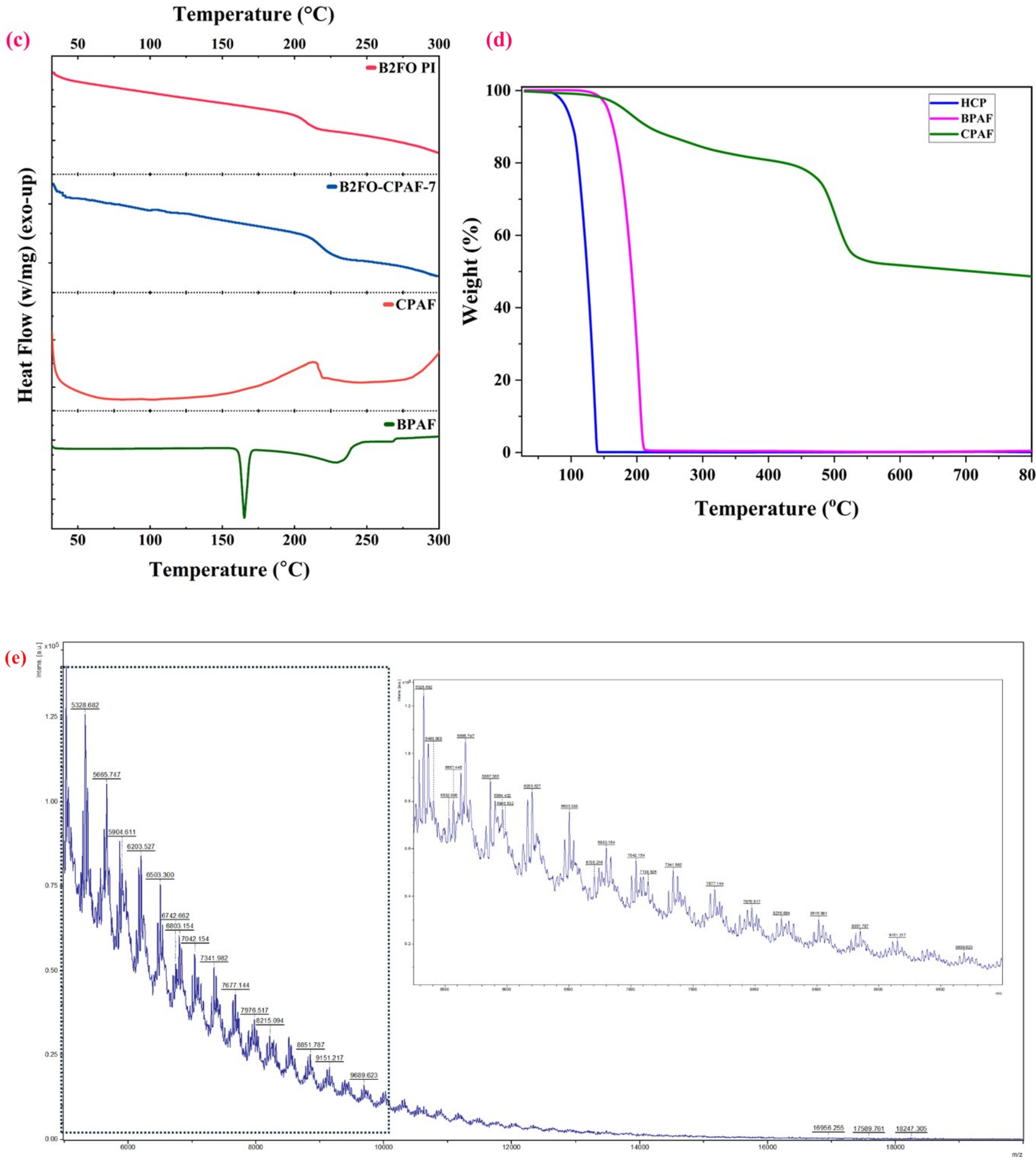


Fig. S 1: ^{1}H NMR spectra of (a) BPAF and (b) hyperbranched CPAF polymer, (c) DSC thermograms of BPAF, CPAF polymer, B2FO PI, and B2FO-CPAF-7 hybrid, (d) TGA curves of HCP, BPAF, and CPAF, and (e) MALDI TOF of CPAF.

