

An Inherently Flame-retardant Bio-based Poly(ethylene 2,5-furandicarboxylate) Copolyester with High Impact Toughness and UV Shielding

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Electronic Supplementary Information

Abstract Bio-based 2,5-furandicarboxylic acid polyesters offer significant promise for reducing energy and environmental crises. However, their intrinsic flammability remains a critical limitation, and conventional flame-retardant strategies often compromise their mechanical properties, hindering their practical applications. Herein, a 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-based comonomer (DDP) was used to synthesize flame-retardant poly(ethylene furandicarboxylate-co-phosphaphenanthrene) (PEFDn). The covalent integration of DDP confers intrinsic flame retardancy, avoiding the plasticization and migration issues associated with additive-type systems. Upon thermal decomposition, the DOPO-derived moieties release phosphoric acid and radical scavengers, promoting char formation and suppressing flame propagation. Furthermore, density functional theory (DFT) calculations combined with non-covalent interaction (NCI) analysis revealed that DOPO dimer molecules adopt a stable parallel-displaced π - π stacking configuration, potentially facilitating microphase separation and enhancing the energy dissipation capability. PEFD₁₀ achieves a UL-94 V-0 rating while simultaneously increasing impact toughness from 1.5 kJ/m² to 14.7 kJ/m². Importantly, PEFDn maintained acceptable oxygen-barrier properties. PEFD₁₀ also exhibited high transparency and UV-shielding performance. The combination of intrinsic flame safety, impact-toughness resistance, UV shielding, and an oxygen barrier ensures reliable protection of electrical components and long-term operational stability. The integration of multiple critical properties within a single bio-based material represents a novel approach for enabling sustainable polymer solutions for high-performance electrical applications.

Keywords Poly(ethylene 2,5-furandicarboxylate); DDP; Superior flame retardancy; High impact toughness; UV shielding

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INTRODUCTION

In the prevailing global energy crisis and the urgent need to mitigate environmental pollution, developing renewable bio-based materials has become a key strategy to substitute traditional plastics and foster sustainable development.^[1] Among these, 2,5-furandicarboxylic acid (FDCA), derived entirely from biomass such as corn, non-food crops, straw, and sawdust, has been recognized as a highly promising monomer.^[2,3] In 2004, the U.S. Department of Energy identified FDCA as one of the

twelve most valuable biomass-derived platform chemicals of the 21st century. The subsequent commercialization of the YXY process (FDCA production process) by the Avantium–BASF joint venture Synvina in 2016 marked a key step toward large-scale production. Advances in FDCA technology have positioned FDCA-based polyesters as attractive alternatives to petroleum-based counterparts.^[4] Notably, poly(ethylene 2,5-furandicarboxylate) (PEF) demonstrates superior oxygen barrier properties approximately seven times greater than those of poly(ethylene terephthalate) (PET), making it particularly suitable for applications such as electronic component casings, where it effectively mitigates oxidation of metallic parts and enhances long-term device reliability.

Despite their promising sustainability profile, FDCA-based polyesters, composed exclusively of C, H, and O, inherit the in-

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herent flammability typical of most polymers, thereby posing significant ignition risks. To date, only a few studies have investigated the flame-retardant modifications of FDCA-based polyesters, and most have reported severe deterioration in mechanical properties.^[5–9] For example, Ding *et al.* developed a flame-retardant DPGE using diphenylphosphinic chloride and genistein,^[5] followed by melt compounding with poly(ethylene 2,5-furandicarboxylate-co-terephthalate) (PEFT20). PEFT20-3 showed a limiting oxygen index (LOI) of 31.4% with a UL-94 V-0 rating. However, its flexural and impact strengths were dramatically reduced to 26% and 9%, respectively, compared with those of PEFT20. Although the introduction of triglycidyl isocyanurate (TGIC) into PEFT20-3 partially mitigated the loss of mechanical properties, it resulted in diminished flame-retardant performance (Fig. 1a). Similarly, Wang *et al.*^[6] reported a copolyester obtained through melt polycondensation of 1,6-hexanediol (HDO), 2-carboxyethyl (phenyl)phosphinic acid (CEPPA), and FDCA. The resulting PHFC10 displayed an increased LOI of 25% (compared with 21.9% for PHF) and improved UL-94 performance from an unrated to V-2 rating. However, the tensile strength and elongation at break of the PHF were reduced to 71% and 8.2%, respectively. Further incorporation of 1 wt% TiO₂ led to slight improvements in flame retardancy, but again compromised the mechanical strength (Fig. 1b). Consequently, enhancing flame retardancy and mechanical performance remains a critical technical challenge in the design of FDCA-

based polyesters.

Integrating flexible long-chain alkyl units is a widely used strategy to enhance the toughness of polymers, although typically at the cost of strength and stiffness.^[10,11] Alternatively, the introduction of rigid aromatic rings can induce π - π interactions and microphase separation, thereby strengthening interchain cohesion and improving impact resistance, a strategy considered more appealing for advanced polymer design.^[12,13] 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), a rigid aromatic monomer with proven gas- and condensed-phase flame-retardant effects,^[14–17] appears to be an effective additive capable of simultaneously enhancing the flame retardancy and mechanical properties of polymers. DOPO is incorporated into the polymer matrix through physical blending; however, the weak interfacial interactions between DOPO and the polymer matrix prevent the effective enhancement of the mechanical properties and even result in their deterioration.^[18,19] In addition, their gradual migration to the polymer surface and subsequent leaching during long-term use poses potential environmental and health risks. To overcome these limitations, a strategy of covalently incorporating DOPO groups into the polymer backbone was employed, which ensured strong interfacial compatibility and long-term multifunctional stability.

A bio-based flame-retardant comonomer (DDP) was copolymerized with PEF *via* melt polycondensation to yield a sustainable polymer with integrated flame retardancy, tough-

