Macromolecular Materials and Engineering

www.mame-journal.de

REVIEW OPEN ACCESS

Phosphorus-Free Flame-Retardant Strategies for Epoxy Resins

Yong Guo[1] | Qingshan Yang[1] | Siqi Huo[1,2] | Boyou Hou[1] | Pooya Jafari[1] | Tao Chu[1] | Hao Wang[1,2] | Pingan Song[1,3]

[1]Centre For Future Materials, University of Southern Queensland, Springfield, Australia | [2]School of Engineering, University of Southern Queensland, Springfield, Australia | [3]School of Agriculture and Environmental Science, University of Southern Queensland, Springfield, Australia

Correspondence: Siqi Huo (siqi.huo@unisq.edu.au) | Hao Wang (hao.wang@unisq.edu.au) | Pingan Song (pingan.song@usq.edu.au)

Received: 25 June 2025 | **Revised:** 17 August 2025 | **Accepted:** 20 August 2025

Funding: The authors acknowledge the financial support received from the Australian Research Council (No. LP220100278, DP240102628, DE230100616, and DP230103008, IM250100102).

Keywords: epoxy resin | flame retardancy | mechanical property | phosphorus-free

ABSTRACT

Driven by the principles of sustainable development and green chemistry, phosphorus-free flame-retardant systems have become a key focus in the development of high-performance polymers because they feature improved ecological safety relative to phosphorus-based systems. This review focuses on two main phosphorus-free flame-retardant strategies: (i) additive phosphorus-free flame retardants and (ii) intrinsically phosphorus-free flame-retardant epoxy resins. Emphasis is placed on the relationship between chemical structure and comprehensive properties, including flame retardancy, thermal properties, and mechanical performance. The flame-retardant modes-of-action for the phosphorus-free flame-retardant epoxy systems are also summarized. Finally, current challenges and future development opportunities are presented. This work is expected to facilitate the development of phosphorus-free flame-retardant systems.

1 | Introduction

Thermosetting polymers characterized by multiple epoxy groups in their molecular chains are commonly referred to as epoxy resins (EPs). These polymers typically undergo crosslinking reactions with curing agents, such as diamines, polyamines, or anhydrides, forming a densely crosslinked 3D network [1]. This structure imparts superior durability, strong chemical resistance, and effective electrical insulating capabilities, resulting in extensive use across coatings, adhesives, electrical insulation, and structural composites [2–5]. However, as EPs are increasingly utilized in advanced technological fields such as aerospace, high-speed communication (e.g., 5G), and electronic packaging, their intrinsic flammability has emerged as a critical limitation, impeding broader applications [6–8]. Upon exposure to heat or open flame, EPs are prone to thermal degradation and the release of toxic gases, posing significant threats to both equipment safety and human health [9–11]. Therefore, efforts to increase flame resistance in EP-based materials are critical topics in current materials science studies [12].

Abbreviations: CCT, Cone calorimetry test; DDM, 4,4-Diaminodiphenylmethane; DDS, 4,4-Diaminodiphenylsulfone; DGEBA, Bisphenol A- diglycidyl ether; DGEBA/DDM, DDM-cured DGEBA; EPs, Epoxy resins; FRs, Flame retardants; HRC, Heat release capacity; LOI, Limiting oxygen index; MCC, Microscale combustion calorimetry; NA, Not applicable; OPFRs, Organophosphorus FRs; pHRR, Peak of heat release rate; SEM, Scanning electron microscopy; T_g, Glass transition temperature; TG-FTIR, Thermogravimetry–Fourier transform infrared spectroscopy; THR, Total heat release; TSP, Total smoke production; △pHRR, pHRR variation compared to control sample; △THR, THR variation compared to control sample; △TSP, TSP variation compared to control sample; XPS, X-ray photoelectron spectroscopy.

Conventional approaches primarily involve incorporating flame retardants (FRs) into the resin matrix [13, 14]. Inorganic intumescent FRs, such as aluminum hydroxide or expandable graphite, are effective; however, they generally require high loading levels (>20 wt.%), which can adversely affect the mechanical properties and processability of the epoxy system [15, 16]. In contrast, halogen-based FRs are highly effective in flame suppression, but their combustion generates considerable toxic and corrosive emissions, posing severe environmental and health hazards [17–22]. As a result, their use has been increasingly restricted or banned in many regions. In recent years, phosphorus-containing FRs (e.g., 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, ammonium polyphosphate, and phenyl phosphate esters) have been extensively investigated as promising alternatives to halogenated FRs [23–29]. The synergistic interaction between phosphorus and nitrogen significantly promotes char formation while suppressing heat and smoke release during combustion. These organophosphorus compounds achieve an optimal balance among flame-retardant efficacy, additive loading levels, and fundamental material properties [30–32]. Despite their widespread use and relatively favourable flame-retardant efficiency, increasing evidence has raised serious concerns regarding the environmental and health risks of organophosphorus FRs (OPFRs) [33]. Several OPFRs and their thermal degradation byproducts exhibit notable biotoxicity, bioaccumulation potential, and environmental persistence, which may lead to long-term ecological consequences [34]. Additionally, certain OPFRs have been identified as endocrine-disrupting chemicals and potential carcinogens, posing risks to both wildlife and human populations [35, 36]. Their high mobility in environmental media (e.g., water and air) further exacerbates the risk of widespread exposure, including through indoor dust and food chains. These findings underscore the urgent need to develop inherently safer and environmentally sustainable flame-retardant systems as alternatives to conventional phosphorus-based materials.

In recent years, phosphorus-free flame-retardant strategies have garnered increasing attention due to their potential to overcome the ecological and human safety concerns caused by conventional FRs, while maintaining desirable material properties. Structural design approaches based on intrinsic flame-retardant functionalities, synergistic interactions, and molecular-level engineering have shown promise in enhancing flame retardancy without compromising thermal stability or mechanical performance. However, a comprehensive understanding of how these structural modifications influence the multifunctional properties of epoxy systems remains limited. Therefore, this review systematically summarizes recent progress in phosphorus-free flame-retardant strategies for EPs, focusing on the relationship between molecular structure and key performance indicators, such as flame retardancy, thermal stability, and mechanical properties. This review also focuses on phosphorus-free flame-retardant mechanisms, discusses their modes of action, and points out current challenges along with corresponding development directions.

This review categorizes phosphorus-free flame-retardant (FR) strategies into two main types: (i) additive phosphorus-free FRs and (ii) intrinsically phosphorus-free flame-retardant epoxy systems. Representative material categories for additive phosphorus-free FRs include boric acid-derived compounds and C═N/C≡N-containing compounds. For intrinsically phosphorus-free flame-retardant epoxy systems, the main categories include benzene/C═C-rich flame-retardant EPs, deoxybenzoin/benzene-based flame-retardant EPs, C═N-containing flame-retardant EPs, and benzene/polyepoxy-based flame-retardant EPs. In addition, common flame-retardant evaluation methods include the limiting oxygen index (LOI) test, which determines the lowest oxygen concentration needed to sustain combustion under defined conditions; the UL-94 vertical burning test, which assesses the flammability of plastics by measuring their ability to self-extinguish when ignited in a vertical orientation; and the cone calorimetry test (CCT), which analyzes fire performance by recording parameters such as heat release rate, smoke generation, and mass loss under controlled heat exposure. Within the CCT, -△pHRR represents the decrease in peak heat release rate, -△THR corresponds to the reduction in total heat release, and -△TSP indicates the decline in total smoke production, each benchmarked against commercial reference materials.

2 | Additive Phosphorus-Free FRs

2.1 | Boric Acid-Derived Compounds as FRs

Boric acid compounds have attracted considerable attention as FRs because of their eco-friendliness, thermal stability, and multiple flame-retardant mechanisms [37]. They exhibit clean-burning behavior without producing hazardous or corrosive byproducts. Therefore, boric acid-based FRs are regarded as cleaner options than conventional phosphorus-based FRs, effectively suppressing flames while minimizing secondary pollution [38]. In terms of flame-retardant mechanism, boric acid compounds primarily act in the condensed phase. Upon heating, boric acid undergoes dehydration to form metaboric acid, which further converts into boron oxide [39]. This boron oxide forms a dense glassy layer that shields the substrate below from high temperatures and oxidative attack, thereby significantly slowing down thermal degradation [40]. Moreover, boron oxide contributes to generating a resilient carbonaceous residue, providing additional insulation against heat [41].

Zhang et al. [42] synthesized a phosphorus-free, hyperbranched polyborate additive-type FR named HBPB (Figure 1a), which was incorporated into an EP system cured with 4,4′-diaminodiphenylsulfone (DDS). As shown in Figure 1f, the epoxy composite containing 9 wt.% HBPB (denoted as 9 wt.% HBPB/EP) achieved a limiting oxygen index (LOI) of 30.2% and passed the UL-94 V-0 rating, indicating excellent flame retardancy. Cone calorimeter test (CCT) results further demonstrated that the peak heat release rate (pHRR), total heat release (THR), and total smoke production (TSP) of 9 wt.% HBPB/EP decreased by 39.7%, 8.4%, and 26.7%, respectively, compared to the neat EP/DDS system. The main action of HBPB occurs in the condensed state, while its effectiveness during gas-phase combustion remains limited. While burning, the hyperbranched molecular backbone of HBPB undergoes early thermal degradation, producing boron-containing fragments such as B–O–C, B–C, and $B(OH)_2$ [43]. These fragments readily interact with free radicals and hydrogen-containing species generated from the thermal cracking of organic compounds. Notably, the reversible nature of these interactions facilitates drying and charring processes occurring in the epoxy matrix. Furthermore, the

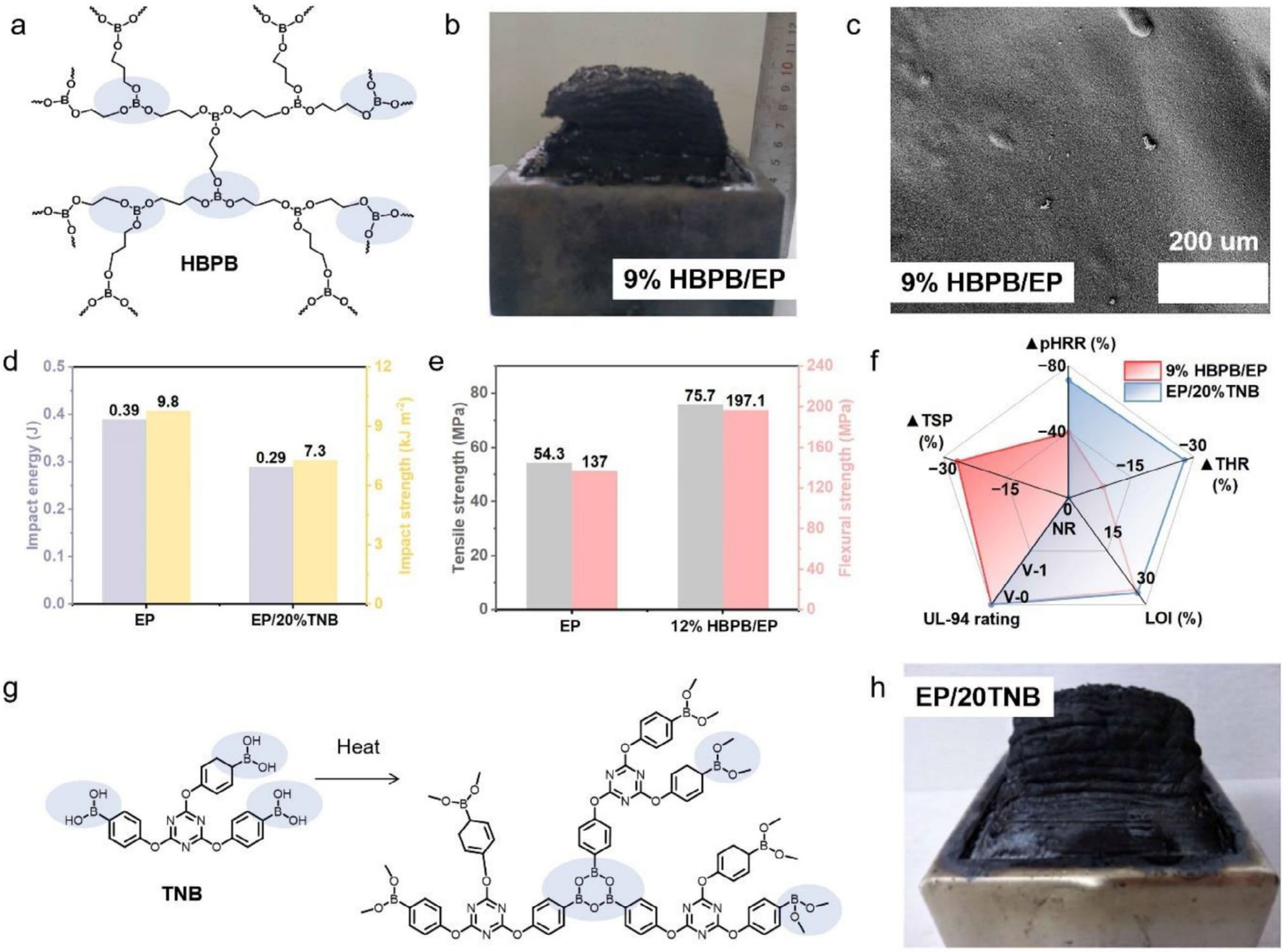

FIGURE 1 | (a) Illustration of the chemical structure of HBPB [42], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (b) Digital photos of 9 wt.% HBPB/EP after CCT [42], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (c) SEM micrograph of char surface of 9 wt.% HBPB/EP after CCT [42], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (d) Impact properties of EP and EP/20TNB. (e) Tensile strength and flexural strength of EP and 12 wt.% HBPB/EP. (f) Performance comparison of 9 wt.% HBPB/EP and EP/20%TNB. (g) Diagram of the thermal dehydration of boric acid to boroxine [47]. (h) Digital photos of EP/20TNB after CCT [47].

boron-containing fragments contribute to char layer formation and participate in the repair and reconstruction of the inherently fragile carbonaceous structure, resulting in a more robust and cohesive char layer [44]. As shown in Figure 1b,c, a dense and expanded char layer is formed after combustion. The char layer protects the underlying material from oxygen infiltration, thereby suppressing flames and limiting the emission of smoke, heat, and harmful gases [45, 46]. Apart from flame retardancy, the EP composite containing 12 wt.% HBPB also exhibited outstanding mechanical performance. As illustrated in Figure 1e, its tensile strength and flexural strength reached 75.7 and 197.7 MPa, representing increases of 39.3% and 43.9%, respectively, compared to the EP.

