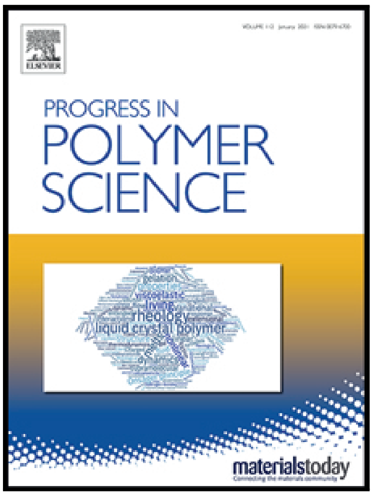

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Phosphorus-containing flame retardant epoxy thermosets: Recent Advances and Future Perspectives

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Abstract

Their pervasive use in industrial applications renders the development of environmentally benign flame-retardant epoxy (EP) thermosets a timely and important goal. The last two decades have witnessed the rise of phosphorus (P)-containing flame retardants for EP due to their high flame retardancy efficiency, low toxicity, multiple modes of action, molecular diversity and other favorable properties. P-containing flame retardants are classified into two types: reactive and additive, according to whether they participate in the curing process. Recent advances in both of these classes of P-containing flame retardants motivate this comprehensive review on the design and synthesis of P-containing flame retardants and their impact on the material properties of EP thermosets. This review focuses on the state-of-the-art knowledge of P-containing flame retardants and their effects on flame retardancy, thermal stability and mechanical properties of the resultant EP. First, representative flame-retardant mechanisms are reviewed. Subsequently, practical applications of P-containing flame-retardant EP thermosets are presented. Finally, the key challenges associated with P-containing flame retardants for EP thermosets are highlighted, and opportunities for future research in the field are proposed.

Keywords

Epoxy thermoset; Phosphorus-containing flame retardants; Flame retardancy; Thermal stability; Mechanical properties

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Nomenclature

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AHRR	Average of heat release rate
AI	1-(3-Aminopropyl)-imidazole
APP	Ammonium polyphosphate
BAMPO	Bis(m-aminophenyl)methylphosphine oxide
BDP	Bisphenol A bis(diphenyl phosphate)
BIM	Benzimidazole
CNT	Carbon nanotube
CTP-EP	Hexa-[4-(glycidyloxycarbonyl) phenoxy]cyclotriphosphazene
CY	Char yield
D230	O, O'-Bis(2-aminopropyl)polypropyleneglycol
DETA	Diethylenetriamine
DDS	4, 4’-Diaminodiphenyl sulfone
DDM	4, 4’-Methylene-dianiline
DGEBA	Diglycidyl ether of bisphenol A
DICY	Dicyandiamide
DMA	Dynamic mechanical analysis
DOPO	9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DSC	Differential scanning calorimetry
EHPP	Phosphonohydrazidic acid
EP	Epoxy resin

FT-IR	Fourier transform infrared spectroscopy
GO	Graphene oxide
h-BN	Hexagonal boron nitride
HGCP	Hexaglycidyl cyclotriphosphazene
HRR	Heat release rate
IFR	Intumescent flame retardant
IPDA	Isophorone diamine
LDH	Layered double hydroxide
LOI	Limited oxygen index
MeHHPA	Methylhexahydrophthalic anhydride
MeTHPA	Methyl tetrahydrophthalic anhydride
MCC	Micro combustion calorimeter
MMT	Montmorillonite
mPDA	Resorcinol
NR	No rating
PA	Phytic Acid
PEI	Polyethylenimine
PEPA	1-Oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2]octane
PHRR	Peak heat release rate
PMDA	Pyromellitic dianhydride
PN	Phenol novolac
POSS	Polyhedral oligomeric silsesquioxane
PPA	Polyphosphamide
rGO	Graphene
SDR	Smoke density rate

SEM	Scanning electron microscopy
SPR	Smoke production release
$T_{2\%}$	Temperature at which the thermoset undergoes 2 wt% of weight loss
$T_{5\%}$	Temperature at which the thermoset undergoes 5 wt% of weight loss
$T_{10\%}$	Temperature at which the thermoset undergoes 10 wt% of weight loss
TEPA	Tetraethylenepentamine
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TGDDM	4, 4’-Tetradiglycidyl diaminodiphenyl methane
THE	Total heat evolved at the flame out
THR	Total heat release
TPP	(4-Carboxybutyl) triphenylphosphonium bromide
TSP	Total smoke production
TSR	Total smoke release
TTI	Time to ignition

1. Introduction

Polymeric materials have been ubiquitous in modern society since their discovery [1-4]. As important thermoset polymers, epoxy resins (EPs) feature high mechanical strength, outstanding adhesion, chemical resistance, and good electrical insulation, all of which enable EPs to find extensive applications in construction, automotive, electronics and aerospace areas [5-8]. Nevertheless, the EPs are intrinsically flammable, suffer a low limited oxygen index (LOI) and cannot pass the UL-94 burning test (see Table 1), and thus their universal use has posed a great fire threat to human life and property. Flammability has significantly restricted its practical applications, such as in the electrical & electronic industries where a desirable flame retardancy requirement, e.g., a V-0 rating during vertical burning tests is needed. Hence, this has driven the development of efficient flame retardants for creating flame-retardant EP thermosets.

Table 1. Thermal properties and flammability of the common P-free EP thermosets.

EP monomer	Curing agent	T_g (^oC)	CY (%)	LOI (%)	UL-94 rating	PHRR (kW/m^2)	THR (MJ/m^2)	Ref.
DGEBA	DDM	147 ^{a}	16.2 ^{c}	26.0	NR	1725 ^{e}	60.2 ^{e}	[9]
DGEBA	DDS	206 ^{b}	18.6 ^{d}	22.5	NR	1208 ^{f}	80.3 ^{f}	[10]
DGEBA	IPDA	127 ^{a}	8.0 ^{d}	/	NR	2550 ^{e}	96.0 ^{e}	[11]
DGEBA	MeTHPA	138 ^{b}	6.5 ^{d}	20.1	NR	1150 ^{f}	86.3 ^{f}	[12]
DGEBA	PEI	44 ^{b}	/	18.3	NR	1770 ^{e}	98.5 ^{e}	[13]
DGEBA	BIM	156 ^{b}	12.5 ^{d}	21.5	NR	1335 ^{f}	95.0 ^{f}	[14]

$^{a,\,b}$ T_g is determined by DSC and DMA;

$^{c,\,d}$ CY is obtained from TGA under N_2 flow at 735 and 800 ^oC;

$^{e,\,f}$ PHRR and THR are collected from cone calorimeter test under a heat flux of 35 and 50 kW/m^2.

Traditionally, halogen-based flame retardants (FRs), especially brominated FRs, have been considered to be highly effective in improving the flame retardancy of EPs. Unfortunately, there are many concerns on the application of brominated FRs because of the potential emission of toxic smoke and bioaccumulation of bromine [15-17]. For the sake of environmental concerns, some of the halogen-based FRs have been gradually phased out, thus stimulating the development of halogen-free FRs in recent years [18-20]. Among all halogen-free FRs, phosphorus (P)-containing FRs stand out as among the most promising candidates, and have been applicable to many polymer matrices, including EPs, because of their low toxicity, high efficiency, multiple flame-retardant mechanisms, and molecular diversity [21, 22].

P-containing FRs are classified into two main types: (i) reactive; and (ii) additive [23] according to whether they participate in the curing process of the EPs. Figure 1 illustrates the development roadmap of P-containing FRs for EP thermosets, showing some representative chemical structures. Since the late 1990s, both types of P-containing FRs for EP thermosets have witnessed great progress and to date have increasingly developed into four subcategories: P-containing epoxy resins and P-containing curing agents for reactive types; and multi-group P-containing additives and multi-functional P-containing additives for additive types. For the reactive P-containing FRs, as early as 1997, Camino *et al.* [24] reported the use of BAMPO as a flame-retardant curing agent to prepare intrinsically flame-retardant EP and its corresponding carbon fiber-reinforced composite. The resultant EP resins and composites exhibited high LOI values because of the intumescent flame-retardant behavior of BAMPO. Regarding the multi-group P-containing additives, Altstädt *et al.* [25] reported a phosphorus/nitrogen-containing flame-retardant additive (DOPO-Cyan-O). The addition of 20 wt% of DOPO-Cyan-O enables the final EP thermoset to achieve a LOI value of >30%, indicating a high flame-retardant efficiency. Moreover, the overall performance of the resultant EP is well maintained, demonstrating a great potential in practical applications. With respect to multifunctional P-containing additives, Hu *et al.* [26] have recently covalently grafted a PPA on the surface of graphene nanosheets to prepare a nanoscale P-containing flame retardant (PPA-*g*-GNS). PPA-g-GNS can significantly increase the LOI value, and remarkably reduce the PHRR and TSP of the resultant EP nanocomposite, indicative of improved flame retardancy and smoke suppression.

