



Review

Flame-Retardant Fiber-Reinforced Composites: Advances and Prospects in Multi-Performance Synergy

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Abstract

Fiber-reinforced polymer composites, particularly carbon fiber and glass fiber reinforced composites, are widely used in cutting-edge industries due to their excellent properties, such as light weight and high strength. This review systematically compares and summarizes recent research advances in flame retardancy for carbon fiber-reinforced polymers and glass fiber-reinforced polymers. Focusing on various polymer matrices, including epoxy, polyamide, and polyetheretherketone, the mechanisms and synergistic effects of different flame-retardant modification strategies—such as additive flame retardants, nanocomposites, coating techniques, intrinsically flame-retardant polymers, and advanced manufacturing processes—are analyzed with emphasis on improving flame retardancy and suppressing the “wick effect.” The review critically examines the challenges in balancing flame retardancy, mechanical performance, and environmental friendliness in current approaches, highlighting the key role of interface engineering in mitigating the “wick effect.” Based on this analysis, four future research directions are proposed: implementing green design principles throughout the material life cycle; promoting the use of natural fibers, bio-based resins, and bio-derived flame retardants; developing intelligent responsive flame-retardant systems based on materials such as metal–organic frameworks; advancing interface engineering through biomimetic design and advanced characterization to fundamentally suppress the fiber “wick effect”; and incorporating materials genome and high-throughput preparation technologies to accelerate the development of high-performance flame-retardant composites. This review aims to provide systematic theoretical insights and clear technical pathways for developing the next generation of high-performance, safe, and sustainable fiber-reinforced composites.

Keywords: fiber-reinforced polymers; composite materials; flame-retardant modification; resin matrix; mechanical strength



Academic Editors: Dong-Jun Kwon and Fubin Luo

Received: 10 November 2025

Revised: 9 December 2025

Accepted: 12 December 2025

Published: 16 December 2025

Citation: Zhang, Z.; Han, F.; Li, H.; Li, T.; Yang, B.; Hu, J.; Pan, Y.-T. Flame-Retardant Fiber-Reinforced Composites: Advances and Prospects in Multi-Performance Synergy. *J. Compos. Sci.* **2025**, *9*, 703. <https://doi.org/10.3390/jcs9120703>

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1. Introduction

Fiber-reinforced polymer (FRP) composites, as cornerstone materials of modern industry, play an indispensable role in aerospace, national defense, military industry, and high-end equipment manufacturing. Their development level is directly related to national technological progress and industrial upgrading [1–3]. Among them, composites reinforced with carbon fibers and glass fibers dominate. Carbon fibers (CFRP), with their outstanding specific strength, specific modulus, and fatigue resistance, are the preferred choice for load-bearing and lightweight structures. Glass fibers (GFRP), by virtue of their

excellent insulation, corrosion resistance, and cost advantages, are widely used in electrical engineering, construction, and anti-corrosion applications [4–6]. These fibers are typically combined with polymer matrices through processes such as lamination, filament winding, and compression molding to form components with superior macroscopic properties. However, the polymer matrices that constitute the core of these composites are mostly composed of carbon and hydrogen elements, making them inherently flammable. More severely, during combustion, the fibers can induce a significant “wick effect,” similar to a candle wick, continuously drawing molten polymer to the flame zone. This leads to rapid flame spread and a sharp increase in heat release rate and accompanies the generation of large amounts of smoke and toxic gases, a phenomenon more pronounced for glass fibers [7–9]. This safety defect, caused by the combined intrinsic material characteristics and composite structure, has become a bottleneck restricting the application of FRP composites in scenarios with stringent fire safety requirements.

To tackle this challenge, flame-retardant technologies have progressed from rudimentary methods to refined strategies. Early approaches primarily used simple physical blending of additive flame retardants, which often compromised mechanical properties and caused interfacial incompatibility. Recent research has shifted toward multiscale, multi-mechanism synergistic systems and precise control. For instance surface engineering and coating techniques (e.g., biomass coatings) create interfacial flame-retardant barriers; nanotechnology (e.g., POSS, MXene) enhances char layer quality; advanced manufacturing (e.g., 3D printing) controls fiber orientation to alter heat transfer and combustion paths; and molecular design develops intrinsic flame-retardant resins that integrate mechanical strength with inherent fire resistance, avoiding the drawbacks of additive approaches [10–12].

Despite significant achievements, current research remains fragmented, lacking a unified analytical framework that spans different resin matrices and reinforcing fibers to systematically reveal the intrinsic “structure-function-performance” relationships. In particular, there is a lack of in-depth comparison and analysis of the commonalities and specificities in flame-retardant strategies between CFRP and GFRP systems. Furthermore, the influence of the “wick effect” has not been fundamentally addressed at the interface level, and the application of novel nanomaterials such as metal–organic frameworks (MOFs) in flame retardancy remains limited and underexplored.

Therefore, the objective of this review is to provide a comprehensive and critical analysis of the latest research progress and development trends in flame retardancy for CFRP and GFRP composites. It systematically elucidates the intrinsic relationships among “structure–function–performance,” with a particular focus on synergistic approaches. This review aims to draw attention to the overreliance on singular flame-retardant strategies and the prevalent lack of synergistic design. Innovatively, it proposes four future research directions to address core challenges such as inherent flammability and the “wicking effect,” while also summarizing past FRP studies based on different flame-retardant strategies. The discussion centers on flame-retardant strategies for various polymer matrices (e.g., epoxy resin (EP), polyamide (PA), and polyether ether ketone (PEEK)), provides an in-depth analysis of the differential impact of the “wicking effect” in CFRP and GFRP systems along with corresponding mitigation approaches, and critically evaluates the effectiveness and limitations of existing flame-retardant methods in simultaneously enhancing flame retardancy, mechanical properties, and environmental sustainability.

The novelty of this review lies in its dual-thread narrative—“synergistic flame retardancy” and “green development”—which runs throughout the text. While emphasizing the fundamental goal of flame retardancy, it also focuses on the full-lifecycle sustainability of materials, covering green pathways such as natural fibers, bio-based resins,

and bio-derived flame retardants. Furthermore, although nanomaterials like MOFs have been widely studied for interfacial enhancement in composites, their application in flame retardancy—especially in synergizing with multiple flame-retardant modes—remains highly innovative. This review also offers forward-looking perspectives on functionalization, intelligence, and synergistic utilization in this context. In Section 2, we introduce key flame-retardant testing methods and evaluation standards. Combined with the data and figures presented later in the text, this will enable readers to better assess different flame-retardant strategies. Through this review, we aim to help readers clearly grasp the cutting-edge advances and persistent challenges in flame-retardant technology for fiber-reinforced composites and to provide theoretical insights and directional guidance for promoting the research and development of next-generation high-performance, high-safety, and environmentally friendly composite materials [13–16].

2. Flame Retardancy Test Methods

In research, a set of test methods and evaluation index systems are typically employed to comprehensively and deeply assess the flame-retardant performance and fire safety of fiber-reinforced polymer composites.

2.1. Limiting Oxygen Index (LOI) Test

The Limiting Oxygen Index test is used to quantitatively evaluate the ignitability of materials. Conducted on an oxygen index apparatus, it measures the minimum volume concentration percentage of oxygen in a nitrogen-oxygen mixture gas flow required to sustain steady burning of a specimen. A higher LOI value indicates that the material is more difficult to ignite in air, signifying superior flame-retardant performance [17–19].

2.2. UL-94 Vertical Burning Test

The UL-94 test is employed to evaluate the burning behavior and self-extinguishing capability of materials in a vertical orientation, thereby assessing their flame retardancy.

In this test, bar-shaped specimens are vertically mounted and subjected to two brief applications of a specified flame source to their bottom end. Based on the afterflame time and afterglow time after each flame removal, as well as the occurrence of burning drips, materials are classified into different flame retardancy grades such as V-0, V-1, V-2, or NR (Not Rated). The V-0 grade represents the most superior retardant performance. A material achieves the V-0 rating if, after both flame applications, the afterflame times (T1 and T2) for each individual specimen are less than or equal to 10 s, the total afterflame time for all five specimens in a set does not exceed 50 s, and no burning drips are produced [20].

2.3. Cone Calorimeter (CCT) Test

The Cone Calorimeter test, based on the oxygen consumption principle, is the most authoritative laboratory-scale method for evaluating material fire reaction properties under simulated real fire conditions. The test involves exposing a specimen to a specific external radiant heat flux and recording the entire process from ignition to extinction. It provides a series of key parameters, including the Heat Release Rate (HRR), Peak Heat Release Rate (PHRR), Total Heat Release (THR), Time to Ignition (TTI), and Total Smoke Production (TSP). These parameters are used to analyze the material's fire intensity, development rate, and smoke generation characteristics [21].

2.4. Analysis of Fire Performance Index (FPI) and Average Effective Heat of Combustion (AEHC)

FPI and AEHC are two key analytical parameters derived from Cone Calorimeter results:

The Fire Performance Index (FPI) is a key indicator for comprehensively evaluating the fire safety of a material. It is defined as

$$FPI = \frac{TTI}{PHRR}.$$

A higher FPI value indicates that the material is more difficult to ignite and exhibits weaker fire intensity when burning, implying a lower fire hazard.

Average Effective Heat of Combustion (AEHC) is a core parameter used to determine the operating mechanism of flame retardants. It is calculated as $AEHC = THR / \text{Mass Loss}$. A significant decrease in the AEHC value suggests that the flame retardant primarily acts in the gas phase by inhibiting the combustion reaction. Conversely, if the AEHC value remains largely unchanged, the flame-retardant action occurs mainly in the condensed phase (e.g., through char formation) [21].

3. Flame-Retardant Carbon Fiber-Reinforced Polymer Composites (CFRPs)

CFRPs are widely used in both military and civilian applications due to their excellent properties, including low weight, high strength, and resistance to high temperatures, offering significant potential for advanced engineering applications [22]. As a reinforcement material, carbon fiber can effectively enhance or impart a variety of functional properties to polymer matrices, such as flame retardancy, thermal conductivity, electromagnetic shielding, and high mechanical strength. However, the intrinsic flame-retardant capability of CFRPs remains inadequate. When exposed to fire, CFRPs are prone to ignition and can release toxic gases [23], prompting intensive efforts to develop effective strategies to improve their flame-retardant performance.

Research on flame-retardant CFRPs has explored a wide range of polymer matrices, including epoxy resin-based CFRPs [24,25], polyamide-based CFRPs [26], polyimide-based CFRPs [27,28] and polyurethane-based CFRPs [29], among others. Each matrix system brings unique properties and challenges to flame-retardant design. The following sections will provide a detailed overview and discussion of flame-retardant CFRPs with different resin matrices, focusing on the mechanisms, modification strategies, and performance characteristics of each system.

3.1. Epoxy Resin-Based (EP) CFRP Flame-Retardant Composites

Epoxy resin (EP), a commonly used polymer mainly composed of carbon, hydrogen, and oxygen, contains epoxy functional groups before curing and typically features aliphatic or heterocyclic segments within its backbone [30], which contribute to its inherent flammability. During the initial stage of combustion, EP absorbs a substantial amount of heat until it reaches its decomposition temperature, leading to chain scission and the formation of reactive radicals such as $\cdot OH$ and $\cdot O$ [31]. The resulting small combustible molecules further react with oxygen, generating flames and dense smoke. Moreover, due to the high crosslinking density of EP, limited char formation occurs in the condensed phase, rendering it ineffective in suppressing the propagation of combustion [30].

Biomass-based materials are considered among the most environmentally friendly alternatives. Li et al. [32] employed a layer-by-layer self-assembly technique to deposit chitosan (CS) and phytic acid (PA) biobased coatings (Figure 1a) onto carbon fiber fabrics, forming CS/PA@CF structures that effectively enhanced both the flame retardancy and mechanical properties of EP. The flame-retardant performance of the EP composite modified with CS/PA@CFRP was evaluated through LOI and UL-94 tests. Results demonstrated an LOI value of 31%, along with a dramatic reduction in TTI from 103 s to 6 s, confirming enhanced fire resistance (Figure 1d). Cone calorimetry analysis (Figure 1c) revealed a 35.1% decrease in TTI relative to unmodified EP, accompanied by substantial reductions in PHRR (85.4%) and THR (70.99%). Smoke emission parameters, including TSP and

CO₂ release (CO₂P), were similarly suppressed. Notably, the char yield reached 65.63%, underscoring the material's superior fire safety characteristics. Concurrently, mechanical properties showed remarkable improvement: impact strength surged to 128.7 kJ/m² (an 800% enhancement over pure EP). Regarding the flame-retardant mechanism, Figure 1e indicates a significant reduction in gaseous pyrolysis products for CS/PA@CFRP. Raman analysis further reveals that the introduction of the CS/PA coating markedly increases the degree of carbonization of CFRP, thereby compensating for the inherent deficiency of EP. While previous studies on layer-by-layer self-assembly modification of CFRP have primarily focused on mechanical performance, such as Fu et al., who enhanced the mechanical performance of CFRP using GO/SiO₂ via a self-assembly modification strategy [33]. Li's work further addressed the gap in flame-retardant applications by employing a coating–self-assembly approach, which not only demonstrated the synergy between sustainability and performance but also achieved concurrent improvements in both mechanical and thermal properties [32].