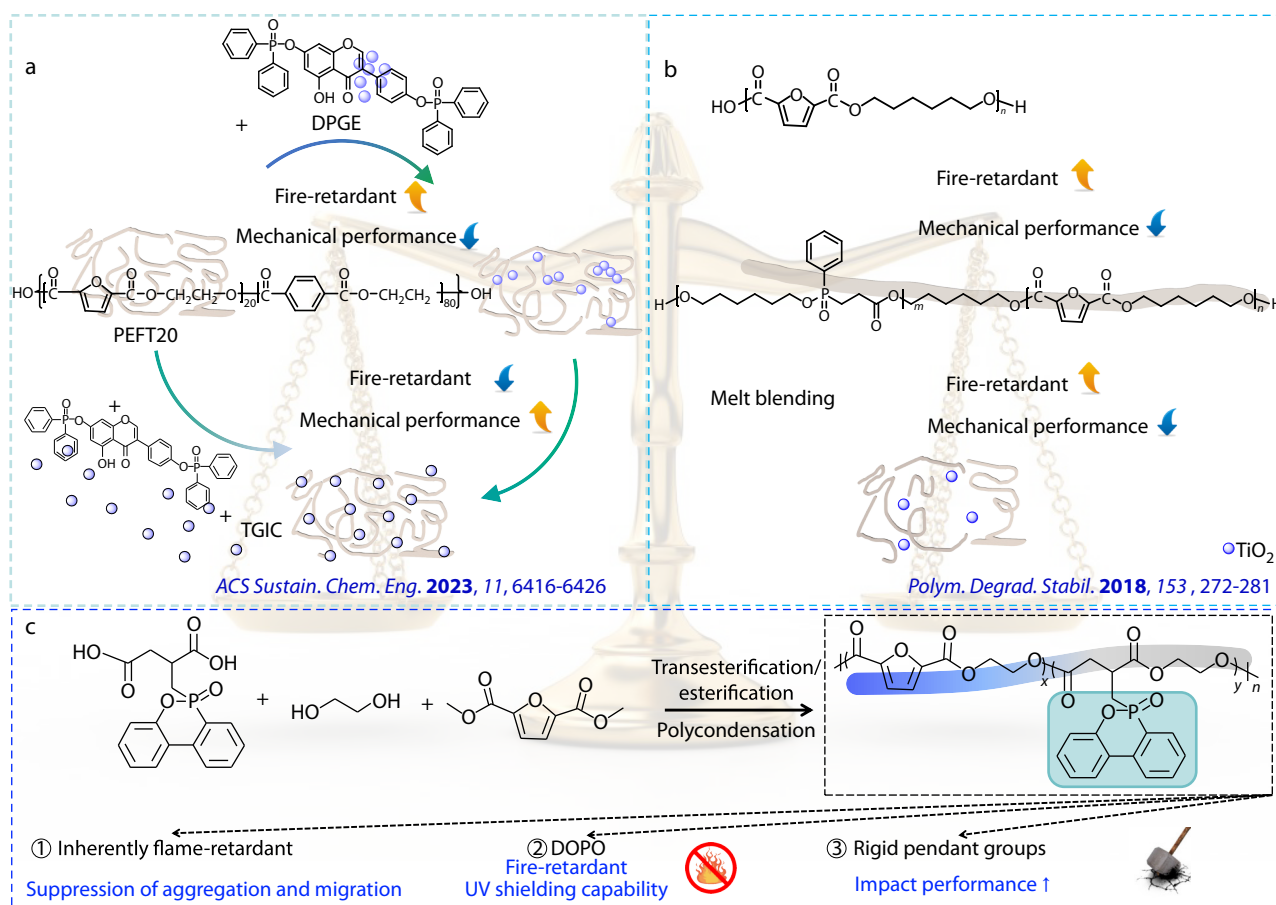


Fig. 1 (a, b) Previous work to improve the fire safety of FDCA-based polyester^[5,6]; (c) Present work to design flame-retardant PEF.

ness, and UV shielding (Fig. 1c). Notably, the intrinsic flame retardancy significantly suppressed the leaching of migratory additives. DOPO generates phosphorus-containing radicals and phosphorus-containing acids during thermal decomposition, which quench flame radicals and catalyze char formation, thereby enhancing the flame retardancy of the polymer. Furthermore, π - π interactions between DOPO enhance the impact toughness, while the photodegradation of UV shielding capability ensures long-term durability in outdoor applications. This study presents a sustainable approach for synthesizing a novel multifunctional monomer for PEF, demonstrating its strong potential for broader practical applications.

EXPERIMENTAL

Materials

Dimethyl-2,5-furandicarboxylate (DMFD 99%) was obtained from Hangzhou Yunshang New Material Technology Co., Ltd. (Hangzhou, China). DOPO, itaconic acid (IA), and xylene were purchased from Shanghai McLean Biochemical Co., Ltd. (Shanghai, China). Acetone, ethylene glycol (EG, 99%), and deuterated trifluoroacetic acid (*d*-TFA, 99.9%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Chloroplatinic acid (H_2PtCl_6), isopropyl alcohol, tin(II) bis(2-ethylhexanoate) (95%), triphenyl phosphate (TPP, 98%), antimony trioxide (Sb_2O_3 , 99.5%), and hexafluoroisopropanol (HFIP) were supplied by Aladdin Reagent Co., Ltd. (Shanghai, China).

Preparation of PEFDn

The flame-retardant monomer, DDP, was synthesized from DOPO and IA according to our previously reported procedure.^[20]

The synthesis of the PEFDn copolyester was conducted via transesterification and melt polycondensation, as depicted in Fig. 1(c). DMFD, DDP, and EG were introduced into a three-necked flask in stoichiometric ratios, and the exact quantities of each reagent are listed in Table 1. Then, the transesterification catalyst, tin(II) bis(2-ethylhexanoate), was added at an amount equivalent to 0.1% of the total molar quantity of DMFD + DDP. The reaction mixture was heated to 170 °C under a nitrogen atmosphere combined yield of methanol and water exceeded 95% of the theoretical value. Sb_2O_3 and TPP were introduced into the mixture in an equimolar ratio relative to tin(II) bis(2-ethylhexanoate). Subsequently, the temperature was increased to 200 °C and the pressure was gradually reduced to 40 Pa. Polycondensation was terminated upon reaching a constant torque, yielding the target products, PEF and PEFDn.

Characterization

The intrinsic viscosity (η) of PEF and PEFDn was measured at 25

°C using a Ubbelohde viscometer with 0.5 g/dL solutions in phenol/1,1,2,2-tetrachloroethane (50 wt%/50 wt%). Molecular weights and distributions were determined by gel permeation chromatography (GPC) using an Agilent PL-GPC 220 system at 40 °C with chloroform as eluent (1 mL/min flow rate) and sample concentration of 1.0 mg/mL. ^1H -NMR spectra were recorded at 298 K on a Bruker AVANCE NEO 600 spectrometer using *d*-TFA as the solvent.

Thermal stability was evaluated by thermogravimetric analysis (TGA) using a Mettler-Toledo instrument under N_2 /air atmosphere from 50 °C to 800 °C at 20 °C/min. Differential scanning calorimetry (DSC, Mettler-Toledo DSC 1) measurements were conducted under N_2 atmosphere from 0 °C to 250 °C with the following program: heating at 10 °C/min, cooling at 5 °C/min, and 3 min isotherms at both 0 °C and 250 °C. Vicat softening temperatures (VST) were determined according to GB/T 1633-2000 using a CEAST 6911 tester (sample dimensions: 10 mm $\times$ 10 mm $\times$ 4 mm; load: 0.45 MPa, heating rate: 2.0 °C/min).

The vertical burning (UL-94) test was conducted with a 5400 vertical burning tester (Suzhou Yangyi Vouch Testing Technology Co., Ltd.) according to ASTM D3801 using a 100 mm $\times$ 13 mm $\times$ 3.2 mm sample. Following ASTM D2863-97, LOI was determined using a 5801 digital oxygen index analyzer (Suzhou Yangyi Vouch Testing Technology Co., Ltd.) with 100 mm $\times$ 6.5 mm $\times$ 3.2 mm specimens. The combustion behaviors of PEF and PEFDn were investigated using a Cone Calorimeter 6810 (Suzhou Yangyi Vouch Testing Technology Co., Ltd.) according to GB/T 16172:2007 at 35 kW/m², with samples of 100 mm $\times$ 100 mm $\times$ 3.2 mm.

Thermal stability and gaseous degradation products were investigated by thermogravimetric analysis/infrared spectroscopy/mass spectroscopy (TG-IR-MS) (PerkinElmer, TGA 8000-Spectrum two-Clarus SQ8T, USA) from 50 °C to 800 °C at 10 °C/min under 50 a nitrogen flow. A scanning electron microscope (Verios G4 UC, Thermo Scientific, USA) was used to examine the morphologies of the gold-sprayed samples. The sample was dissolved in HFIP and spin-coated onto a pre-cleaned silicon wafer. After complete solvent evaporation, atomic force microscopy (AFM, Veeco, USA) was performed. The graphitization degree of the char residues was evaluated by micro-Raman spectroscopy (Renishaw inVia Reflex) via I_D/I_G ratio analysis.

The tensile properties were measured according to ASTM D638 using a Zwick/Roell Z1.0 tester (Germany) at 10 mm/min. The dumbbell-shaped samples measured 35 mm $\times$ 2 mm $\times$ 1 mm, with five tests per sample. Unnotched Izod impact tests were conducted on a GT-7045-HML impact tester using 10 mm $\times$ 4 mm $\times$ 80 mm samples with five replicates for each sample. The O_2 permeability was measured at 23 °C and 50% relative humidity using Labthink VAC-V2 according

Table 1 Composition and the molecular weight of PEF and PEFDn.

Sample	Theo.		Actual.		$[\eta]$ (dL/g)	GPC	
	n_{DMFD} (mol%)	n_{DDP} (mol%)	n_{DMFD} (mol%)	n_{DDP} (mol%)		M_n (g/mol)	PDI
PEF	100	0	100	0	0.69	2.9×10^4	1.8
PEFD ₃	97	3	96.9	3.1	0.67	2.5×10^4	2.0
PEFD ₅	95	5	94.8	5.2	0.67	2.4×10^4	2.0
PEFD ₇	93	7	92.8	7.2	0.74	3.0×10^4	1.9
PEFD ₁₀	90	10	90.3	9.7	0.68	2.4×10^4	2.1

to GB/T 1038–2000, with sample thicknesses of 200 μm and a diameter of 9.7 cm, respectively. Ultraviolet-visible (UV-Vis) spectra were analyzed using a Lambda 950 UV/Vis/NIR model with a sample thickness of 200 μm .