Chen et al. [47] developed a boron/nitrogen-containing FR (TNB), incorporating it into the EP system cured with 4,4-Diaminodiphenylmethane (DDM). As shown in Figure 1f, compared with 9 wt.% HBPB/EP, the EP composite containing 20 wt.% TNB (EP/20%TNB) exhibits significantly enhanced flame retardancy and heat suppression. The LOI reaches 31.2%, and the UL-94 test achieves a V-0 rating. Furthermore, CCT results demonstrate that the PHRR and THR of EP/20%TNB are diminished by 71.3% and 27.8%, respectively, compared to the EP/DDM system. These excellent performances can be attributed to two main factors. First, the high loading level of TNB contributes directly to flame retardancy. Second, during combustion, TNB forms cyclic boroxine structures (Figure 1g), which synergize with the triazine moieties to enhance char formation, leading to a dense, intumescent carbonaceous layer (Figure 1h). In addition, the triazine units decompose to generate numerous nitrogen-containing inert gases during the gas state, effectively diluting flammable volatiles [48]. However, as shown in Figure 1d, the high TNB content in EP/20%TNB induces weakening of mechanical performance.

In summary, boron-containing oligomeric FRs, boric acid-derived compounds—contain reactive groups like B–OH, which may participate in chemical bonding with epoxy groups, are well compatible with EPs and can achieve effective flame-retardant performance at relatively low loading levels while maintaining favorable mechanical properties [49, 50]. Although B-based FRs offer advantages such as environmental benignity, low smoke generation, heat release suppression, and enhanced char formation, they also face certain limitations. Specifically, their combustion inhibition in the gaseous state is relatively limited, and high loading levels may compromise the mechanical integrity of the final material. Furthermore, in accordance with the Classification, Labelling and Packaging (CLP) Regulation and Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), certain borates have been classified as reproductive toxicants due to their potential to impair fertility. Nevertheless, their use is still permitted under strict labeling requirements and concentration limits (typically below 5.5%). To mitigate these limitations, the integration of additional phosphorus-free flame-retardant elements, such as nitrogen and silicon, is recommended. These combinations are expected to produce synergistic effects, thereby enhancing overall flame retardancy while maintaining favorable mechanical properties at low additive levels.

2.2 | C═N/C≡N-Containing Compounds as FRs

When compounds containing C═N and C≡N functional groups are incorporated as FRs into EP matrices, their flame-retardant performance can be significantly enhanced through thermally induced crosslinking reactions [51, 52]. Specifically, the unsaturated bonds present in aromatic Schiff base structures—namely C═N and C≡N—undergo crosslinking at elevated temperatures, producing a stable, carbon-rich barrier [53, 54]. The resulting carbonaceous layer effectively blocks heat transfer and greatly suppresses the emission of flammable volatiles [55]. During the gaseous state, the thermal decomposition of nitrogen-containing components leads to the generation of nonflammable gases, such as CO_2 and nitrogenous species (e.g., N_2, NH_3, or NO_x) [56]. These inert gases dilute flammable gases and oxygen in the combustion zone, thereby suppressing flame propagation through a gas-phase dilution mechanism [57]. Overall, the combined effects of condensed-phase char formation and gas-phase inert gas release endow C═N/C≡N-containing compounds with strong flame-retardant efficacy, making them promising functional additives for improving flame retardancy of EPs [58].

Wang et al. [59] proposed a feasible multi-crosslinking strategy for enhancing the fire retardant performance of EP by introducing an unprecedented additive FR (BPPDN, Figure 2a) containing self-crosslinkable groups. The curing process was initiated using DDS, leading to the development of a multi-network architecture within the EP matrix. As shown in Figure 2d, the composite containing 15 wt.% BPPDN (15BPPDN/EP) achieved an LOI of 27.5% and passed the UL-94 test at the V-0 level. CCT results (Figure 2f) further demonstrated that, compared with the unmodified EP/DDS system, the PHRR and THR of 15BPPDN/EP diminished by 22.2% and 40%, correspondingly. In the condensed phase, the aromatic Schiff base segments containing C═N and C≡N functionalities undergo thermal crosslinking at elevated temperatures, forming a stable carbonaceous char (Figure 2b), which acts as a strong thermal barrier and inhibits the release of flammable volatiles. FT-IR analysis of the residual char (Figure 2c) confirmed the cyclization and crosslinking of C═N and C≡N groups. In the gas phase, the crosslinking of the phthalide moieties promotes CO_2 release and facilitates the trimerization of C≡N groups, contributing additional inert gases that suppress combustion. Moreover, the incorporation of BPPDN did not compromise the material's inherent optical and mechanical properties. The 15BPPDN/EP composite retained high transparency, excellent UV-blocking capability, and superior dielectric performance, along with outstanding mechanical strength, including tensile and flexural strength of 108 and 127 MPa, and impact strength (23 $kJ \cdot m^{-2}$).

Lv et al. [60] synthesized a novel FR, PBA-Salen, which contains C═N and boron (Figure 2g), and incorporated it into EP, cured using DDM. The resulting EP composite containing 4.7 wt.% PBA-Salen exhibited a LOI of 29.1%, meeting the criteria for UL-94 V-1 classification and demonstrating enhanced resistance to ignition and flame spread. However, the observed suppression of heat and smoke was less effective than expected. This suboptimal performance may be attributed to the relatively low loading level of PBA-Salen (4.7 wt.%), which is likely insufficient to produce a protective char structure capable of shielding the underlying material during combustion.

Wang et al. [61] developed a novel FR, DBA-Ph, featuring C═C and C≡N functionalities (Figure 2j), and incorporated it into the EP system cured with DDS. Compared to 15 wt.% BPPDN and PBA-Salen, the composite containing 20 wt.% DBA-Ph (denoted as DP-20) exhibited significantly enhanced flame retardancy, with an LOI of 34.9% and meeting the UL-94 V-0 standard. As shown in Figure 2f, CCT results demonstrated that DP-20 exhibited superior heat suppression performance compared to the BPPDN-based system, showing 40% and 39.7% reductions in PHRR and THR, respectively. Digital photographs and SEM images of the post-combustion residues (Figures 2h–i) revealed that the DP-20 samples developed a dense and continuous carbonaceous barrier at the surface. The formation of this char structure results from the combined action of the crosslinked network generated during combustion. Enhanced crosslinking improved the char's integrity and density, effectively protecting the polymer beneath against thermal and oxidative damage, thereby disrupting the combustion process and enhancing fire resistance.

In summary, C═N and C≡N-containing compounds exhibit flame-retardant effects through dual-phase mechanisms. During the gas phase, they emit nonflammable gases that dilute flammable volatiles, effectively hindering flame spread. During the condensed phase, these compounds thermally crosslink to generate a dense, cohesive char that functions as a robust barrier against heat and oxygen. However, achieving optimal flame-retardant performance typically requires a relatively high additive loading (more than 15 wt.%), which may limit their applicability in certain high-performance applications.

2.3 | Summary of Additive Phosphorus-Free FRs

According to Table 1, additive phosphorus-free FRs can achieve satisfactory flame-retardant performance; however, their effectiveness is generally low and they typically require relatively high additions (usually 10–20 wt.%) to markedly enhance the LOI and attain a UL-94 V-0 classification. Such high loadings often compromise key material characteristics, including mechanical performance and optical clarity [62]. Moreover, the CCT results indicate that these FRs show limited ability to suppress heat

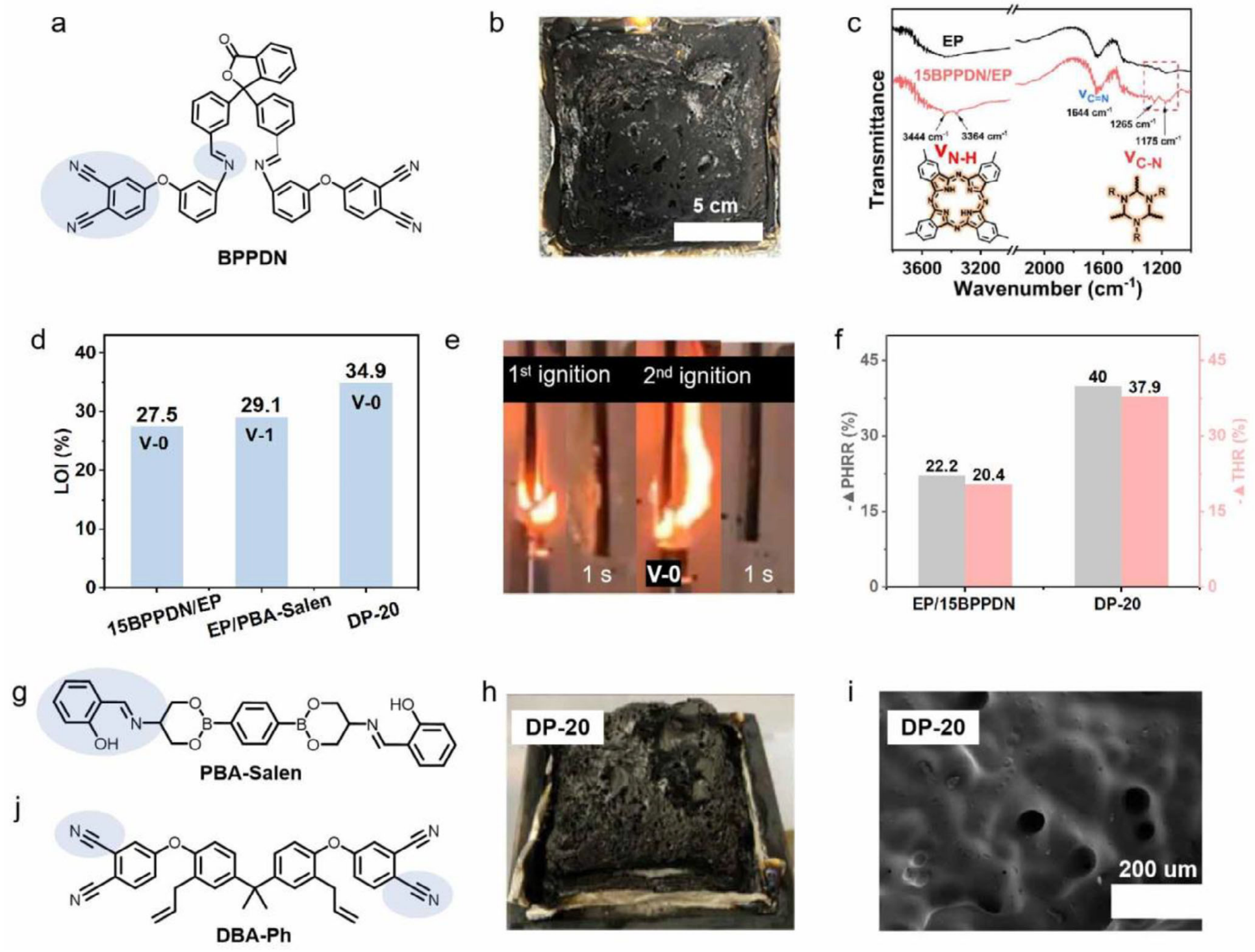

FIGURE 2 | Illustration of chemical structures of (a) BPPDN [59], Copyright 2024. Reproduced with permission from Elsevier Science Ltd, (g) PBA-Salen [60], Copyright 2022. Reproduced with permission from Elsevier Science Ltd and (j) DBA-Ph [61]. (b) SEM micrograph [59], Copyright 2024. Reproduced with permission from Elsevier Science Ltd and (c) FT-IR of char residue of 15BPPDN/EP after CCT [59], Copyright 2024. Reproduced with permission from Elsevier Science Ltd. (d) LOI and UL-94 results of three FRs. (e) Digital photos of the DP-20 burning process during the UL-94 [61]. (f) PHRR and THR comparison of 15BPPDN/EP and DP-20. (h) Digital photos [61] and (i) SEM micrograph of char residue of DP-20 [61].

TABLE 1 | Summary of comprehensive performances for EPs containing additive phosphorus-free FRs.

Ref.	Flame-retardant group	Sample name	FR loading (wt.%)	LOI (%)	UL-9 rating	-△ pHRR (%)	-△ THR (%)	-△ TSP (%)	Tensile strength (MPa)	Flexural strength (MPa)
[42]	B	9% HBPB/EP	9	30.2	V-0	39.7	8.4	26.7	75	175
[47]	B	EP/20%TNB	20	31.2	V-0	71.3	27.8	NA	NA	NA
[59]	C=N and C≡N	15BPPDN/EP	15	27.5	V-0	22.2	20.4	38.7	108	127
[60]	C=N and B	EP/PBA-Salen	4.7	29.1	V-1	NA	NA	NA	NA	NA
[61]	C=C and C≡N	DP-20	20	34.9	V-0	40.0	37.9	28.1	NA	NA

release during combustion, as confirmed by a low reduction in THR. They mainly function in the condensed phase during combustion, which induces crosslinking and char formation to inhibit combustion. Due to their relatively weak activity in the gas phase, their efficiency is usually lower than FRs with active gas-phase mechanisms. Furthermore, in most cases, additive phosphorus-free flame retardants do not readily form strong covalent bonds with the epoxy matrix. As a result, the long-term stability of such flame-retardant EP composites may be compromised due to potential issues such as additive migration and phase separation. Therefore, future research should focus on optimizing the molecular structures of phosphorus-free flame retardants to enhance their flame-retardant efficiency, form chemical bonds with the epoxy matrix, and mitigate adverse effects on the overall performance.