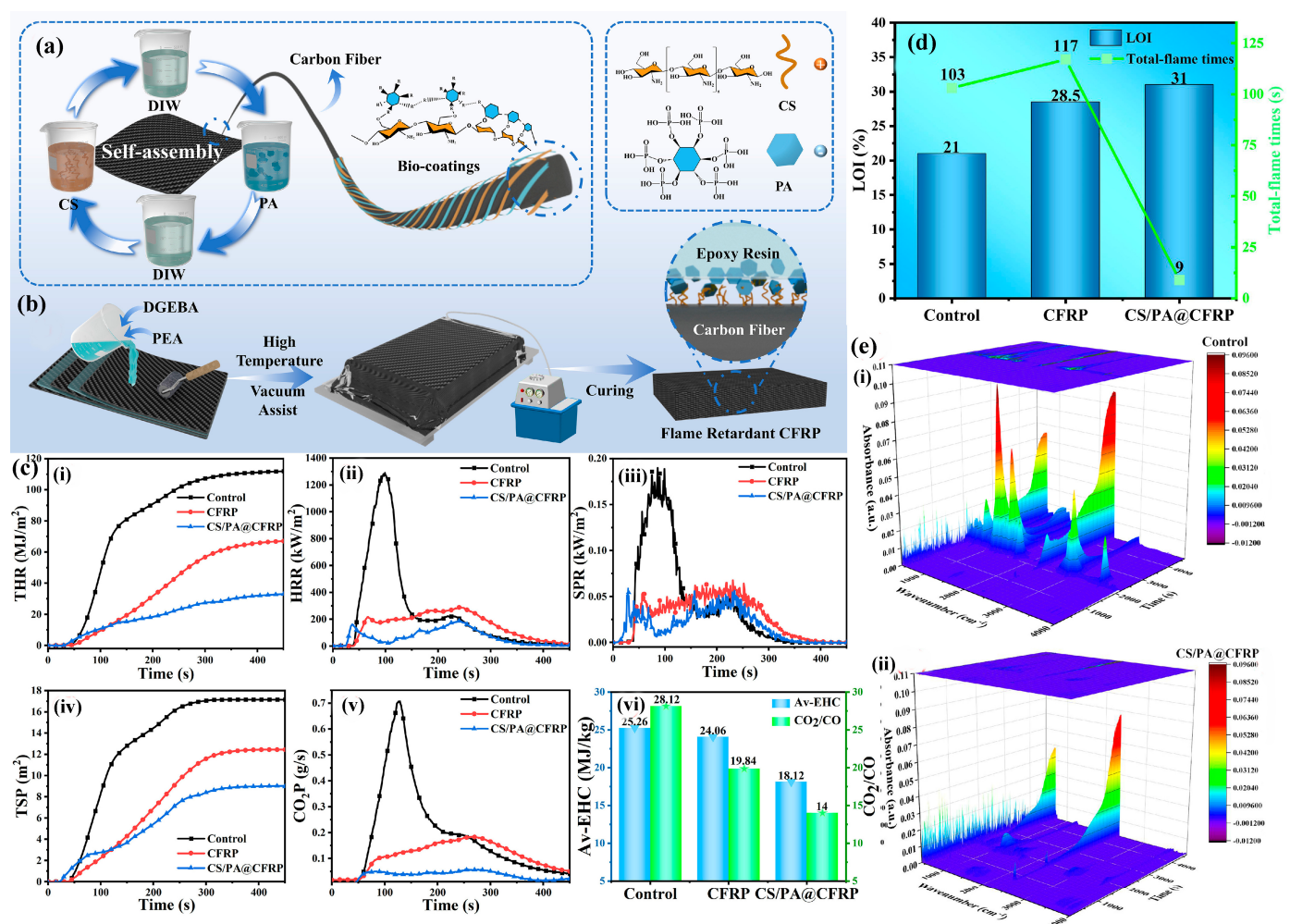


Figure 1. (a) LbL procedure of bio-based flame retardant coatings (CS/PA) constructed on carbon fiber cloths. (b) Preparation process of CFRP and CS/PA@CFRP by vacuum assisted hand layup method. (c) Cone calorimeter curves of (i) Total Heat Release (THR), (ii) Heat Release Rate (HRR), (iii) Smoke Production Rate (SPR), (iv) Total Smoke Production (TSP), (v) CO₂ product curves. (CO₂P), (vi) Av-EHC and CO₂/CO with different samples. (d) Real-time images of VFT of graph of LOI values and combustion time. (e) 3D FTIR spectra of (i) Control and (ii) CS/PA@CFRP [32].

For traditional flame retardant (FR) materials, the relatively large particle size [34] can significantly affect the mechanical properties of composites. To address this issue, Yang et al. [35] developed a method that enhances flame retardancy while maintaining mechanical performance. Ammonium polyphosphate (APP) was reacted with an amine curing agent, followed by probe sonication to obtain HF-APP (with slightly larger particle size) and SHF-APP (with smaller particle size), which both types exhibit diameters of approximately 0.12 μm . The flame-retardant efficacy of EP/CFRP composites modified with HF-APP and SHF-APP was quantitatively assessed. LOI measurements revealed values of 49% and 45% for HF-APP and SHF-APP formulations, respectively, indicating superior oxygen deprivation capability. Comparative analysis of combustion parameters showed HF-APP's enhanced performance, exhibiting 74.25% and 72.5% reductions in PHRR and THR relative to unmodified EP (Figure 2). These results confirm the exceptional fire suppression characteristics achieved through APP particle size optimization. Regarding mechanical strength, the smaller diameters of HF-APP and SHF-APP reduced the waviness of fiber bundles in the composite, resulting in an approximately 8.6% increase in compressive strength. As shown in the figure, in terms of flexural strength, both HF-APP/CFRP and SHF-APP/CFRP outperformed conventional APP/CFRP. In terms of flexural strength, short-beam shear strength, and interlaminar fracture energy, SHF-APP exhibits greater advantages over HF-APP. However, regarding flame-retardant performance, excessively small particles fail to form a continuous and compact char layer, resulting in lower values during combustion tests. Yang's work demonstrated that tuning flame-retardant particle size can synergistically enhance mechanical properties and further innovatively proposed particle downsizing combined with functionalized curing of the flame retardant [36], providing a new design pathway for other flame-retardant fillers as well [35].

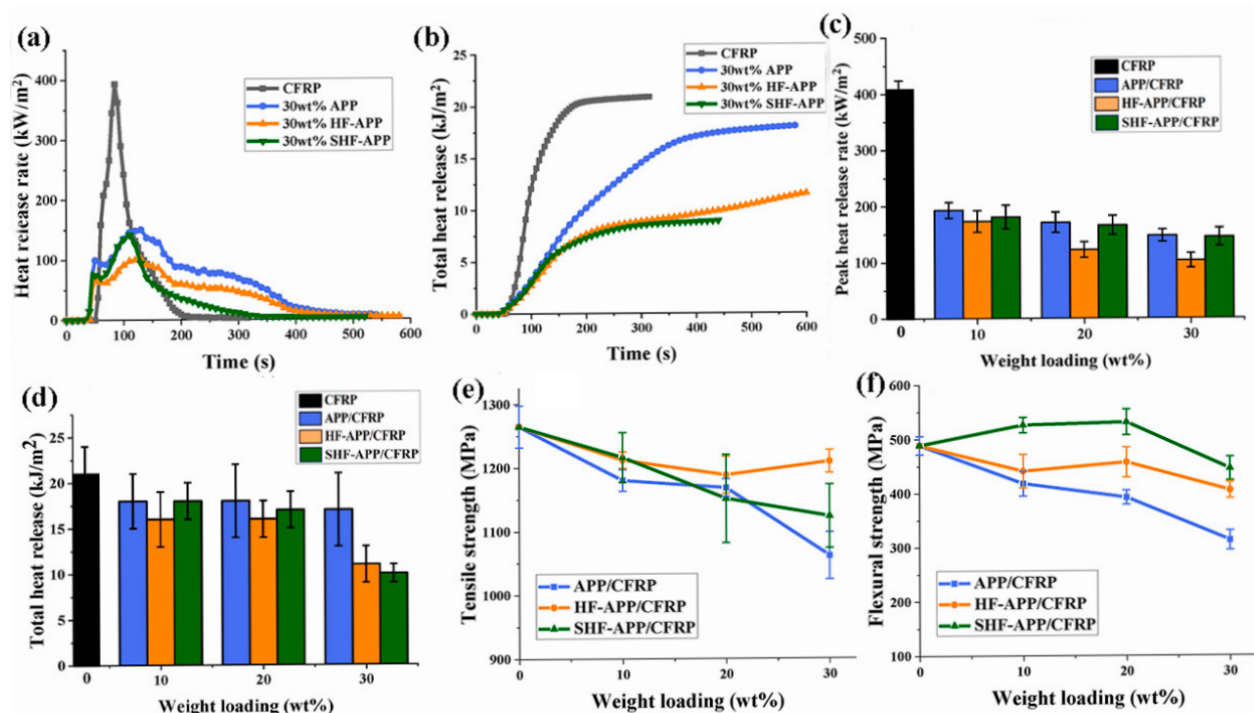


Figure 2. Flame retardant characteristics of CFRPs containing APP, HF-APP, and SHF-APP. (a) typical heat release rate versus time curves; (b) total heat release versus time curves; (c) effects of weight loadings on (c) the peak heat release rate and (d) the total heat release. Strengths of CFRPs with different weight loadings of APP, HF-APP, and SHF-APP particles: (e) tensile strength and (f) flexural strength [35].

Zou et al. [37] synthesized a novel phosphorus-based flame retardant (DPO) [38] and investigated its effectiveness in enhancing the flame retardancy of epoxy-based CFRP compared with a commercial additive, DOPO-HQ. Their study proposed the concept of the “contradictory effect” of phosphorus flame retardants (PFRs). As illustrated in the synthesis scheme, DPO was prepared from DOPO-HQ through a multi-step reaction (Figure 3a). The key distinction lies in the oxidation state of phosphorus: it exists in a high oxidation state in DPO, whereas in DOPO-HQ, it exhibits the opposite configuration. As shown in Figure 3c–e, the HRR, THR, and CO₂P profiles revealed that CF/EP/7%DPO and CF/EP/16%DOPO-HQ exhibited similar trends, both showing notable improvements over neat CF/EP, with DOPO-HQ demonstrating slightly superior performance. Regarding the gas-phase flame-retardant mechanism, as shown in the FTIR spectra (Figure 3b), the characteristic peaks of typical combustion products—including ether compounds (1172 cm^{−1}), aromatic species (1510 cm^{−1}), and hydrocarbons (2930 cm^{−1})—were significantly reduced, particularly for CF/EP/16%DOPO-HQ. In the condensed phase, CF/EP/7%DPO formed a denser, more spherical char structure, indicating a more compact and thermally stable carbonaceous layer. Zou’s work innovatively addressed the balance between subjective and objective weighting in selecting flame retardants, emphasizing that both the oxidation state and thermal stability of PFRs should be comprehensively considered when optimizing the flame retardancy of CF/EP composites.

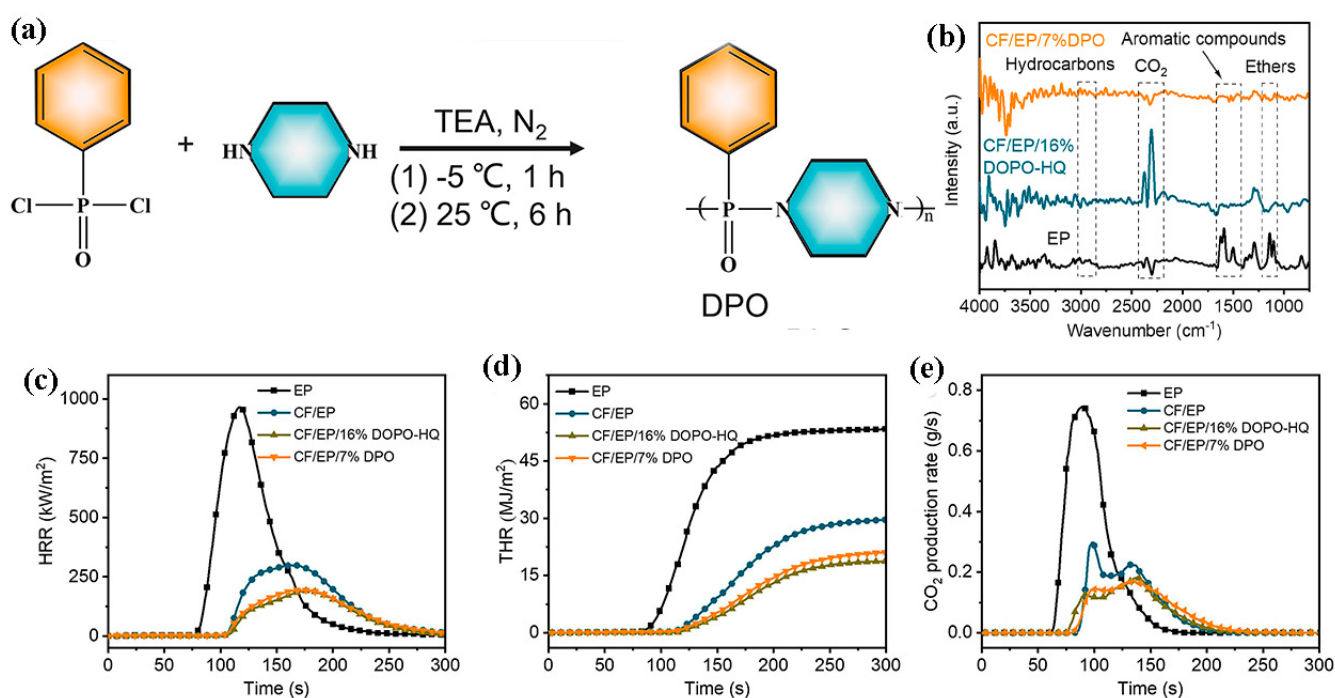


Figure 3. (a) Synthesis route of DPO; combustion characteristics of CF/EP composites at 65 kW/m². (b) FTIR spectra of thermal decomposition gas products of flame-retardant CF/EP composites at the maximum degradation rate. (c) HRR. (d) THR. (e) CO₂ release [37].