Density functional theory (DFT) calculations combined with non-covalent interaction (NCI) analysis were used to analyze the toughening mechanism. Low-energy DOPO dimers were optimized using the dispersion-corrected $\omega\text{B97X-D}$ functional with the 6-31+G(d) basis set, as implemented in Gaussian 16.^[21] To characterize and visualize intermolecular interactions, non-covalent interaction (NCI) analyses were performed, including quantum theory of atoms in molecules (QTAIM) and the independent gradient model based on Hirshfeld partitioning (IGMH).^[22–24] Electrostatic potential (ESP) mapping was performed on van der Waals (vdW) surfaces. Visualization of all NCI descriptors was performed using VMD 1.9.3, with data generated by Multiwfn 3.7.^[25]

RESULTS AND DISCUSSION

Synthesis and characterization of PEF and PEFDn

PEFDn contained 3% (PEFD₃) to 10% (PEFD₁₀) of the DDP units.

The intrinsic viscosity (η) of PEF and PEFDn is between 0.67 and 0.74 dL/g, with number-average molecular weight (M_n) of 2.4×10^4 – 3.0×10^4 g/mol, and polydispersity index (PDI) of 1.8 to 2.1, as shown in Table 1 and Fig. 2(a). This indicates that the molecular weights of the samples are close to each other, ensuring that the overall performance can be evaluated in subsequent tests.

The molecular structure of the polymer was characterized by FTIR and ¹H-NMR spectroscopy, as illustrated in Figs. 2(b) and 2(c). Furan ring-related bending motion bands (753, 824, and 953 cm^{-1}), furan ring breathing band (1014 cm^{-1}), and C=C in the furan ring (1511 and 1575 cm^{-1}) were detected in PEF. Additionally, the C—O of ester carbonyl peak in PEF appears at 1270 cm^{-1} , the ester carbonyl group (C=O) band is observed at 1722 cm^{-1} and C—H of CH₂ group band appears around 2927 and 2863 cm^{-1} .^[26] Moreover, the characteristic P—O absorption band of the DDP unit appeared in PEFDn at 917 cm^{-1} . The chemical shifts of PEF are primarily at 7.48 (a) and 4.89 ppm (b), corresponding to the furan ring and CH₂ in ethylene glycol, respectively. Furthermore, PEF exhibits very small absorption peaks at approximately 4.78 and 4.28 ppm, which can be owing to the methylene protons of the diethy-

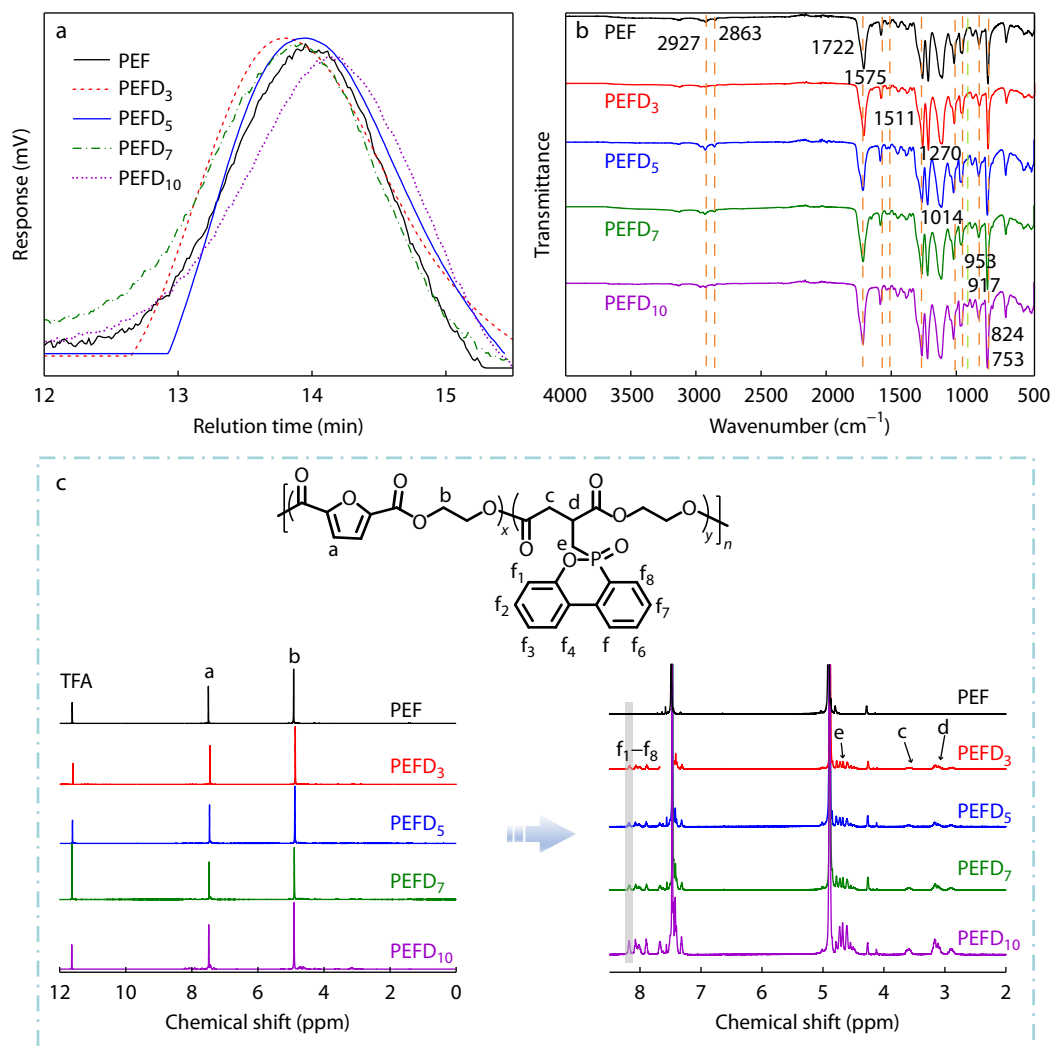


Fig. 2 (a) GPC curves, (b) FTIR spectra and (c) ¹H-NMR spectra of PEF and PEFDn.

lene glycol (DEG) unit^[27]. The introduction of DDP led to the emergence of novel chemical shifts within PEFDn, belonging to protons (f_1 – f_8) on the benzene ring of DOPO and CH_2 (c, e) and CH (d) on the butyl chain, respectively. The calculation of the DDP and DMFD content in PEFDn is based on the ratio of the characteristic absorption peaks f_4 and a (Eqs. 1 and 2). High-molecular-weight PEFDn was successfully synthesized, as illustrated in Table 1.

$$n_{\text{DDP}} = \frac{I_{f_4}}{\frac{1}{2}I_a + I_{f_4}} \times 100\% \quad (1)$$

$$n_{\text{DMFD}} = \frac{\frac{1}{2}I_a}{\frac{1}{2}I_a + I_{f_4}} \times 100\% \quad (2)$$

Thermal Stability and Thermal Property

The thermal stabilities of PEF and PEFDn in N_2 and air were evaluated using TGA (Figs. 3a, 3b and Table S1 in the electronic supplementary information, ESI). Both PEFDn and PEF decomposed under N_2 . The DDP introduction minimally affected the initial decomposition temperature ($T_{5\%}$) and maximum decomposition rate temperature (T_{max}), ranging 366–373 °C and 411–418 °C, respectively. Fortunately, the maximum decomposition rate (R_{max}) of PEFDn was significantly lower than that of PEF, and the char residue at 800 °C increased sharply. Notably, PEFD₁₀ exhibited an increased char yield of 12.66% at 800 °C compared with 0% for PEF. This enhancement originates from polyphosphoric acids or polyphosphate derived from DDP decomposition, which catalyzes polymer dehydration into char.^[28] The improved char-forming abilities of the polymers promote the development of a thermal-insulating barrier, which effectively restricts the diffusion of heat, oxygen, and pyrolytic volatiles dur-

ing thermal decomposition, thus inhibiting flame propagation.^[29] Following the initial decomposition of PEFDn and PEF into a char layer in air, the char layer undergoes a subsequent reaction with oxygen at high temperatures, thereby demonstrating a two-stage decomposition trend (Figs. 3c and 3d). The $T_{5\%}$ and $T_{\text{max}1}$ of PEFDn were similar to those of PEF, but $T_{\text{max}2}$ was greatly delayed with increasing DDP content. The $T_{\text{max}2}$ raised from 536 °C for PEF to 551–577 °C for PEFDn, demonstrating the formation of thermally more stable char residues.