3 | Intrinsically Phosphorus-Free Flame-Retardant EPs

3.1 | Benzene/C=C-Rich Flame-Retardant EPs

EPs containing benzene rings and C=C unsaturated bonds exhibit flame-retardant behavior primarily through condensed-phase mechanisms. Upon thermal exposure, the conjugated benzene structures enhance thermal stability and promote the formation of aromatic char layers [63]. Simultaneously, C=C double bonds undergo crosslinking reactions when heated, producing a denser and more cohesive char structure. This carbonaceous residue serves as a protective layer that limits the transfer of heat and oxygen into the underlying matrix [64]. Additionally, the aromatic structure promotes increased residual char formation and improves the graphitic nature of the residue, thereby boosting its thermal insulation performance [65, 66]. However, the gas-phase flame inhibition effect is limited due to the absence of significant nonflammable gas release.

Zhang et al. [67] synthesized a bio-based epoxy monomer from curcumin (Figure 3a), which was subsequently cured with DDS to produce an intrinsically flame-retardant EP (DGEC/DDS). Compared with the conventional petroleum-based system DGEBA/DDS, DGEC/DDS exhibited a notably elevated glass transition temperature (T_g) of 300 °C, in contrast to 215 °C for DGEBA/DDS, indicating its superior thermal stability. As shown in Figure 3b, the DGEC/DDS resin obtained a UL-94 V-0 rating, indicating superior fire resistance. Microscale combustion calorimetry (MCC) data showed that DGEC/DDS exhibited decreases of 80.2%, 74.8%, and 59.4% in heat release capacity (HRC), peak heat release rate (PHRR), and total heat release (THR), respectively, relative to DGEBA/DDS, highlighting its outstanding flame-retardant efficiency. This excellent performance results from combined actions occurring in both condensed and gaseous states. Within the condensed phase, the DGEC/DDS system enhances char formation, creating a dense char layer that protects the substrate by blocking heat and oxygen penetration [68]. Meanwhile, during the gaseous phase, abundant nonflammable CO_2 is emitted, which aids in heat dissipation and dilutes oxygen and combustible gases, further suppressing flame spread. Moreover, as shown in Figure 3c, DGEC/DDS exhibited a tensile strength of 65.9 MPa, which is significantly greater compared to 56.1 MPa for DGEBA/DDS, indicating that the improvement in flame retardancy was achieved without sacrificing the mechanical performance.

Lu et al. [69] prepared a bio-based epoxy monomer (RESEP) from resveratrol (Figure 3d), which was subsequently cured with DDM to produce an intrinsically flame-retardant EP. The resulting RESEP/DDM system exhibited a T_g of 335 °C, which is the highest value reported to date among bio-based EP, indicating exceptional thermal stability. RESEP/DDM exhibited an LOI of 31.8% and passed the UL-94 test with a V-0 classification (Figure 3e). Its effectiveness against flames mainly results from the rapid generation of a compact char layer in the condensed phase, coupled with the emission of large quantities of inert gases in the gas phase, together suppressing flame spread. RESEP/DDM also demonstrated excellent mechanical performance, exhibiting tensile strength at 76.0 MPa and tensile modulus reaching 3499.3 MPa, which reflects outstanding rigidity and load-bearing capacity.

Song et al. [70] synthesized a bio-based epoxy monomer, HCA-EP (Figure 3f), which was subsequently cured with DDM to obtain an intrinsically flame-retardant EP. In Figure 3b, the HCA-EP/DDM system achieved an LOI of 32.6%, surpassing those of RESEP/DDM and DGEC/DDS, indicating outstanding fire-retardant performance. Although its UL-94 rating was V-1, the total after-flame time ($t_1 + t_2$) was only 11 s, suggesting excellent fire resistance. CCT results revealed substantial declines in PHRR, THR, and TSP by 60%, 34%, and 30%, respectively, compared to the DGEBA/DDM system. The primary flame-retardant mechanism involves generating a protective char layer within the condensed phase. This was confirmed by digital and microscopic observations of the post-CCT residues (Figure 3g), revealing the formation of a dense carbonaceous layer which effectively protects the substrate from thermal and flammable gas exposure [71]. Moreover, HCA-EP/DDM exhibited outstanding mechanical performance. As shown in Figure 3c, the tensile strength reached 98.3 MPa, significantly higher than that of RESEP/DDM and DGEC/DDS. The flexural strength was also notably high at 158.9 MPa. This remarkable mechanical performance is attributed to the compact molecular structure of hydroxycinnamic acid, which promotes efficient chain packing and stress transfer, thereby enhancing the overall mechanical integrity of the cured network.

Overall, benzene/C=C-based EPs mainly achieve fire resistance by generating a protective carbonaceous layer within the condensed phase. This thermally formed carbonaceous barrier acts as an effective shield against heat and flammable volatiles. Additionally, the release of substantial amounts of CO_2 during the gas phase helps suppress flames by diluting combustible gases and oxygen, thereby offering a secondary gas-phase flame-retardant function. Comparative data indicate that epoxy systems containing two or more benzene rings exhibit superior flame-retardant performance, particularly in achieving the V-0 rating in the UL-94 test. The improvement can be attributed to the greater aromatic content and increased molecular rigidity, facilitating rapid generation of stable, graphitized char during thermal decomposition, which enhances both char yield and thermal protection. However, while multi-ring aromatic structures enhance flame retardancy, they tend to compromise mechanical performance. Specifically, resins with multiple benzene rings typically show reduced tensile strength and impact resistance. This is primarily due to increased steric hindrance, which interferes with effective chain packing and crosslinking density. Moreover, the higher rigidity leads to greater brittleness and reduced strain tolerance, making the material more susceptible to fracture under mechanical stress. Therefore, when designing intrinsically flame-retardant EPs of this type, a balance between flame retardancy and mechanical integrity must be carefully considered. Future research should focus on molecular design strategies such as incorporating flexible segments, optimizing the functionality of reactive groups, or constructing intramolecular synergistic structures to achieve high flame-retardant efficiency while maintaining or enhancing mechanical performance. Such approaches

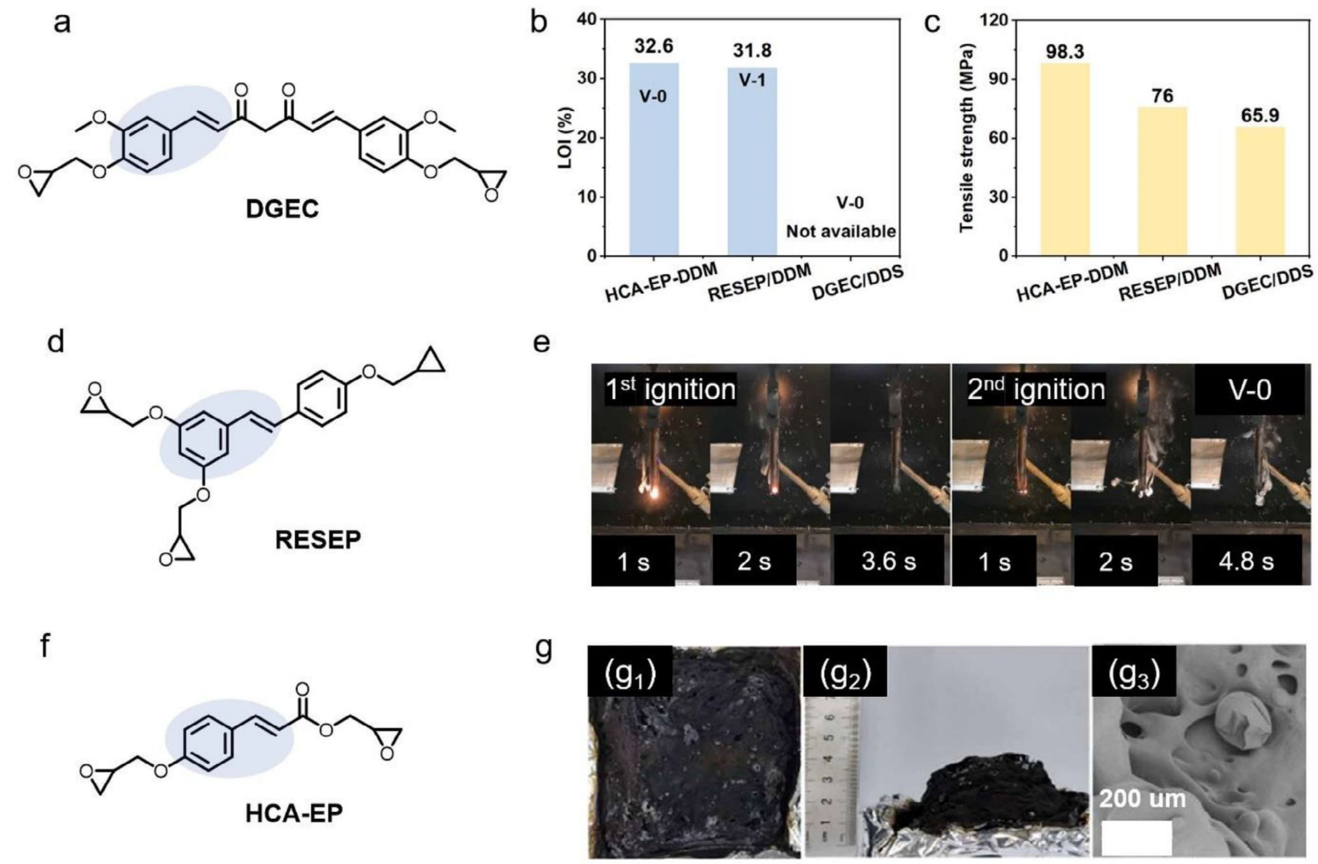

FIGURE 3 | Illustration of chemical structures of (a) DGEC [67], Copyright 2023. Reproduced with permission from Elsevier Science Ltd, (d) RESEP [69], Copyright 2022. Reproduced with permission from Elsevier Science Ltd and (f) HCA-EP [70], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (b) LOI and UL-94 of three flame-retardant EPs. (c) Tensile strength results of three flame-retardant EPs. (e) Digital photos of the RESEP/DDM burning process during the UL-94 [69], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (g) (g_1 and g_2) Digital photos and (g_3) SEM micrograph of char residue of HCA-EP after CCT [70], Copyright 2022. Reproduced with permission from Elsevier Science Ltd.

are essential to meet the multifaceted requirements of advanced high-performance polymer applications.

3.2 | Deoxybenzoin/Benzene-Based Flame-Retardant EPs

Deoxybenzoin/benzene-based EPs demonstrate inherent flame retardant properties, primarily attributed to their unique deoxybenzoin/benzene backbone [72–74]. This highly conjugated and rigid structure not only imparts excellent thermal stability but also significantly facilitates a protective carbonaceous char developing during thermal decomposition [75]. A compact char structure effectively limits thermal conduction and blocks flammable gases from escaping during the condensed phase [76]. Moreover, the abundant phenolic —OH present in the flavonoid framework plays a critical role in enhancing thermal crosslinking reactions. Upon exposure to elevated temperatures, these —OH groups can undergo condensation and polymerization, further stabilize the matrix and reinforce the integrity of the char residue [77]. Deoxybenzoin/benzene-based EPs undergo thermal degradation that produces significant amounts of non-flammable gases like CO_2 and water vapor, reducing the levels of combustible gases and oxygen near the flame front. This contributes to a secondary flame inhibition mechanism via gas-phase dilution.

Dai et al. [78] synthesized a bio-based epoxy monomer DGEG (Figure 4a) from genistein, which was subsequently cured with DDM to produce DGEG/DDM. This system exhibited outstanding flame-retardant properties, achieving an LOI value of 33.1% alongside a UL-94 V-0 classification. MCC data showed significant reductions in pHRR, THR, and TSP by 36.9%, 48.5%, and 64.4%, respectively, compared to unmodified EP/DDM. Digital photographs before and after LOI testing (Figure 4b), after CCT (Figure 4e), along with SEM images of the char residue (Figure 4c), revealed a continuous and robust char layer formed on the material's surface. During combustion, the compact char structure hinders the intrusion of oxygen and flammable volatiles into the material and insulates the underlying polymer from external heat, thereby enhancing fire resistance. In addition to its flame-retardant behavior, the DGEG/DDM system demonstrated robust mechanical behavior. The tensile and flexural strength reached 92 MPa and 141 MPa, respectively, representing increases of 19.5% and 33% over EP/DDM. These improvements are ascribed to the highly aromatic and rigid conjugated backbone of the genistein-derived epoxy monomer, which contributes to enhanced crosslinking density, network stiffness, and efficient stress transfer within the cured resin.