In Zou’s study, the incorporation of DPO did not significantly improve the overall flame-retardant performance, yet it further clarified the respective roles of phosphorus species: high-oxidation-state phosphorus (DPO) contributing primarily to the condensed phase, and low-oxidation-state phosphorus (DOPO-HQ) acting mainly in the gas phase. This raises an important question: could phosphorus flame retardants combining both high and low oxidation states offer superior flame-retardant efficiency in fiber-reinforced composites? Yu et al. recently synthesized a phosphorus-based flame retardant (POG-DOPO) containing both oxidation states, which exhibited strong gas-condensed phase synergy,

though its thermal stability remained insufficient [39]. Therefore, achieving effective cooperation between high- and low-oxidation-state phosphorus while simultaneously balancing flame retardancy and thermal stability will be a key focus of our future work [37].

3.2. Polyamide-Based (PA) CFRP Flame-Retardant Composites

Polyamide (PA) is a high molecular weight polymer composed of repeating amide groups ($-\text{CONH}-$) linked through covalent bonds. It exhibits excellent wear resistance, chemical stability, and mechanical strength, making it one of the most widely produced and applied thermoplastic engineering plastics [40]. As a typical organic material rich in carbon and hydrogen, PA is highly flammable under elevated temperatures. Consequently, improving the flame retardancy of fiber-reinforced composites based on PA has become an urgent necessity. Prior to 2020, relatively few studies focused on enhancing the flame-retardant performance of carbon fiber reinforced polyamide (CF/PA) composites, with most research emphasizing their thermodynamic behavior. Efforts to improve flame resistance were mainly limited to the incorporation of flame retardants, such as halogen-, phosphorus-, or nitrogen-based additives [41]. Physical blending remains the most straightforward and cost-effective approach; however, it suffers from notable drawbacks—halogenated flame retardants exhibit poor thermal stability and release toxic smoke during combustion [42,43], while phosphorus-based additives (e.g., red phosphorus) often show poor compatibility with the polymer matrix. Therefore, enhancing the compatibility of existing flame retardants or developing alternative types of flame-retardant CF/PA composites is of critical importance. Achieving simultaneous synergy across the material system's overall performance also remains a critical challenge to be resolved.

CFRPs have become indispensable in aerospace applications, yet their finite service life results in substantial annual waste accumulation, necessitating effective recycling solutions [44]. In response, Zhu et al. [45] developed a 3D-printed polyamide composite reinforced with recycled carbon fiber (rCF). As depicted in Figure 4a, their methodology encompasses the complete recycling chain from fiber recovery to final product fabrication. This work combined rCF, POSS, and a phosphorus-based flame retardant, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), to prepare a flame-retardant rCF/PA composite (FR rCF/PA) via 3D printing, achieving high thermal stability and flame retardancy performance. Prior to this, 3D printing technology had already been applied in the fabrication of flame-retardant fiber-reinforced composites. For instance, Geoffroy et al. demonstrated the feasibility of 3D printing in the field of flame-retardant materials by preparing flame-retardant ethylene–vinyl acetate (EVA) filaments incorporating EG and aluminum hydroxide [46]. Similarly, Li et al. fabricated flame-retardant thermoplastic polyurethane (TPU) materials via 3D printing [47]. However, the influence of different structural orientations (longitudinal or transverse, Figure 4b) in 3D-printed CFRPs on their flame-retardant performance remains unclear. Zhu et al. conducted a detailed investigation on this aspect.

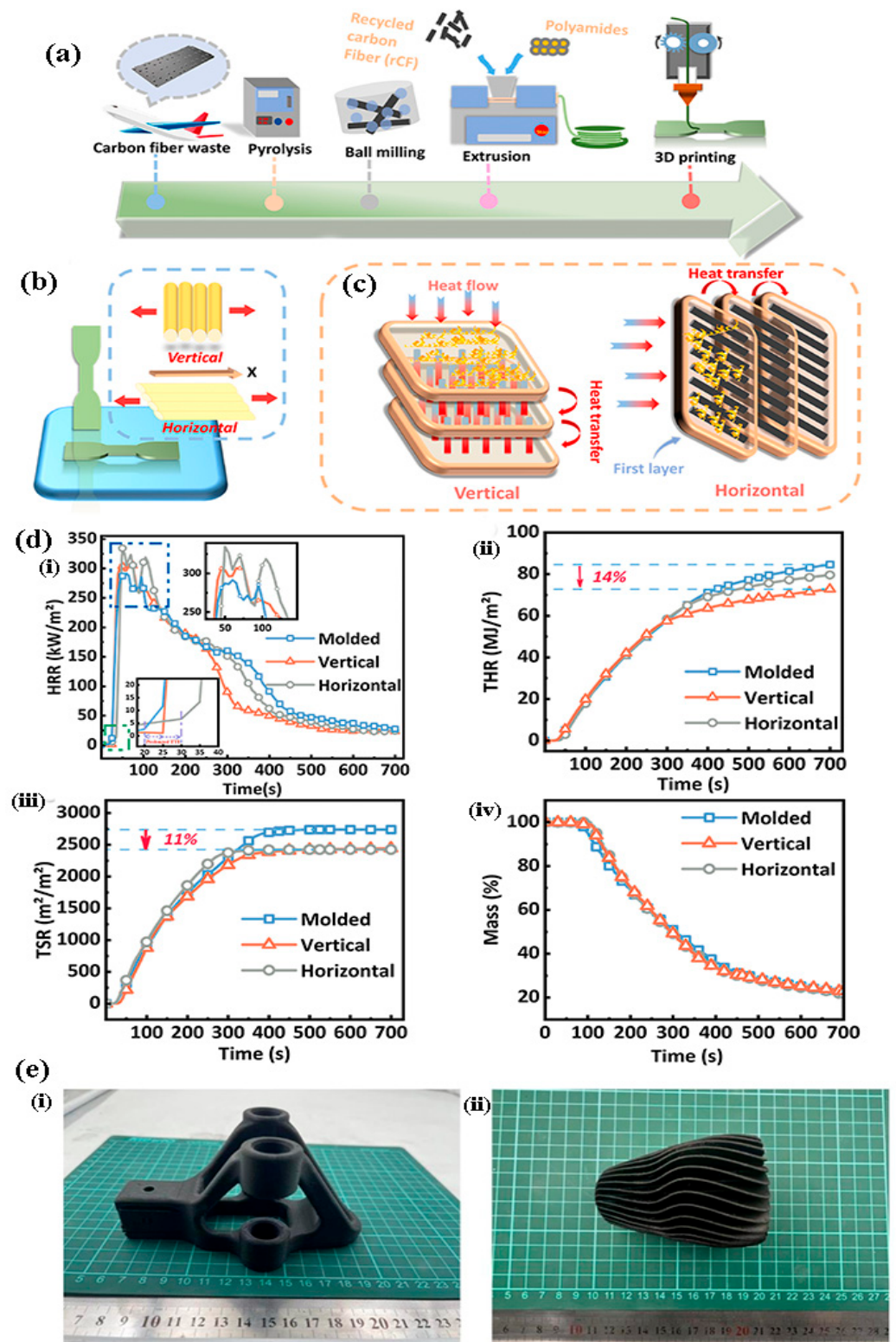


Figure 4. (a) The process involves recovering and reprocessing carbon fiber for subsequent applications. (b) Horizontal and vertical indicate specimens printed horizontally and vertically in the tensile direction. (c) Differential response of differently oriented fibers to heat within the matrix. (d) Performance characterization of composites (i) HRR profiles. (ii) Cumulative THR profiles. (iii) TSR profiles. (iv) Flexural stress of injection-molded specimens. (e) 3D printed parts of FR rCF/PA. (i,ii) Various complex structures [45].

As shown in the UL-94 and LOI results (Table S3), although both the horizontally and vertically (Figure 4c) printed samples achieved a V-0 rating, the LOI value of the printed samples was 7.6% higher than that of the rCF/PA. In the CCT, the TTI of the molded sample was 21 s, whereas those of the 3D-printed horizontal and vertical fiber samples were 31 s and 25 s, respectively. This indicates that the printed samples provide a longer escape time during the early stage of combustion. The superior performance of the horizontally printed sample may be attributed to the fiber alignment parallel to the heat flux direction, which facilitates preferential longitudinal heat transfer, resulting in more uniform heating and delayed ignition [48]. As shown in Figure 4d(i), HRR values during the first stage of burning showed little difference between molded and 3D-printed samples. However, in the second stage, the HRR of the 3D-printed samples dropped sharply, especially for the vertically oriented samples. The THR and TSR values of the 3D-printed samples decreased by 14% and 11% (Figure 4d(ii,iii)), respectively, compared to the molded samples. In terms of tensile strength, all 3D-printed samples exhibited a significant improvement compared with the molded ones. These superior properties may be attributed to the oriented alignment of rCF induced by the 3D printing process, which also contributes to anisotropic flame-retardant behavior. Moreover, Zhu et al. fabricated a variety of complex-structured flame-retardant rCF/PA composites (Figure 4e), demonstrating the versatility of 3D printing technology and its potential applicability in producing components with intricate geometries across diverse engineering fields. In summary, Zhu's work demonstrates that the application of 3D printing technology synergizes manufacturing flexibility with overall material performance. The use of rCF, combined with the synergistic application of the silicon-based flame retardant POSS and the phosphorus-based flame retardant DOPO, aligns with green development trends. Furthermore, the integration of these two halogen-free flame retardants—silicon- and phosphorus-based—represents a promising direction for future research [45]. The application of 3D printing technology in CFRPs with other matrix materials will be discussed in the following sections [49,50].

CFRP/PA6, as a member of the carbon fiber reinforced polyamide family, is a thermoplastic matrix with excellent chemical resistance and mechanical strength. It has been widely applied in the transportation, electrical and electronic, and construction industries, which impose stringent requirements on its flame retardancy [51,52]. The development of flame-retardant coatings offers an efficient strategy to enhance the fire resistance of CFRP/PA6 [53]. Kovács Z et al. [54] investigated a series of flame-retardant coatings for CFRP/PA6 composites. Initially, they applied coatings composed of EG combined with RP and EG combined with magnesium oxide (MgO) onto the PA6 matrix, reinforced with carbon fibers, resulting in two composite systems: PA6/CF/5%RP/5%EG and PA6/CF/5%MgO/5%EG. In CCT, as shown in Figure 5a, both flame-retardant coatings significantly reduced the PHRR compared with the uncoated sample (PA6/CF), with a maximum reduction of approximately 27%. This improvement is attributed to the formation of a continuous char layer on the surface during coating combustion, which acts as a protective barrier, while the high thermal inertia of EG further prolongs TTI. Data from Table S4 (No.2) indicate that the RP-containing coating exhibits superior overall flame-retardant performance compared with the MgO-based coating, likely due to the synergistic interaction between carbon fibers, EG, and RP, which stabilizes the incorporation of RP within the PA6 matrix. Originally, the compatibility between RP and thermoplastic matrices was limited. The incorporation of CF and EG not only improved the interfacial compatibility of RP but also enhanced its intrinsic stability. In the flame-retardant modification of thermoplastic matrices, fiber reinforcement itself can serve as an effective means to enhance the performance of flame retardants—a factor that is often overlooked [54].

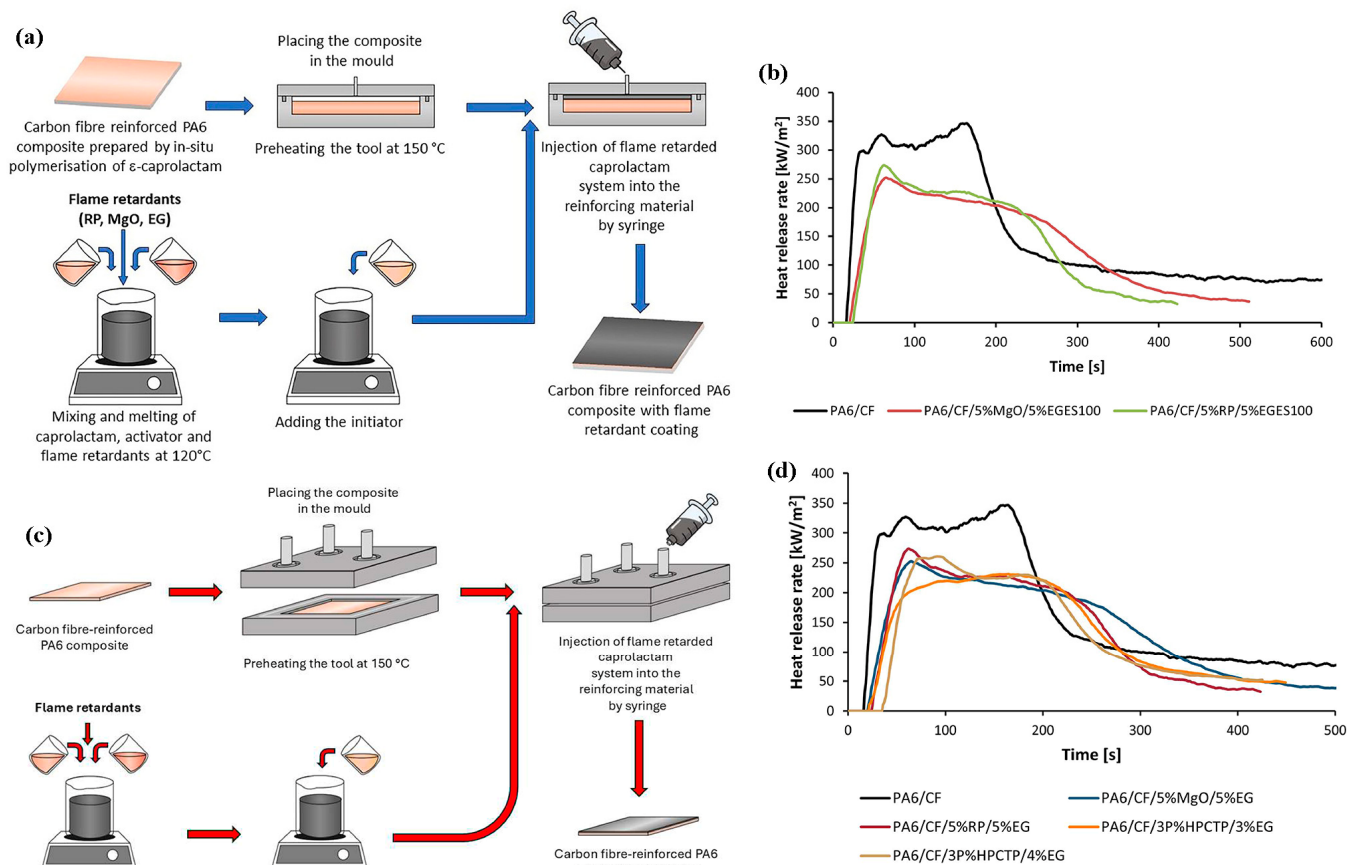


Figure 5. (a) Key steps in the preparation of carbon fiber-reinforced polyamide 6 composites (b) HRR comparisons between reference and flame-retarded polyamide 6 samples, tested via mass loss calorimetry (MLC) [54]. (c) Key steps in the preparation of carbon fiber-reinforced polyamide 6 composites. (d) HRR trends as a function of temperature during pyrolysis-combustion flow calorimetry [55].