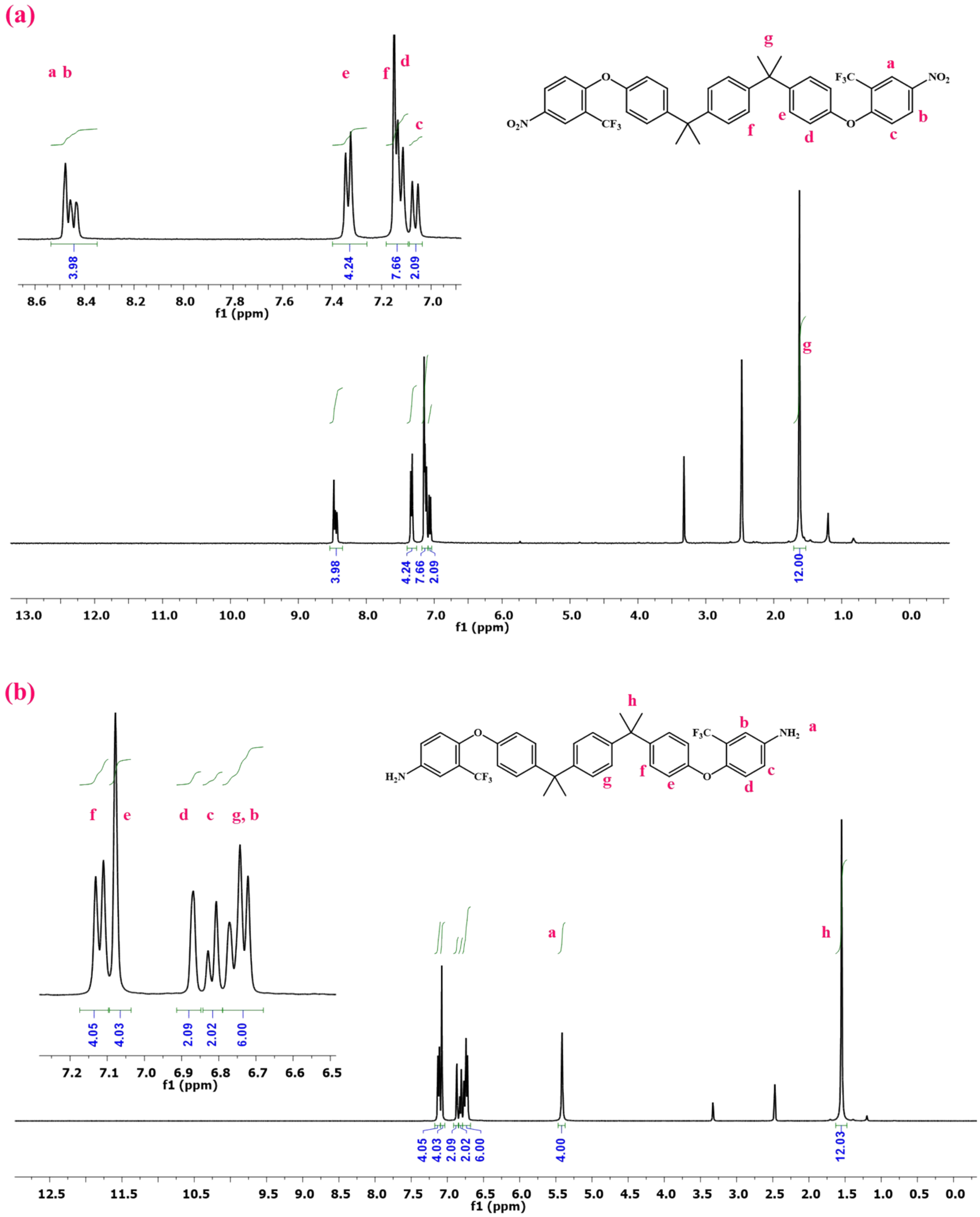


Fig. S 2: ^{1}H NMR spectra of (a) B2FDN and (b) B2FDA.