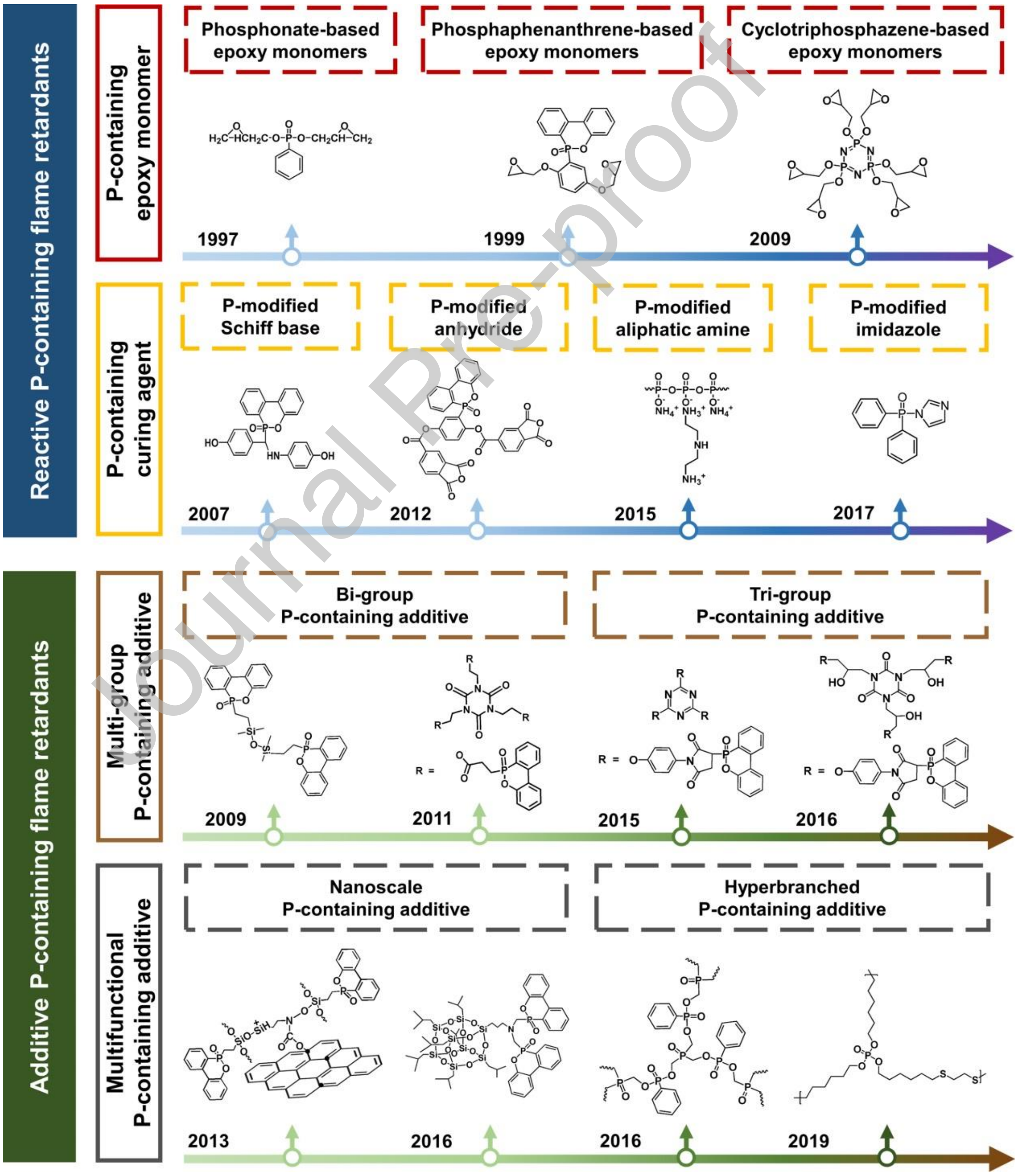

Fig. 1. The development roadmap of reactive and additive P-containing FRs: representative

P-containing epoxy resins and curing agents, and multi-group and multifunctional P-containing additives.

To date, several reviews have been written focusing on the significant advances in the preparation and flame-retardant performances of flame-retardant EP thermosets based on P-containing FRs [27, 28]. Unfortunately, there remains a remarkable lack of a critical review on the design and synthesis of P-containing FRs and their impacts on the overall performances of EP thermosets. This critical review will focus on the state-of-the-art of both reactive P-containing FRs (P-containing epoxy monomer and curing agent) and additive ones ((multi-group, multifunctional (hyperbranched and nanoscale) P-containing additives)) for EP (see Figure 2), and will also highlight their impact on the overall properties, such as flame retardancy, smoke suppression, glass transition and mechanical strength, of the resultant EP composites. Flame-retardant mechanisms of typical P-containing FRs in EP will also be discussed, followed by some practical industrial applications of the resultant flame-retardant EPs. Finally, this review presents some key challenges associated with P-containing FRs for EP, and proposes their future development directions and opportunities.

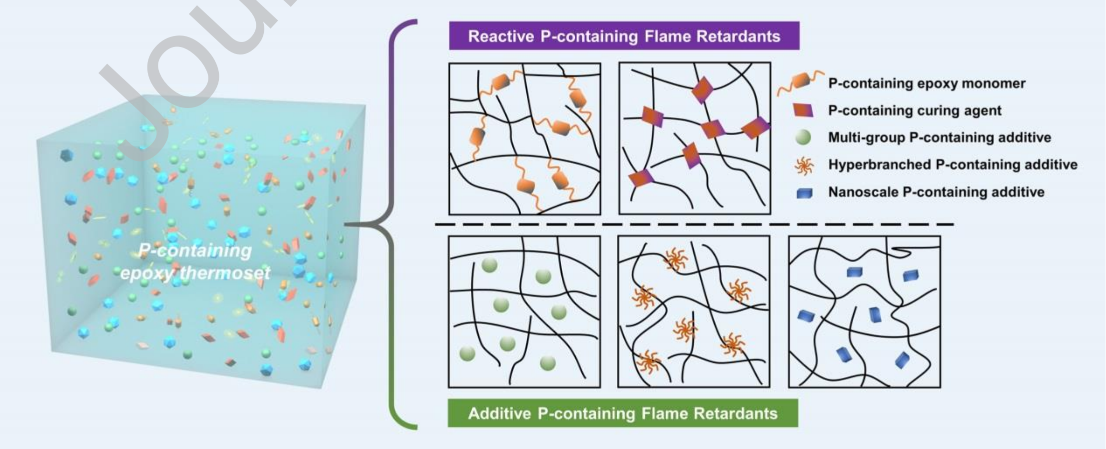

Fig. 2. Specific P-containing flame retardants for EP thermosets reviewed in this work. Reactive P-containing flame retardants: P-containing epoxy monomers and curing agents; and additive P-containing flame retardants: multi-group, hyperbranched and nanoscale P-containing additives.

2. Curing reaction and thermal decomposition of EP thermoset

Epoxy resins, which is one class of low-molecular-weight prepolymers with more than one epoxy group, was first synthesized by the Russian chemist Prileschajew in 1909 [29]. The epoxy groups in the resin can be cured by a variety of curing agents, such as amine, phenol, anhydride and imidazole (see Figure 3) under certain conditions [30, 31]. The cured products generate a 3D highly crosslinked network, and their properties (e.g., mechanical properties, thermal stability and flammability) are dependent on the chemical structure of both epoxy resins and curing agents as well as the crosslinking density.

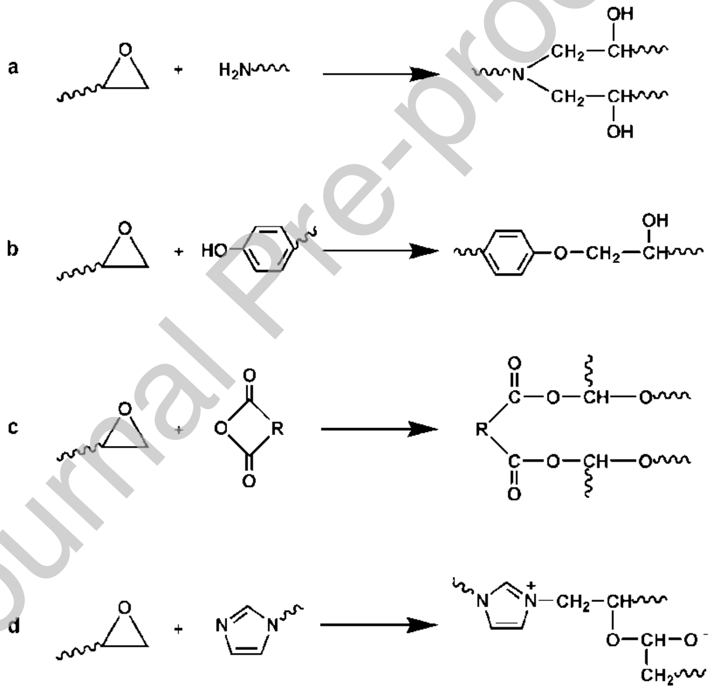

Fig. 3. Four typical curing reactions between epoxy resins and curing agents: reactions of epoxy group and a) amine, b) phenol, c) anhydride and d) imidazole. a-c) [30], Copyright 2010. Reproduced with permission from Multidisciplinary Digital Publishing Institute; and d) [31], Copyright 1987. Reproduced with permission from Elsevier Science Ltd.

Conventional EP thermosets comprise mainly carbon, hydrogen and oxygen, and thermally degrade to release a large amount of heat, combustible gas and smoke at high temperatures (≥ 300 ^{o}C). Their thermal decomposition is a complex multiple-step process (see Figure 4). Upon exposure to high temperatures or a heat flux, the EP begins to degrade and undergo competitive dehydration and dehydrogenation reactions, associated with the secondary alcoholic groups, giving rise to the formation of H_2O and H_2 (see Figure 4a) [30, 32]. The cross-linked structure then further decomposes *via* aliphatic-chain scission due to the breakdown of thermally weak C-O bonds (see Figures 4b and 4c) [33]. For the amine-cured EPs, the C-N bonds are less thermostable than the C-O bonds, and thus also undergo scission at this stage [33]. Finally, there is a further breakdown of products of the aliphatic chain release into the gaseous phase as combustible volatile fragments to feed the flame. Meanwhile, the EP segments after dehydration can undergo the aromatic Claisen rearrangement (see Figure 4d), yielding thermostable 1, 2, 4-trisubstituted benzene and its derivatives [34], which contribute to the carbonization. In addition, the cyclization of EP segments can also promote the charring process (see Figure 4e) [34, 35]. In brief, the release of volatile combustible fragments and the formation of a thermostable char are two competitive reactions during the thermal degradation and combustion of the EP.