The phase-transition temperatures of PEF and PEFDn were studied using DSC, as shown in Fig. 3(e). The DDP segment has been demonstrated to cause a significantly disrupts the regularity of chains, thereby destroying the crystallization of PEFDn.^[30] The glass transition temperature (T_g) of PEFDn was comparable to PEF, with variations within 1 °C. Consequently, PEFDn can be utilized within the same temperature range as PEF, while maintaining its heat resistance, rendering it suitable for daily applications. This hypothesis is further substantiated by the consistent Vicat softening temperature (between 92.4 and 93.6 °C) of PEF and PEFDn (Fig. 3f).

Fire Safety

The flame retardancy of the polymers was characterized using a UL-94 test and LOI, and the detailed results are presented in Fig. 4. PEF exhibits high flammability, as evidenced by its low LOI value of 21.0%, and it only passes the UL-94 V-2 rating. Upon ignition, the PEF produces copious molten droplets with sustained flaming, facilitating rapid cotton ignition and substantially increasing the likelihood of secondary fire incidents. With the introduction of DDP, the droplet of PEFDn slowed down, and the LOI value increased significantly. The remarkably low 3 wt% DDP loading enables PEF to pass the UL-94 V-0 rating, which is attributable to the DDP dual-phase flame retardant mechanism

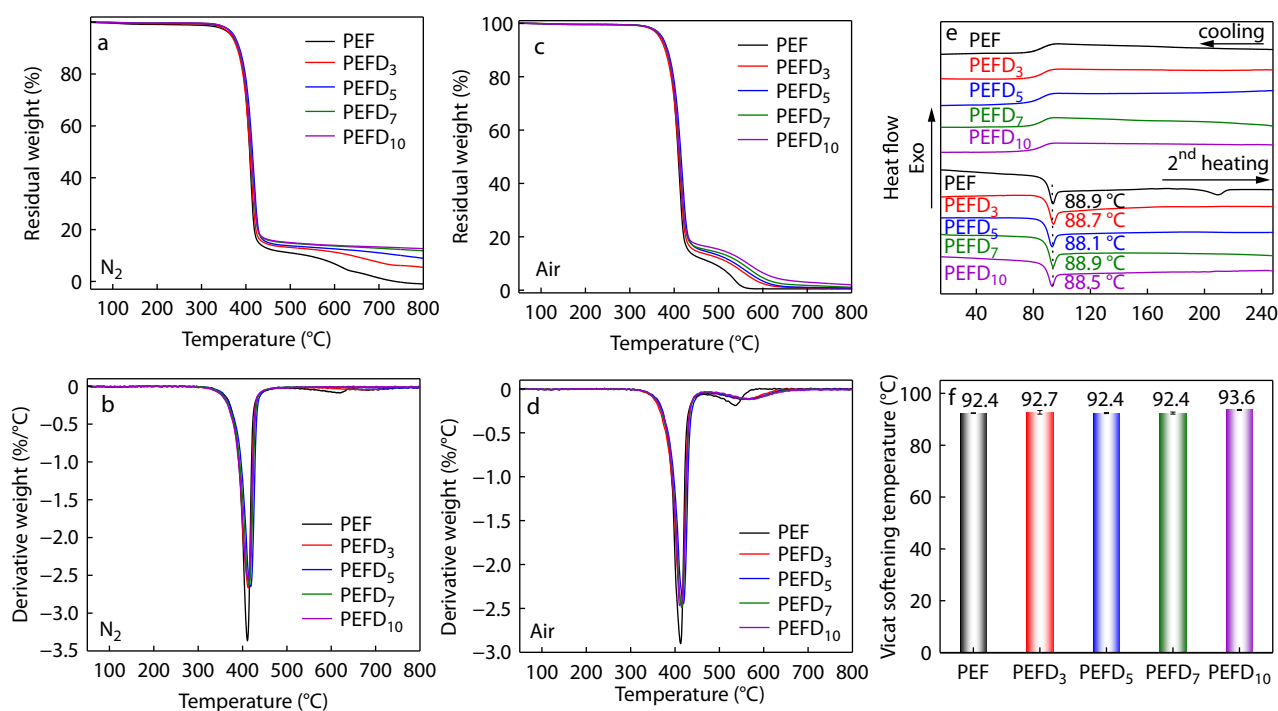


Fig. 3 (a, c) TGA and (b, d) DTG curves in (a, b) N_2 and (c, d) air, (e) DSC curves and (f) vicat softening temperature of PEF and PEFDn.

involving the gas phase. The elevated LOI (28.0%) of PEFD₅ was significantly higher than that of the flame-retardant standard. With a further increase in DDP, PEFD₁₀ achieved an LOI value of 30.8% and successfully passed the UL-94 V-0 rating. Because of the decomposition of DDP, phosphorus-containing free radicals (P·, PO·) are generated, which trap the H·, HO· free radicals generated by the thermal cracking of polymers and slow down the combustion.

Cone calorimetry, an advanced technique for quantitatively characterizing the heat release and smoke production during combustion, was employed to evaluate the fire behavior of polymer systems.^[31,32] Thermal radiation is an important factor in fire fatalities, as shown in Fig. 5 and Table 2. The PEF has a peak heat release rate (PHRR) of 1067 kW/m² with a total heat release (THR) of 92 MJ/m². Owing to the introduction of DDP, the risk of thermal radiation was gradually reduced. PEFD₁₀ exhibited a PHRR of 737 kW/m² and THR of 63 MJ/m², corresponding to 30.9% and 31.5% reductions relative to PEF (1067 kW/m² and 92 MJ/m², respectively). Fire danger is usually assessed using the fire growth rate (FIGRA = PHRR/t-PHRR), with lower values indicating a longer flashover time and more escape time.^[33–35] The FIGRA of PEF is 7.6 kW/(m²·s), and that of PEFD₁₀ is 5.3 kW/(m²·s), which decreases by 30.3%. Furthermore, PEFDn exhibited significantly higher char yields than PEF, with PEFD₁₀ exhibiting the most pronounced increase (98.2%), which is in agreement with the TGA results. These enhancements stem from the decomposition of DDP units to provide phosphoric acid or polyphosphate, which catalyze the promotion of char formation and improves the

flame-retardant performance.^[36]

Notably, the total smoke production (TSP) of PEFD₁₀ and PEFD₅ was higher than that of PEF (Fig. S1 and Table S2 in ESI). This phenomenon can be attributed to incomplete combustion, as evidenced by the marked increase in the CO/CO₂ ratio of PEFD₁₀ from 0.0275 to 0.2152 for PEF. Furthermore, the average heat combustion (Av-EHC) of the PEF undergoes a gradual decline with the addition of DDP, which means that the degree of burning of volatile gases is reduced.^[37] This phenomenon may be due to the phosphorus radical quenching flame generated from the DDP during burning.^[38]

Flame-retardant Mechanism

Condensed phase

The char residues after cone were characterized by SEM and Raman spectroscopy, providing a preliminary investigation into the condensed-phase mechanism of DDP. The char residues of PEF appear light gray and exhibit a sparse, loose, and discontinuous morphology in the SEM images, thus hindering their capacity to provide effective protection to the substrate (Fig. 6a). However, the char residues of PEFD₅ and PEFD₁₀ were more complete, dense, and continuous than those of PEF, although the char residues of PEFD₅ and PEFD₁₀ showed a porous structure because of the various gases produced during burning. It effectively inhibits the transfer of heat, "fuel" and oxygen during combustion, thereby reducing the generation of complete combustion products (converted to heat and gases), while increasing char residues and significantly reducing fire hazards. In addition,