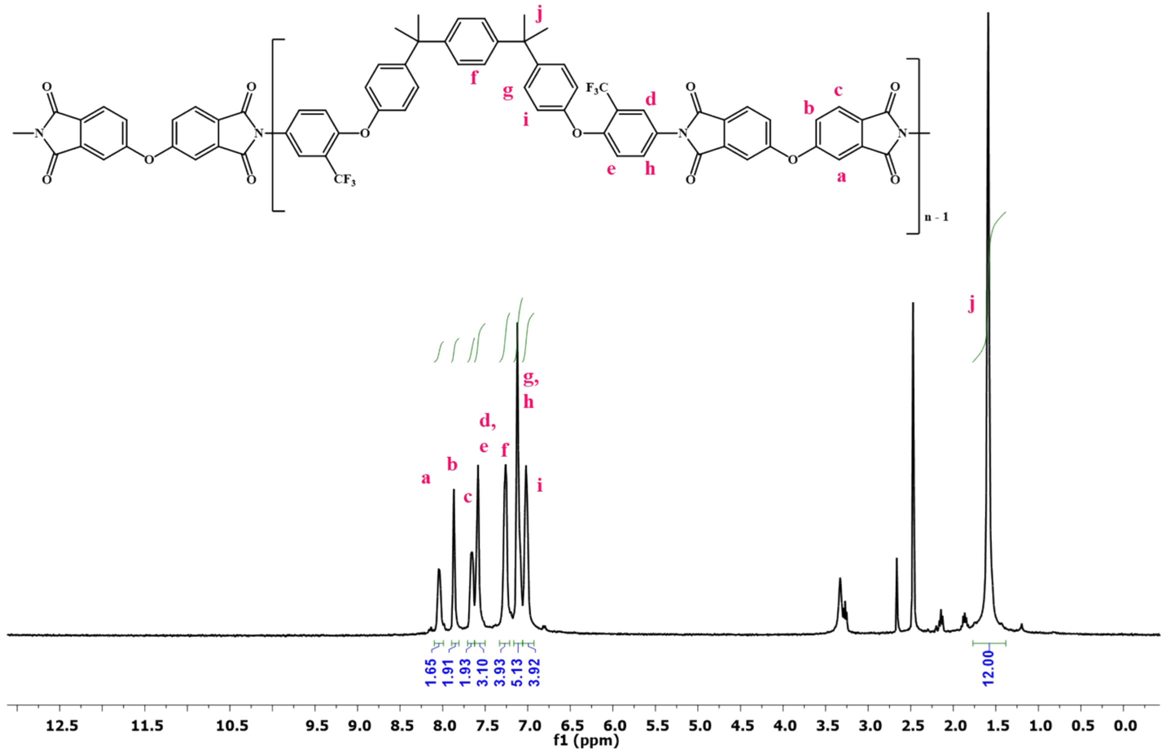


Fig. S 3: ^{1}H NMR spectrum of B2FO PI.

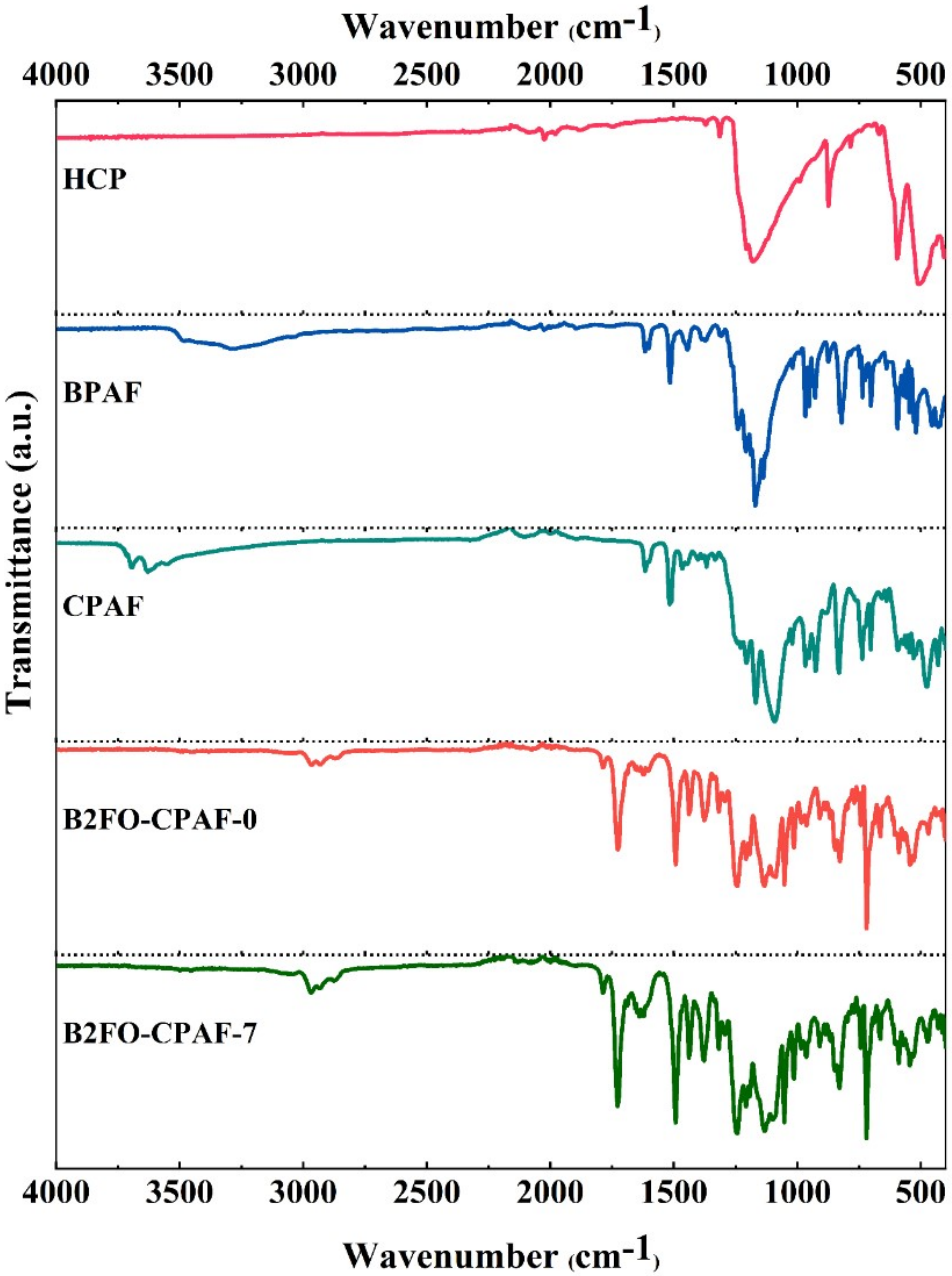


Fig. S4. ATR-FTIR spectra of HCP, BPAF, CPAF polymer, B2FO PI and B2FO-CPAF PI hybrid films.