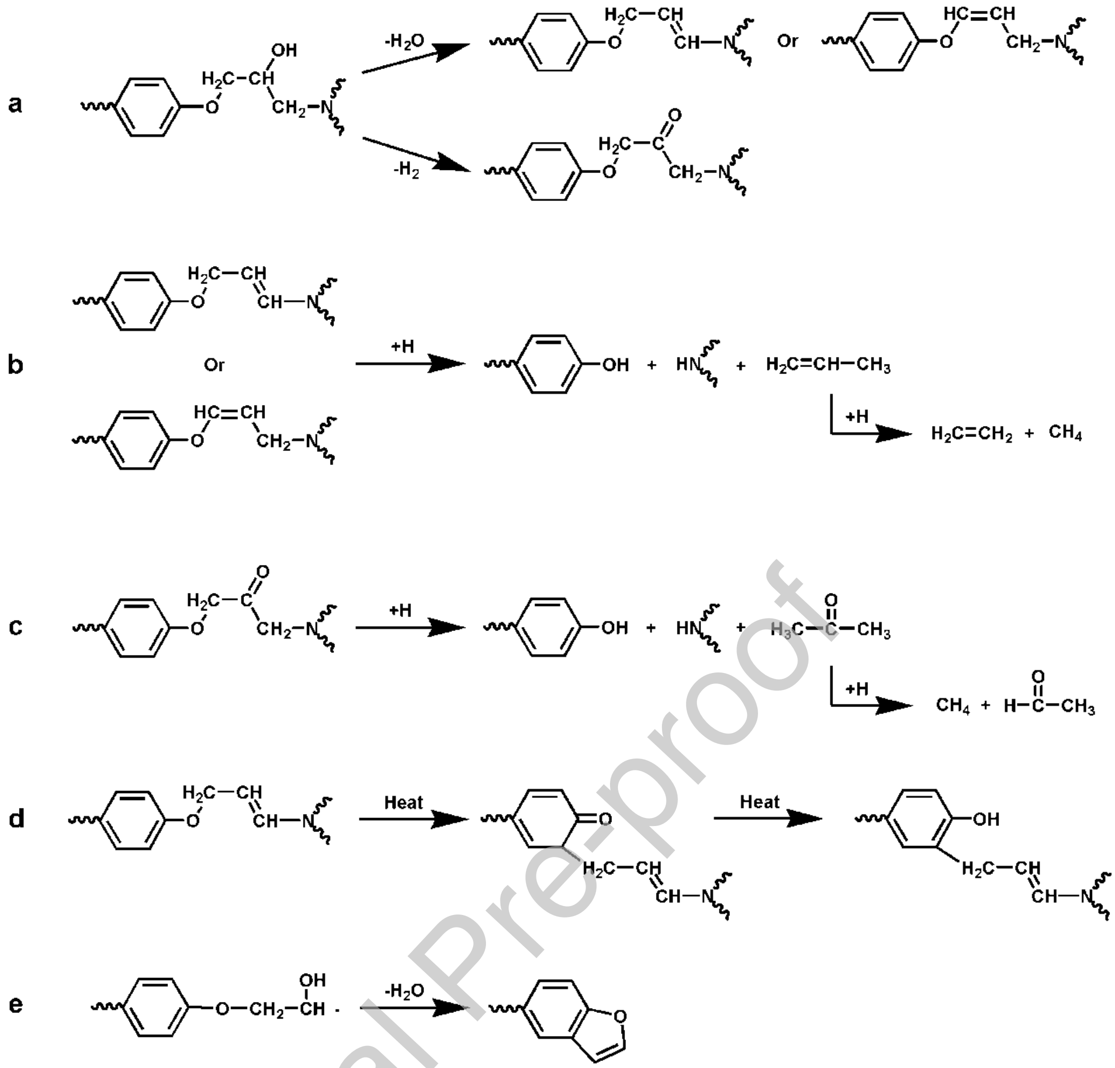

Fig. 4. Thermal decomposition pathways of the amine-cured epoxy thermosets. a) The dehydration and dehydrogenation of secondary alcoholic groups in the epoxy backbone; b, c) the scission of aliphatic chain in the epoxy backbone; d) the aromatic Claisen rearrangement of epoxy segments; and e) the cyclization of epoxy segments. a) [32], Copyright 1970. Reproduced with permission from John Wiley & Sons Inc.; b, c) [33], Copyright 1995. Reproduced with permission from John Wiley & Sons Inc.; and d, e) [34], Copyright 2004. Reproduced with permission from John Wiley & Sons Inc.

3. Flame-retardant mechanism of P-containing FRs

Until now, a variety of P-containing FRs have been synthesized for EPs, and their flame-retardant mechanisms have also been extensively studied [36-38]. In general, the flame-retardant mechanism of P-containing FRs can be divided into: (i) gaseous-phase mechanism; and (ii) condensed-phase mechanism (see Figure 5) according to the phase where they function [39-42]. The phosphorus is a multivalent element and can exist in any valance of -3, 0, +1, +3, and +5. Previous work has demonstrated that flame-retardant mechanisms of P-containing FRs are usually determined by their oxidation states in the flame retardants. The FRs with P in a higher oxidation state (+3, +5) exhibit a condensed phase mechanism whereas those with P in a lower oxidation state (0, +1) primarily display a gaseous-phase mechanism [43]. For instance, during combustion, phosphine oxides play an important role in the gaseous phase, and phosphates mainly function in the condensed phase. For many P-containing FRs, both the gaseous phase and the condensed phase mechanisms coexist and interplay.

In the condensed phase, P-containing FRs function through promoting the char-formation. Specifically, upon exposure to elevated temperatures they generate (poly)phosphoric acid species during combustion of polymers, which can promote the carbonization of the EP matrix by dehydration reactions [39, 43]. The as-created char can act as a physical barrier against both heat and mass, thus significantly hindering the transfer of both heat and combustible fragments between the underlying polymer and the combustion zone. As a result, the EP shows enhanced flame retardancy. In the gaseous phase, at high temperatures, P-containing FRs decompose to release many P-containing radicals, such as PO•, HPO• and HPO_2•, which can capture the highly active secondary free radicals, including H• and HO• generated by degradation of the EP matrix [41, 44]. By terminating these active free radicals, the combustion of EP will be significantly interrupted and suppressed, giving rise to improved flame retardancy.

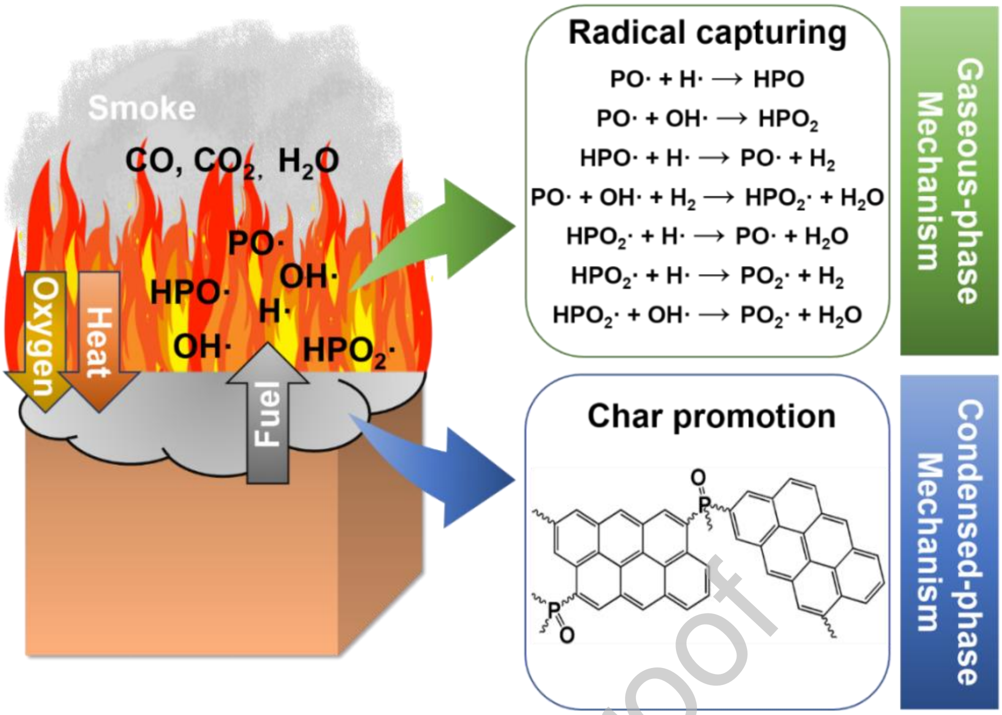

Fig. 5. The flame-retardant mechanism of P-containing flame retardants: radical capturing effect in the gaseous phase and char promotion effect in the condensed phase.

In addition, introducing synergistic flame-retardant groups or elements has emerged as an effective way to strengthen either of the flame-retardant mechanisms of P-containing flame retardant [10, 45, 46]. For example, nitrogen (N)-containing groups, such as triazine, triazole and triazine-trione, decompose to release inert N-containing gases during combustion, which can strengthen the gaseous-phase mechanism by diluting the concentration of both O_2 and fuels. In addition, silicon (Si)- and boron (B)-containing groups can promote the formation of a compact and glassy char during combustion, thus underpinning the condensed-phase mechanism. In summary, the flame-retardant mechanism of P-containing FRs can be regulated *via* the rational design of their chemical structures.