Kovács Z et al. [55] reported flame-retardant coatings containing hexaphenoxycyclophosphazene (HPCTP) and EG for CFRP/PA6 composites. HPCTP, as a member of the cyclophosphazene family, has been previously explored by Di et al., who employed hexaphenoxycyclophosphazene (HPCP) with PA6 via melt spinning to successfully prepare flame-retardant PA6 exhibiting an after-flame time of approximately 1.5 s and no smoldering time [56]. This prior work demonstrated the feasibility of using cyclophosphazene compounds to enhance the flame retardancy of PA6. Building on this, Kovács Z et al. developed a composite flame-retardant coating combining HPCTP and EG to improve the flame retardancy of CFRP/PA6 (PA6/CF/HPCTP/EG). Moreover, they innovatively employed an inner-membrane coating fabrication process, as shown in Figure 5a–c.

As shown in Table S4 (No.2), the flame-retardant coating exhibited excellent performance, with TTI extended by up to 19 s and THR reduced by approximately 37%. The advantage of HPCTP as a flame retardant lies in its solubility in ϵ -caprolactam, allowing it to be incorporated without affecting polymerization. However, this work did not clarify whether the inner-membrane coating process contributes to the overall improvement in flame retardancy, which represents a potential direction for further research [55].

The challenge in flame-retardant modification of PA matrices primarily lies in the poor interfacial compatibility between the flame retardant and PA, which complicates both coating techniques and direct physical blending approaches. From the perspective of synergistic modification via processing, advantages can be achieved by simultaneously

improving interfacial compatibility and mechanical performance—for example, through 3D printing, which presents significant potential. For the modification of the flame retardant itself, multi-component systems (e.g., POSS–DOPO synergy) or structural optimization (e.g., HPCTP) can enhance compatibility with thermoplastic matrices. Ideally, the combination of these two strategies would maximize performance, though achieving such synergy remains highly challenging.

3.3. Other Resin-Based CFRP Flame-Retardant Composites

As established in prior research, 3D-printed thermoplastic composites demonstrate significant potential for advanced engineering applications. Similarly, Yang et al. [57] applied 3D orthogonal weaving technology to CFRP/PEEK composites (Figure 6a) shows the material preparation process), endowing the material with excellent bending properties and flame retardancy. In contrast to conventional 2D lamination techniques that are prone to interlayer delamination [58], Yang first employed CF/PEEK as the warp and weft yarns, followed by the introduction of Kevlar yarns woven in a vertical Z-pattern. This architecture effectively reinforced the overall structural integrity of the composite. In CCT, the 3D CF/PEEK composite could not be ignited directly by an alcohol lamp (Figure 6b), and its decomposition temperature reached as high as 548 °C. During heating, the material darkened and showed a slight mass loss (Figure 6c), which is likely due to the inherent high thermal stability and self-extinguishing nature of PEEK [57]. As shown in Figure 6d, in the bending performance test, the 3D CF/PEEK composite retained good mechanical properties even after 360 s of exposure to heat, with the inherent high thermal stability of PEEK and the self-extinguishing behavior of Kevlar yarn [59,60].

Among these materials, CFRP/PEEK systems have gained particular prominence in industrial and aerospace sectors, primarily due to the outstanding thermomechanical characteristics inherent to the semi-crystalline PEEK polymer matrix. However, most improvements to this type of composite have focused on enhancing its mechanical properties. For example, Dai et al. fabricated a CFRP/PEEK composite with a carbon fiber content of up to 66 wt%, achieving tensile and flexural strengths exceeding 1000 MPa at room temperature [61]. In contrast, advancements in the flame-retardant performance of these materials remain limited, making this an important direction for future development of CFRP/PEEK composites.

Polycarbonate (PC) has emerged as a prominently advancing engineering thermoplastic in contemporary materials science [42], but studies on its flame-retardant properties remain limited. Shang et al. [62] reported a composite system consisting of polyphenylene sulfide (PPS), short carbon fibers (SCF), and polycarbonate (PPS/SCF/PC) (Figure 6g). They first investigated the influence of SCF on the flame retardancy of PC with different thicknesses. Experimental results (Figure 6f) showed that in thick-walled samples, the reinforcement effect of SCF alone significantly improved the flame-retardant performance of PC. When the SCF content reached 10 wt%, the LOI value increased to 31.4%, meeting the UL-94 V-0 standard. However, at a reduced thickness of 1.6 mm, the effectiveness of SCF was notably diminished, likely due to the accelerated dripping behavior in thinner samples, which disrupted the char-forming effect of SCF (Table S5).

To address this limitation, Shang introduced PPS—known for its thermal stability and inherent charring capability—into the SCF/PC system. As shown in the corresponding Figure 6e and Table S6, the incorporation of PPS effectively enhanced the flame-retardant performance, with the 20PPS/6SCF/PC (3.2 mm) sample exhibiting the best results. The synergistic effect between the inherently carbonizable PPS and the high thermal conductivity of SCF enabled rapid self-extinguishing behavior while effectively suppressing flame propagation.

Moreover, PPS addition in the SCF/PC system reduced the heat release rate and improved the residual mass, as evidenced by cone calorimetry data, although the TSP increased slightly—remaining lower than that of pure PC. This was attributed to the radical-quenching mechanism of PPS during combustion. Overall, the incorporation of PPS complemented the reinforcing effect of SCF, jointly enhancing the comprehensive flame retardancy of PC. The co-action of PPS and SCF formed a stable and compact char layer, which served as an effective thermal barrier and oxygen shield. Furthermore, the combination of PPS and SCF created an “alloy-like” reinforcement effect, providing a promising strategy for improving the performance of fiber-reinforced polymer composites. This represents an ideal synergy between reinforcing fibers and flame retardants, in contrast to conventional approaches where one primarily enhances the other. Here, the two components complement each other, akin to an alloy, leveraging each other’s strengths. Expanding this approach could offer greater improvements in flame-retardant performance while potentially enhancing mechanical properties as well [62].

Yu et al. [63] designed a method to enhance the flame retardancy of carbon fiber-reinforced vinyl ester (CF/VER) composites by introducing nanofiber interlayers. Using electrospinning technology, a nanofibrous membrane (FPM) composed of the flame retardant pentaerythritol phosphate (PEPA) and the inherently flame-retardant engineering plastic polyethersulfone (PES), which possesses a high char yield, was fabricated (Figure 7a). The FPM was alternately layered with CF/VER to prepare the composite (CF/VER@FPM). When the thickness of FPM in CF/VER@FPM reached 50 μm , the composite exhibited the best flame-retardant performance, with the LOI value increasing to 33.5%, approximately 30% higher than that of the unmodified CF/VER. In addition, the 50 μm FPM effectively reduced the combustion intensity, with the THR decreasing by approximately 26.4% (Figure 7b(i)), and showed excellent smoke suppression, lowering the TSP value by about 30.4%. The average effective heat of combustion (av-EHC) was only 40% of that of pure CF/VER. The outstanding flame-retardant performance originates from the synergistic effects of PEPA and PES. PES, with its inherent flame retardancy, releases SO_2 during combustion, which not only dilutes the flammable gases but also scavenges free radicals [64]. Meanwhile, in the gas phase, PEPA generates phosphorus-containing radicals that further inhibit flame propagation. In the condensed phase, the degradation products of PEPA and PES, including phosphorus- and sulfur-containing species, catalyze and promote the formation of a stable char layer, thereby enhancing flame retardancy. Overall, the introduction of the electrospun nanofibrous FPM interlayer not only imparts remarkable flame-retardant performance but also improves the structural integrity of the laminate by reducing the likelihood of interlayer fracture between the carbon fiber plies. Even so, nano-intercalation has not consistently improved the mechanical performance of the material system. While toughness is somewhat enhanced, other mechanical properties show no clear trend, exhibiting considerable uncertainty. The advantage of nano-intercalation lies in separating the fiber-reinforced layer from the flame-retardant layer, preventing mutual interference. However, issues such as interfacial compatibility between the interlayer and fibers, as well as the effect of interlayer thickness on performance, remain critical considerations. Although the authors employed electrospinning to mitigate these effects, true synergistic enhancement was not fundamentally achieved [63].

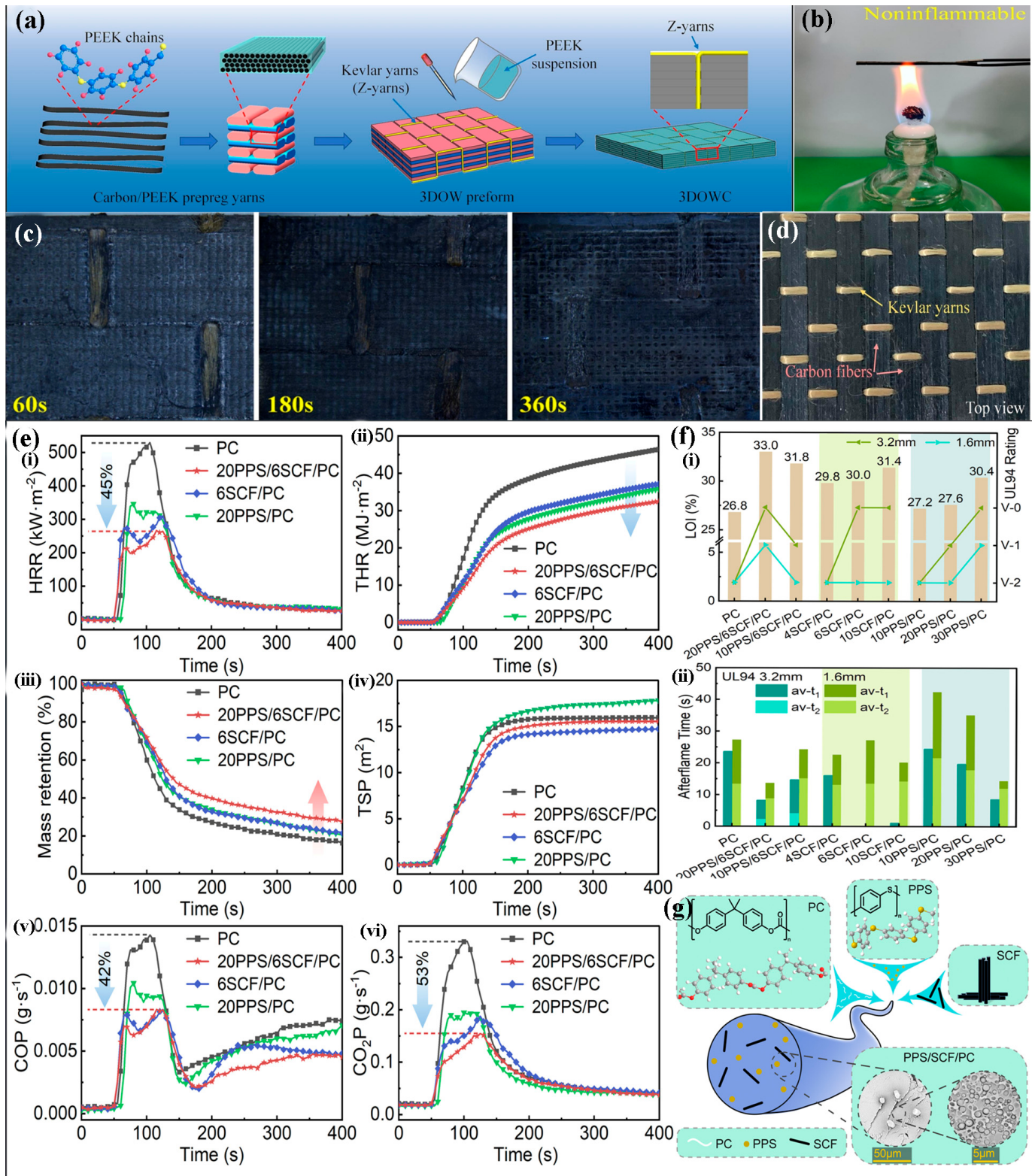


Figure 6. (a) Preparation process of 3D CF/PEEK composites; flame-retardant performance. (b) Burning test. (c) As-prepared composite with the surface color changes. (d) 3D CF/PEEK preform [40]. (e) Cone calorimeter curves obtained for the PC composites studied: (i) HRR curves, (ii) THR curves, (iii) mass retention rate curves, (iv) TSP curve, (v) COP curves, (vi) CO_2P curves. (f) Results of LOI measurement and vertical burning test obtained for the PC composites studied: (i) LOI value and UL94 rating; (ii) Afterflame time. (g) Preparation schematic and component dispersion characteristic of PPS/SCF/PC composites [62].