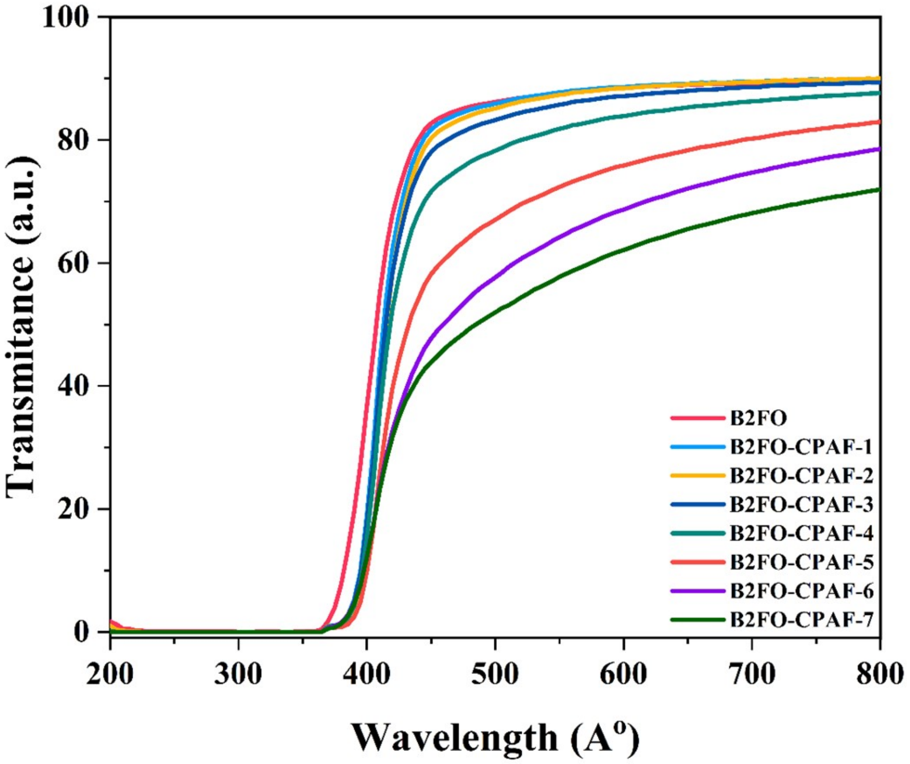


Fig. S5: UV-visible spectra of B2FO PI and B2FO-CPAF PI hybrid films.