4. Reactive P-containing FRs

EP thermosets are fabricated *via* a curing reaction between the EP and a curing agent. Generally, reactive P-containing FRs serve as either P-containing EP monomers or curing agents to endow the cured EPs with intrinsic flame retardancy. Compared with additive P-containing FRs, the reactive FRs feature two advantages. The first advantage is that the reactive P-containing FRs do not leach out or migrate to the sample surface during their practical applications because they are covalently linked into the polymer network [47]. Another advantage is that the reactive P-containing FRs with a predesigned structure can endow EPs with integrated performances. For instance, the cured cyclotriphosphazene-based EPs exhibit an integrated performance portfolio: outstanding flame retardancy, improved mechanical properties and enhanced T_g [48, 49]. In addition, many P-modified imidazoles can be used as latent curing agents and the resultant EP/P-modified-imidazole mixtures can maintain an uncured state at the room temperature for a long time, but cure rapidly under heating [14]. This class of EP mixtures show a great potential in composite prepregs and large-scale industrial production. The development of both reactive P-containing FRs will be highlighted and discussed in the following sections.

4.1. P-containing EP monomers

This section mainly focuses on four classes of reactive P-containing EPs from phosphaphenanthrene-, cyclotriphosphazene-, phosphonate- and phosphate-based EP monomers.

4.1.1. Phosphaphenanthrene-based EP monomers

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), as a commercial P-containing FR, features high flame retardancy efficiency, high thermal stability, and good oxidation resistance due to its special phosphaphenanthrene structure [50-52]. Because of the active P-H group in DOPO, many DOPO derivatives have been synthesized for the preparation of phosphaphenanthrene-containing EP monomers. For instance, Wang and co-workers [53-57] reported the synthesis of a series of DOPO-containing EP monomers (see Figures 6a-6d), which were cured by several common curing agents, such as DDS, PN, and DICY. Detailed compositions and performances for the resultant flame-retardant EP thermosets are summarized in Table 1. All EP thermosets exhibit excellent flame retardancy (LOI ≥ 27% and V-0 rating during UL 94 tests) when the phosphorus content reaches a certain concentration. The glass transition temperature (T_g) of the final EP thermosets shows a strong dependence on the kind of curing agents used. Additionally, the CYs for these EP systems at 700 ^oC under air atmosphere are relatively high, indicating their good charring capability, as evaluated by TGA. Fang and co-workers [58] synthesized a flame-retardant EP monomer (denoted as DPBAEP, see Figure 6e), which was added to the TGDDM/DDS system to prepare an inherent flame-retardant EP thermoset. In this EP thermoset, both the LOI values and the UL 94 ratings increase with the increasing content of phosphorus, and finally reach up to 33.4% and V-0, respectively (see Table 2). To unveil the action mechanism behind, the surface morphology and chemical compositions for the residual chars after the LOI test are investigated by SEM and FT-IR. The results indicate that the DOPO moieties react with the EP matrix to generate a compact and continuous char layer, which can inhibit the heat transfer, flame propagation, and droplet generation during combustion, thus leading to an intrinsically flame retardant EP thermoset. Obviously, directly introducing DOPO will significantly lower the T_g value of the EP thermoset due to the end-capping reaction between P-H bonds and epoxy groups, which is not conducive to industrial applications. In contrast, DE-2 and DPBAEP with two epoxy groups can effectively avoid end-capping reaction, which are more suitable for industrial applications.

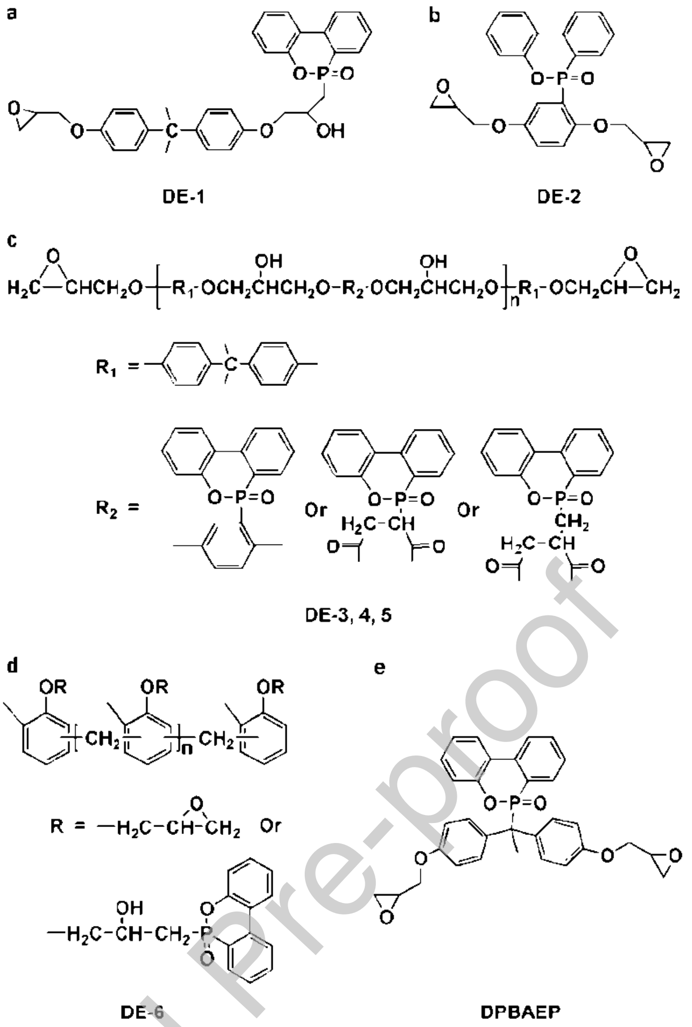

Fig. 6. A series of phosphaphenanthrene-based EP monomers. a) [53], Copyright 1999. Reproduced with permission from John Wiley & Sons Inc.; b) [54], Copyright 1999. Reproduced with permission from John Wiley & Sons Inc.; c) [55, 56], Copyright 2000. Reproduced with permission from John Wiley & Sons Inc.; d) [57], Copyright 2001. Reproduced with permission from Elsevier Science Ltd.; and e) [58], Copyright 2017. Reproduced with permission from SAGE Publications Ltd.

Table 2. Flame retardancy and thermal stability of phosphaphenanthrene-based EP thermosets cured by different common curing agents.

EP monomer	Curing agent	P content [a] (wt%)	LOI (%)	UL-94 rating	T_g (^{o}C)	CY [d] (%)	Ref.
DE-1	DDS	2.49	30	V-0	124 [b]	18.7	[53]
	PN	2.23	27	V-0	117 [b]	20.7	

DE-2	DDS	4.50	32	V-0	254 ^{b}	32.0	[54]
	PN	4.80	34	V-0	181 ^{b}	37.0	
	DICY	7.20	36	V-0	198 ^{b}	28.0	
DE-3	DDS	2.89	32	V-0	/	/	[55]
	PN	2.89	32	V-0	/	/	
DE-4	DDS	2.20	/	V-0	143 ^{b}	27.5	[56]
DE-5	DDS	2.24	/	V-0	140 ^{b}	27.8	[56]
DE-6	DDS	3.63	33	V-0	178 ^{b}	29.5	[57]
	PN	3.29	28	V-0	155 ^{b}	41.0	
	DICY	3.83	38	V-0	169 ^{b}	27.9	
TGDDM + DPBAEP	DDS	0.50	33.4	V-0	244 ^{c}	4.2	[58]

^{a} P content in the cured EP;

$^{b,\,c}$ T_g is determined by DMA and DSC;

^{d} CY is obtained from TGA at 700 ^{o}C under air flow.

4.1.2. Cyclotriphosphazene-based EP monomers

Cyclotriphosphazene is a cyclic ring consisting of alternating N and P atoms, exhibiting a high char yield, excellent thermal stability, and excellent flame retardancy [59, 60]. Hence, the cyclotriphosphazene group is often introduced into EP to improve the flame retardant performances because of the synergistic effect between P and N in the ring [37]. Among all cyclotriphosphazene-containing compounds, the commercially available hexachlorocyclotriphosphazene is recognized as an important starting material for the synthesis of cyclotriphosphazene-based EP monomers because its active chlorine atoms can be replaced by many different substituents *via* a nucleophilic substitution reaction.

El Gouri and co-workers [61] reacted hexachlorocyclotriphosphazene with 2,3-epoxy-1-propanol to synthesize the HGCP as a cyclotriphosphazene-containing

EP monomer, which was blended with a commercial epoxy resin (DGEBA) and a curing agent, DDM, to fabricate an intrinsic flame-retardant EP thermoset. The results show that 20 wt% of HGCP enables the final EP thermoset to reach a UL94 V-0 rating, in addition to leading to a significantly suppressed smoke generation because the HGCP can work in both the condensed phase and the gaseous phase. Specifically, (i) in the condensed phase, it promotes the formation of an intumescent and P-rich char as a barrier to inhibit the diffusion of gaseous products and the transfer of both heat and oxygen. In the gaseous phase, non-combustible gases, such as CO_2, NH_3, and N_2 generated by the decomposition of HGCP, can dilute the combustible gases and thus slow the combustion process.

Meanwhile, Wang *et al.* [62-65] prepared four kinds of cyclotriphosphazene-based EP monomers (see Figure 7), which were then cured by different commercially-available curing agents. As shown in Table 3, all the reported EP thermosets achieve relatively high LOI values (> 28%) and a UL-94 V-0 rating, suggesting outstanding flame retardancy. Moreover, the resultant EP thermosets exhibit high thermal resistance (T_gs > 130 °C) and strong charring capability (CYs > 20%) because of the polyfunctional EP monomers containing thermostable cyclotriphosphazene groups.