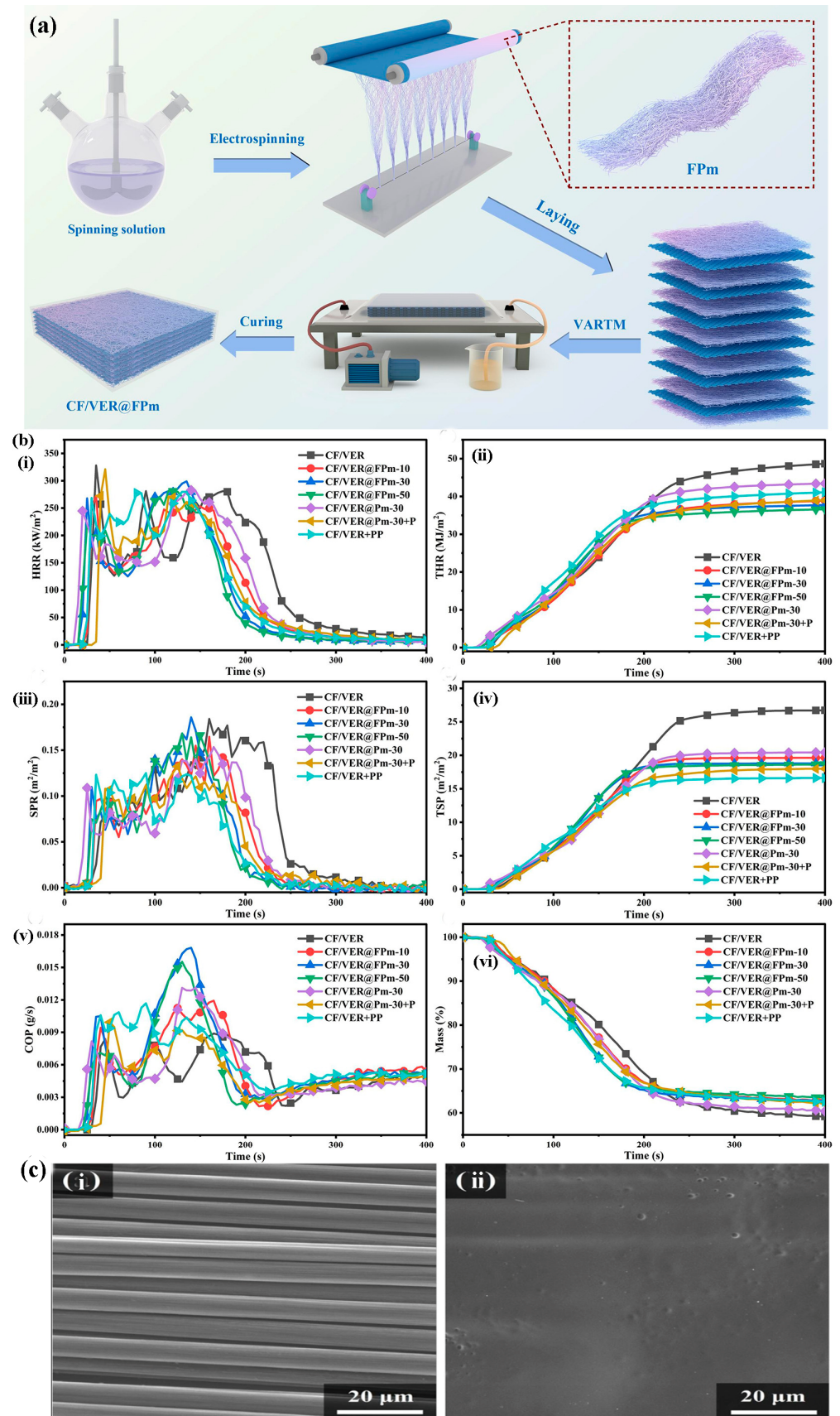


Figure 7. (a) Schematic of the preparation of FPm and composite (Purple represents FPm, and blue represents the carbon fiber fabric). (b) Cone calorimetry results of composites: (i) HRR curve, (ii) THR curve, (iii) SPR curve, (iv) TSP curve, (v) COP curve, and (vi) mass loss curve. (c) (i) SEM of CF/VER after cone calorimetry test, (ii) SEM of CF/VER@FPm-10 after cone calorimetry test [63].

CFRPs, as the most common resin-based composites, have seen a wide variety of flame retardants and thermoplastic materials used to enhance their performance. It is clear that there are significant differences among different matrix materials, and variations in thickness and material content can lead to substantial differences in both fire resistance and structural integrity characteristics.

Currently, modifications of EP and PA matrices have been comprehensively developed in both aspects. PEEK, when reinforced with carbon fiber, exhibits excellent mechanical properties, and the use of 3D printing technology further diversifies its fabrication methods. However, research investigating the fire-resistant characteristics of CF/PEEK composites remains limited in the current literature.

Research on other matrix materials is also advancing, especially with the application of electrospinning technology. The selection of textile architectures (e.g., plain versus twill weave configurations) critically influences material properties, thereby advancing the technological progress of CFRP systems.

4. Flame-Retardant Composites of Glass Fiber Reinforced Polymers (GFRPs)

GFRP composites represent an important class of structural materials consisting of glass fiber reinforcements embedded in polymer matrix systems [65]. They exhibit high tensile strength while maintaining relatively low density [66–68]. GFRPs demonstrate excellent corrosion resistance, electrical insulation, and thermal insulation. However, the high-temperature resistance and flame retardancy of such materials remain relatively poor. This limitation, similar to that observed in carbon fiber-reinforced composites, primarily arises from the inherently low flame resistance of the resin matrix. In addition, the glass fiber content significantly influences the overall flame-retardant performance of the composites. The incorporation of glass fibers may also alter the thermal stability of the system and induce a “wick effect,” which further accelerates the combustion process. Therefore, the introduction of flame retardants or the development of hybrid composites with other functional materials has become an effective strategy to enhance the flame retardancy of glass fiber-reinforced composites.

4.1. Epoxy Resin-Based (EP) GFRP Flame-Retardant Composites

Xiao et al. [69] developed a flame-retardant GFRP composite by incorporating DOPO-GL-DCDA as a flame retardant and combining it with PA-modified boron nitride (BN) and aluminum oxide (Al_2O_3) (Figure 8a) [69]. The glass fiber-reinforced epoxy (GFREP) composite demonstrated remarkable improvements in both fire resistance and heat transfer capabilities.

The flame resistance evaluation through LOI and UL-94 testing revealed substantial improvements for the hybrid composites. The EP/40% (Al_2O_3 + BN)/GF system achieved an LOI of 55%, while its modified counterpart EP/40% (Al_2O_3 + BN)/mGF reached 56%, corresponding to 139% and 143% enhancements, respectively, over the unmodified epoxy matrix (Figure 8b). However, due to the “wick effect” [70], the EP/40% (Al_2O_3 + BN)/GF composite could only achieve a V-2 rating in the UL-94 test. In contrast, the use of modified glass fibers (mGF), which improved interfacial compatibility with the epoxy matrix, enabled the composite to reach the V-0 level (Figure 8b). In the CCT analysis, the EP/40% (Al_2O_3 + BN)/mGF system exhibited a significant reduction in PHRR, THR, and TSP values (Figure 8c–g and Table S7 No.1). The synergistic presence of mGF and ceramic fillers (Al_2O_3 and BN) effectively enhanced the condensed-phase flame retardancy of the composite, as evidenced by the decreased AEHC. Meanwhile, the flame retardant primarily acted in the gas phase. Within the DOPO-GL-DCDA structure, thermolysis of the DOPO moiety

released phosphorus-containing radicals, which combined with active radicals ($H\cdot$ and $OH\cdot$) to quench the combustion process and interrupt the gas-phase chain reactions. The complementary flame-retardant mechanisms in both the gas and condensed phases endowed the composite with outstanding overall flame retardancy. Xiao's work is notable for the synergistic enhancement of flame retardancy and thermal conductivity. After treating EP/GF with DOPO-GL-DCDA for flame retardancy, BN and Al_2O_3 were incorporated to improve thermal conductivity and further reinforce flame resistance. In fiber-reinforced materials, increased thermal conductivity often compromises flame-retardant performance; however, the addition of Al_2O_3 fills voids and defects in EP/GF, substantially mitigating the conflict between these two properties. This represents an effective and strategic approach [69].

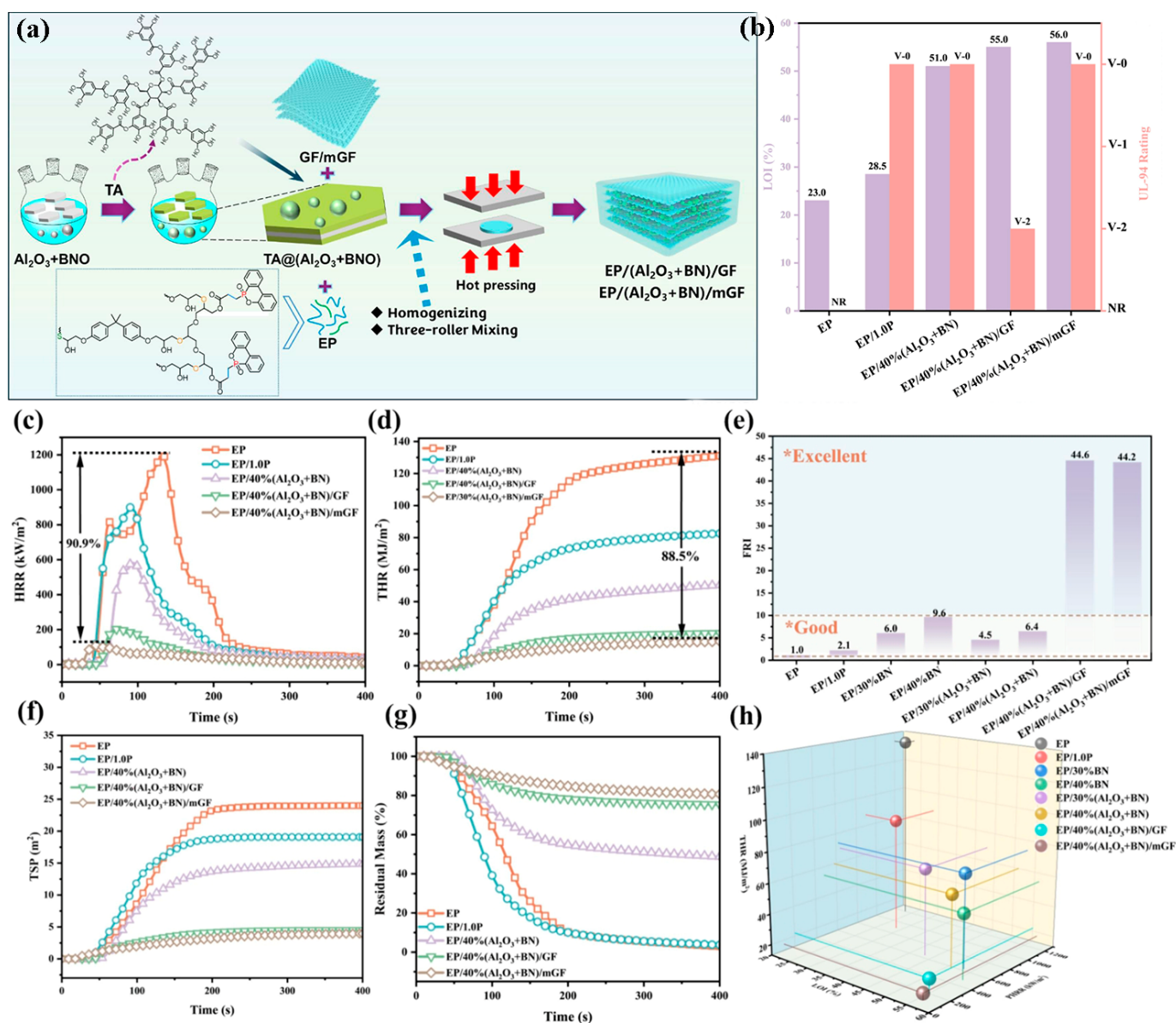


Figure 8. (a) Preparation process of GFREP. (b) LOI and UL-94 ratings. (c) HRR curves. (d) THR curves. (e) FRI. (f) TSP curves. (g) Residual mass. (h) LOI, PHRR and THR comparison of epoxy composites [69].