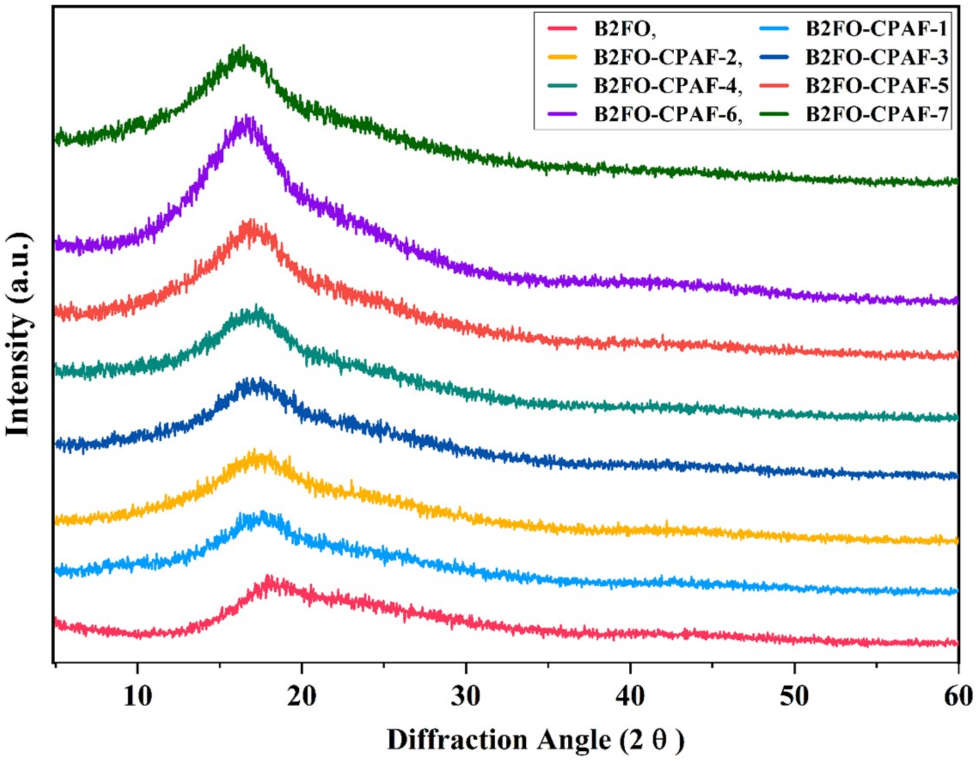
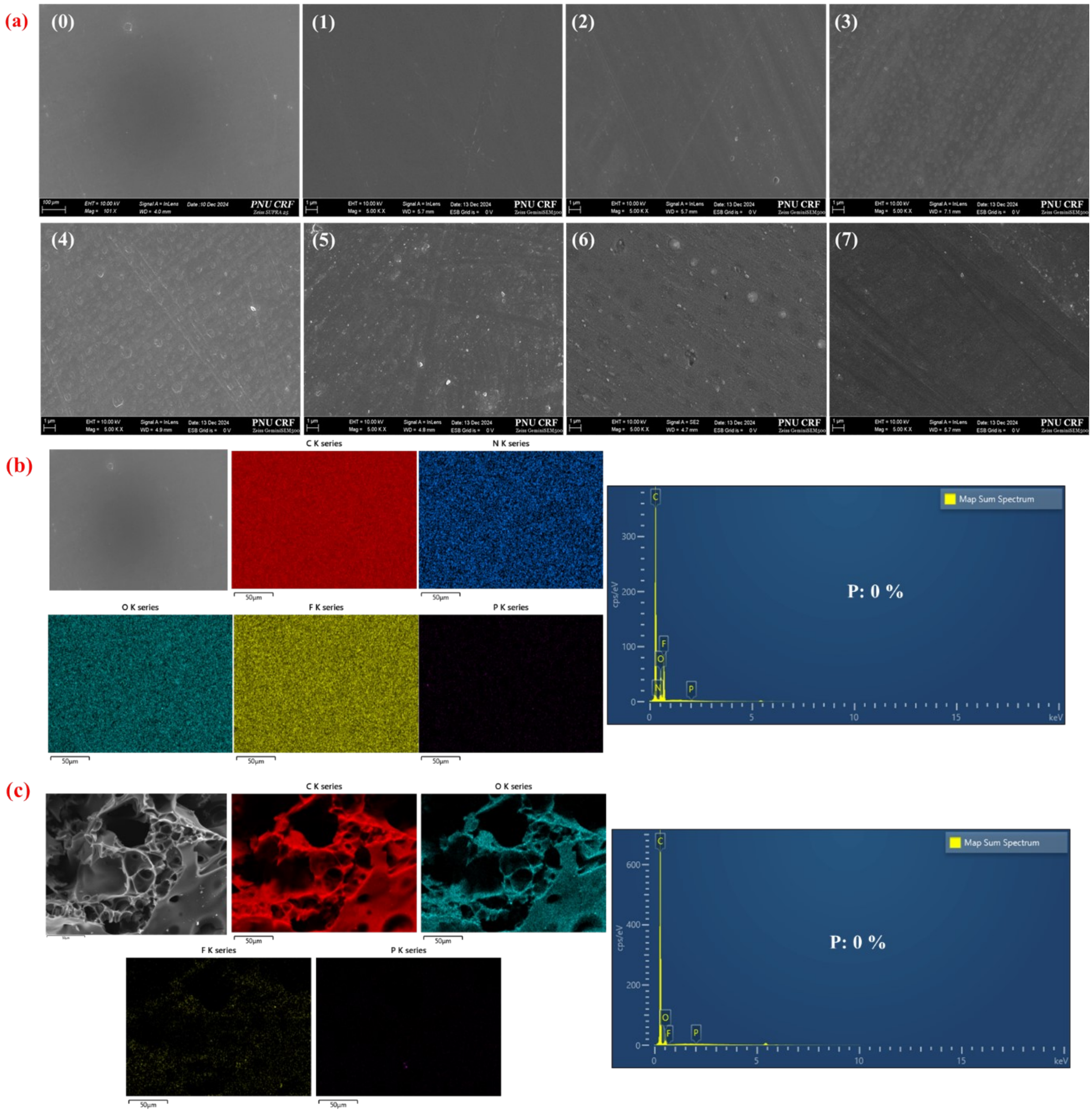


Fig. S6: WAXD patterns of B2FO PI and B2FO-CPAF PI hybrid films.