Wang et al. [79] synthesized a bio-based epoxy monomer (DGELU) from luteolin (Figure 4g) and cured it with DFA

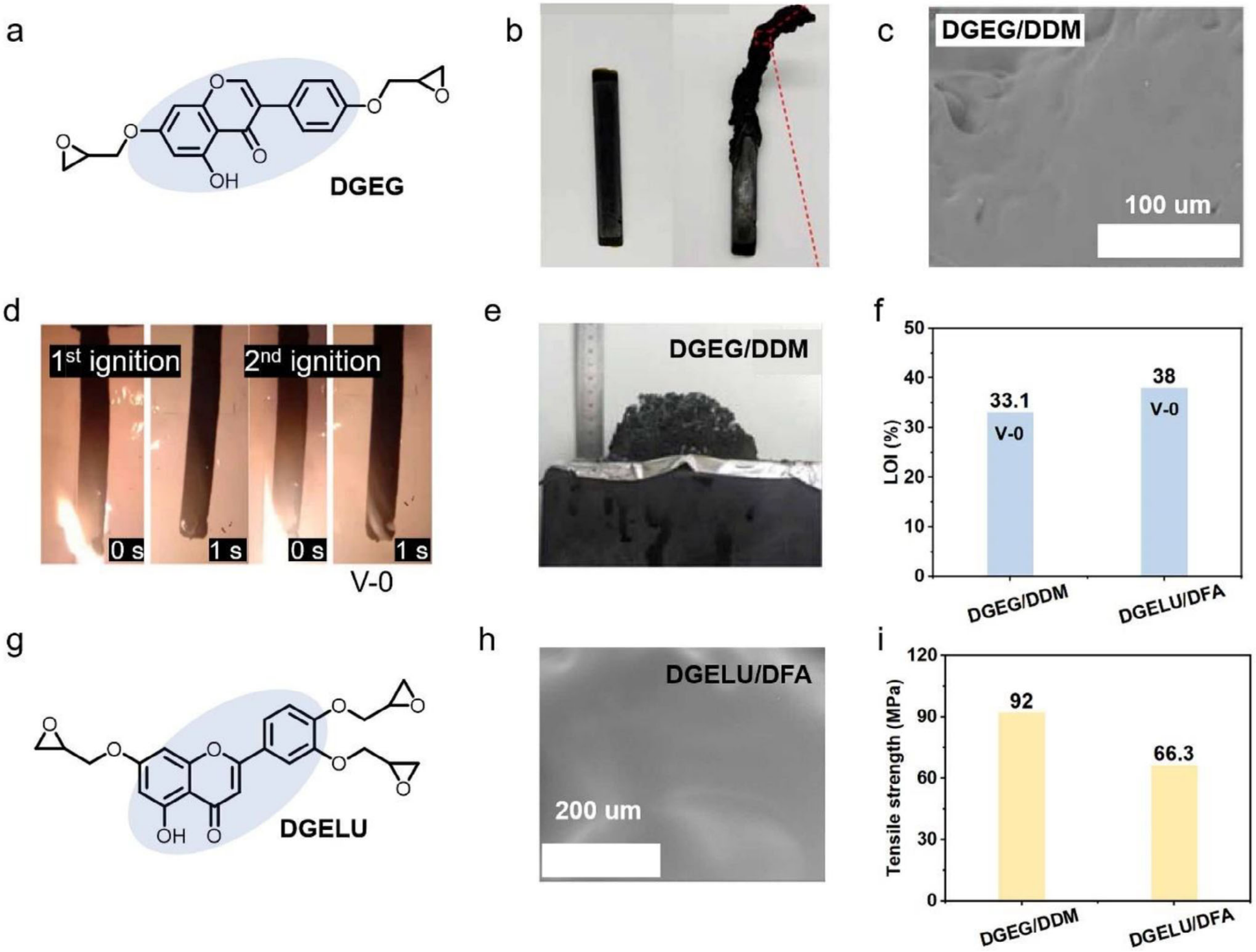

FIGURE 4 | Illustration of chemical structures of (a) DGEG [78], Copyright 2019. Reproduced with permission from Elsevier Science Ltd, and (g) DGELU [79], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (b) Digital photos and (c) SEM micrograph of char residue of DGEG/DDM after LOI [78], Copyright 2019. Reproduced with permission from Elsevier Science Ltd. (d) Digital photos of the DGELU/DFA burning process during the UL-94 [79], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (e) Digital photos of char residue of DGEG/DDM after CCT [78], Copyright 2019. Reproduced with permission from Elsevier Science Ltd. (f) LOI and UL-94 results of DGEG/DDM and DGELU/DFA. (h) SEM micrograph of char residue of DGELU/DFA after CCT [79], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (i) Tensile strength of DGEG/DDM and DGELU/DFA.

to obtain the inherently flame-retardant EP (DGELU/DFA). As shown in Figure 4f, the DGELU/DFA system exhibited a significantly higher LOI of 38% compared to DGEG/DDM. During the UL-94 test (Figure 4d), the material achieved a V-0 rating and self-extinguished within just 2 s, demonstrating excellent non-flammability. Moreover, the application of DGELU/DFA as a flame-retardant coating on wood surfaces imparted remarkable fire protection. Compared with untreated wood, the coated samples exhibited substantial reductions in PHRR, THR, and TSP by 55.8%, 12.4%, and 11.5%, respectively, indicating efficient inhibition of thermal release and smoke generation during combustion. SEM observations (Figure 4h) showed a tightly packed and uniform char structure on the surface, indicating that DGELU/DFA achieves flame resistance primarily through condensed-phase action. The high charring efficiency suggests that most of the thermal degradation products are trapped within the condensed phase rather than contributing to combustion during the gas phase. Apart from excellent flame-retardant properties, the DGELU/DFA system also demonstrated favorable mechanical performance. Its tensile strength reached 66.3 MPa, which is significantly greater than the conventional DGEBA/DDM (53.8 MPa), indicating enhanced structural integrity and rigidity. This improvement is mainly attributed to the rigid aromatic backbone and multiple functional groups present in the DGELU molecule, which contribute to a higher crosslinking density and more robust polymer network, thereby improving load-bearing capacity. However, based on Figure 4i, the tensile strength of DGELU/DFA is slightly lower than that of the DGEG/DDM system cured with DDM. This difference is likely due to the use of different curing agents. DFA and DDM vary in terms of curing kinetics, crosslinking behavior, and molecular interactions, which can affect the final network architecture and the efficiency of stress transfer, ultimately influencing the mechanical performance of EPs.

To summarize, deoxybenzoin/benzene-based EPs exhibit outstanding flame-retardant performance, particularly in UL-94 vertical burning tests, where some systems demonstrate complete non-flammability under ambient oxygen concentrations. The flame-retardant action mainly occurs in the condensed phase. Benefiting from the highly aromatic and rigid backbone of deoxybenzoin/benzene-based structures, these materials possess excellent thermal stability and can rapidly form a dense, continuous char layer upon thermal decomposition. This carbonaceous barrier effectively insulates the substrate from external thermal exposure and oxygen, thereby suppressing further degradation and volatile release. Although studies focusing on the gas-phase flame-retardant mechanism of deoxybenzoin/benzene-based systems remain limited, available evidence suggests that their thermal degradation can produce significant amounts of nonflammable gases such as CO and CO_2. These gases contribute to flame inhibition through dilution of flammable volatiles and oxygen near the combustion zone. Moreover, due to their rigid, conjugated molecular skeletons, deoxybenzoin/benzene-based EPs generally exhibit outstanding mechanical performance, featuring high tensile strength, stiffness, and thermal stability. This combination of intrinsic flame retardancy and robust mechanical performance positions deoxybenzoin/benzene-based systems as promising candidates for high-performance applications in flame-retardant coatings, electronics, and structural composites.

3.3 | C═N-Containing Flame-Retardant EPs

C═N-based flame-retardant EPs have garnered significant interest due to their inherent charring capability and high thermal stability. The imine (C═N) functionality, commonly found in Schiff base and related aromatic structures, significantly contributes to strengthening condensed-phase flame retardancy. Under high-temperature conditions, C═N bonds undergo thermal crosslinking and cyclization reactions, rapidly generating thermally robust carbonaceous residue [80–82]. It forms a protective layer that reduces thermal conduction, shields the polymer beneath, and suppresses the release of flammable gases [83]. Furthermore, the decomposition of nitrogen-containing groups can yield inert gases such as N_2, NH_3, and CO_2, which reduce the concentration of combustible gases near the flame, aiding gas-phase flame suppression [84]. This dual-phase flame-retardant mechanism allows C═N-based epoxy systems to achieve favorable performance in LOI and UL-94 tests, particularly when combined with aromatic or conjugated backbones that enhance structural rigidity.

Nabipour et al. [85, 86] successively developed two inherently flame-retardant epoxy monomers containing C═N bonds, named VTA-EP (Figure 5a) and HMF-GAN-EP (Figure 5d), both of which were cured using DFA to produce thermosetting resins demonstrating superior flame-retardant performance. The VTA-EP/DFA system demonstrated excellent flame inhibition capability, with an LOI value reaching 38.5% and successfully passing the UL-94 test with a V-0 rating (Figure 5b). CCT results further confirmed its effectiveness, with PHRR and THR decreased by 88.4% and 87.8%, respectively, relative to the unmodified EP. In comparison, the HMF-GAN-EP/DFA system showed even more remarkable flame-retardant properties, with an LOI of 40% and a UL-94 V-0 rating. Notably, $t_1 + t_2$ was only 2 s, indicating a highly self-extinguishing nature that rendered the material nearly non-flammable under ambient oxygen conditions. MCC results corroborated this, showing reductions in PHRR and THR of 91.7% and 73.2%, respectively, relative to the conventional DGEBA/DDM system. Besides flame retardancy, both resins showed excellent performance in tensile strength, measuring 60.8 and 67.9 MPa, surpassing the standard DGEBA/DDM. This mechanical enhancement stems from the rigid Schiff base structure and the resulting high crosslinking density, which reinforces the network integrity. Moreover, both VTA-EP/DFA and HMF-GAN-EP/DFA displayed promising degradability due to the dynamic and reversible nature of the C═N bonds in their molecular backbones. As illustrated in Figure 5c, these materials can be fully degraded under mildly acidic conditions, highlighting their potential for environmental sustainability and recyclability.

Xie et al. [87] developed a C═N base-containing epoxy monomer, PH-ODA-EP (Figure 5g), which was subsequently cured with DDM to prepare the intrinsically flame-retardant EP (PH-ODA-EP/DDM). As shown in Figure 5e, this system exhibited a superior LOI of 40.5%, outperforming both VTA-EP/DFA and HMF-GAN-EP/DFA, and successfully earned a V-0 rating according to UL-94 standards. CCT analysis disclosed remarkable flame-retardant efficiency, showing a 90.9% reduction in PHRR and a 72.0% reduction in THR relative to the conventional DGEBA/DDM system. Post-combustion digital photographs (Figure 5h) and SEM images (Figure 5i) of the char residue confirmed the presence of thick, compact carbon-rich residue. This dense char, attributed to the Schiff base and aromatic structures, effectively suppressed heat transfer in the condensed phase [88]. During the gas phase, the release of nonflammable gases further contributed to flame inhibition through self-extinguishing effects. Along with its superior flame resistance, PH-ODA-EP/DDM also demonstrated outstanding mechanical performance. As shown in Figure 5f, its tensile strength reached 103.6 MPa, significantly surpassing that of VTA-EP/DFA and HMF-GAN-EP/DFA. The flexural strength was also remarkably high at 157.9 MPa. The enhancement in mechanical performance is primarily attributed to the rigid molecular structure of PH-ODA-EP and the high crosslinking density achieved through curing with DDM, which together reinforce the polymer network and significantly improve its mechanical strength.

In summary, intrinsically flame-retardant EPs based on C═N structures exhibit outstanding fire resistance. These systems demonstrate significant improvements in LOI, achieve V-0 ratings in UL-94 tests, and show marked reductions in PHRR and THR during CCT, indicating excellent flame inhibition and thermal shielding capabilities. The enhanced performance is predominantly linked to the introduction of C═N moieties into the molecular structure, which not only imparts high thermal stability and char-promoting ability, but also facilitates the creation of a robust, carbon-rich protective layer during decomposition, reinforcing the condensed-phase flame-retardant mechanism. Additionally, the thermal degradation of C═N bonds releases nonflammable gases that dilute combustible volatiles and oxygen, thereby improving flame suppression in the gas phase. Moreover, C═N-based epoxy monomers typically possess rigid, highly aromatic backbones, which contribute to the formation of tightly crosslinked networks upon curing. This structural rigidity contributes to flame resistance while markedly enhancing the mechanical strength and dimensional stability of the resulting materials.

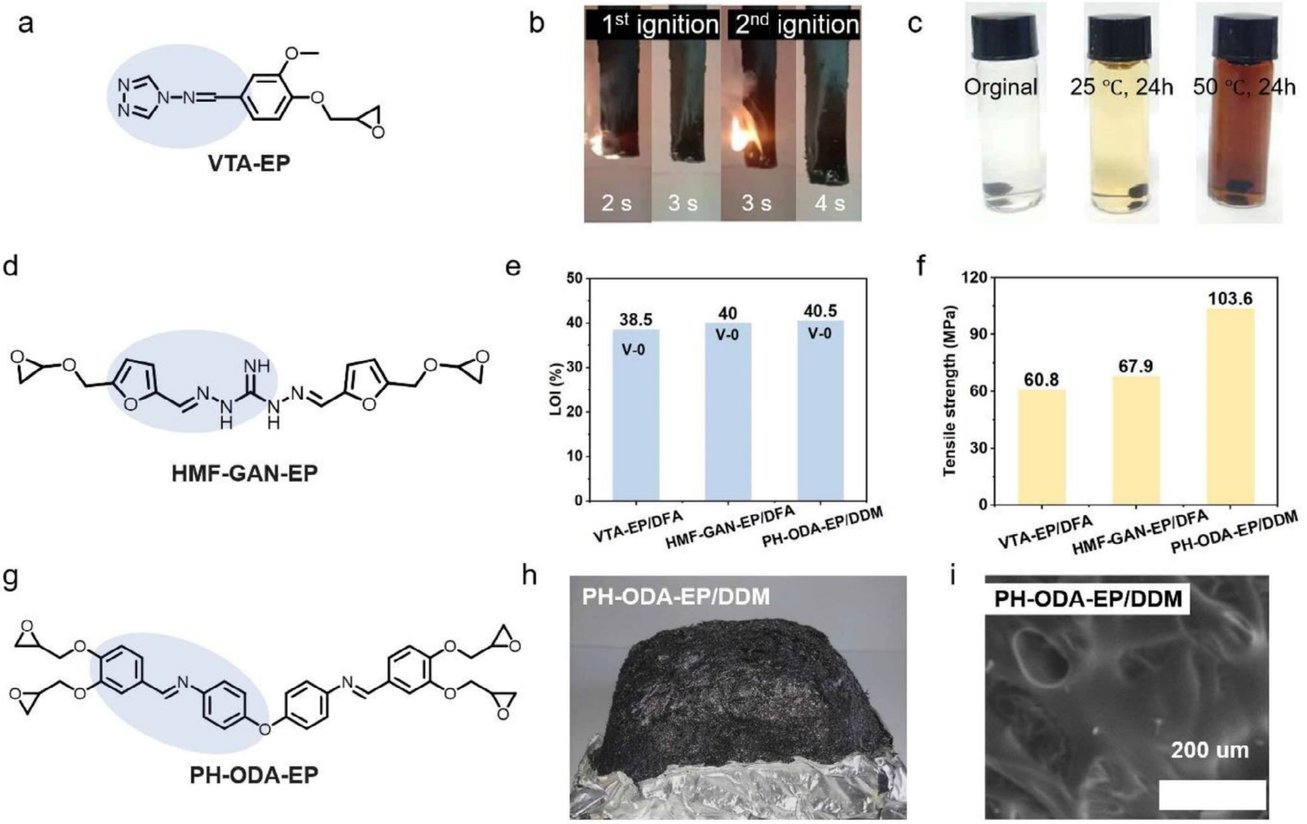

FIGURE 5 | Illustration of chemical structures of (a) VTA-EP [85], Copyright 2021. Reproduced with permission from Elsevier Science Ltd, (d) HMF-GAN-EP [86], Copyright 2023. Reproduced with permission from Elsevier Science Ltd, and (f) PH-ODA-EP [87], Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (b) Digital photos of the VTA-EP/DFA burning process during the UL-94 [85], Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (c) digital photographs of VTA-EP/DFA in 0.1 M sulfuric acid solution (H_2O/DMF (v/v) = 2: 8) [85], Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (e) LOI and UL-94 results of three flame retardant EPs. (f) Tensile strength results of three flame retardant EPs. (h) Digital photos and (i) SEM micrograph of char residue of PH-ODA-EP/DDM after CCT [87], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