Zhi et al. [71] reported a glass fiber–reinforced vanillin-based epoxy resin composite (VH/GF) as an intrinsically flame-retardant EP system. This epoxy was synthesized from a bio-based monomer derived from vanillin, offering both environmental sustainability and excellent flame-retardant performance. For comparison, Zhi et al. also prepared a conventional glass fiber–reinforced bisphenol A diglycidyl ether epoxy (DGEBA) composite (DG/GF). The VH/GF composite self-extinguished just 1 s after ignition, and for all tested formulations, the LOI values reached 90% or higher, indicating excellent flame resistance (Table S8 No.2). As shown in Figure 9a–d, the formulation GF6VH4 performed particularly well. The vanillin-modified composite demonstrated superior fire safety performance relative to the GF6DG4 control, with dramatic reductions observed across all critical flammability metrics: an 80.9% decrease in peak heat release rate, 79.4% lower total heat release, 92.0% suppression of peak smoke production, and 94.8% reduction in total smoke production. However, the earlier decomposition of the alkyl segments in vanillin led to a shortened TTI value. In the smoke density test, GF6VH4 also exhibited outstanding performance, with a maximum smoke density reduction of 86.23%. This is attributed to the strong smoke-suppressing ability of the vanillin-based resin, which promotes char formation on the surface of the glass fibers. In summary, based on both the α_v -EHC and FGI values (Table S7 No.2), the VH/GF material exhibited excellent flame-retardant performance. Zhi's work represents an exploration of intrinsic flame retardancy in fiber-reinforced composites and provides a viable strategy for the development of sustainable, green flame-retardant materials. For modifications of the EP matrix, VH/GF outperforms DG/GF across all aspects, achieving maximal synergy between mechanical performance and thermal stability. This highlights the advantages of intrinsically flame-retardant matrices combined with fiber-reinforced composites, particularly when using bio-based materials—a strategy that warrants greater attention in future research [71].

Yuksel Yilmaz et al. [72] incorporated MXene nanosheets and functionalized MXene nanosheets into glass fiber-reinforced EG composites to improve both flame retardancy and mechanical performance [73]. As shown in Figure 9e, the burning rate of the MXene-reinforced glass fiber composites (M-C) and functionalized MXene composites (FM-C) decreased with increasing MXene content. The flame propagation rate decreased with increasing content of MXene nanosheets and functionalized MXene nanosheets, with reductions of 22.17% and 25.5% observed for 0.5M-C and 0.5FM-C, respectively. The layered structure of MXene nanosheets serves as a barrier, effectively reducing smoke generation during combustion, and their uniform dispersion further enhances flame-retardant performance [74]. During combustion, the vaporization and expansion of the resin can cause separation between the fibers and the matrix [75] (Figure 9f), which may compromise the safety of the material. However, the bottleneck of this strategy lies in the interfacial compatibility between nanomaterials and the matrix. Study [75] indicates that during combustion, resin vaporization and expansion can lead to fiber–matrix separation, severely compromising material integrity and posing potential risks for long-term safety. This reflects the inherent conflict between flame-retardant and mechanical performance under extreme conditions. Consequently, Ayten's work is significant not only for demonstrating the flame-retardant potential of MXene but also for highlighting the common interfacial challenges in current nanocomposites. It points to future research directions: whether surface functionalization or the construction of three-dimensional network structures can strengthen interfaces to achieve synergistic enhancement of flame retardancy and mechanical performance [72,76].

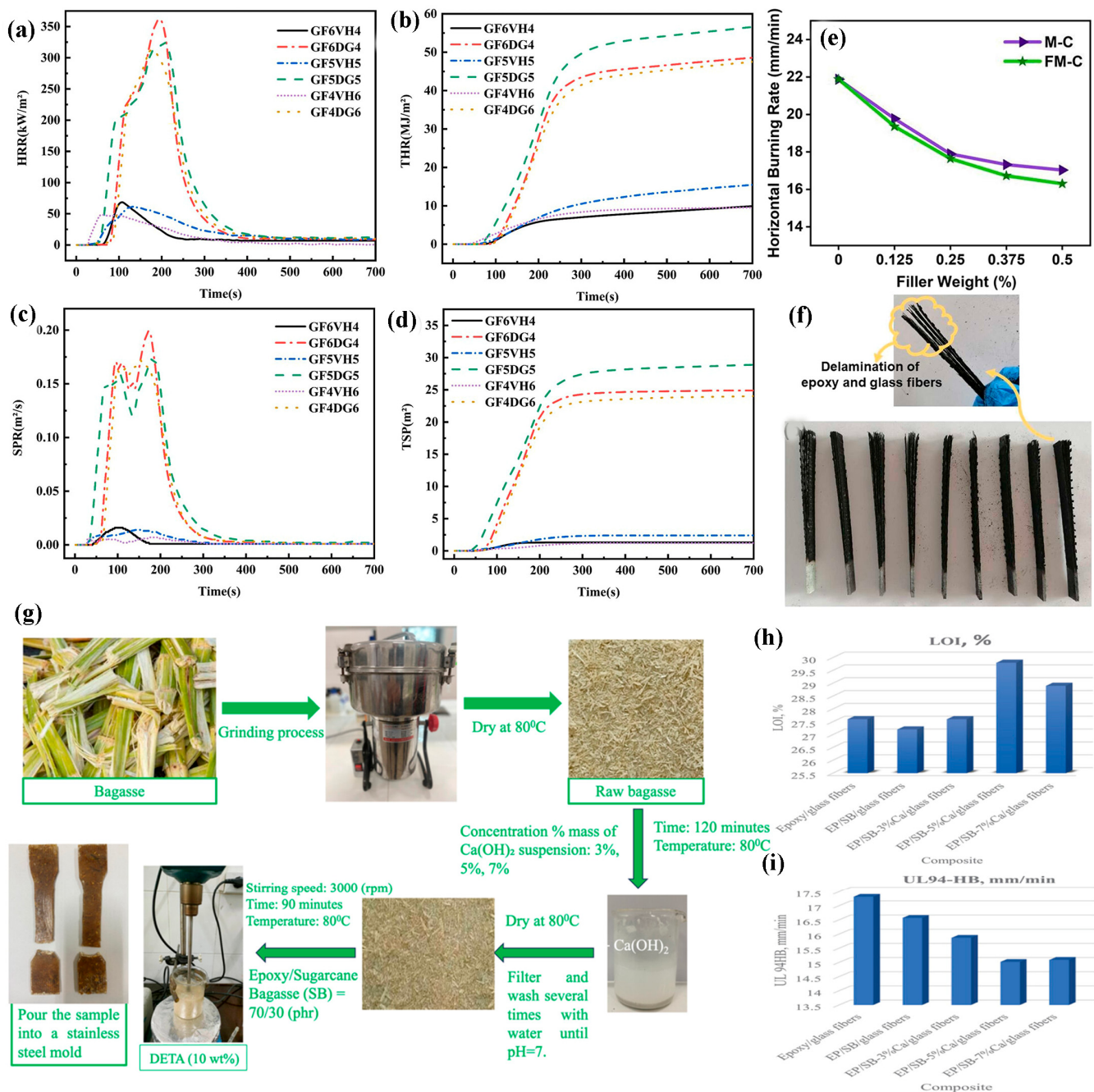


Figure 9. Combustion performance of composite systems: (a) HRR profiles; (b) THR evolution; (c) SPR trends; (d) TSP characteristics [71]; (e) HRR of M and FM reinforced composites; (f) images of composite specimens after the test [72]. (g) Manufacturing process of epoxy resin-based composite materials reinforced with sugarcane bagasse; flame retardant properties of epoxy composite materials reinforced with sugarcane bagasse. (h) LOI; (i) UL-94 [77].

Multifiber-reinforced composites are currently gaining attention due to their prospective applications. For instance, Nguyen et al. [77] reported EP composite reinforced with both sugarcane bagasse fibers and glass fibers (Figure 9e), which exemplifies the synergy in multi-fiber materials. Previous studies have primarily focused on natural fiber-reinforced composites, such as Fong et al.'s work on sugarcane bagasse fiber and nanosilica-reinforced epoxy [78], and Cerqueira et al.'s investigation of sugarcane bagasse fiber-reinforced polypropylene [79]. Reports on the synergistic reinforcement of natural fibers with glass fibers remain limited. The innovation in Nguyen's study lies in treating sugarcane bagasse fibers with limewater instead of the more commonly used NaOH, which not only offers a

more environmentally friendly approach but also significantly enhances flame-retardant performance. EP composites reinforced with limewater-treated sugarcane bagasse and glass fibers (EP/SB-7%Ca/glass fibers) demonstrated excellent performance in surface properties, mechanical strength, and flame retardancy. As shown in Figure 9h,i the combination of sugarcane bagasse fiber reinforcement, limewater treatment, and glass fiber addition progressively improved the flame-retardant performance of the EP matrix, with EP/SB-7%Ca/glass fibers achieving the optimal balance across all metrics. The close integration between sugarcane bagasse fibers and glass fibers forms a dense structure, while limewater treatment increases the carbon content, resulting in a composite with superior flame-retardant and mechanical properties. This work not only enhances the performance of glass fiber-reinforced composites through the inclusion of agricultural waste but also aligns with sustainable development principles, providing a promising strategy for future modification of fiber-reinforced materials. The significance of this work lies in its successful conversion of agricultural waste into high-value functional components, transforming waste into resources. Without compromising performance, it substantially enhances the material's sustainability index, providing an inspiring approach for the development of high-performance, eco-friendly composites [77].

4.2. Other Resin-Based GFRP Flame-Retardant Composites

Graphene nanosheets, as a classical type of graphene-based nanomaterials, have been widely applied across various fields over the past two decades. Combining graphene nanosheets with glass fibers to form glass fiber/graphene nanosheet-reinforced nanocomposites represents an effective strategy to compensate for the poor thermal properties of glass fibers. Papageorgiou et al. [80] utilized this approach to fabricate graphene/glass fiber-hybrid reinforced PP composites. In CCT (Figure 10a and Table S9 No.1), glass fiber-reinforced polypropylene (PP-GF) exhibited no significant improvement in flammability compared with neat PP. However, with the incorporation of graphene nanosheets (GNP), a slight reduction in flammability was observed. Among the samples, only PP-GF16-GNP20 demonstrated self-extinguishing behavior, with the highest TTI of 88 s (Table S10 No.1). The contribution of GNP arises from its ability to accumulate and form an active char layer during combustion, which serves as a protective barrier to slow down burning. A GNP content of 10 wt% exhibited the optimal flame-retardant effect, whereas higher contents may lead to excessive hardness in the protective layer, introducing defects that compromise the barrier performance. This simple physical blending method exhibits low flame-retardant efficiency and fails to fundamentally address the “wicking effect.” Apart from relatively straightforward manufacturability, it offers limited advantages [80].

Vinyl ester resin (VER), which combines the favorable properties of epoxy resin and unsaturated polyester resin, serves as an excellent matrix for fiber-reinforced composites. However, due to its high carbon-hydrogen content, VER is inherently flammable. To develop flame-retardant glass fiber-reinforced vinyl ester resin (VER) composites, Zhang et al. [81] strategically incorporated a DOPO-based vinylimidazolium salt (VIDOP) as a multifunctional reactive flame-retardant crosslinker into the VER network via chemical copolymerization. The design's ingenuity lies in VIDOP's role not as a physical additive, but as a structural participant in VER crosslinking: its vinyl group copolymerizes with the VER backbone, while the DOPO-derived moiety anchors onto the resin framework via ionic bonding (Figure 10b). This molecular-level engineering imparts exceptional flame retardancy to the VIDOP25/VER/GF composite. As shown in Figure 10d and Table S9 No.2, the incorporation of VIDOP significantly improved the overall flame-retardant performance, reducing THR by 21.6% and TSP by 10.9%. The primary action of VIDOP occurs in the gas phase. However, the presence of GF disrupts the formation of a continuous, compact char

layer in the VER matrix, thereby compromising condensed-phase flame retardancy. Notably, Zhang et al. demonstrated that incorporating flame-retardant structures as crosslinking agents into the polymer network not only achieves exceptional fire resistance via the VIDOP mechanism but also improves the composite's storage modulus. This molecular-level integration of flame-retardant functionality directly into the polymer backbone represents a promising research direction [81].