(a)
(0)
(1)
(2)
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(5)
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PNU CRF
(b)
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O K series
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Map Sum Spectrum
P: 0 %
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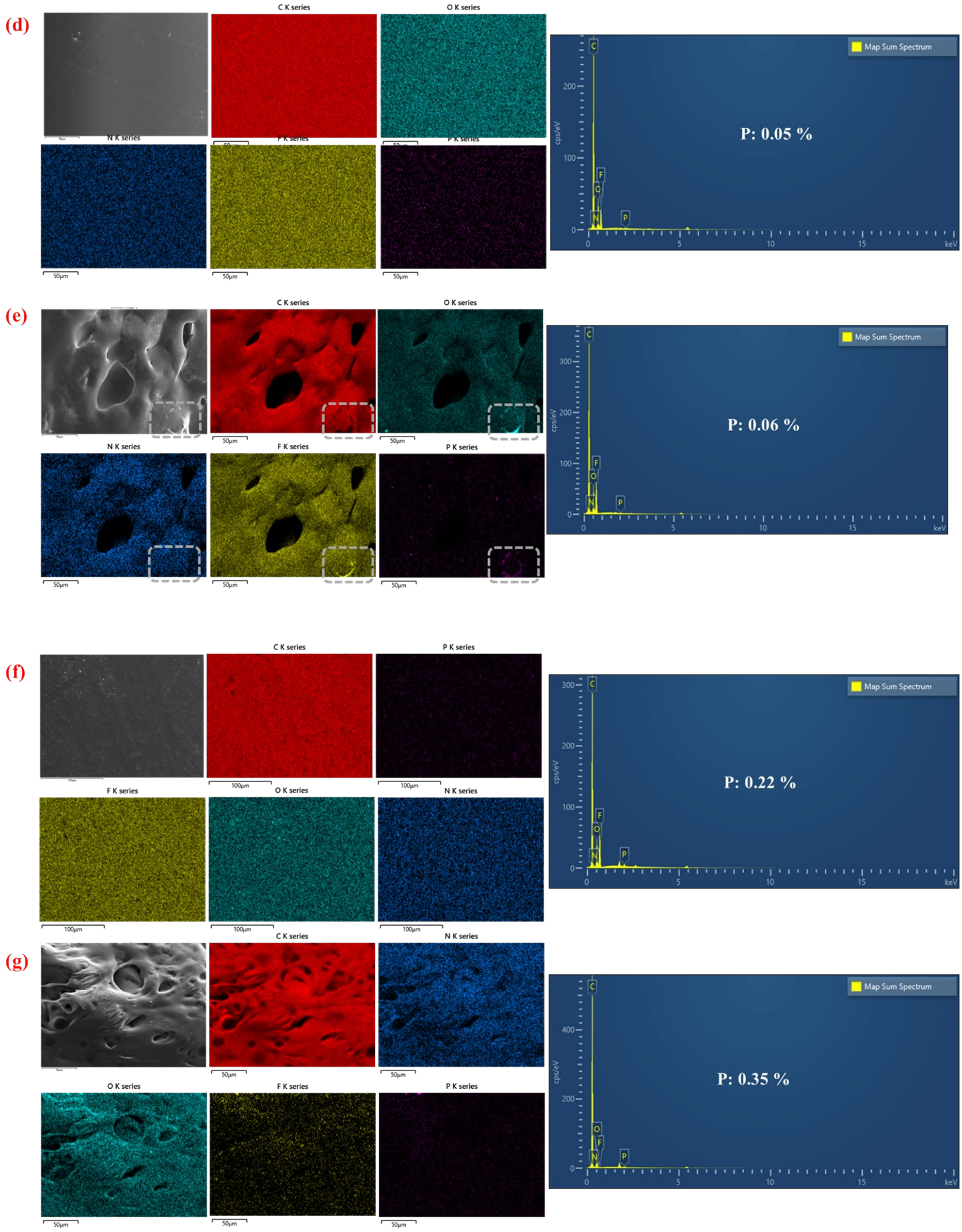

Fig. S7: Surface SEM images of the films (a), along with k-electron XPS (EDS) mapping, SEM images, and EDS patterns of B2FO both before and after flame exposure (b and c), as well as B2FO-CPAF-3 (d and e) and B2FO-CPAF-7 (f and g).