Additionally, Li *et al.* [66] have recently synthesized a P-based EP monomer, CTP-EP, with the reaction of hexachlorocyclotriphosphazene, *p*-hydroxybenzaldehyde and epichlorohydrin, as shown in Figure 8a. The CTP-EP with ester groups appear to be susceptible to hydrolysis. However, a 3D highly-crosslinked structure is formed after the curing of CTP-EP/DDM, thus helping to prevent the water attack on ester groups. All the final cyclotriphosphazene-based EP thermosets exhibit high LOI values (> 31%) with a UL94 V-0 rating regardless of the type of curing agents (see

Table 3). Compared to the common DGEBA/DDM system, the T_g and CY of CTP-EP/DDM increased from 155 °C to 167 °C, and from 14.1% to 39.0%, respectively. The combustion behaviors of CTP-EP/DDM thermosets are comprehensively evaluated by cone calorimetry under an incident heat flux of 50 kW/m^2, with the HRR and THR curves shown in Figures 8b and 8c. The PHRR, THR, and TSP values for the CTP-EP/DDM thermosets decrease by 74.5%, 38.8%, and 61.0%, respectively, relative to those for the DGEBA/DDM thermoset because of the formation of an intumescent and continuous char layer (see Figures 8e). The performance comparisons strongly indicate the superior flame retardancy and smoke suppression properties of the CTP-EP/DDM thermoset to those of the DGEBA/DDM. The exceptional thermal and flame-retardant performance portfolio has also been reported elsewhere [48, 49]. Overall, the cyclotriphosphazene-based EP thermosets exhibit excellent flame retardancy, high heat resistance, and good charring capability, and thus can be applied in electric and electronic sectors.

The reported cyclotriphosphazene-based EP thermosets above feature great flame retardancy and high heat resistance due to the multifunctionality of cyclotriphosphazene-based EP monomers and high thermostability of the cyclotriphosphazene rings, which have thus attracted a great deal of attention in recent years. However, the high price of hexachlorocyclotriphosphazene has significantly discouraged the applications of cyclotriphosphazene-based EP thermosets in the industry.

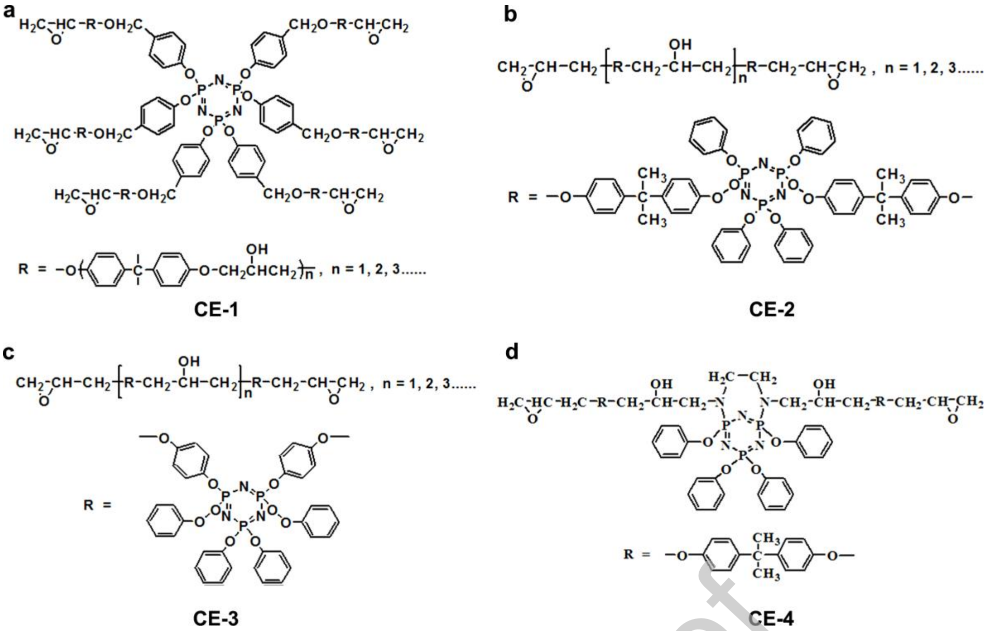

Fig. 7. Four typical cyclotriphosphazene-based EP monomers. a) [62], Copyright 2009. Reproduced with permission from Elsevier Science Ltd.; b) [63], Copyright 2012. Reproduced with permission from American Chemical Society; c) [64], Copyright 2012. Reproduced with permission from Royal Society of Chemistry; and d) [65], Copyright 2012. Reproduced with permission from American Chemical Society.

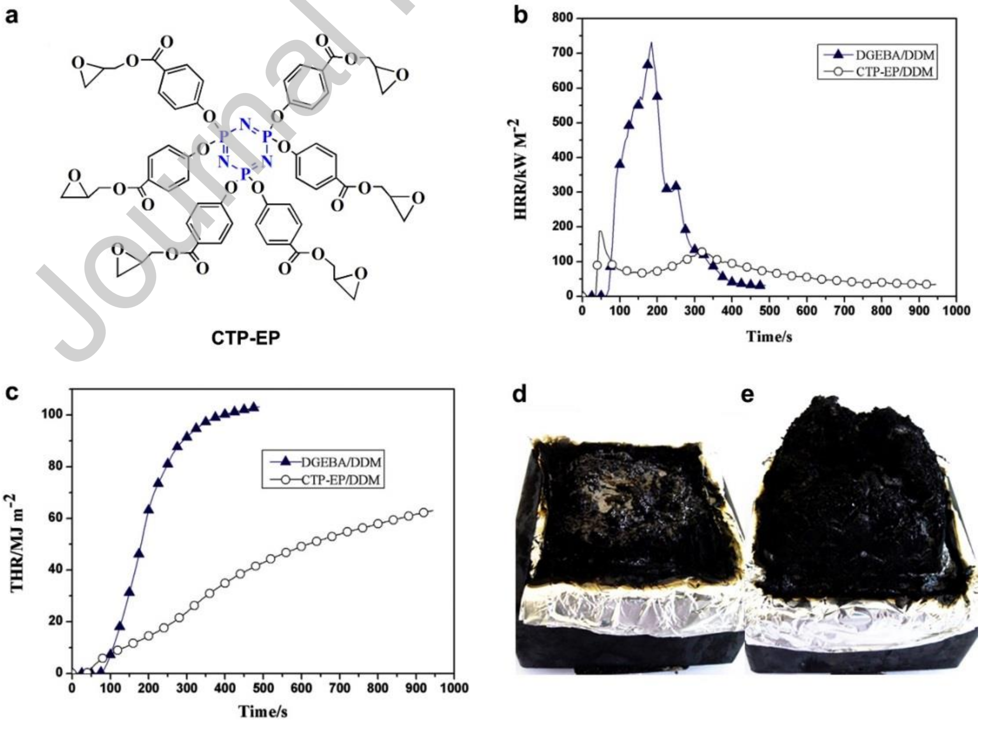

Figure 8. CTP-EP and the properties of the cured CTP-EP. a) Chemical formula of CTP-EP; b) HRR and c) THR curves of DGEBA/DDM and CTP-EP/DDM thermosets; and digital

photographs of residual chars of d) DGEBA/DDM and e) CTP-EP/DDM systems. [66], Copyright 2014. Reproduced with permission from Elsevier Science Ltd.

Table 3. Flame retardancy and thermal stability of the reported cyclotriphosphazene-based EP thermosets cured by different common curing agents.

EP monomer	**Curing agent**	**P content [a] (wt%)**	**LOI (%)**	**UL94 Rating**	**T_g (^oC)**	**CY (%)**	**Ref.**
CE-1	DDM	2.40	28.5	V-1	137.5 [b]	23.5 [d]	[62]
	DICY	2.52	31.2	V-0	133.8 [b]	42.4 [d]	
	PN	2.18	33.5	V-0	144.6 [b]	56.2 [d]	
	PMDA	2.38	32.9	V-0	138.2 [b]	54.6 [d]	
CE-2	DDM	/	31.6	V-0	156.6 [b]	26.68 [e]	[63]
	DICY	/	32.4	V-0	159.2 [b]	33.24 [e]	
	PN	/	30.2	V-0	166.5 [b]	37.72 [e]	
CE-3	MeTHPA	/	36.5	V-0	156.8 [b]	42.19 [e]	[64]
	DDM	/	39.2	V-0	166.1 [b]	42.85 [e]	
	PN	/	38.7	V-0	170.4 [b]	48.32 [e]	
CE-4	DDS	/	32.5	V-0	159.8 [b]	38.48 [e]	[65]
	DDM	/	31.1	V-0	157.7 [b]	31.01 [e]	
	PN	/	30.8	V-0	164.6 [b]	36.30 [e]	
CTP-EP	DDM	5.8	33.5	V-0	167 [c]	39.0 [f]	[66]
	DDS	5.6	34.3	V-0	/	/	
	mPDA	6.4	31.8	V-0	/	/	

[a] P content in the cured EP;

[b, c] T_g is determined by DSC and DMA, respectively;

[d, e, f] CY is obtained from TGA under N_2 flow at 650, 750 and 700 ^oC, respectively.

4.1.3. Phosphonate- and phosphate-based EP monomers

In addition, the phosphonate- and phosphate-based EP monomers have also been developed for creating intrinsically flame-retardant EP thermosets (see Figure 9)

[67-70]. For instance, Ma *et al.* [71] have recently prepared two kinds of biomass-vanillin-derived phosphonate-based EP monomers (EP1 and EP2), with their chemical structures presented in Figure 10a. Two bio-based flame retardant EP thermosets (EP1-DDM and EP2-DDM) are fabricated by curing with DDM. As shown in Figure 10b, the DGEBA-DDM system fails to pass the UL-94 test, with a low LOI value of only 24.6%, whereas both EP1-DDM and EP2-DDM systems achieve a V-0 rating and their LOI values reach 31.4% and 32.8%, respectively. In addition, both EP1-DDM and EP2-DDM exhibit much higher CYs (see Figure 10c), and generate a more continuous and intumescent char in comparison to the DGEBA-DDM, which accounts for the significantly improved flame-retardant performance. Notably, a high T_g of ~214 °C (see Table 4), a high tensile strength of ~80.3 MPa, and a tensile modulus of ~2709 MPa are observed for vanillin-derived phosphonate-based EP because of their relatively rigid structure. However, they suffer a low thermal stability, as reflected by a low $T_{5\%}$ values (< 300 °C) because of the thermally unstable diethyl phosphite, which has also been reported in other diethyl-phosphite-containing EPs systems [72, 73].