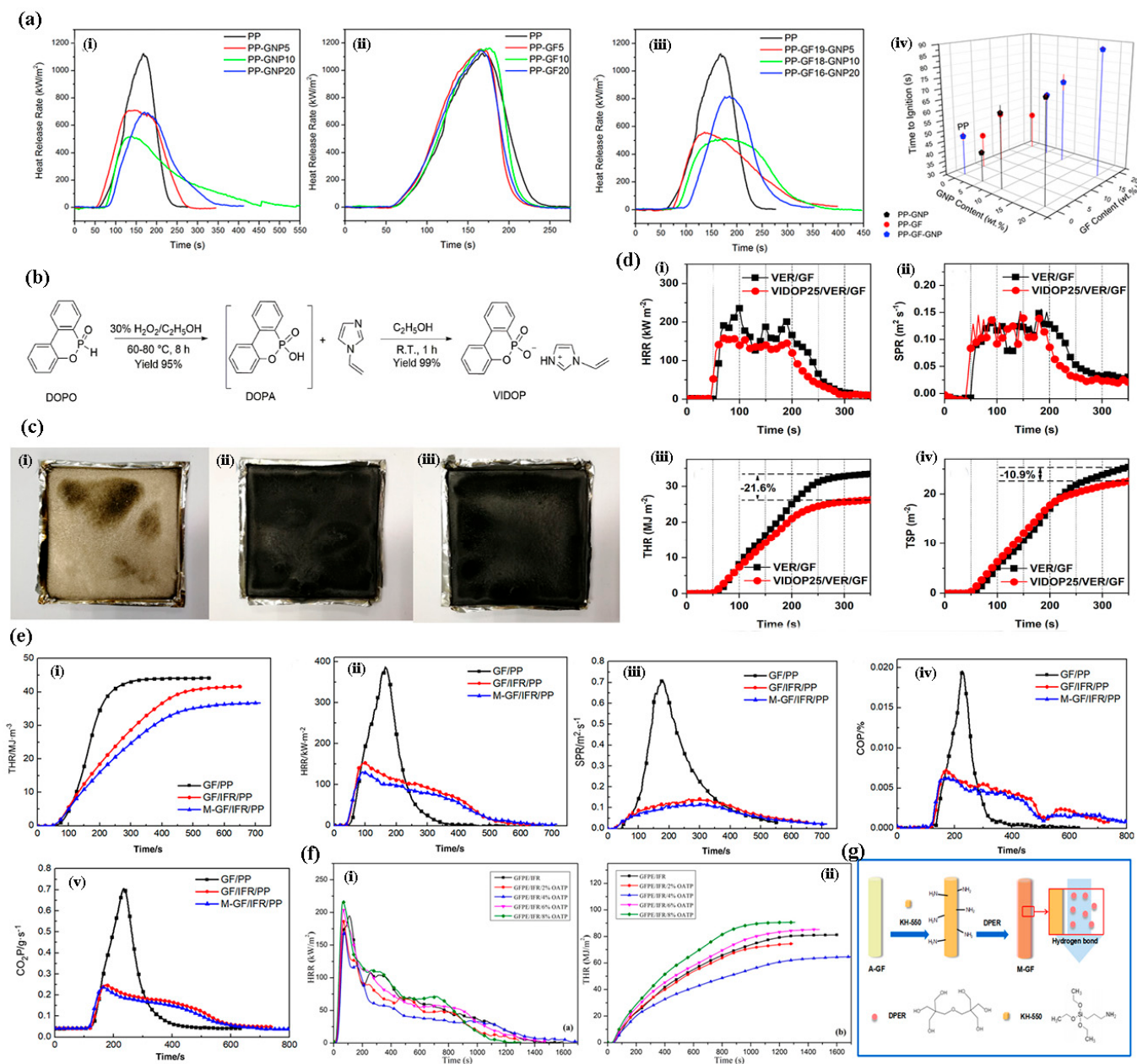


Figure 10. (a) (i–iii) Heat release rate curves of PP and nanocomposites filled with GNP, GF and GF-GNP; (iv) time to ignition for all samples under study [80]. (b) Synthesis route of VIDOP. (c) Digital photographs of residues after cone calorimeter testing: (i) GF/PP; (ii) GF/IFR/PP; (iii) M-GF/IFR/PP [81]. (d) presents the cone calorimeter results comparing VER/GF and VIDOP25/VER/GF composites, showing their respective heat release rate (HRR, i), total heat release (THR, ii), smoke production rate (SPR, iii), and total smoke production (TSP, iv) profiles [82]. (e) Cone calorimeter test results of PP composites: (i) THR, (ii) HRR, (iii) SPR, (iv) CO product curves, (v) CO₂ product curves. (f) (i) HRR and (ii) THR curves of GFPE/IFR/OATP composites (g) Preparation of the DPER modified GFs [83].

However, the incorporation of glass fibers significantly reduced the overall flame-retardant performance of PP, primarily due to the “wick effect” induced by GF. To address this issue, Xue et al. [82] combined bulk flame-retardant and interfacial flame-retardant strategies [82]. They employed a silane coupling agent to anchor dipentaerythritol (DPER) onto GF, reinforcing the PP matrix, while simultaneously IFR to obtain M-GF/IFR/PP. The advantage of this approach lies in the synergistic action of DPER as a char-forming agent with IFR, which facilitates the formation of a dense carbon layer on the material surface (Figure 10c), resulting in excellent flame-retardant performance. As shown in Figure 10e and Table S9 No.3, M-GF/IFR/PP exhibited superior performance across various combustion tests. The LOI reached 29.5%, achieving UL-94 V-0 classification, while the PHRR and THR values decreased significantly by 66.2% and 16.8%, respectively, compared with GF/PP. The incorporation of IFR slightly reduced the TTI due to its early-stage decomposition, but this had minimal impact on the overall flame-retardant performance. In summary, the introduction of DPER not only increased the surface roughness of GF, mitigating the wick effect, but also enhanced the formation of the IFR-derived char layer, demonstrating the effectiveness of combining bulk and interfacial flame-retardant strategies. This approach successfully demonstrates the feasibility of converting the detrimental “wick effect” into a beneficial “char-forming platform” through interface engineering, representing a sophisticated strategy to mitigate the inherent limitations of GF [82].

Chen et al. [83] similarly employed IFR to enhance the flame retardancy of GFPE. In their previous work, Chen synthesized a novel IFR using ammonium polyphosphate (APP) as the acid source and poly(1,3-diaminopropane-1,3,5-triazine-cored pentaerythritol phosphate) (PDTBP) as the carbon source, exhibiting good thermal stability and char-forming ability (Figure 10g). In this study, Cheng et al. further introduced organically modified attapulgite (OATP) as a synergistic additive with IFR to improve the flame retardancy of GFPE. The effect of OATP content on flame retardancy displayed a non-linear trend, with GFPE/IFR/4%OATP showing optimal performance (Figure 10f and Table S9 No. 4), reducing PHRR and THR by 12.1% and 20.1%, respectively, compared with GFPE/IFR. However, the OATP/IFR system could not fully mitigate the wick effect induced by GF. Although the LOI increased, none of the samples achieved a UL-94 classification. During combustion, OATP can form metal oxides that enhance the stability of the char layer. Excessive OATP, however, reduces the proportion of IFR and interferes with its carbonization process, thereby diminishing the overall flame-retardant performance. While Chen’s work successfully demonstrates the feasibility of constructing a synergistic flame-retardant system by incorporating nano-synergists to simultaneously enhance mechanical and flame-retardant properties, the OATP/IFR synergistic system fails to address the fundamental combustion challenges posed by the “wick effect.” [83].

GFRPs have found extensive applications in aerospace, telecommunications, and other industries owing to their favorable combination of lightweight properties, cost-effectiveness, ease of processing, and recyclability. However, current modifications of GFRP materials are often limited in scope, typically focusing on a single performance aspect rather than offering comprehensive enhancements. Moreover, current research on GFRPs demonstrates a pronounced orientation toward communication technology applications, resulting in a disproportionate focus on electrical conductivity. As a result, less attention has been paid to flame retardancy and mechanical safety, and fire performance tests are often insufficient or incomplete.

Future research should prioritize multifunctional modification approaches for GFRPs and investigate innovative fabrication methods to address the increasing requirements for high-performance, flame-retardant composites.

5. Overview and Prospects of Flame-Retardant Strategies for Fiber-Reinforced Materials

Fiber reinforcement is a widely adopted approach to enhance the performance of resin-based materials, primarily improving their mechanical properties and physicochemical characteristics. Different types of fiber-reinforced materials exhibit distinct advantages and have been extensively applied in the construction, aerospace, automotive, and battery industries.

In this review, we mainly discussed two of the most common synthetic fiber-reinforced materials: CFRP and GFRC. As described above, the inherent flammability of the resin matrix, combined with the wick effect induced by fiber incorporation, results in poor flame-retardant performance for composites reinforced solely with fibers. This limitation is particularly pronounced in glass fiber-reinforced materials [84]. Consequently, researchers have been actively exploring strategies to enhance the flame retardancy of fiber-reinforced composites.

5.1. Additive Flame-Retardant Approach

The additive flame-retardant approach is the most commonly employed strategy for improving the flame retardancy of fiber-reinforced composites. In early studies, researchers primarily relied on physical blending to enhance flame-retardant performance, directly incorporating halogen-, nitrogen-, or phosphorus-based or intumescent flame retardants.

Halogen-based flame retardants, although widely used commercially due to their effective flame-retardant performance, release toxic halogenated gases and carcinogenic compounds during combustion, leading to restrictions on their use in most countries [85].

Subsequently, phosphorus-based flame retardants have gained significant attention as environmentally friendly alternatives. Typical phosphorus-based flame retardants include APP, RP, HPCTP, and DOPO derivatives, as discussed above. Their advantages lie in their dual action in both the gas and condensed phases: in the gas phase, thermal decomposition generates phosphorus-containing radicals ($\text{PO}\cdot$, $\text{HPO}\cdot$) that quench highly reactive radicals ($\text{H}\cdot$, $\text{OH}\cdot$) and interrupt the combustion chain reaction; in the condensed phase, phosphorus-based flame retardants promote char formation, producing a dense carbon layer that protects the matrix. However, these flame retardants often suffer from poor compatibility with polymer matrices and limited thermal stability.

Nitrogen-based flame retardants are another class of low-toxicity, environmentally friendly additives. Nevertheless, their action is largely limited to the gas phase, resulting in relatively low flame-retardant efficiency, which is why they are commonly used in combination with other flame retardants.

Consequently, in recent years, efforts have focused on modifying and improving additive flame-retardant systems beyond simple physical blending.

Incorporating nanofillers represents an effective strategy for improving the flame retardancy of fiber-reinforced composites. Common nanomaterials include graphene nanosheets (GNP), MXene nanosheets, and POSS, as previously summarized. POSS, with its three-dimensional structure, can satisfy nearly all performance requirements for modified polymers. As a flame retardant, POSS offers the advantage of directly modifying the resin matrix, enhancing the decomposition temperature of the matrix, and promoting the formation of flame-resistant species and a protective char layer [86]. For example, Choi et al. [87] and Liu et al. [88] utilized POSS to modify PP and EP, respectively, resulting in nanocomposites with excellent flame-retardant performance. Furthermore, POSS can be used to enhance the efficiency of phosphorus-based flame retardants and IFR.

IFR, a halogen-free flame retardant primarily composed of phosphorus and nitrogen, is also an effective strategy to improve the low efficiency of nitrogen-based flame retardants. As mentioned above, Xue et al. [82] and Chen et al. [83] synthesized novel IFRs with tailored carbon sources to modify fiber-reinforced materials. The introduction of POSS can further enhance the effect of IFR, as recently confirmed by Marie Combeau et al. [89].

Coating methods provide an alternative to physical blending by applying flame-retardant additives as surface layers on fiber-reinforced materials, addressing issues of poor stability and interfacial adhesion. Kovács Z et al. demonstrated that coating RP-based flame retardants significantly improved flame-retardant performance [55]. This approach transforms a bulk flame-retardant mode into an interfacial flame-retardant mode, simultaneously enhancing mechanical properties and thermal stability [90,91]. Recently, flame-retardant coatings have evolved toward green synthesis, bio-based materials, and nanocomposites. For instance, the CS/PA coating discussed above is a typical bio-based flame-retardant layer. MOFs, recognized in the 2025 Nobel Prize in Chemistry, have rapidly developed as excellent carriers for flame retardants in coatings [16]. MOF-decorated graphene oxide (MOFs-GO) has been reported as an effective flame-retardant coating for EP matrices [92], and bio-based MOF coatings such as BNNS@PA@Fe-MOFs provide simple, environmentally friendly, and efficient flame retardancy [93]. Although numerous studies have explored MOFs for resin matrix modification [94,95], their application in fiber-reinforced materials remains limited. We consider this a promising direction for the future development of flame-retardant coatings for fiber-reinforced composites. MOFs can serve as carriers for flame retardants or be grown in situ on fiber surfaces to enhance the mechanical performance of fibers. Meanwhile, MOF materials offer the advantage of intelligent responsiveness, enabling functionalities such as self-healing [96,97] and early-stage damage [98] detection in materials. For example, this application can be extended from corrosion indication to early fire warning and even synergistic mechanical damage detection. This would significantly enhance the safety and multifunctional integration of fiber-reinforced composites. Specifically, MOFs can be engineered as intelligent carriers to encapsulate fluorescent probes or other signaling molecules. Upon exposure to initial combustion conditions—such as elevated temperature, specific gaseous pyrolysis products, or initial smoldering—the MOF structure could undergo controlled decomposition or pore-gate opening, releasing the encapsulated indicators. This would provide a visual or measurable early warning signal prior to full flame development, enabling timely intervention. Furthermore, by integrating functional fillers (e.g., conductive nanoparticles, strain-sensitive dyes) within MOFs or combining MOFs with self-reporting polymer matrices, the system could also monitor mechanical integrity in real time. Under stress or micro-damage, the MOF-based interface could release detectable signals or exhibit altered optical/electrical properties, thereby achieving dual functionality: early fire warning and structural health monitoring. These capabilities are of significant importance for enhancing FRI safety and achieving synergistic performance.

5.2. Intrinsic Flame-Retardant Approach

Although additive flame-retardant strategies are fast and effective, they cannot fully address the environmental concerns associated with flame-retardant additives. In this context, intrinsic flame retardancy offers significant advantages. To date, intrinsic flame-retardant modifications have primarily focused on EP-based matrices. Bio-based monomers, such as vanillin, isosorbide, and eugenol [99], have been used to prepare intrinsically flame-retardant EP. The key feature of intrinsic flame retardancy is the covalent integration of flame-retardant elements directly into the polymer backbone.

For example, Zhi et al. synthesized an EP monomer from vanillin to achieve enhanced flame resistance [71]. Earlier, Kumar et al. first prepared vanillin-derived EP monomers

reinforced with natural jute fibers, achieving UL-94 V-0 classification [100]. Similarly, Huang et al. [101] and Liu et al. [102] prepared EP monomers from isosorbide, attaining UL-94 V-0 ratings with ease.

EP, as the most commonly used matrix for various fiber-reinforced materials, has been extensively explored for intrinsic flame-retardant development and represents a promising direction for green materials. However, its application in fiber-reinforced composites remains limited. Future studies could focus on developing intrinsically flame-retardant fiber-reinforced EP materials, ensuring both excellent flame-retardant performance and mechanical properties.

6. Future Directions for Flame-Retardant Fiber-Reinforced Materials

This article systematically reviews recent advances in flame retardancy of CFRP and GFRP composites. Table 1 comprehensively summarizes flame-retardant strategies across various resin matrices—including EP, PA, PEEK, and polycarbonate—with natural fiber-reinforced composites included for comparison. The progression evident in this analysis demonstrates a clear evolution from simple physical blending toward multi-scale, multi-dimensional synergistic design.