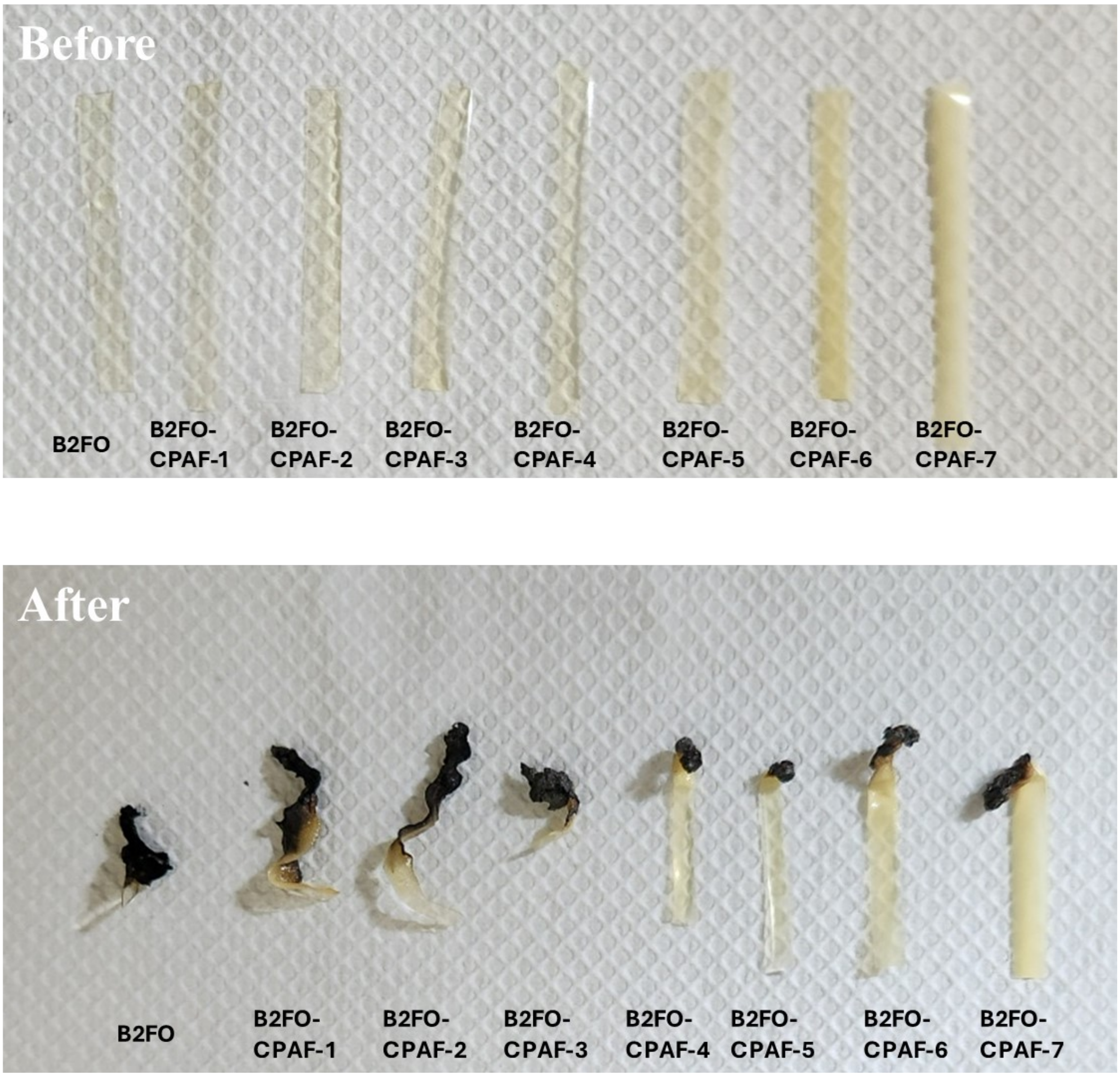

Fig. S8: Digital images of B2FO PI and B2FO-CPAF PI hybrid films before and after flame exposure.

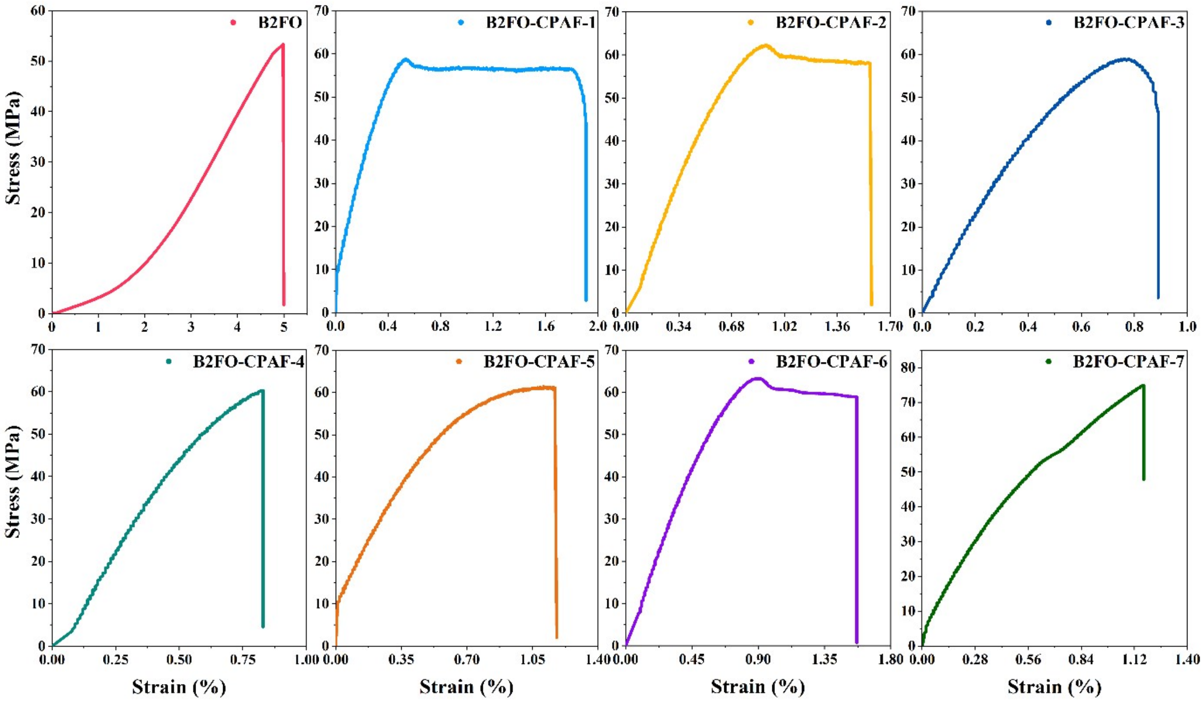

Fig. S9. Stress-strain curves of B2FO PI and B2FO-CPAF PI hybrid films.