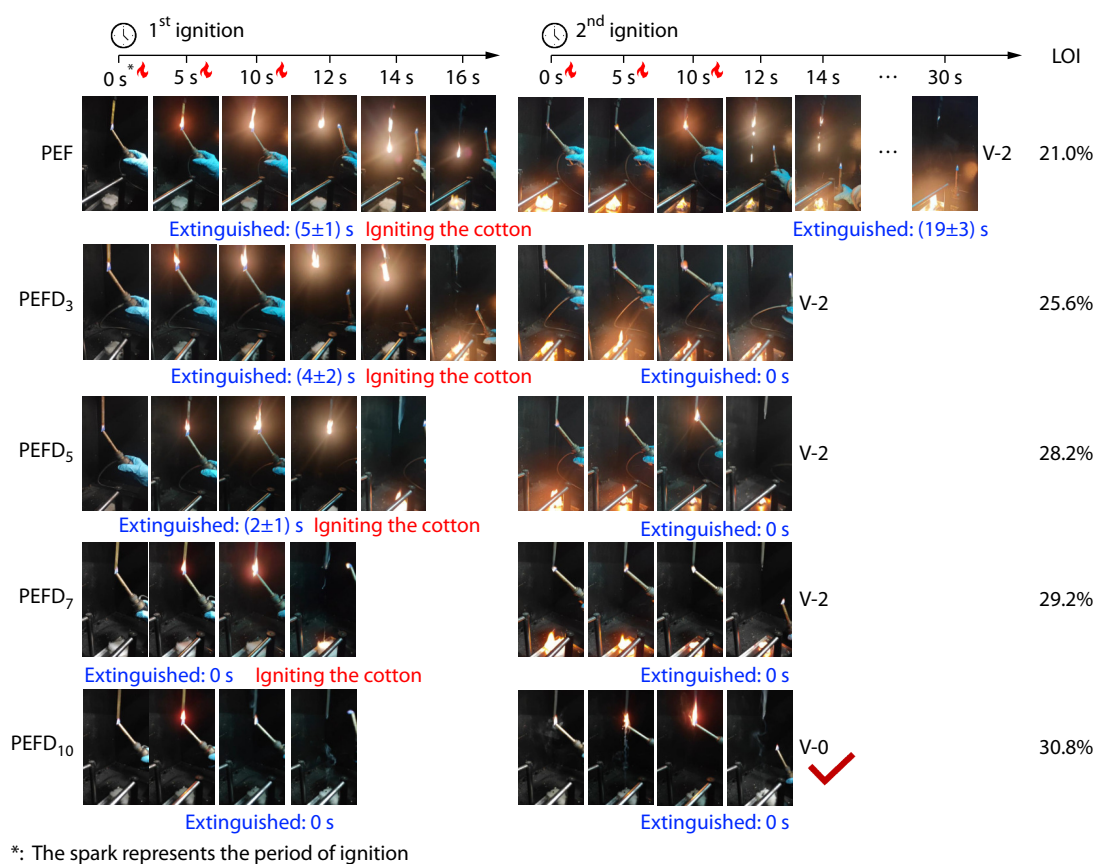


Fig. 4 Photos during UL-94 and results of LOI for PEF and PEFDn.

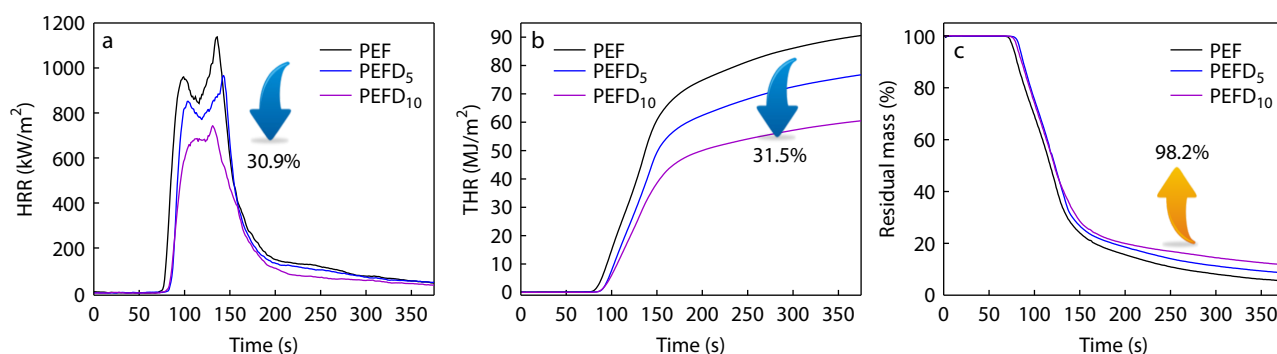


Fig. 5 (a) Heat release rate, (b) total heat release, (c) residual mass of PEF, PEFD₅, and PEFD₁₀.

Table 2 The results of PEF and PEFDn from Cone.

Sample	PHRR (kW/m ²)	t-PHRR	TTI	THR (MJ/m ²)	FIGRA (kW/(m ² ·s))	Av-EHC (MJ/kg)	RC (wt%)
PEF	1067±71	140±5	73±2	92±1	7.6	29.4±0.8	5.7±0.2
PEFD ₅	964±2	139±4	78±1	76±1	6.9	28.8±0.6	8.9±0.3
PEFD ₁₀	737±6	138±7	76±1	63±4	5.3	25.1±1.7	11.3±0.5

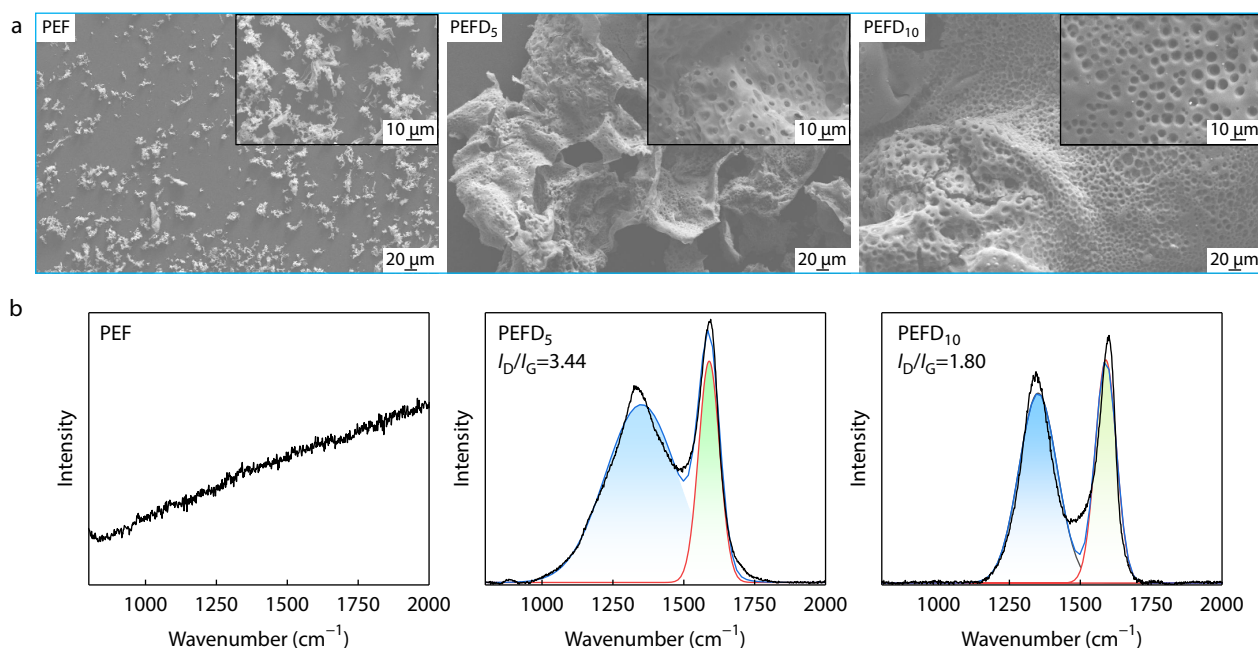


Fig. 6 (a) The SEM images and (b) Raman spectra of the char residuals after the Cone of PEF, PEFD₅, and PEFD₁₀.

tion, the residues of PEF exhibited negligible Raman signals, which can be attributed to the minimal amount of char retained in the residue (Fig. 6b). The introduction of DDP results in two distinct band at 1360 (D band, disordered graphite) and 1580 cm⁻¹ (G band, ordered graphite).^[39,40] The I_D/I_G values climb gradually as the DDP content decreases, from 3.44 (PEFD₅) to 1.80 (PEFD₁₀). The pronounced graphitic ordering within ash contributes to the development of a compact and robust structure, thereby significantly improving its barrier efficiency.^[41,42] This is in good agreement with the SEM results.