In another work, Liu *et al.* [74] reported the preparation of one bio-based EP thermoset from a eugenol-derived phosphate-based EP monomer (BEU-EP, see Figure 10d). As-prepared BEU-EP/DDM is featured by its extraordinary flame retardancy, e.g., a LOI of 38.4%, a UL-94 V-0 rating (see Table 4) and a ~85.1% reduction in PHRR relative to the control DGEBA/DDM sample under a heat flux of 50 kW/m^2 (see Figure 10e). Likewise, the BEU-EP/DDM sample also exhibits an increased char yield (see Figure 10f), which is mainly responsible for enhanced flame retardancy.

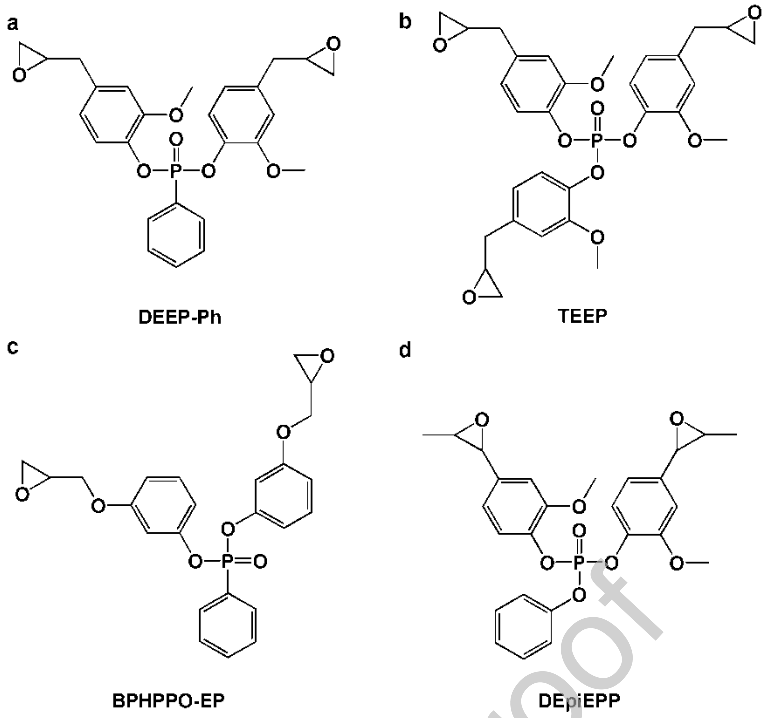

Fig. 9. Two typical phosphonate-based EP monomers: a) DEEP-Ph and c) BPHPPO-EP); and two representative phosphate-based EP monomers: b) TEEP and d) DEpiEPP. a, b) [67], Copyright 2019. Reproduced with permission from Multidisciplinary Digital Publishing Institute; c) [68], Copyright 2007. Reproduced with permission from Elsevier Science Ltd.; and d) [69], Copyright 2019. Reproduced with permission from American Chemical Society.

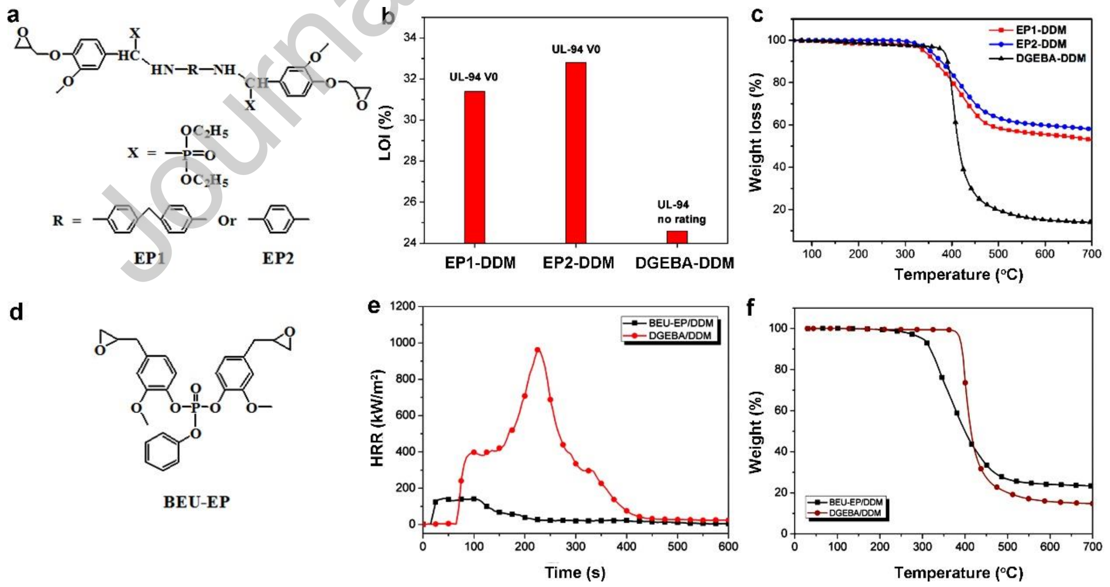

Fig. 10. Two phosphonate-based EP monomers and one phosphate-based EP monomer, and the properties of the cured EPs. a) Chemical formulas of EP1 and EP2; b) UL-94 ratings and LOI values for EP1-DDM, EP2-DDM, and DGEBA-DDM samples; c) TGA curves of EP1-DDM,

EP2-DDM, and DGEBA-DDM samples under N_2 flow; d) chemical formula of BEU-EP; e) HRR curves of BEU-EP/DDM and DGEBA/DDM samples; and f) TGA curves of BEU-EP/DDM and DGEBA/DDM samples under N_2 flow. a-c) [71], Copyright 2017. Reproduced with permission from American Chemical Society; and d-f) [74], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

Table 4. Flame retardancy and thermal stability of the reported phosphonate- and phosphate-based EP thermosets cured by different curing agents.

EP monomer	**Curing agent**	**P content [a] (wt%)**	**LOI (%)**	**UL-94 Rating**	**T_g (^oC)**	**CY (wt%)**	**Ref.**
BPHPPO-EP	DDS	7.79	34.0	/	/	51.8 [d]	[68]
EP1	DDM	6.50	31.4	V-0	183 [b]	53.0 [e]	[71]
EP2	DDM	7.18	32.8	V-0	214 [b]	58.0 [e]	[71]
BEU-EP	DDM	5.18	38.4	V-0	112 [c]	23.4 [e]	[74]

[a] P content in the cured EP;

[b, c] T_g is determined by DSC and DMA;

[d, e] CY is obtained from TGA under a N_2 condition at 800 and 700 ^oC.

4.2. P-containing curing agents

This section reviews four kinds of P-containing curing agents: P-modified Schiff-base, anhydride, aliphatic amine and imidazole.

4.2.1. P-modified Schiff-base curing agents

Schiff base is a class of common compound with an electron-deficient C=N bond, and can readily react with phosphorus-based compounds containing active P-H bond, such as DOPO and diethyl phosphite to form P-modified Schiff bases [7, 75]. The phosphorus-modified Schiff bases contain secondary amine groups, which can participate in the cross-linking curing reaction of the EP, and thus are often used as co-curing agents to prepare inherently flame-retardant EP thermosets. Therefore, to date a large number of studies have been reported on the application of phosphorus-modified Schiff-base curing agents towards flame-retardant EP thermosets [76-80].

Liu and co-workers [81] reported the fabrication of a DOPO-modified Schiff-base (D-bp, see Figure 11a) serving as a co-curing agent to improve the flame retardancy of the DGEBA/DDM thermoset. The DGEBA/D-bp/DDM thermoset exhibits a LOI value as high as 39.7% and a UL-94 V-0 rating at a phosphorus content of only 0.5 wt%. Both the PHRR and THR of the resultant EP thermosets gradually reduce with an increase in the content of phosphorus under an incident heat flux of 35 kW/m^2. Notably, the PHRR decreases from 939.2 to 535.1 kW/m^2 (a ~43% reduction), and the THR reduces from 227.4 to 121.9 MJ/m^2 (reduced by ~46%) when the phosphorus content increases to 1.0 wt%. However, the relatively low activity of secondary amine groups in D-bp reduces the crosslink density and the T_g value of the final EP thermoset. Such a phenomenon is also observed in other flame-retardant EP systems with phosphorus-modified Schiff-base curing agents [82-84].

Meanwhile, Cai and co-workers [85] developed two phosphorus-modified Schiff-base curing agents (DAP and AP, see Figures 11b and 11c) respectively derived from DOPO and diethyl phosphite, and compared their flame-retardant performances and corresponding mechanisms. The DAP derived from DOPO exhibits better flame retardancy efficiency than the AP derived from diethyl phosphite under the same addition. The significant enhanced flame retardancy of EP thermosets modified with DAP is due to the combination of the phosphorus-rich char, the free radical scavenging effect of phosphorus-based free radicals, and the diluting effect of nitrogen-based nonflammable gases. In contrast, the mismatching of the formation of the char layer with the release of gaseous products results in an inferior flame retardance of the AP-modified EP thermoset.