3.4 | Benzene/Polyepoxy-Based Flame-Retardant EPs

Benzene/Polyepoxy-based flame-retardant EPs exhibit excellent intrinsic flame retardancy, primarily attributed to the synergistic effects between their highly aromatic benzene-based backbones and multifunctional epoxy groups. These structural features facilitate the formation of a densely crosslinked network during curing. Upon thermal decomposition, the aromatic rings provide outstanding thermal stability, promoting early-stage carbonization and the rapid development of a dense, cohesive char coating [89]. This char barrier effectively blocks thermal conduction and suppresses the emission of flammable gases in the condensed phase. Moreover, the high functionality of polyepoxy groups contributes to increased crosslinking density, which enhances the structural integrity of the cured resin under high temperatures and further improves its thermal shielding capability. The char layer not only isolates the underlying substrate from external oxygen but also suppresses heat feedback during combustion, forming a synergistic "char-thermal insulation" flame-retardant mechanism [90]. During combustion, these resins release non-flammable gases like CO_2 and H_2O that reduce the concentration of flammable species and oxygen around the flame front, thereby enhancing flame inhibition in the gas phase. Collectively, benzene/polyepoxy-based EPs achieve a balanced and efficient flame-retardant performance through dual-action mechanisms in both the condensed and gas phases, making them highly promising candidates for intrinsic flame-retardant systems.

Ou et al. [91] synthesized a benzene-containing trifunctional EP named TEPEU (Figure 6a) using eugenol and subsequently cured it with DDS to prepare a flame-retardant EP, TEPEU/DDS. The rigid aromatic backbone and multiple crosslinking sites endowed the material with a high T_g of 294.5 °C, while maintaining favorable processability. The TEPEU/DDS system reached an LOI value of 28.7% and obtained a UL-94 V-1 rating (Figure 6b). MCC results revealed that, compared with the conventional DGEBA/DDS system, the reductions in PHRR and THR were 29.8% and 40.3%, respectively. This improved fire resistance mainly resulted from the substantial carbonaceous residue generated in the condensed phase, promoted by the aromatic rings and DDS (Figure 6d). SEM images of the char residue following the UL-94 test revealed a smooth, dense, and continuous char layer that efficiently blocked heat and oxygen transfer. During the gas phase, non-flammable CO_2 played a major role in diluting combustible gases. In terms of mechanical properties, the TEPEU/DDS thermoset exhibited enhanced rigidity, with values of 0.407 GPa for hardness and 4.693 GPa for Young's

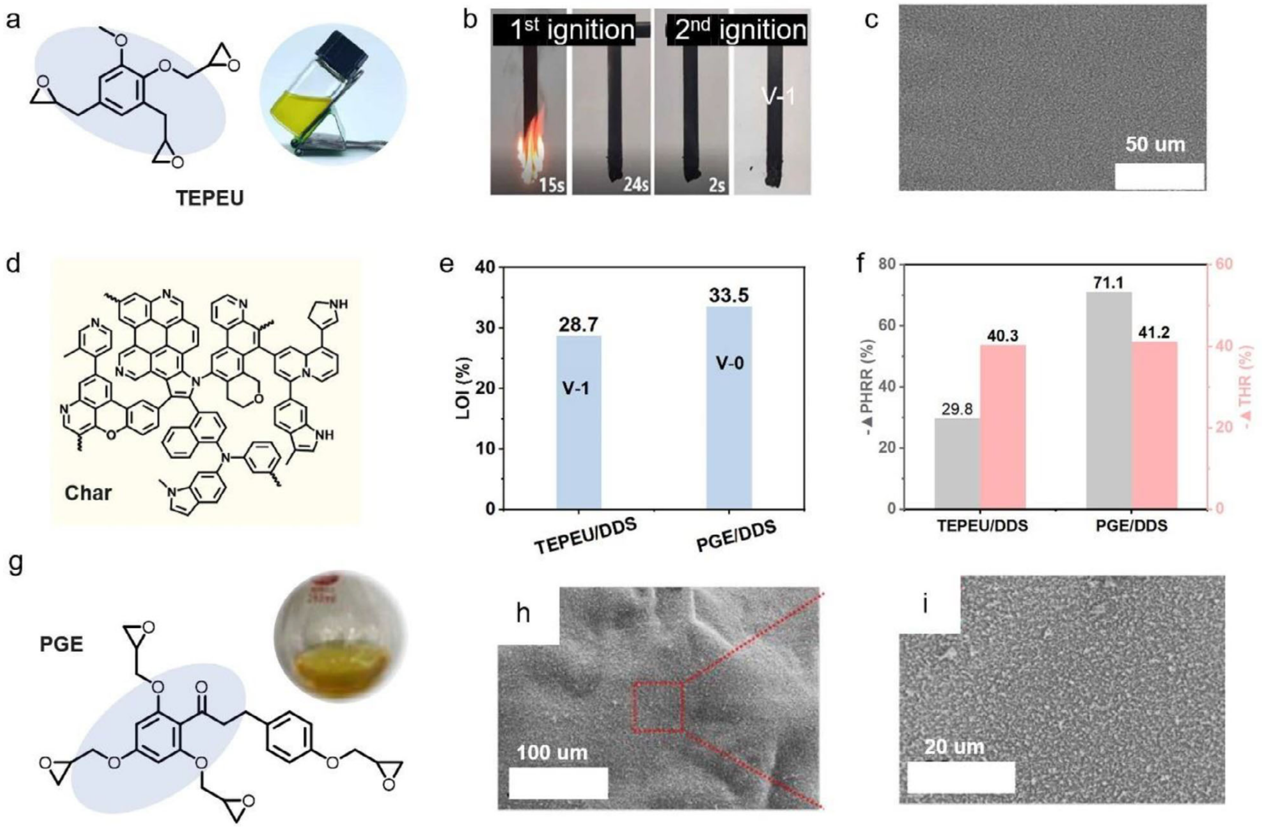

FIGURE 6 | Illustration of chemical structures and digital photos of (a) TEPEU [91], Copyright 2025. Reproduced with permission from Elsevier Science Ltd and (g) PGE [92], Copyright 2023. Reproduced with permission from American Chemical Society. (b) Digital photos of the TEPEU/DDS burning process during the UL-94 [91], Copyright 2025. Reproduced with permission from Elsevier Science Ltd. (c) SEM of char residue of TEPEU/DDS after CCT [91], Copyright 2025. Reproduced with permission from Elsevier Science Ltd. (d) Chemical structures of char residue [91], Copyright 2025. Reproduced with permission from Elsevier Science Ltd. (e) LOI and UL-94 results of TEPEU/DDS and PGE/DDS. (f) -△PHRR and -△THR results of TEPEU/DDS and PGE/DDS. (h-i) SEM micrograph of char residue of PGE/DDS after UL-94 [92], Copyright 2023. Reproduced with permission from American Chemical Society.

modulus, both markedly exceeding the corresponding 0.273 and 3.327 GPa measured for the conventional DGEBA/DDS system, indicating improved resistance to deformation. However, the measured impact resistance was slightly reduced compared to the conventional system, with a marginal decline observed in the TEPEU-based formulation. This decrease in toughness likely stems from the denser crosslinked structure, which hinders polymer chain movement and reduces the material's capacity to absorb and dissipate energy during sudden mechanical stress. Consequently, while the TEPEU/DDS system excels in rigidity and structural strength, it experiences a trade-off in terms of impact durability.

Ying et al. [92] synthesized a tetrafunctional EP (PGE) using pinoresinol as a bio-based precursor (Figure 6g). After curing with DDS, the resulting flame-retardant epoxy thermoset (PGE/DDS) exhibited a high T_g of approximately 259.2 °C, owing to its rigid molecular backbone. As shown in Figure 6e, compared with the TEPEU/DDS system, PGE/DDS demonstrated superior flame retardancy, achieving an elevated LOI value of 33.5% along with a UL-94 classification of V-0. In terms of combustion behavior (Figure 6f), PGE/DDS showed enhanced heat suppression performance. MCC results indicated that, relative to the conventional DGEBA/DDS system, the PHRR and THR of PGE/DDS decreased significantly by 71.1% and 41.2%, respectively. Post-UL-94 SEM analysis (Figures 6h–i) revealed a compact and uniform char layer generated during combustion, which is closely associated with the rigid aromatic structure. Most aromatic fragments retained in the condensed phase helped stabilize the resulting carbon-rich residues. This protective char barrier effectively inhibited the release of flammable volatiles, thereby enhancing flame resistance. Production of inert gases during the gas-phase reactions further helped suppress combustion by diluting flammable species. Regarding mechanical performance, PGE/DDS outperformed the DGEBA/DDS system. The Young's modulus of PGE/DDS reached 5.41 GPa, significantly higher than that of DGEBA/DDS (3.92 GPa). Additionally, the hardness increased by approximately 25%, from 0.28 to 0.35 GPa. These improvements are a consequence of the increased crosslinking density and chain rigidity of the PGE-based network.

In summary, for benzene/polyepoxy-based flame-retardant EP systems, structures containing a single benzene ring generally exhibit limited flame-retardant performance. This is primarily because multi-aromatic ring structures tend to undergo thermal rearrangement more readily during decomposition, resulting in robust char networks that significantly strengthen thermal shielding in the condensed stage. Additionally, such structures

TABLE 2 | Summary of comprehensive performances of the intrinsically phosphorus-free flame-retardant EPs.

Ref.	Flame-retardant group	Sample name	LOI (%)	UL-94 rating	-△ pHRR (%)	-△ THR (%)	-△ TSP (%)	Tensile strength (MPa)	Flexural strength (MPa)
[70]	C=C and benzene	HCA-EP-DDM	32.6	V-1	59.8	33.7	29.9	98.3	158.9
[69]	C=C and benzene	RESEP/DDM	31.8	V-0	NA	NA	NA	76.0	NA
[67]	C=C and benzene	DGEC/DDS	NA	V-0	NA	NA	NA	65.9	NA
[78]	Deoxybenzoin and benzene	DGEG/DDM	33.1	V-0	36.9	48.5	64.4	92	141
[79]	Deoxybenzoin and benzene	DGELU/DFA	38.0	V-0	NA	NA	NA	66.3	NA
[85]	C=N	HMF-GAN-EP/DFA	40.0	V-0	NA	NA	NA	67.9	NA
[87]	C=N	PH-ODA-EP/DDM	40.5	V-0	90.9	72.0	NA	103.6	157.9
[86]	C=N	VTA-EP/DFA	38.5	V-0	88.4	87.8	NA	60.8	NA
[91]	Benzene and polyepoxy	TEPEU/DDS	28.7	V-1	NA	NA	NA	NA	NA
[92]	Benzene and polyepoxy	PGE/DDS	33.5	V-0	NA	NA	NA	NA	NA

contribute to improved thermal stability and provide potential gas-phase flame-retardant synergy. While the number of epoxy groups does not directly determine flame retardancy, it significantly influences the crosslinking density and thermal degradation behavior of the cured network, thereby indirectly affecting the flame-retardant properties. Overall, the quantity and distribution of aromatic units remain the dominant factors governing flame-retardant performance. Therefore, molecular designs that incorporate multiple aromatic rings along with high epoxy functionality are generally more effective in achieving improved flame-retardant performances. Multifunctional groups and rigid molecular frameworks contribute significantly to improved structural performance, reflected in elevated stiffness and enhanced surface durability. However, this structural modification inevitably compromises the material's flexibility. Specifically, the elevated crosslinking density and rigid chain segments restrict molecular mobility, thereby reducing the material's ability to dissipate energy under stress. As a result, the elongation at break and impact resistance tend to decrease. Therefore, achieving a balance between mechanical rigidity and toughness remains a key consideration in the structural design of high-performance thermosetting resins.

3.5 | Summary of Intrinsically Phosphorus-Free Flame-Retardant EPs

According to Table 2, phosphorus-free flame-retardant EPs generally exhibit favourable flame-retardant performance, primarily attributed to the high content of rigid structures within their molecular framework. These rigid moieties facilitate the development of robust and compact char layers upon thermal decomposition, greatly improving the material's ability to resist combustion in the condensed phase. Meanwhile, a high crosslinking density indirectly contributes to flame retardancy by improving the structural compactness and thermal stability of the epoxy network. This enhancement facilitates carbonization at elevated temperatures, leading to the development of continuous and dense char layers. Such char layers effectively block oxygen and heat transfer, reinforcing the condensed-phase flame-retardant mechanism. Additionally, the highly crosslinked network restricts the release of combustible low-molecular-weight volatiles, thereby reducing the concentration of flammable gases during combustion. Therefore, high crosslinking density indirectly boosts flame retardancy by optimizing thermal degradation behavior and promoting char formation. In contrast, gas-phase flame suppression is modest and primarily depends on diluting flammable volatiles to inhibit combustion. In summary, phosphorus-free EPs mainly rely on protective char formation in the condensed phase, enhanced by the combined effect of inert gases released in the gas phase. For mechanical properties, phosphorus-free flame-retardant EPs exhibit relatively high mechanical strength, mainly attributed to the abundant rigid aromatic frameworks and high crosslinking density. These factors collectively enhance the material's rigidity and network compactness, resulting in increased tensile modulus and hardness. However, the presence of rigid structures often restricts the mobility of molecular chains, which may cause a reduction in elongation at break and consequently adversely affect the material's toughness.