Gaseous phase

The gaseous decomposition products of PEF and PEFD₁₀ were studied by IR-MS. The principal characteristic absorption peaks of PEF align with those of PEFD₁₀, occurring at 2360, 668 (CO₂),

1769 (carbonyl compounds), and 1288–1167 cm⁻¹ (ethers),^[43,44] as shown in Figs. 7(a) and 7(b). This indicates that the introduction does not alter the decomposition pathway of the polymer. However, PEFD₁₀ exhibited a significantly lower absorption intensity than PEF, indicating that DDP suppressed the formation of volatile gases. A greater quantity of decomposition products remained in the condensed phase, which was consistent with the cone results. To analyze the changes in the pyrolysis products in more detail, representative products were selected for evaluation (Figs. 7c–7f). The reduction in hydrocarbons, carbonyl compounds, and ethers decreases the amount of combustible volatile products (fuel), thereby reducing the heat release. Concurrently, a decline in CO₂ levels mitigates the risk of asphyxiation.

The MS results further clarified the flame-retardant mechanism of PEFD₁₀. At $T_{5\%}$ and $T_{\max}$, the main peak positions of PEF and PEFD₁₀ were the same, that is, the decomposition products were the same (Figs. 7g–7j and Table S3 in ESI). This indicated that DDP did not alter the primary decomposition pathway of PEF. However, the introduction of DDP significantly increases the yield of macromolecular species, suggesting that it inhibits thermal decomposition and consequently retards combustion. Key fragments at m/z 112, 156, 182, and 210 correspond to vinyl- and carboxyl-terminated compounds generated through the β -hydrogen scission of ester bonds (Fig. 7k, Chain scission I).^[45] However, as the temperature increased to $T_{\max}$, both PEF and PEFD₁₀ exhibited a prominent peak at m/z 96, corresponding to 2-furaldehyde, via alkyl-oxygen or acyl-oxygen (Fig. 7k, chain scission II and chain scission III).^[46] The thermal decomposition pathways of PEF generate a substantial number of free radicals.^[47] The flame-retardancy mechanism of DOPO primarily occurs in the gas phase. It creates free radicals (at m/z 47, 63, 152, and 169) that quench those produced by the thermal decomposition of polymers, thereby inhibiting chain reactions and slowing combustion. These findings are in good agreement with the TG results. Before and after the introduction of DDP, the $T_{5\%}$

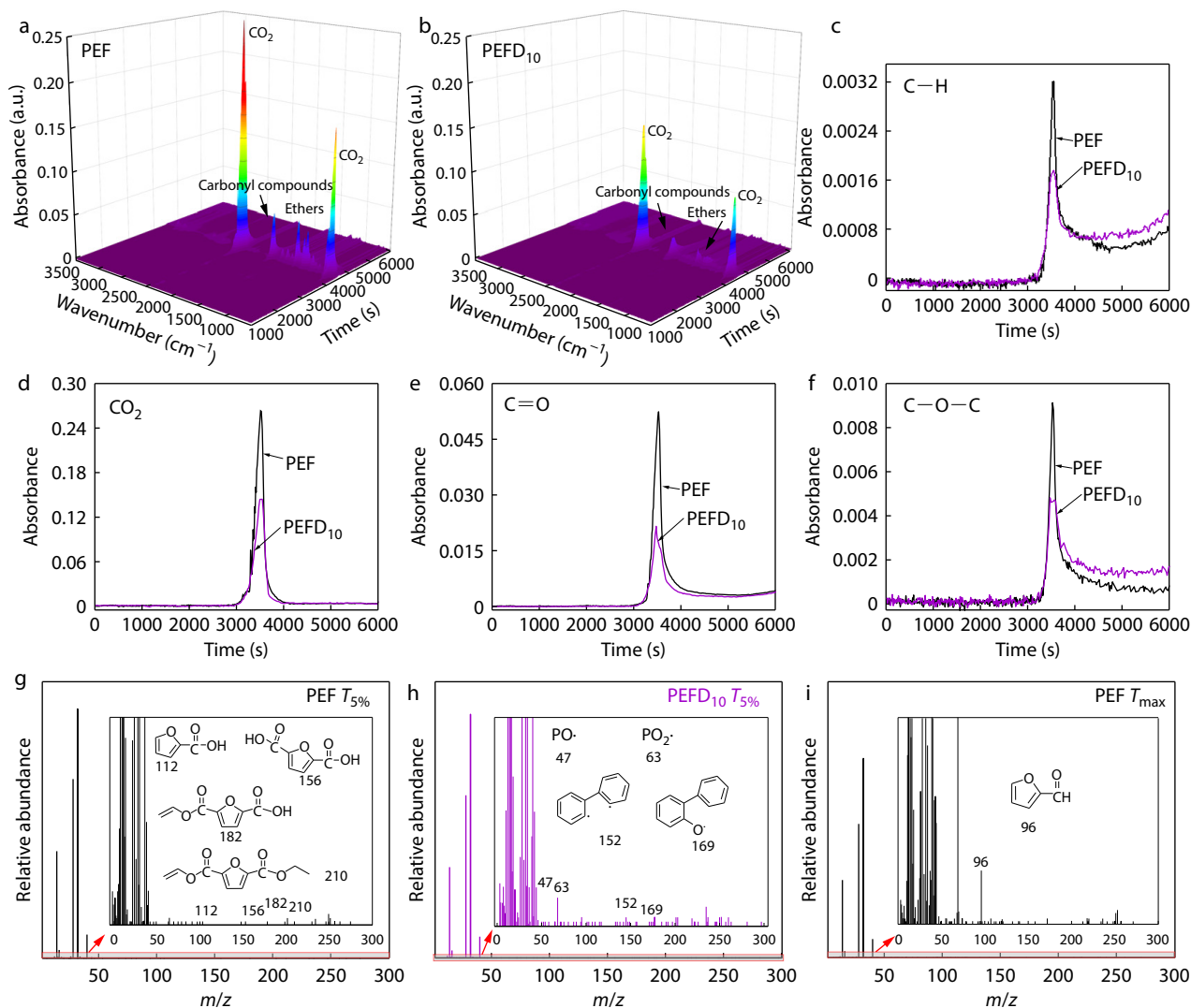
of the polymer remained almost unchanged, whereas $T_{\max}$ was delayed and $R_{\max}$ decreased. A schematic representation of PEFD₁₀'s flame-retardant mechanism appears in Fig. 7(l).

In conclusion, phosphoric acid derived from DOPO decomposition triggered matrix dehydration and promoted char formation through esterification. Meanwhile, as combustion proceeds, the decomposition pathways of PEF and PEFD₁₀ change from β -hydrogen cleavage to free radical reactions. Phosphorus-containing radicals ($\text{PO}\cdot/\text{HPO}\cdot$) derived from DOPO effectively scavenge polymer-derived $\text{H}\cdot/\text{OH}\cdot$ radicals, thereby suppressing chain propagation reactions and retarding combustion.

Mechanical properties

The effect of DDP on the mechanical properties of the PEF was investigated through tensile and unnotched impact tests, as illustrated in Fig. 8 and Fig. S2 (in ESI). The tensile properties of PEFD_n and PEF were almost the same (Fig. 8a). This challenges the prevailing notion that enhancing flame retardancy inevitably leads to a decline in the tensile properties, as previously documented in the literature (Fig. 8b).^[5,6,8,11]

Surprisingly, the impact strength of PEFD_n gradually increased as more DDP was introduced. PEFD₁₀ achieves an 8.6-