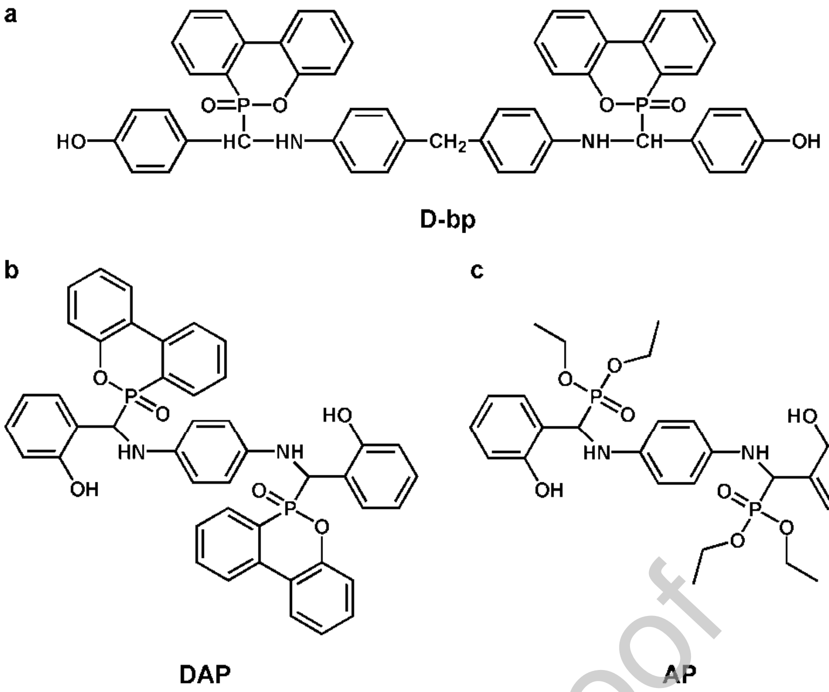

Fig. 11. Three representative P-modified Schiff-base curing agents: a) D-bp, b) DAP and c) AP. a) [81], Copyright 2015. Reproduced with permission from Elsevier Science Ltd.; and b, c) [85], Copyright 2016. Reproduced with permission from John Wiley & Sons Inc.

Recently, Huo *et al.* synthesized four types of highly efficient DOPO-modified Schiff bases with different N-containing heterocycles (see Figures 12a-12d), respectively named as BPD, DPT, DIB, and DTA [86-89]. The EP thermosets modified with these Schiff bases exhibit relatively high T_gs (see Table 5) because they possess at least two secondary amine groups and thus can effectively avoid the end-capping reaction. Meanwhile, the CYs of these EP thermosets gradually increase with the increasing content of phosphorus, probably because of the promotion effect of phosphorus on the char formation. Notably, as shown in Table 5, these EP thermosets exhibit high LOI values (≥ 36%) with a UL-94 V-0 rating when the P content is as low as only 0.75 wt%. Additionally, the PHRR and THR values of these EP thermosets are much lower than those of the unmodified EP thermosets (see Figures 12e-12h) under a heat flux of 50 kW/m^2 because of the synergistic effect between phosphaphenanthrene and nitrogen-containing heterocycles. During combustion, both components work cooperatively by interrupting the combustion reaction in the gaseous phase, and promoting the formation of a compact char in the condensed phases (see Figures 12i-12l). In general, these Schiff-base curing agents can not only significantly improve flame retardancy but also retain high heat resistance for the EP thermoset.

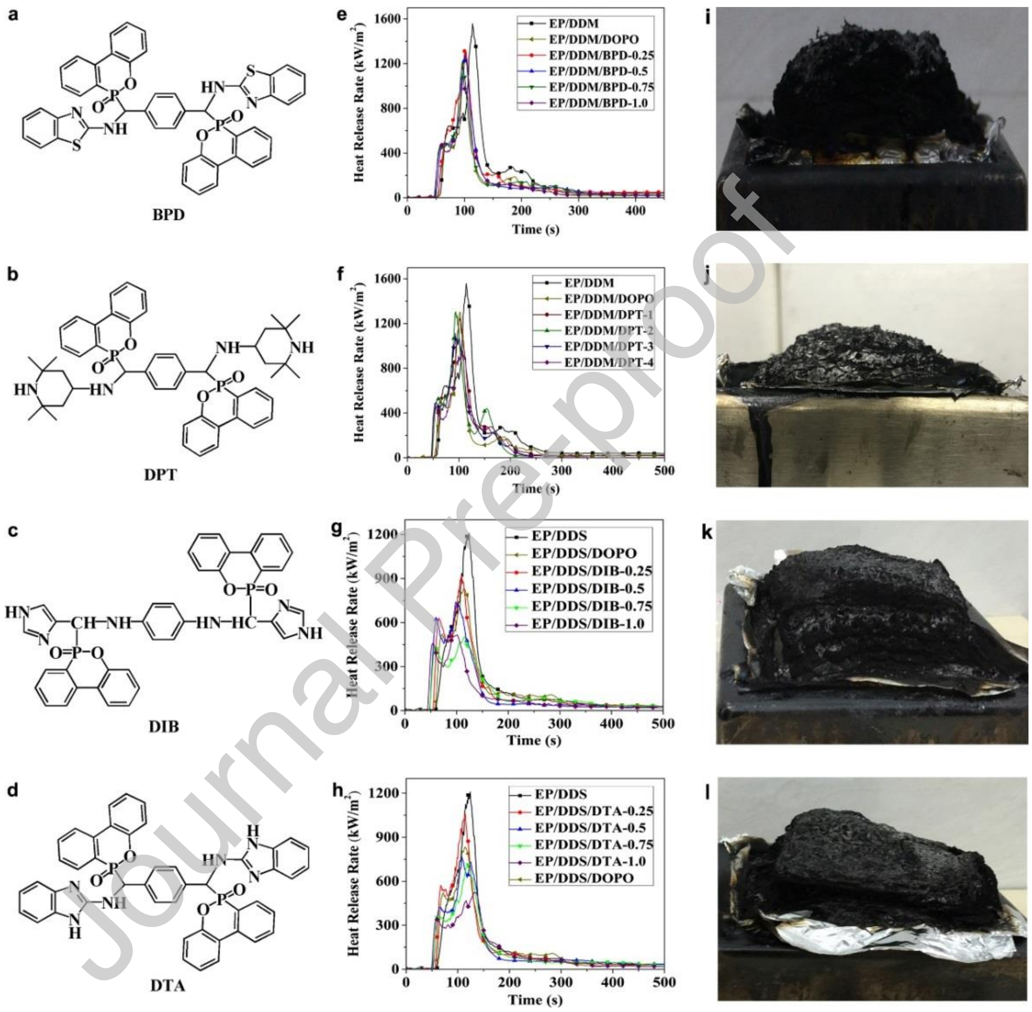

Fig. 12. Four P-modified Schiff-bases and their impacts on the flame retardancy of epoxy thermosets. a-d) Chemical formulas of BPD, DPT, DIB and DTA; e-h) HRR curves of EP thermosets modified with BPD, DPT, DIB and DTA; and i-l) char residues of EP thermosets modified with BPD, DPT, DIB and DTA. a, e, i) [86], Copyright 2018. Reproduced with permission from John Wiley & Sons Inc.; b, f, j) [87], Copyright 2017. Reproduced with permission from Elsevier Science Ltd.; c, g, k) [88], Copyright 2019. Reproduced with permission from Elsevier Science Ltd.; and d, h, l) [89], Copyright 2019. Reproduced with permission from

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Table 5. Flame retardancy and thermal stability of EP thermosets modified with BPD, DPT, DIB and DTA.

Curing agent	**P content** [a] **(wt%)**	**T_g** [b] **(°C)**	**$T_{5\%}$** [c] **(°C)**	**CY** [d] **(wt%)**	**LOI (%)**	**UL-94 rating**	**Reduction (%)** [e]		**Ref.**
							PHRR	**THR**	
DDM + BPD	0.75	160	310	18.1	36.9	V-0	21.7	31.4	[86]
DDM + DPT	0.75	169	322	17.8	36.5	V-0	28.6	30.9	[87]
DDS + DIB	0.75	186	347	24.0	36.8	V-0	58.4	27.3	[88]
DDS + DIB	0.75	192	339	23.5	36.7	V-0	41.1	24.2	[89]

[a] P content in the cured EP;

[b] T_g is determined by DSC;

[c] $T_{5\%}$ is tested by TGA under N_2 flow;

[d] The CY is obtained by TGA under N_2 flow at 800 °C;

[e] PHRR and THR are collected from cone calorimeter test under a heat flux of 50 kW/m^2.

4.2.2. P-modified anhydride curing agents

The anhydride curing agent is also widely used a hardener for EPs because of its low volatility, toxicity, cost, and long pot life. The EP thermosets cured with the anhydride curing agent often exhibit excellent electrical properties and dimensional stability [90-92]. As a result, many phosphorus-containing anhydride derivatives have recently been synthesized to create intrinsically flame-retardant EP thermosets. For instance, Liang *et al.* [93] reported the synthesis of a DOPO-containing anhydride curing agent (BPAODOPE, see Figure 13a) and its use as a co-curing agent of MeHHPA for the EP. Upon the phosphorus content increasing to 1.75 wt%, the resultant EP system reaches a UL-94 V-0 rating. A LOI value of above 30% cannot be achieved until the phosphorus content increases to 2.25 wt% because many thermally weak C-O bonds exist in the anhydride-cured EPs. Meanwhile, both the tensile strength and the impact strength of the final EP thermoset with 2.25 wt% of phosphorus decrease by 26.5% and 45.1%, respectively, relative to the neat EP thermoset. The decreased mechanical strength of the EP thermoset is primarily due to the reduced crosslinking density because of the excess amount of BPAODOPEs.