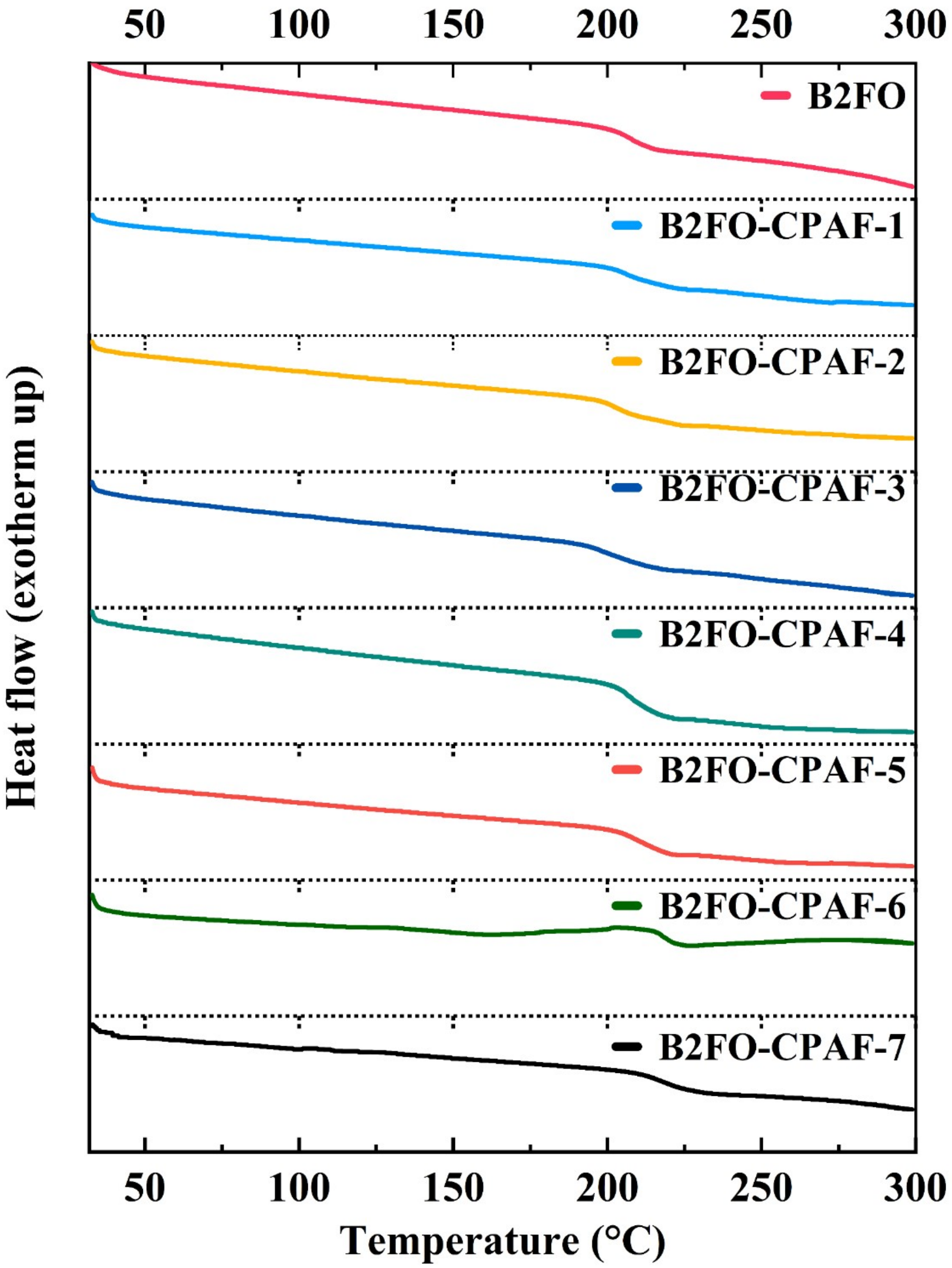

Fig. S10. DSC thermograms of B2FO PI and B2FO-CPAF PI hybrid films.

1. X. Tang, X. Huang, *Chapter 14 - synthesis and assembly chemistry of inorganic polymers*, in *Modern inorganic synthetic chemistry*, R. Xu, W. Pang, and Q. Huo, Editors, Elsevier, Amsterdam, 2011, Chapter 14.