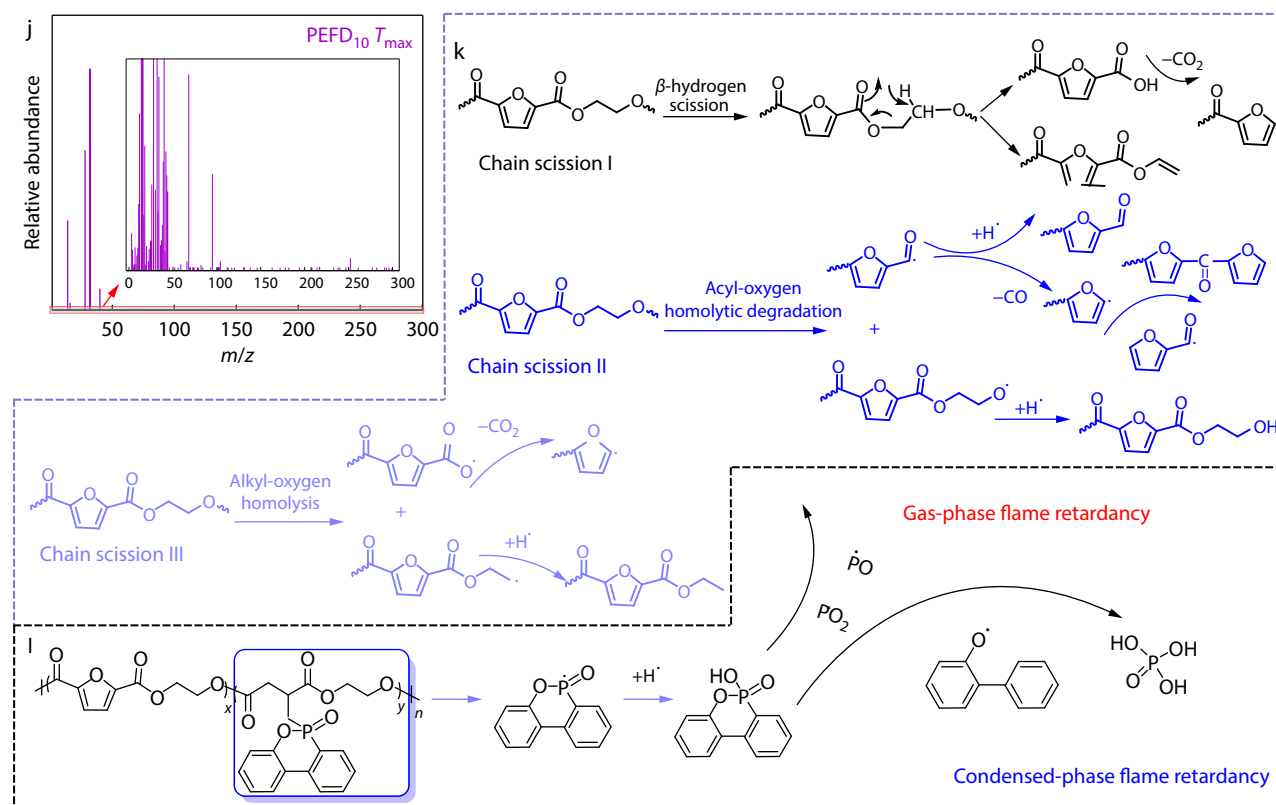


Fig. 7 (a, b) 3D TG-FTIR results of PEF and PEFD₁₀, (c–f) time-dependent absorption profiles of key pyrolysis volatile species, (g–j) MS results of PEF and PEFD₁₀, (k) thermal degradation mechanism of PEF, and (l) flame retardant mechanism of PEFD₁₀.

fold enhancement in impact strength (from 1.5 kJ/m² to 14.7 kJ/m²), demonstrating exceptional impact toughness (Fig. 8c). As is evident from the SEM image (Fig. 8d), the impact fracture surface of the PEF is characterized by a smooth and flat appearance, which is indicative of a typical brittle fracture.^[48] However, the section of PEFD₁₀ exhibited substantial cracking, which is indicative of plastic deformation. The dissipation of energy resulting from this process can impede the initiation or propagation of cracks, thereby enhancing toughness.^[49,50] More specifically, the presence of DOPO pendant groups induces microphase separation (Fig. 8e), which absorbs additional energy during impact, thereby enhancing the impact strength. This was reported in Hu's work.^[51]

To elucidate the role of the DOPO-based units in promoting microphase separation, a DOPO dimer model was optimized at the ω B97X-D/6-31+G(d) level. The resulting geometry exhibits a characteristic parallel-displaced stacking configuration with an interlayer distance of 3.54 Å—well within the van der Waals range and a horizontal offset of 1.63 Å, minimizing electrostatic repulsion between aromatic rings. These features highlight the adaptive molecular adjustments that optimize intermolecular interactions. ESP maps (Fig. 8f) show a uniform π -electron cloud distribution over aromatic rings, with complementary positive/negative regions at the stacking interface, favoring stable sliding i -stacking. The ESP map also revealed complementary positive/negative regions along the aromatic planes, favoring stable π - π association. IGMH analysis showed that the plots of the $\text{sign}(\lambda_2)\rho(r)$ function

mapped on the isosurface of the g^{inter} descriptor demonstrated the regions of the negative function around the aromatic rings shown in green, indicating the attractive nature of these interactions (Fig. 8g). The types of intermolecular interactions can be revealed via reduced density gradient (RDG) scatterplots. The RDG scatterplots (Fig. 8h) display pronounced green spikes with $\text{sign}(\lambda_2)\rho$ values greater than -0.04 , indicative of dispersion and van der Waals interactions as the dominant forces. We further analyzed the dimeric species using Bader's quantum theory of atoms in molecules (QTAIM) (Fig. 8i). QTAIM analysis revealed multiple bond critical points (BCPs) between the two aromatic rings. The electron density $\rho(r)$ and Laplace value $\nabla^2\rho(r)$ of these BCPs were consistent with the characteristics of typical non-covalent π - π interactions, confirming the directional delocalization of the electron cloud between the aromatic rings.

This flame-retardant polyester exhibited excellent impact toughness, making it a promising candidate for applications in electrical appliance casings and switch components.

O₂ Barrier Property and UV Shielding Capability

It is well known that oxygen is a significant factor in the aging of metal parts within the electronic components. Therefore, the oxygen barrier properties of polymers used in electronic component casings are critical. The oxygen barrier performances of PEF and PEFD_n are shown in Fig. 9(a). The introduction of DDP reduced the crystallization capability of the polymer (as shown in Fig. 3e), consequently lowering its barrier performance. However, its permeability coefficient is still lower than that of PET.^[52]