4 | Overview of Phosphorus-Free Flame-Retardant Strategies

Table 3 provides a comprehensive overview of various phosphorus-free flame-retardant strategies, highlighting their respective advantages and limitations to offer a clear comparison of their performance and applicability. Phosphorus-free additive FRs (Figure 7a) possess significant advantages, including simple synthesis processes and ease of application. Their synthetic routes are generally straightforward, characterized by mild reaction conditions, abundant raw materials, and low cost, rendering them suitable for large-scale industrial production. In practical applications, these FRs can be directly incorporated into EP matrices as additives, demonstrating excellent processing compatibility. Despite the absence of phosphorus, phosphorus-

TABLE 3 | Overview of the phosphorus-free flame-retardant strategies with their corresponding advantages and shortcomings.

Strategies	Advantages	Limitation
Additive phosphorus-free FRs	✓ Easy to synthesize and apply ✓ Good flame-retardant effect	• High loading levels • Adversely effects on mechanical properties and transparency • Poor compatibility with EP
Intrinsically phosphorus-free flame-retardant EPs	✓ No additional FRs needed ✓ Biobased ingredient ✓ Good flame-retardant performance ✓ Good thermal stability and mechanical robustness	• High cost • Complex preparation process • Unsatisfactory toughness

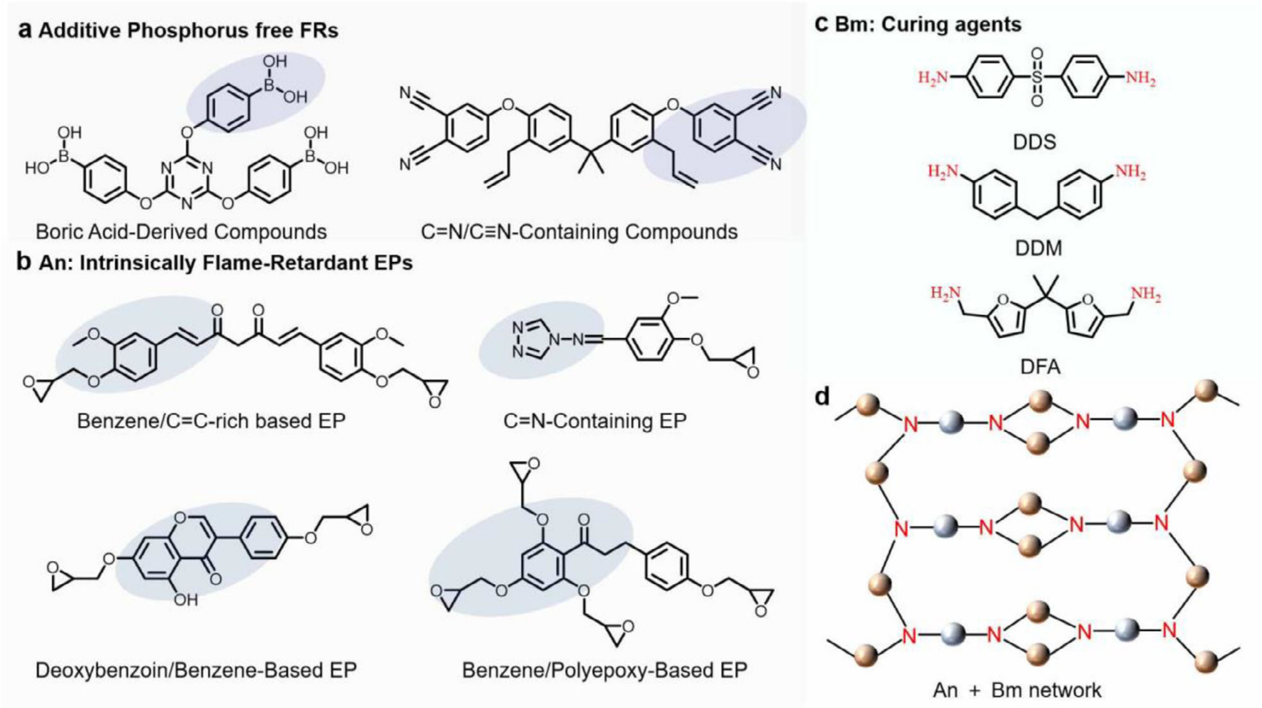

FIGURE 7 | The chemical structures of representative (a) additive phosphorus-free FRs, (b) intrinsically phosphorus-free flame-retardant EPs, and (c) curing agents. (d) Schematic diagram of the cross-linked (An + Bm) network [1].

free FRs achieve flame retardancy through multiple mechanisms such as physical barrier effects, heat absorption, and intumescent char formation. For instance, compounds containing borate ester and $C{=}N/C{\equiv}N$ groups can significantly enhance the LOI and UL-94 rating, reduce the heat release, and prolong the ignition time, thereby effectively improving the overall fire safety performance of the material. However, phosphorus-free FRs have certain limitations. To meet specified flame retardant standards (e.g., UL-94 V-0, and LOI > 28%), relatively high loading levels (typically exceeding 20 wt.%) are usually required, which not only increases material costs but also poses challenges to processing and final material properties. Moreover, high additive content often induces interfacial defects and stress concentrations within the polymer matrix, thereby diminishing tensile strength, impact toughness, and other mechanical properties. Additionally, high loading levels of phosphorus-free FRs usually reduce the transparency of EPs, limiting their applications in optical and electronic packaging fields that require high transparency. Furthermore, as phosphorus-free FRs are mostly macromolecular additives, their compatibility with EP is relatively poor, frequently leading to uneven dispersion, sedimentation, and agglomeration, which adversely affect flame retardancy and comprehensive performances.

Intrinsic phosphorus-free flame-retardant epoxy resins (Figure 7b), when cured with the curing agents shown in Figure 7c, form a highly cross-linked (An + Bm) network as illustrated in Figure 7d. A key advantage of this system is its ability to achieve excellent flame retardancy intrinsically, without the need for additional flame-retardant additives. Their LOI can readily reach 30%, and the UL-94 rating can attain V-0, thereby circumventing common compatibility and dispersion issues associated with additive phosphorus-free FRs. This markedly enhances the overall uniformity and thermal stability. In addition, intrinsic phosphorus-free flame-retardant EPs are commonly derived from bio-based sources and serve as sustainable alternatives to bisphenol A-based systems, promoting green and environmentally responsible development. Moreover, these EPs typically demonstrate superior thermal stability and excellent mechanical properties, maintaining material strength and rigidity while ensuring outstanding flame-retardant performance, thus meeting the stringent requirements of high-performance engineering applications. However, the preparation processes for intrinsic phosphorus-free flame-retardant EPs have yet to be industrialized, facing certain technical barriers and challenges in scalable production, which result in relatively high manufacturing costs and limit their widespread adoption in industrialization. Additionally, these materials exhibit deficiencies in toughness; compared with conventional EPs, they show reduced elongation at break and impact strength, which restricts their suitability for applications demanding high toughness and deformability. In summary, although intrinsic phosphorus-free flame-retardant EPs excel in flame retardancy and comprehensive mechanical performance, their high cost, processing difficulties, and insufficient mechanical toughness must be addressed through molecular design and process optimization to enable broader application and commercialization.

In addition to EPs, phosphorus-free flame-retardant strategies have also been actively investigated in other polymer systems, such as polyurethane and polypropylene. For example, Luo et al. [93] demonstrated that strongly nucleophilic potassium salts, such as potassium formate and potassium maleate, can induce molecular rearrangements and thus catalyze self-pyrolysis of polymers. This process facilitates the proactive release of carbon dioxide before ignition, thereby achieving intrinsic flame retardancy in polyurethane materials. Furthermore, isocyanurate-based flame retardants offer high thermal stability, excellent char-forming ability, and good compatibility, making them promising candidates for halogen- and phosphorus-free flame-retardant systems. Chen et al. [94]. synthesized a novel tris(2-hydroxyethyl) isocyanurate-based char-forming agent via melt polycondensation using tris(2-hydroxyethyl) isocyanurate. When applied to polypropylene, the resulting composite exhibited excellent charring ability and flame-retardant performance, as evidenced by improved LOI values and UL-94 ratings. Therefore, these works highlight the potential of phosphorus-free flame retardants in diverse polymeric materials.

5 | Conclusions and Perspectives

5.1 | Conclusions

Driven by the principles of sustainable development and green chemistry, phosphorus-free flame-retardant systems have become a promising research focus for enhancing the flame retardancy of polymers. Unlike traditional phosphorus-based FRs, phosphorus-free alternatives effectively prevent the generation of toxic, corrosive, and environmentally harmful byproducts during burning, providing better ecological safety. This makes them particularly attractive for applications requiring environmentally friendly and low-toxicity materials. This review centers on the structure–property relationship, systematically summarizing and comparing representative phosphorus-free flame-retardant strategies in EP systems. Emphasis is placed on elucidating the mechanisms by which these molecular designs influence flame retardancy, thermal stability, mechanical strength, and other critical performance characteristics. Studies have shown that the incorporation of rigid aromatic backbones, multi-functional groups, or highly crosslinked networks enables phosphorus-free EPs to generate thick and resilient char structures, which effectively insulate heat and block flammable volatiles. Simultaneously, such structural features help maintain mechanical strength without compromising thermal performance. With the synergistic advancement of molecular engineering and integrated structural-function design, phosphorus-free flame-retardant EPs hold great potential for broader applications in high-performance, low-environmental-impact functional materials.

5.2 | Challenges

Despite significant advancements in the phosphorus-free flame-retardant strategies for EPs, several challenges remain:

(1) Complexity in Molecular Design, Synthesis, and Scalability Issues: Phosphorus-free FRs and intrinsically flame-retardant EPs often rely on rigid aromatic frameworks or multifunctional structures to achieve superior thermal stability and char-forming ability. However, these molecular architectures typically involve lengthy and complex synthetic routes with high raw material costs, making the process difficult to scale up industrially. Currently, many high-performance phosphorus-free flame-retardant systems remain at the laboratory research stage. The expensive starting materials, intricate synthesis procedures, and potential environmental concerns significantly hinder their commercialization and broader practical application.

(2) Compromised Toughness and Flexibility: To improve char-forming ability and thermal resistance, rigid molecular segments and highly crosslinked networks are commonly introduced. While effective in enhancing flame retardancy, these structural features often restrict polymer chain mobility, resulting in reduced toughness and inferior impact resistance. Balancing flame retardancy with mechanical toughness remains a key challenge.

(3) Lower Flame Retardancy Than Phosphorus-Containing Systems: Phosphorus-free flame-retardant systems, especially additive-type Phosphorus-Free FRs, generally exhibit lower flame retardancy compared to phosphorus-containing systems. This is likely attributed to their insufficient gas-phase flame inhibition effects, as reflected in lower LOI values and inferior UL-94 classifications.

5.3 | Opportunities

(1) AI-Driven Design and Process Optimization of Phosphorus-Free Flame-Retardant EPs: The application of AI-assisted design, particularly machine learning and deep learning algorithms, enables the identification of more efficient and cost-effective raw material combinations. Furthermore, these techniques can simulate and predict synthesis reaction conditions and pathways, assisting researchers in planning optimal synthetic routes and forecasting key material properties such as flame retardancy and mechanical performance [95–98]. This approach significantly reduces experimental time and resource consumption. In terms of large-scale production, AI-driven process optimization facilitates the evaluation of reaction controllability and industrial adaptability, thereby promoting the scale-up and refinement of synthesis procedures, lowering production costs, and minimizing environmental impacts.

(2) Balancing Flame Retardancy with Mechanical Toughness: To address the trade-off between flame retardancy and mechanical toughness, two main strategies have been proposed. First, the incorporation of flexible chain segments (e.g., siloxane units) or dynamic covalent bonds (e.g., Diels–Alder linkages) into the polymer structure imparts appropriate chain mobility and stress-relaxation capacity, thereby significantly improving the elongation at break and impact toughness of the material. Second, the synergistic integration of nanofillers (such as graphene, MXene, etc.) not only builds micro-scale thermal and mass transfer barriers that enhance the compactness of the char layer and further reinforce flame retardancy, but also markedly improves the overall mechanical strength and toughness through interfacial interactions and nano-reinforcement mechanisms [99–101].

(3) Multiscale Characterization and Modeling for Mechanistic Insights into Phosphorus-Free Flame-Retardant Mechanisms: Current research generally attributes the flame-retardant performance of phosphorus-free materials to the formation of dense char layers in the condensed phase. However, the detailed reaction pathways and structural evolution mechanisms remain insufficiently understood. To gain deeper mechanistic insights, it is essential to integrate multiscale characterization techniques, such as TG-FTIR, Raman spectroscopy, XPS, and SEM, with theoretical approaches including molecular dynamics simulations and pyrolysis kinetics modeling. This combined strategy enables comprehensive analysis of microstructural transformations, thermal degradation behavior, and gas-condensed phase interactions during combustion [102]. Such mechanistic studies will provide a solid theoretical basis to guide the targeted creation of phosphorus-free flame retardants, promoting their accurate formulation and broad implementation of efficient flame-retardant systems.

Acknowledgements

The authors acknowledge the financial support received from the Australian Research Council (Nos. LP220100278, DP240102628, DE230100616, and DP230103008, IM250100102).

Open access publishing facilitated by University of Southern Queensland, as part of the Wiley - University of Southern Queensland agreement via the Council of Australian University Librarians.

Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

References

1. Y. Guo, Q. Yang, S. Huo, et al., “Recyclable Fire-Retardant Bio-Based Thermosets: From Molecular Engineering to Performances and Applications,” *Progress in Polymer Science* 2025, 162, 101935.
2. Q. S. Yang, J. Wang, X. Chen, et al., “A Phosphorus-Containing Tertiary Amine Hardener Enabled Flame Retardant, Heat Resistant and Mechanically Strong yet Tough Epoxy Resins,” *Chemical Engineering Journal* 468 (2023): 143811.
3. G. F. Ye, S. Q. Huo, C. Wang, et al., “Strong yet Tough Catalyst-Free Transesterification Vitrimer with Excellent Fire-Retardancy, Durability, and Closed-Loop Recyclability,” *Small* 20 (2024): 2404634.
4. C. Wang, G. F. Ye, Q. Zhang, H. Wang, S. Q. Huo, and Z. T. Liu, “Closed-Loop Recyclable, Self-Catalytic Transesterification Vitrimer Coatings with Superior Adhesive Strength, Fire Retardancy, and Environmental Stability,” *ACS Materials Letters* 7 (2024): 210.
5. H. Wang, S. Q. Huo, V. Chevali, et al., “Carbon Fiber Reinforced Thermoplastics: from Materials to Manufacturing and Applications,” *Advanced Materials* 37 (2025): 2418709.
6. P. F. Liu, X. Wang, X. W. Jiang, et al., “A High-Performance Flame Retardant Liquid Synthesized on the Basis of DOPO Hydrolysis Products Avoids the Defects of DOPO,” *Polymer Degradation and Stability* 232 (2025): 111116.
7. G. F. Ye, S. Q. Huo, C. Wang, et al., “Durable Flame-Retardant, Strong and Tough Epoxy Resins with Well-Preserved Thermal and Optical Properties via Introducing a Bio-Based, Phosphorus-Phosphorus, Hyperbranched Oligomer,” *Polymer Degradation and Stability* 207 (2023): 110235.
8. Q. Chen, L. Liu, A. L. Zhang, et al., “An Iron Phenylphosphinate@Graphene Oxide Nanohybrid Enabled Flame-Retardant, Mechanically Reinforced, and Thermally Conductive Epoxy Nanocomposites,” *Chemical Engineering Journal* 454 (2023): 140424.
9. S. Q. Huo, P. A. Song, B. Yu, et al., “Phosphorus-Containing Flame Retardant Epoxy Thermosets: Recent Advances and Future Perspectives,” *Progress in Polymer Science* 2021, 114, 101366.
10. N. N. Song, Y. F. Suo, F. Rong, et al., “Construction of an Organic Iron Phosphate/Graphite Carbon Nitride Hybrid System for Improved Fire Safety of Epoxy Resin,” *Materials Today Sustainability* 26 (2024): 100789.
11. N. N. Song, Z. W. Chen, Y. Yu, et al., “Electrolytic Manganese Residue to Metal Phosphides via Ball Milling: Enhancing Flame Retardancy, Mechanical Properties, and Electrical Conductivity of Epoxy Resin,” *Applied Surface Science* 638 (2023): 158154.
12. G. F. Ye, S. Q. Huo, C. Wang, et al., “A Transparent Epoxy Vitrimer with Outstanding Flame Retardancy, Toughness, and Recyclability Enabled by a Hyperbranched P/N-Derived Polyester,” *Construction and Building Materials* 2025, 470, 140673.
13. B. R. Yang, N. N. Song, Z. W. Chen, et al., “Fabrication of a Cinnamaldehyde-Based bi-DOPO Flame Retardant with Excellent Glass Transition Temperature, Fire Safety and Mechanical Properties for Epoxy Resins,” *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 681 (2024): 132815.
14. Z. W. Ma, J. B. Feng, S. Q. Huo, et al., “Mussel-Inspired, Self-Healing, Highly Effective Fully Polymeric Fire-Retardant Coatings Enabled by Group Synergy,” *Advanced Materials* 36 (2024): 2410453.
15. Y. Guo, Z. W. Chen, Y. Yu, et al., “A New-Type Terephthalonitrile Derivative Flame Retardant of bi-DOPO Compound with Hydroxyl and Amino Groups on Epoxy Resin,” *Journal of Applied Polymer Science* 139 (2022): 52209.

16. C. Li, Z. T. Ba, B. C. Wu, et al., “Bio-Inspired Construction of Hydrophobic Mg(OH)2/Co-MOF/DOPO Hybrids for Simultaneously Improving Flame Retardancy and Mechanical Properties of Poly(L-Lactic acid) Composites,” *Chemical Engineering Journal* 504 (2025): 158853.

17. H. N. Wang, S. Q. Huo, C. Wang, et al., “A P/N/Si-Containing Hyperbranched Flame Retardant for Improving Mechanical Performances, Fire Safety, and UV Resistance of Epoxy Resins,” *Progress in Organic Coatings* 193 (2024): 108562.

18. J. S. Wang, J. Wang, S. Yang, et al., “Phosphorus-Derived Imidazolium Salts with Varied Oxidation States: Tailoring Latency, Mechanical Properties, and Flame Retardancy in Single-Component Epoxy Resins,” *Polymer Degradation and Stability* 237 (2025): 111325.

19. X. N. Zhang, T. Bai, P. C. Zhou, et al., “Non-Phosphorus Glucosyl Schiff Bases for Smoke Inhibition and Mechanical Enhancement of Epoxy Resin Composites,” *Polymer Degradation and Stability* 223 (2024): 110715.

20. Z. W. Chen, Y. Guo, Y. P. Chu, et al., “Solvent-Free and Electron Transfer-Induced Phosphorus and Nitrogen-Containing Heterostructures for Multifunctional Epoxy Resin,” *Composites Part B: Engineering* 240 (2022): 109999.

21. H. Rong, Y. Guo, Z. W. Chen, et al., “Synergistic Effect of Phenyl Phosphoric Acid Derivatives and DOPO on Multifunctional Epoxy Resin: Fire Safety, Mechanical Properties, Transparency and Hydrophobicity,” *Polymer Degradation and Stability* 216 (2023): 110471.

22. B. X. Du, Z. H. Guo, P. A. Song, H. Liu, Z. P. Fang, and Y. Wu, “Flame Retardant Mechanism of Organo-Bentonite in Polypropylene,” *Applied Clay Science* 45 (2009): 178–184.

23. G. F. Ye, S. Q. Huo, C. Wang, et al., “Fabrication of Flame-Retardant, Strong, and Tough Epoxy Resins by Solvent-Free Polymerization with Bioderived, Reactive Flame Retardant,” *Sustainable Materials and Technologies* 2024, 39, 00853.

24. J. S. Wang, J. Wang, S. Yang, et al., “Development of Single-Component Epoxy Resin with Superb Thermal Stability, Flame Retardancy, Smoke Suppression, and Latency via Cu-Based Phosphorus/Imidazole-Containing Complex,” *Polymer Degradation and Stability* 228 (2024): 110906.

25. C. Wang, S. Q. Huo, G. F. Ye, et al., “Construction of an Epoxidized, Phosphorus-Based Poly(styrene butadiene styrene) and Its Application in High-Performance Epoxy Resin,” *Composites Part B: Engineering* 268 (2024): 111075.

26. C. Wang, S. Q. Huo, G. F. Ye, et al., “Strong Self-Healing Close-Loop Recyclable Vitrimers via Complementary Dynamic Covalent/Non-Covalent Bonding,” *Chemical Engineering Journal* 500 (2024): 157418.

27. T. Chu, Y. X. Lu, B. Y. Hou, et al., “Engineering Amine-Modified Ammonium Polyphosphate for Enhancing Flame Retardancy and Smoke Suppression of Vinyl Ester Resin,” *Construction and Building Materials* 475 (2025): 141174.

28. Y. Guo, H. Rong, Y. Yu, et al., “A Facile Method for Synthesis of Novel Phenyl Phosphates Flame Retardants and Their Application in Epoxy Resin,” *Journal of Applied Polymer Science* 139 (2022): 53100.

29. Q. Chen, J. B. Feng, Y. J. Xue, et al., “An Engineered Heterostructured Trinity Enables Fire-Safe, Thermally Conductive Polymer Nanocomposite Films with Low Dielectric Loss,” *Nano-Micro Letters* 17 (2025): 168.

30. S. Gaan, G. Sun, K. Hutches, and M. Engelhard, “Effect of Nitrogen Additives on Flame Retardant Action of Tributyl Phosphate: Phosphorus–nitrogen Synergism,”*Polymer Degradation and Stability* 2008, 93, 99–108.

31. S. Deh, F. Gähr, and M. Buchmeiser, “Synergistic Effects in the Pyrolysis of Phosphorus-Based Flame-Retardants: the Role of Si- and N-Based Compounds,” *Polymer Degradation and Stability* 2016, 130, 155–164.

32. J. Alongi, C. Colleoni, G. Rosace, and G. Malucelli, “Phosphorus- and Nitrogen-Doped Silica Coatings for Enhancing the Flame Retardancy of Cotton: Synergisms or Additive Effects?,” *Polymer Degradation and Stability* 98 (2013): 579–589.

33. I. van der Veen and J. de Boer, “Phosphorus Flame Retardants: Properties, Production, Environmental Occurrence, Toxicity and Analysis,” *Chemosphere* 88 (2012): 1119.

34. S. W. Yuan, Y. N. Han, M. Ma, et al., “Aryl-Phosphorus-Containing Flame Retardants Induce Oxidative Stress, the p53-Dependent DNA Damage Response and Mitochondrial Impairment in A549 Cells,” *Environmental Pollution* 250 (2019): 58–67.

35. Q. Zhang, C. Y. Ji, X. H. Yin, L. Yan, M. Y. Lu, and M. R. Zhao, “Thyroid Hormone-Disrupting Activity and Ecological Risk Assessment of Phosphorus-Containing Flame Retardants by in Vitro, in Vivo and in Silico Approaches,” *Environmental Pollution* 210 (2016): 27–33.

36. Q. Zhang, M. Y. Lu, X. W. Dong, et al., “Potential Estrogenic Effects of Phosphorus-Containing Flame Retardants,” *Environmental Science & Technology* 48 (2014): 6995.

37. Y. X. Lu, T. Chu, S. Q. Huo, et al., “Green Synthesis of a P/N/B-Containing Aggregate for Boosting Fire-Retardancy of PA6/Aluminum Diethylphosphinate Composites,” *Polymer Degradation and Stability* 229 (2024): 110949.

38. R. Liu, Y. F. Zhang, Z. Li, R. Wang, and H. X. Yan, “Si, B-Containing Dynamic Covalent Bonds Enable Excellent Flame Retardancy and Reduced Fire Hazards for Cyanate Ester Resin,” *Materials Horizons* 11 (2024): 5094.

39. C. L. He, Y. Guo, X. D. Zhang, et al., “A Phosphorus/Nitrogen/Boron co-Curing Agent for Enhancing Flame Retardancy, Mechanical Properties Transparency of Epoxy Resin,” *Progress in Organic Coatings* 195 (2024): 108667.

40. H. F. Chen, G. Z. Ji, F. Y. Lan, et al., “B/P/N Flame Retardant Based on Diboraspiro Rings Groups for Improving the Flame Retardancy, Char Formation Properties and Thermal Stability of Cotton Fabrics,” *International Journal of Biological Macromolecules* 270 (2024): 132330.

41. C. Chen, J. X. Luan, F. Y. Lan, et al., “Construction and Application of B/P/N Durable Flame Retardant Crosslinking System on Cotton Fabric,” *Industrial Crops and Products* 222 (2024): 119623.

42. Y. B. Zhang, R. Liu, R. Z. Yu, K. M. Yang, L. L. Guo, and H. X. Yan, “Phosphorus-Free Hyperbranched Polyborate Flame Retardant: Ultra-High Strength and Toughness, Reduced Fire Hazards and Unexpected Transparency for Epoxy Resin,” *Composites Part B: Engineering* 242 (2022): 110101.

43. J. F. Zhang, J. Liu, W. W. Gu, et al., “Preparation of Flame-Retardant and Toughened Polycarbonate via Reactive Blending of Polyborosiloxane Elastomer,” *Composites Part A: Applied Science and Manufacturing* 187 (2024): 108505.

44. Z. Zhang, S. H. Wang, X. Jin, et al., “Preparation and Application of Durable and Efficient Flame Retardants: Phosphorus–nitrogen–boron Synergistic Effect, Flame Retardant Properties, Combustion Behavior and Mechanical Properties,” *Cellulose* 31 (2024): 1891.

45. H. L. He, Q. Jiang, Y. H. Wan, et al., “Biological Skin-Inspired Damage Warning and Self-Healing Thermoelectric Aerogel fiber via Coaxial Wet Spinning for Wearable Temperature Sensing,” *Journal of Materials Science & Technology* 250 (2026): 257–271.

46. Z. C. Yu, Y. H. Wan, M. Zhou, et al., “Muscle-Inspired Anisotropic Aramid Nanofibers Aerogel Exhibiting High-Efficiency Thermoelectric Conversion and Precise Temperature Monitoring for Firefighting Clothing,” *Nano-Micro Letters* 17 (2025): 214.

47. S. S. Chen, L. H. Ai, T. Zhang, et al., “Synthesis and Application of a Triazine Derivative Containing Boron as Flame Retardant in Epoxy Resins,” *Arabian Journal of Chemistry* 13 (2020): 2982.

48. X. L. Sha, X. Z. Yang, S. P. Fang, Z. Y. Yang, Z. T. Liu, and Z. H. Fei, “Three Birds with One Stone: Halogen- and Phosphorus-Free Flame-Retardant Thermosetting Resins with High Heat Resistance and Excellent

Mechanical Properties Based on Simple Biobased Feedstocks," *Chemical Engineering Journal* 505 (2025): 158851.

49. S. Q. Huo, T. Sai, S. Y. Ran, et al., "A Hyperbranched P/N/B-Containing Oligomer as Multifunctional Flame Retardant for Epoxy Resins," *Composites Part B: Engineering* 234 (2022): 109701.

50. S. Q. Huo, Z. X. Zhou, J. W. Jiang, et al., "Flame-Retardant, Transparent, Mechanically-Strong and Tough Epoxy Resin Enabled by High-Efficiency Multifunctional Boron-Based Polyphosphonamide," *Chemical Engineering Journal* 427 (2022): 131578.