Table 1. Summary of Characteristics of Flame-Retardant Fiber-Reinforced Materials.

Characteristic Dimension	Carbon Fiber Reinforced Polymer (CFRP)	Glass Fiber Reinforced Polymer (GFRP)	Natural Fiber Reinforced Polymer (NFRPC)
Core Function Positioning	Synergy of High Performance and Flame Retardancy	Balance of Cost, Function, and Flame Retardancy	Unification of Green Sustainability and Flame Retardancy
Characteristic Flame Retardant Types	• Bio-based Coatings: Chitosan/Phytic Acid (CS/PA) • Nano Flame Retardants: Micronized Ammonium Polyphosphate (APP), POSS • Phosphorus-based Flame Retardants: DOPO and its derivatives (e.g., DOPO-HQ, DPO) • Novel Synthetic Flame Retardants: Phosphazene type (e.g., HPCTP)	• Efficient Gas-Phase Flame Retardants: DOPO derivatives (e.g., DOPO-GL-DCDA) • Functional Fillers: Aluminum Hydroxide (Al(OH)3), Boron Nitride (BN), MXene • Intumescent Flame Retardants (IFR): APP-based composite systems • Surface Treatment Agents: Silane coupling agents grafted with flame retardants (e.g., DPER)	• Bio-derived Flame Retardants: Phytic Acid (PA), Tannic Acid (TA), Chitosan (CS), Phosphorylated Lignin • Intrinsically Flame-Retardant Monomers: Vanillin-based, Guaiacol-based epoxy resins • Green Intumescent Systems: Bio-based carbon/acid sources • Mineral Fillers: Expandable Graphite (EG)
Key Flame Retardancy Mechanism	Primarily condensed phase char formation, supplemented by gas phase inhibition. Forms a dense char layer to block heat and mass transfer and trap radicals.	Gas phase inhibition is crucial for extinguishing flames induced by the “wick effect”; condensed phase char formation serves as a supplement.	Strong catalytic char formation is key, building a protective layer to shield the flammable natural fibers.
Performance Synergy Effects	Enhances flame retardancy while maintaining high mechanical properties; can even use flame retardants to improve fiber/matrix interface.	While achieving flame retardancy, it can impart properties like high thermal conductivity, excellent smoke suppression, or higher arc resistance.	Combines flame retardancy with material biodegradability, renewability, and environmental friendliness.

Table 1. Cont.

Characteristic Dimension	Carbon Fiber Reinforced Polymer (CFRP)	Glass Fiber Reinforced Polymer (GFRP)	Natural Fiber Reinforced Polymer (NFRPC)
Unique Functional Advantages	Enables structural-functional integration, providing integrated load-bearing and fire protection solutions for high-end equipment.	Mature technology, controllable cost, and easy-to-achieve flame-retardant functional modification in general industrial fields.	Meets the highest environmental standards, an ideal choice for the circular economy and green design.

As the data indicate, effective flame-retardant modification relies not on simple additive incorporation but on sophisticated molecular and structural designs that achieve synergy between: gas-phase and condensed-phase flame inhibition, flame retardancy and mechanical performance, functional performance and environmental sustainability.

Whether through bio-based interface engineering, 3D-printed fiber orientation control, or molecularly designed intrinsic flame-retardant epoxy systems, success ultimately depends on precisely balancing and enhancing these synergistic interactions.

Despite considerable achievements, challenges and opportunities coexist. Based on a critical analysis of existing systems, future research should focus on breakthroughs in the following directions:

6.1. Lifecycle Design Philosophy Oriented Toward “Green and Circular” Principles

Currently, green development is a major trend across all materials. For flame-retardant fiber-reinforced materials, the green development strategies can be primarily categorized into three aspects: fiber materials, matrix materials, and flame retardants.

For fiber materials, natural fibers are the preferred choice. Natural fibers can be classified into plant-based and mineral-based types. Plant fibers are diverse, including jute, sisal, banana, coconut husk, and fruit fibers. Although these fibers enhance the mechanical properties of resin matrices, they also increase the complexity of achieving flame retardancy. Due to their inherent flammability, coupled with the flammability of the resin matrix, flame-retardant modification of natural fiber-reinforced composites is particularly important. Although some studies have addressed this issue—for example, Yang et al. synthesized an efficient nanoflame retardant PBXY from PA, boric acid, and xylitol to improve the flame retardancy of jute fiber-reinforced EP composites (EP/RF) [103], and N. Beemkumar et al. used bran to enhance basalt fiber and Kevlar fiber-reinforced EP materials—reports specifically focusing on flame-retardant natural fibers remain limited.

For eco-friendly matrix materials, one approach is the bio-based production of EP, as discussed in the previous section. However, this approach is still limited, with reports primarily restricted to EP monomers and few studies on other matrices. This remains a promising future direction, emphasizing the preparation of resin matrices from renewable biomaterials. Another approach involves using degradable polymer matrices such as polylactic acid (PLA). Overall, research on environmentally friendly, bio-fiber-reinforced matrices is scarce, likely due to inherent material limitations, but it remains a field worthy of exploration.

The application of bio-derived flame retardants has become increasingly widespread [103]. Typically, bio-derived flame retardants are phosphorus- or nitrogen-based. A representative bio-phosphorus flame retardant is phytic acid (PA), which produces acidic species at elevated temperatures to promote char formation and is often used synergistically with tannic acid (TA) [104]. Other typical examples include phosphorylated chitosan [105] and phosphorylated lignin [106]. Jiang et al. synthesized an entirely bio-based flame retardant using CS, PA, and epoxidized soybean oil [107], while Zhang et al.

applied a vanillin-derived nitrogen-phosphorus synergistic flame retardant in polyurethane foam, achieving excellent results [108].

Sustainability has transitioned from an option to a necessity. We strongly advocate for lifecycle-oriented design in future research by prioritizing natural fibers or recycled carbon fiber as reinforcements; advancing bio-based intrinsically flame-retardant resins—extending from epoxy to polyamide, polyurethane, and beyond; and promoting bio-derived flame retardants such as phytic acid, chitosan, and lignin to unify high performance with sustainable development.

6.2. *Evolving from “Multi-Element Synergy” to “Intelligent Response”*

While current systems predominantly rely on multi-element synergy (e.g., P, N, Si), future efforts should shift toward intelligent flame-retardant materials. For instance, emerging materials like MOFs can serve as smart carriers for flame retardants, enabling rapid, stimulus-triggered release at early fire stages to maximize efficiency [15,109,110]. Additionally, self-healing char layers offer a revolutionary solution to seal cracks during combustion, forming dynamic and robust barriers that address the fragility of conventional coatings. Alternatively, the feasibility of utilizing electrostatic spinning technology to fabricate core-shell fibers encapsulating flame retardants could be explored, enabling the controlled release of retardants during the initial stages of combustion. Concurrently, the development of self-healing char layers should be investigated. Such layers should not only repair cracks generated during combustion but also synergistically address mechanical damage, thereby establishing a dynamic and stable physical barrier. This represents a transformative approach to overcoming the limitations of current coatings, which often suffer from functional simplicity and susceptibility to failure.

6.3. *Advancing “Interfacial Engineering” to Overcome the Wick Effect*

The “wick effect,” serving as the core mechanism for accelerated flame spread in fiber-reinforced composites, particularly in glass fiber-reinforced systems, essentially involves fibers acting as capillary channels under high temperatures, continuously transporting pyrolytic flammable substances to the flame zone. Traditional interface modifications, such as silane coupling agent treatments [111], primarily focus on enhancing mechanical interlocking and stress transfer between fibers and the matrix. While these approaches improve initial mechanical properties, the interface region often becomes the weak point under extreme fire conditions—first to pyrolyze, fail, and exacerbate the “wick effect.” Therefore, future interface engineering must achieve a transformative shift from mere combustion resistance to proactive flame retardation, constructing the fiber-matrix interface into an intelligent, multifunctional barrier.

With the deepening integration of computer science and artificial intelligence across various fields, the application of biomimetic design, combined with advanced characterization techniques and computational modeling, can profoundly reveal the evolution behavior and failure mechanisms of interfaces under high-temperature conditions. This will provide theoretical guidance for the precise design of interfaces, enabling the development of next-generation composites with inherently enhanced flame-retardant capabilities.

6.4. *Implementing “Materials Genome” and High-Throughput Strategies in Flame Retardancy*

Conventional trial-and-error methods struggle to navigate the extensive combinatorial space of flame retardants, resins, and fibers. We advocate a “materials genome” approach to establish structure-property relationships connecting molecular design, thermal decomposition behavior, and flame-retardant performance. Machine learning models can subsequently predict optimal formulations. When integrated with high-throughput tech-

niques such as 3D printing and electrospinning, this strategy enables rapid iteration and customization, substantially accelerating the development of advanced composites.

7. Conclusions

This review systematically summarizes recent progress in flame-retardant research on CFRP and GFRP composites. Based on current trends in materials science and a critical analysis, the following core conclusions are drawn:

Current research has evolved from early-stage simple physical blending toward sophisticated multi-scale and multi-dimensional designs centered on synergy. This analysis reveals:

Synergy as the key mechanism: Effective flame-retardant systems fundamentally depend on synergistic interactions: between gas-phase and condensed-phase flame retardancy, between flame retardancy and mechanical properties, and between functional performance and sustainability. This principle is evident in nanocomposite interfaces, precisely structured 3D-printed components, and intrinsically flame-retardant resins. Additionally, synergy among multiple fiber types, flame retardants, and fabrication methods is particularly critical.

Converging strategies for addressing the wicking effect: Despite differences in CFRP and GFRP, the fundamental solution lies in interfacial engineering—transforming the vulnerable fiber–matrix interface from a combustion pathway into a robust and flame-retardant barrier.

Limitations of current studies: Most work remains confined to case-specific optimizations, lacking universal design principles. There is insufficient understanding of long-term performance and failure mechanisms under extreme fire conditions. Many flame-retardancy strategies focus narrowly on improving a single property, often neglecting closely related mechanical and thermal performance or offering superficial solutions that fail to address inherent flammability, thus limiting practical impact.

To overcome the aforementioned challenges, propel the field from “incremental improvement” toward “transformative innovation,” and achieve high performance, safety, and sustainability, future research should concentrate on the following four breakthrough directions:

Implement full lifecycle green design: Elevate sustainability from an “add-on attribute” to a “core design criterion,” promoting the use of natural/recycled fiber reinforcements, bio-based intrinsically flame-retardant resins, and bio-derived flame retardants, accompanied by systematic environmental footprint assessment.

Develop smart responsive flame-retardant systems: Focus on intelligent carriers such as MOFs to enable on-demand, targeted release of flame retardants under fire stimuli. Coupled with self-healing char layers, this can create dynamic and stable fire barriers.

Advance multi-scale interfacial engineering: Move beyond traditional compatibility enhancement toward constructing intelligent interphases with multi-level gradient structures or stimulus-responsive functionality, fundamentally suppressing or even utilizing the wicking effect to turn the interface into a strategic asset for fire protection.

Integrate data-driven and high-throughput methods: Actively incorporate machine learning to build “composition–structure–property” databases for flame-retardant composites. Combined with high-throughput fabrication platforms, this will accelerate integrated and personalized rapid manufacturing from molecular design to macro-components.

In summary, the development of next-generation high-performance flame-retardant composites requires breaking down disciplinary barriers and firmly adopting a core paradigm of synergistic design, green priority, and intelligence-driven innovation to achieve an essential unity of fire safety, mechanical performance, and environmental sustainability.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs9120703/s1>, Table S1: The LOI and UL-94 Vertical Burning Tests of Epoxy Resin-Based (EP) CFRP Flame-Retardant Composites; Table S2: The CCT of Epoxy Resin-Based (EP) CFRP Flame-Retardant Composites; Table S3: The LOI and UL-94 Vertical Burning Tests of Polyamide-Based (PA) CFRP Flame-Retardant Composites; Table S4: The CCT of Polyamide-Based (PA) CFRP Flame-Retardant Composites; Table S5: The LOI and UL-94 Vertical Burning Tests of Other Resin-Based CFRP Flame-Retardant Composites; Table S6: The CCT of Other Resin-Based CFRP Flame-Retardant Composites; Table S7: The CCT of Epoxy Resin-Based (EP) GFRP Flame-Retardant Composites; Table S8: The LOI and UL-94 Vertical Burning Tests of Epoxy Resin-Based (EP) GFRP Flame-Retardant Composites; Table S9: The CCT of Other Resin-Based GFRP Flame-Retardant Composites; Table S10: The LOI and UL-94 Vertical Burning Tests of Other Resin-Based GFRP Flame-Retardant Composites.

Author Contributions: Z.Z.: Writing—original draft, Methodology, Investigation. F.H.: Formal analysis, Investigation. H.L.: Investigation, Data curation. T.L.: Investigation, Data curation. B.Y.: Investigation, Data curation. J.H.: Investigation. Y.-T.P.: Writing—review and editing, Methodology, Funding acquisition, Conceptualization. All authors have read and agreed to the published version of the manuscript.

Funding: The National Natural Science Foundation of China (No. 22375023), the Natural Science Foundation of Chongqing (CSTB2024NSCQ-MSX0452), the Natural Science Foundation of Hebei Province (E2024105006) and the Natural Science Foundation of Shandong Province (ZR2024ME040) provided funding for this work. We would like to thank National/Municipal College Student Innovation and Entrepreneurship Training Program (202510007011X) and Beijing Institute of Technology Student Innovation Training Program (BIT2024LH013) for supporting this work.

Data Availability Statement: No new data were created or analyzed in this study.

Conflicts of Interest: The authors declare no competing financial interest.

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