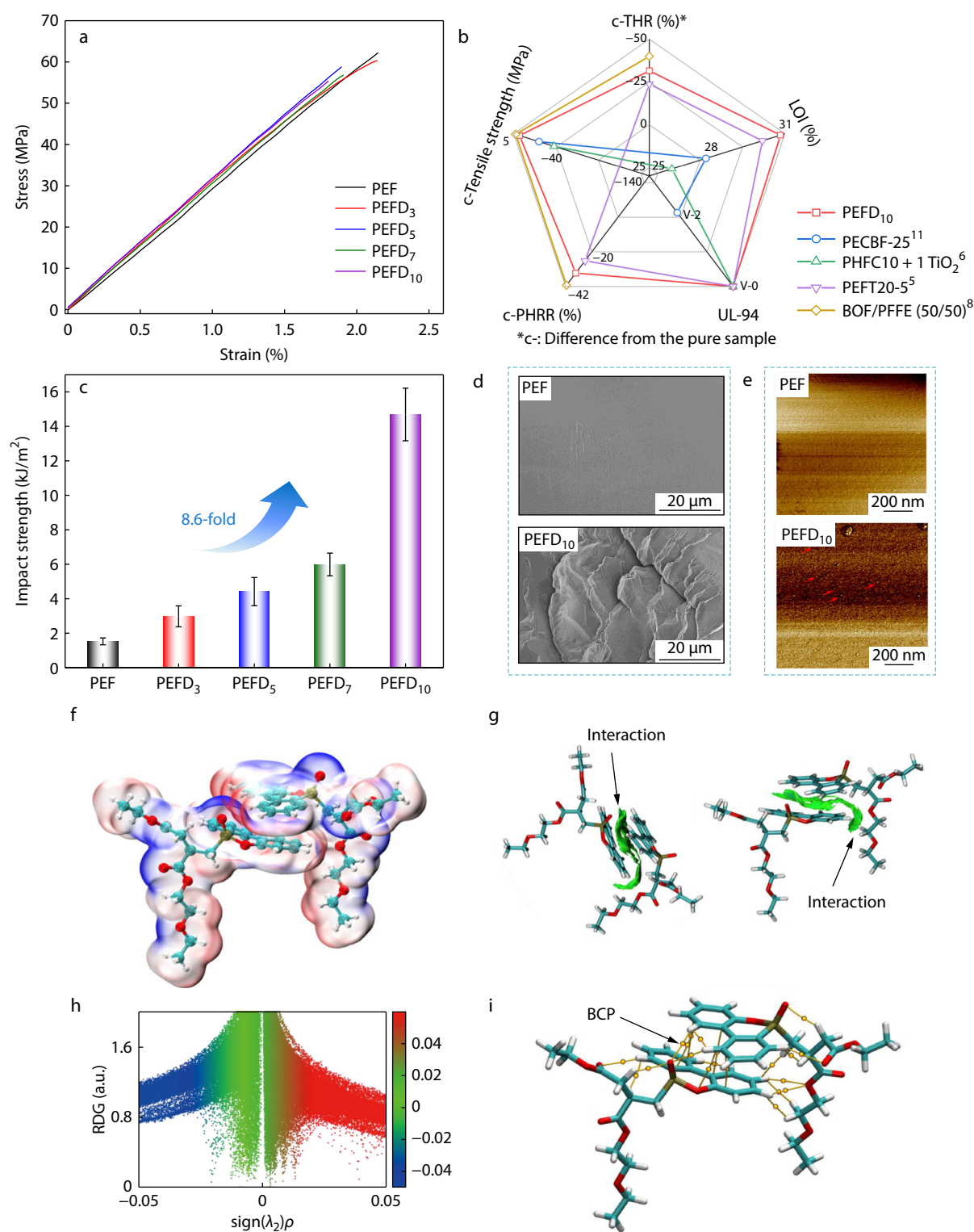


Fig. 8 (a) Stress-strain curves of PEF and PEFD_n; (b) A performance comparison between this work and literature-reported results; (c) Impact strength; (d) SEM images; (e) AFM images of the impact fracture surface of PEF and PEFD₁₀. The red arrow indicates the area where microphase separation occurs. And the non-covalent interaction analysis of the DOPO dimer. (f) Electrostatic potential (ESP) analysis. The default color transition is BWR (Blue-White-Red), the white area corresponds to the region having almost vanished ESP value, while the red and blue points have evidently positive and negative ESP, respectively. (g) IGMH analysis in top view and side view. IGMH isosurface (blue) visualizing the spatial distribution of π - π stacking regions, further confirming the presence and extent of aromatic stacking interactions. (h) Color filled RDG scatter plot. (i) QTAIM analysis identifying bond critical points (BCPs) between aromatic rings, with electron density $\rho(r)$ and $\nabla^2\rho(r)$ values characteristic of π - π interactions.

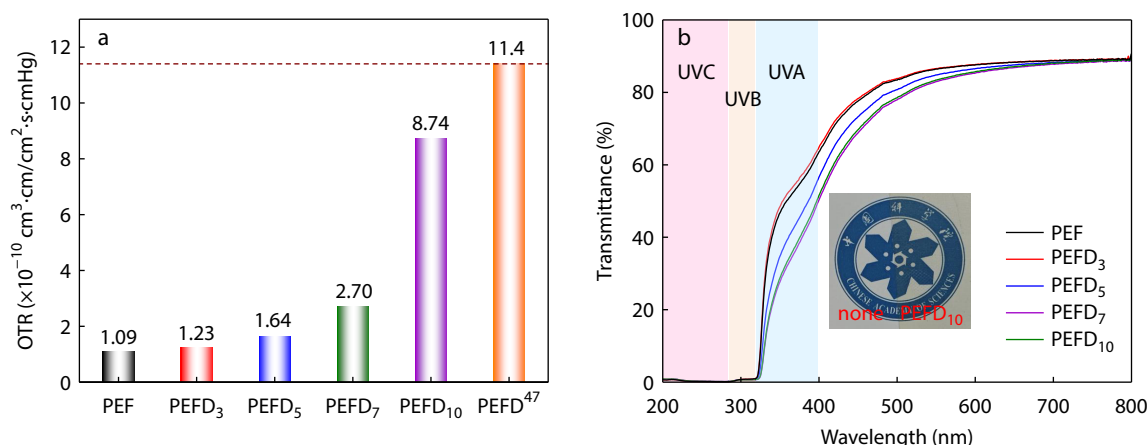


Fig. 9 (a) O_2 barrier properties of PEF, PEFDn and PET (O_2 barrier properties of PET (Burgess *et al.*^{[52])}); (b) Transmittance curves for PEF and PEFD_n, and image of PEFD₁₀ covering paper.

The high UV-shielding capability of outdoor electronic housings significantly enhances their durability by minimizing UV-induced damage to internal electronic components. The UV shielding discussion highlights PEFD's potential of PEFD in outdoor applications. The UV-Vis transmission spectra of PEF and PEFDn are shown in Fig. 9(b). PEF and PEFDn demonstrated effective UV-shielding performance in the UVC and UVB regions. Notably, the UVA shielding capability progressively improved with increasing DDP content. For example, PEF exhibited 64% transmittance at 400 nm, whereas PEFD₁₀ exhibited 50% transmittance, corresponding to a 14% reduction. This reduction resulted from the UV-absorbing capability of the DOPO component in PEFD₁₀.^[53] The large π bonds of aromatic rings in DOPO can absorb UV light through the electronic transition of π electrons under UV-radiation.^[54] Moreover, although PEFD₁₀ exhibits a slightly reduced transmittance in the visible region compared with PEF, it still maintains high transparency, as demonstrated in Fig. 9(b). PEFD₁₀ retains excellent visible-light transparency, achieving an optimal balance between transparency and shielding efficiency.

CONCLUSIONS

In conclusion, we reported a PEF copolyester that combines flame retardancy and high impact resistance. The addition of DDP did not alter the T_g and Vicat softening temperatures of the polymer, demonstrating that it retained its heat resistance. PEFD₁₀ exhibited excellent flame retardancy and achieved a V-0 rating in the UL-94 test. The LOI of the material increased significantly from 21.0% (PEF) to 30.8%, thus meeting the criteria for flame-retardant materials. Meanwhile, the cone revealed a 30.9% reduction in PHRR and a 31.5% decrease in THR compared to PEF, indicating substantially reduced thermal radiation hazards. PEFD₁₀ exhibited a 98.2% increase in char residuals compared with PEF, which significantly enhanced substrate protection. In addition, PEFDn exhibited tensile properties comparable to those of PEF, while demonstrating significantly enhanced impact performance. Notably, PEFD₁₀ showed an 8.6-fold increase in impact strength compared with PEF, along with a substantial improvement in toughness. DFT investigations confirmed that the DOPO dimers adopt an energetically favorable parallel-displaced π - π stacking configuration. This stacking

motif contributes to microphase separation and enhances energy dissipation, offering fundamental insights into the molecular mechanisms underlying the improved impact resistance of DOPO-based materials. Furthermore, while PEFDn exhibits reduced oxygen barrier performance compared to PEF, it still surpasses that of PET. Simultaneously, PEFD₁₀ achieves an optimal balance between optical transparency and UV shielding performance. Sustainable green materials exhibit exceptional multifunctional characteristics, positioning them as an advanced solution for next-generation electrical enclosures.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3478-4>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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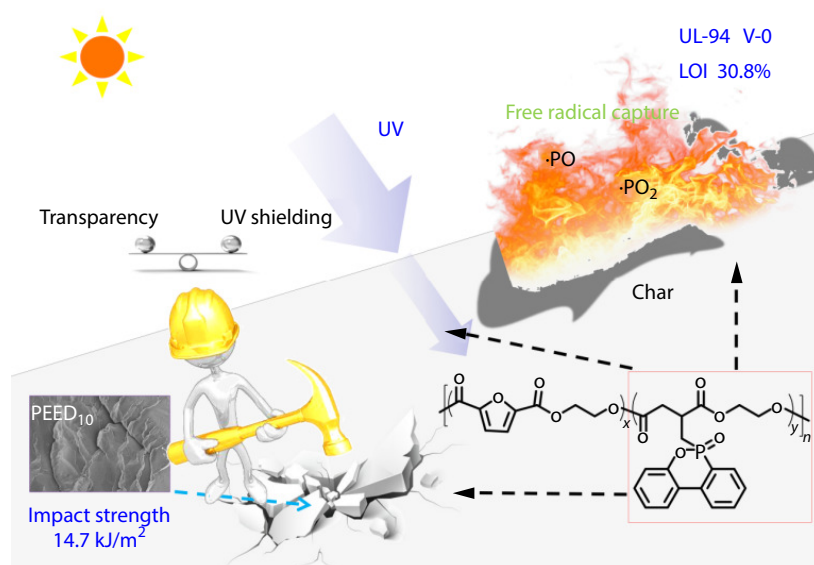
Graphical Abstract

An Inherently Flame-retardant Bio-based Poly(ethylene 2,5-furandicarboxylate) Copolyester with High Impact Toughness and UV Shielding

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In this study, a bio-based poly(ethylene 2,5-furandicarboxylate) (PEF) copolymer was illustrated, integrating intrinsic flame retardancy (UL-94 V-0), exceptional impact toughness (14.7 kJ/m²), and UV shielding via phosphorus-containing segments, overcoming traditional flame retardant trade-offs.



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