51. Y. Guo, H. M. Yang, H. Rong, et al., "Hydrophobicity, Transparency, Mechanically Excellent and Fire Safety Multifunctional Epoxy Resin Based on a Novel DOPO Derivative with Cyano Group," *Progress in Organic Coatings* 185 (2023): 107897.

52. J. W. Li, Q. J. Ma, Q. Y. Liu, and P. L. Zheng, "A P/N Synergistic Flame Retardant Containing Flexible Nitrile Group for Enhancing the Mechanical Properties and Fire Safety of Epoxy Resins," *Journal of Applied Polymer Science* 141 (2024): 54842.

53. N. N. Song, J. Li, B. R. Yang, et al., "Advancing Flame Retardancy, Mechanical Properties, and Hydrophobicity of Epoxy Resins through Bio-Based Cinnamaldehyde Derivative," *Journal of Industrial and Engineering Chemistry* 139 (2024): 185–198.

54. Y. Guo, H. Rong, Z. W. Chen, et al., "A Novel DOPO Derivative Containing Multifunctional Groups Aiming to Improve Fire Safety, Thermal Stability and Curing state towards Epoxy Resin," *Polymer Degradation and Stability* 205 (2022): 110142.

55. R. P. Wang, S. Zhang, S. Du, et al., "Glass-Blowing-Inspired Constructing a Novel Ceramizable Intumescent Flame Retardant for Realizing Superior Flame Retardancy, Smoke Suppression and Water Resistance of Polyethylene Composites," *Composites Part A: Applied Science and Manufacturing* 190 (2025): 108687.

56. H. X. Cheng, J. H. Guo, Y. Ye, et al., "Molecular Design and Properties of Intrinsic Flame-Retardant P-N Synergistic Epoxy Resin," *Journal of Applied Polymer Science* 141 (2024): 54885.

57. Z. Wang, S. Wang, H. F. Chen, et al., "Preparation and Thermostability of a Si/P/N Synergistic Flame Retardant Containing Triazine Ring Structure for Cotton Fabrics," *International Journal of Biological Macromolecules* 260 (2024): 129497.

58. J. B. Feng, Z. W. Ma, J. P. Wu, et al., "Fire-Safe Aerogels and Foams for Thermal Insulation: from Materials to Properties," *Advanced Materials* 34 (2024): 2411856.

59. Y. Wang, L. Zhang, J. H. Liu, et al., "Multi-Functional Flame-Retardant Epoxy Resin Featuring Diverse Crosslinking Networks," *Chemical Engineering Journal* 499 (2024): 156143.

60. Y. Lv, J. G. Dai, L. Xia, L. L. Luo, Y. T. Xu, and L. Z. Dai, "Smoke Suppression and Phosphorus-Free Condensed Phase Flame-Retardant Epoxy Resin Composites Based on Salen-Ni," *Polymer Degradation and Stability* 201 (2022): 109980.

61. R. Wang, P. L. Zheng, J. W. Li, et al., "An Efficient Cross-Linked Phosphorus-Free Flame Retardant for Epoxy Resins," *Acs Omega* 7 (2022): 37170.

62. J. Zhou, Y. Guo, Z. W. Chen, et al., "A Synthesized P/N/S Oligomer Flame Retardant to Construct Superior Flame-Retardant, Transparent, and Mechanical Properties Epoxy Resin," *Materials Today Chemistry* 40 (2024): 102201.

63. S. Wang, F. Sun, Z. B. Ni, et al., "Aromatic Epoxy from Caffeic Acid: Mechanical Properties and Flame Retardancy," *Acs Sustainable Chemistry & Engineering* 12 (2024): 10713.

64. X. Song, Z. P. Deng, C. W. You, et al., "High-Performance and Fire-Resistant Epoxy Thermosets Derived from Plant-Derived Ferulic Acid," *Industrial Crops and Products* 187 (2022): 115445.

65. L. Liu, Q. Y. Gao, J. H. Wang, et al., "Supramolecular Flame Retardants towards Fire Safe Polycarbonate with High Thermal Stability and Smoke-Suppression Properties," *Journal of Materials Science & Technology* 242 (2026): 173.

66. Y. Q. Shi, S. Q. Jiang, J. K. Wu, et al., "Constructing Efficient Flame-Retardant Coatings to Enhance the Performances of Glass fiber Cloth," *Composites Communications* 56 (2025): 102392.

67. Y. Zhang, X. Y. Zhang, P. Wang, Y. D. Liu, M. T. Wan, and K. Zhang, "Phosphorus-Free Curcumin-Derived Epoxy Resin with Exceptional Flame Retardancy, Glass Transition Temperature and Mechanical Properties," *Polymer Degradation and Stability* 215 (2023): 110440.

68. X. R. Bai, Z. Y. Li, Y. T. Dong, X. Y. Gao, and J. J. Meng, "Comprehensive Performance Improvement and Functional Upgrade of Magnolia-Based Epoxy Resins," *Reactive & Functional Polymers* 207 (2025): 106129.

69. C. J. Lu, S. Bian, K. Hu, C. C. Li, K. W. Zheng, and Q. F. Sun, "Biomass-Based Epoxy Resin Derived from resveratrol with High Temperature Resistance and Intrinsic Flame Retardant Properties," *Industrial Crops and Products* 187 (2022): 115500.

70. X. Song, Z. P. Deng, C. B. Li, et al., "A Bio-Based Epoxy Resin Derived from p-Hydroxycinnamic Acid with High Mechanical Properties and Flame Retardancy," *Chinese Chemical Letters* 33 (2022): 4912.

71. Y. Qi, Z. H. Weng, Y. Kou, et al., "Facile Synthesis of Bio-Based Tetra-Functional Epoxy Resin and Its Potential Application as High-Performance Composite Resin Matrix," *Composites Part B: Engineering* 214 (2021): 108749.

72. J. Y. Dai, Y. Y. Peng, N. Teng, et al., "High-Performing and Fire-Resistant Biobased Epoxy Resin from Renewable Sources," *Acs Sustainable Chemistry & Engineering* 6 (2018): 7589.

73. K. A. Ellzey, T. Ranganathan, J. Zilberman, E. B. Coughlin, R. J. Farris, and T. Emrick, "Deoxybenzoin-Based Polyarylates as Halogen-Free Fire-Resistant Polymers," *Macromolecules* 39 (2006): 3553.

74. M. W. Szyndler, J. C. Timmons, Z. H. Yang, A. J. Lesser, and T. Emrick, "Multifunctional Deoxybenzoin-Based Epoxies: Synthesis, Mechanical Properties, and Thermal Evaluation," *Polymer* 55 (2014): 4441.

75. X. Wang, H. X. Niu, J. L. Huang, L. Song, and Y. Hu, "A Desoxyanisoin- and Furfurylamine-Derived High-Performance Benzoxazine Thermoset with High Glass Transition Temperature and Excellent Anti-Flammability," *Polymer Degradation and Stability* 189 (2021): 109604.

76. T. Chu, Y. X. Lu, B. Y. Hou, et al., "The Application of Ammonium Polyphosphate in Unsaturated Polyester Resins: a Mini Review," *Polymer Degradation and Stability* 225 (2024): 110796.

77. S. L. Jin, L. J. Qian, Y. Qiu, Y. J. Chen, and F. Xin, "High-Efficiency Flame Retardant Behavior of bi-DOPO Compound with Hydroxyl Group on Epoxy Resin," *Polymer Degradation and Stability* 166 (2019): 344–352.

78. J. Y. Dai, N. Teng, J. K. Liu, J. X. Feng, J. Zhu, and X. Q. Liu, "Synthesis of Bio-Based Fire-Resistant Epoxy without Addition of Flame Retardant Elements," *Composites Part B-Engineering* 179 (2019): 107523.

79. X. Wang, H. Nabipour, Y. C. Kan, L. Song, and Y. Hu, "A Fully Bio-Based, Anti-Flammable and Non-Toxic Epoxy Thermosetting Network for Flame-Retardant Coating Applications," *Progress in Organic Coatings* 172 (2022): 107095.

80. C. Yang, X. N. Xia, Y. L. Xiao, G. Q. Wei, W. S. Li, and Y. B. Lu, "Degradable, Intrinsically Flame-Retardant, Low-Water-Absorbing Vanillin-Derived Epoxy Thermoset with a Schiff Base Structure," *Polymer Degradation and Stability* 221 (2024): 110666.

81. H. X. Niu, H. Nabipour, X. Wang, L. Song, and Y. Hu *Acs Sustainable Chemistry & Engineering* 9 (2021): 5268.

82. H. Nabipour, X. Wang, L. Song, and Y. Hu, "A High Performance Fully Bio-Based Epoxy Thermoset from a Syringaldehyde-Derived Epoxy Monomer Cured by Furan-Derived Amine," *Green Chemistry* 23 (2021): 501–510.

83. S. Ting, X. Ye, B. Wang, et al., "Transparent, Intrinsically Fire-safe yet Impact-resistant Poly(carbonates-b-siloxanes) Containing Schiff-base and

Naphthalene-Sulfonate," *Journal of Materials Science & Technology* 225 (2025): 11–20.

84. H. Nabipour, S. Rohani, and Y. Hu, "A Bio-Based Epoxy Resin Derived from Syringaldehyde with Excellent Mechanical Properties, Flame Retardant and High Glass Transition Temperature," *Polymer Degradation and Stability* 214 (2023): 110410.

85. H. Nabipour, H. X. Niu, X. Wang, S. Batool, and Y. Hu, "Fully Bio-Based Epoxy Resin Derived from Vanillin with Flame Retardancy and Degradability," *Reactive & Functional Polymers* 168 (2021): 105034.

86. H. Nabipour, X. Wang, B. Kandola, et al., "A Bio-Based Intrinsically Flame-Retardant Epoxy Vitrimer from Furan Derivatives and Its Application in Recyclable Carbon fiber Composites," *Polymer Degradation and Stability* 207 (2023): 110206.

87. W. Q. Xie, S. W. Huang, D. L. Tang, S. M. Liu, and J. Q. Zhao, "Biomass-Derived Schiff Base Compound Enabled Fire-Safe Epoxy Thermoset with Excellent Mechanical Properties and High Glass Transition Temperature," *Chemical Engineering Journal* 394 (2020): 123667.

88. X. H. Sun, W. J. Miao, Y. T. Pan, et al., "Metal-Organic Frameworks: a Solution for Greener Polymeric Materials with Low Fire Hazards," *Advanced Sustainable Systems* 2025, 9, 2400768.

89. Y. J. Xue, M. Zhang, S. Q. Huo, et al., "Engineered Functional Segments Enabled Mechanically Robust, Intrinsically Fire-Retardant, Switchable, Degradable PolyureThane Adhesives," *Advanced Functional Materials* 34 (2024): 2409139.

90. Z. Y. Chen, Y. Y. Wu, S. C. Liu, et al., "Pottery-Inspired Flexible Fire-Shielding Ceramifiable Silicone Foams for Exceptional Long-Term Thermal Protection," *Advanced Functional Materials* 35 (2025): 2413362.

91. H. Y. Ou, J. B. Li, M. Jin, and J. Ren, "Eugenol-Derived Trifunctional Epoxy Resin: Intrinsic Phosphorus-Free Flame Retardancy and Mechanical Reinforcement for Sustainable Polymer Alternatives," *Polymer Degradation and Stability* 239 (2025): 111394.

92. J. Ying, Y. X. Zhang, J. T. Chen, et al., "Facile Synthesis of Phosphorus-Free Biobased Epoxy Resin with Exceptional Flame Retardancy, Mechanical Properties, and Heat Resistance," *Acs Applied Polymer Materials* 5 (2023): 9445.

93. W. Luo, M. Chen, T. Wang, et al., "Catalytic Polymer Self-Cleavage for CO2 Generation before Combustion Empowers Materials with Fire Safety," *Nature Communications* 15 (2024): 2726.

94. W. Chen and G. Liu, "Flame-Retardancy Properties of Tris(2-hydroxyethyl) Isocyanurate Based Charring Agents on Polypropylene," *Journal of Applied Polymer Science* 132 (2015): 41810.

95. P. Jafari, R. R. Zhang, S. Q. Huo, et al., "Machine Learning for Expediting next-Generation of Fire-Retardant Polymer Composites," *Composites Communications* 45 (2024): 101806.

96. Z. W. Chen, C. L. He, K. Wang, et al., "Machine Learning-Driven Molecular Generation for Accelerated Screening of High-Performance Flame Retardants in Epoxy Resin Composites," *Chemical Engineering Journal* 516 (2025): 163946.

97. Z. W. Chen, B. R. Yang, N. N. Song, et al., "Machine Learning-Enabled Rational Design of Organic Flame Retardants for Enhanced Fire Safety of Epoxy Resin Composites," *Composites Communications* 44 (2023): 101756.

98. Z. W. Chen, B. R. Yang, N. N. Song, et al., "Machine Learning-Guided Design of Organic Phosphorus-Containing Flame Retardants to Improve the Limiting Oxygen Index of Epoxy Resins," *Chemical Engineering Journal* 455 (2023): 140547.

99. S. Huo, Y. Guo, Q. Yang, H. Wang, and P. A. Song, "Two-Dimensional Nanomaterials for Flame-Retardant Polymer Composites: a Mini Review," *Advanced Nanocomposites* 2024, 1, 240–247.

100. H. Y. Ma, P. A. Song, and Z. P. Fang, "Flame Retarded Polymer Nanocomposites: Development, Trend and Future Perspective," *Science China-Chemistry* 54 (2011): 302–313.

101. Y. J. Wang, B. F. Guo, L. Y. Lv, et al., "Thermally Induced Cyclic Resistance Transition of a Transparent and Flame-Retardant Layered Oxidized MXene Composite Nanocoating for Remote-Sync Fire Monitoring," *Journal of Materials Chemistry A* 13 (2025): 26255.

102. T. Sai, S. Y. Ran, Z. H. Guo, P. A. Song, and Z. P. Fang, "Recent Advances in Fire-Retardant Carbon-Based Polymeric Nanocomposites through Fighting Free Radicals," *Susmat* 2 (2022): 411–434.