Another phosphaphenanthrene/triazine-containing anhydride curing agent (TDA, see Figure 13b) synthesized by Zhao *et al.* [94] was also used as a co-curing agent of MeHHPA. Benefiting from the synergistic effect of phosphaphenanthrene and triazine, the flame retardancy of the EP thermoset cured by TDA is superior to that of the EP thermoset modified by BPAODOPE at the same phosphorus content. For instance, the EP thermoset with TDA exhibits a LOI value of above 30% and a UL-94 V-0 rating when the phosphorus content is only 1.5 wt%, as compared to 2.25wt% of phosphorus for the BPAODOPE-cured system. It can be inferred that phosphaphenanthrene and triazine groups are capable of working collaboratively in the condensed and gaseous phases to inhibit the combustion of the EP, thus improving the flame-retardant performance. Moreover, because of the rigid phosphaphenanthrene and triazine groups in the TDA, the resultant EP thermoset maintains its high heat resistance (T_g), which is conducive to its practical applications in the industry.

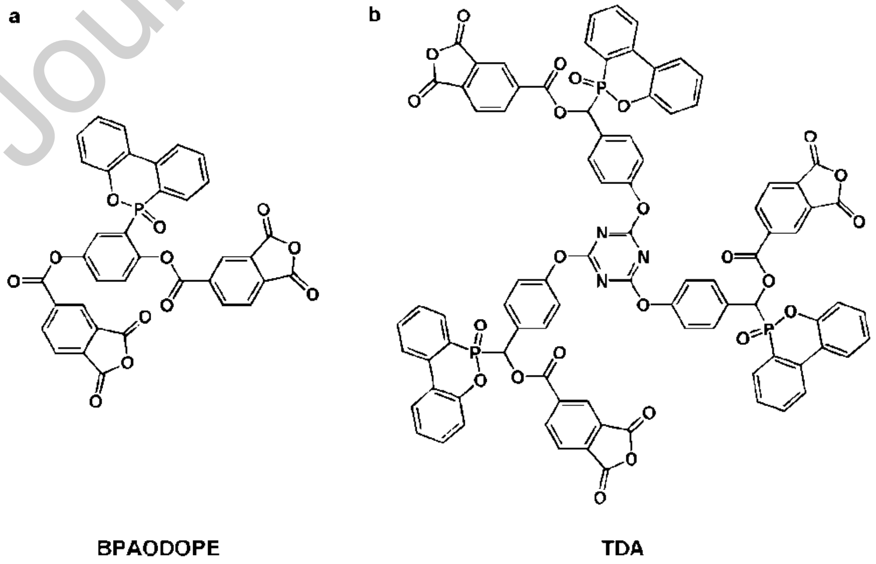

Fig. 13. Two typical P-modified anhydride curing agents: a) BPAODOPE and b) TDA. a) [93],

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4.2.3. P-modified aliphatic amine curing agents

Aliphatic amine curing agents feature many merits, including low viscosity, room temperature curing, and ease of use [95, 96]. However, the unmodified aliphatic amine suffers high volatility, thus compromising the users' health by inhalation. Hence, some modifications are often required to address this issue prior to use. Introducing phosphorus-containing groups is a promising strategy because these groups cannot only impart flame-retardant effect to an aliphatic amine curing agent but can also increase the molecular weight to reduce its volatility.

A variety of phosphorus-modified aliphatic amine curing agents for EP thermosets have been successfully developed in recent years [13, 97-102]. For instance, Wang *et al.* [98] reported a phosphorus-modified aliphatic amine curing agent (DETA-APP) based on the cation exchange of APP and DETA. Unlike the aforementioned flame-retardant curing agents, DETA-APP can directly cure the EP without additional curing agents. The DETA-APP imparts outstanding charring capability, flame retardancy and smoke suppression to the EP thermoset. Compared with the EP thermoset cured by DETA, the PHRR and TSP of the EP thermoset containing only 15 wt% DETA-APP decrease by ~68% and ~79%, respectively, under a heat flux of 35 kW/m^2. The authors believe the DETA-APP acts in both the condensed and gaseous phases during combustion: (i) the phosphorus groups derived from DETA-APP promote the formation of a protective char at relatively low temperatures, and the char layer can significantly delay the decomposition of the EP matrix at high temperatures; (ii) the nitrogen-containing, non-combustible gases generated by the thermal decomposition of DETA-APP can expand the melt char layer, thus leading to an intumescent char which can suppress the transfer of both mass and heat and protect the underlying polymer matrix.

In addition, Shao *et al.* [13, 100] synthesized two kinds of multi-functional phosphorus-modified aliphatic amine curing agents (DPPEI and DPTA), with their chemical structures presented in Figures 14a and 14d. Because of the amorphous structures of DPPEI and DPTA, the final DPPEI-EP and DPTA-EP samples maintain high transmittances above 90% in the visible region, which are very close to those of the controlled EP thermosets cured by PEI and TEPA (PEI-EP and TEPA-EP). The flammability of EP samples is evaluated by a cone calorimeter under a heat flux of 35 kW/m^2. Compared with the PEI-EP sample, the PHRR for DPPEI (30)-EP sample with 30 wt% of DPPEI decreases from 1770 to 645 MJ/m^2 with a ~63.6% reduction, and the TSP decreases from 145.3 to 31.6 m^2 with a ~78.3% reduction (see Figures 14b and 14c). Meanwhile, compared with the TEPA-EP sample, the PHRR for DPTA (12.5)-EP sample with 12.5 wt% of DPTA decreases from 1441 to 820 kW/m^2 (reduced by ~43.1%), and the TSP decreases from 141 to 58 m^2 (reduced by ~58.8%) (see Figures 14e and 14f). Both DPPEI and DPTA can simultaneously confer the EP thermoset with high transparency, good flame retardancy and smoke suppression, thus the final EP thermosets can be used in the fields of gradient coating and light-emitting diodes. For the P-modified aliphatic amine curing agents above, the volatility and high reactivity of aliphatic amine and diphenylphosphinyl chloride are the non-negligible issues during their industrial synthesis.

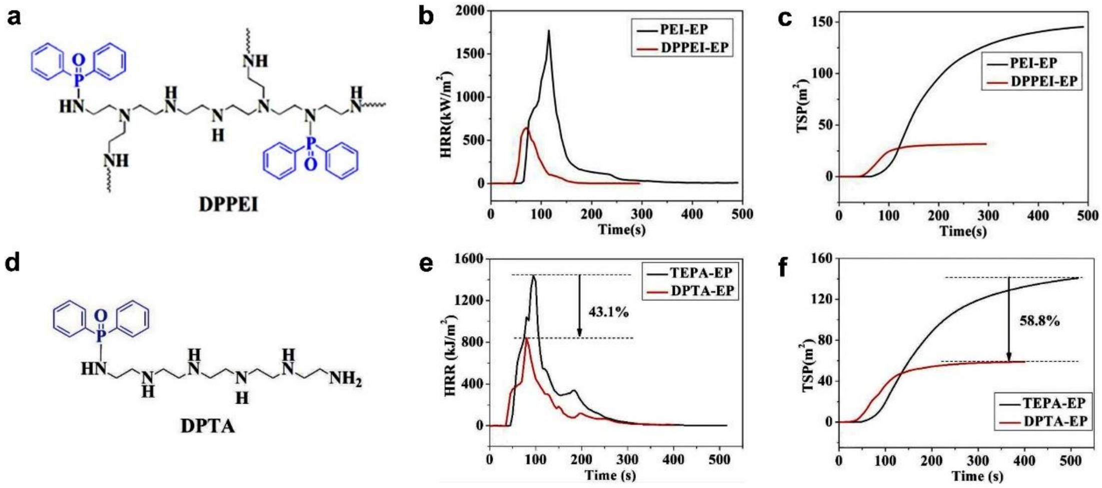

Fig. 14. Two P-modified aliphatic amines and their impacts on the flame retardancy and smoke suppression of epoxy thermosets. a) Chemical structure of DPPEI; b) HRR and c) TSP curves of PEI-EP and DPPEI (30)-EP thermosets; d) chemical structure of DPTA; and e) HRR and f) TSP curves of TEPA-EP and DPTA (12.5)-EP thermosets. a-c) [13], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.; and d-f) [100], Copyright 2019. Reproduced with permission from John Wiley & Sons Inc.

4.2.4. P-modified imidazole curing agents

Unlike the conventional additive type curing agents, imidazole and its derivatives are considered to be a class of anionic polymerization type curing agents, thus possessing a relatively low curing temperature and a fast curing rate [103, 104]. However, the unmodified imidazole normally exhibits extremely high curing activity and can cure EP very quickly even at room temperature. It is thus not suitable as a latent curing agent to prepare one-component EP systems. Introducing functional groups into 1-position and 3-position of the imidazole ring has shown to be an effective approach to tune its curing activity and to enhance its thermal latency [105, 106]. In addition, it has been reported that incorporating phosphorus-containing groups into 1-position and 3-position of imidazole not only enhances thermal latency but also introduces flame-retardant function. For instance, Wang *et al.* [107, 108] synthesized three kinds of phosphorus-modified imidazole curing agents, respectively designated as DPPIO, DPIPP and IDOP (see Figure 15), for the fabrication of one-component EP systems. In these cases, the EP resins with these curing agents remain uncured at the room temperature for a long time, and cure rapidly upon heated, e.g., taking 6.5 min in the DPPIO/EP system to gel at 150 °C. Similar to other phosphorus-containing EP thermosets, the EP thermosets with DPPIO, DPIPP and IDOP exhibit a strong charring capability and good flame retardancy. The resultant EP thermosets achieve a V-0 rating in the UL-94 test and their PHRR under a heat flux of 35 kW/m^2 decrease by 45.4%, 46.1%, and 36.9%, respectively, relative to the EP thermoset cured by imidazole. Therefore, these functionalized imidazole curing agents with phosphorus are applicable to the preparation of one-component flame-retardant EP systems.

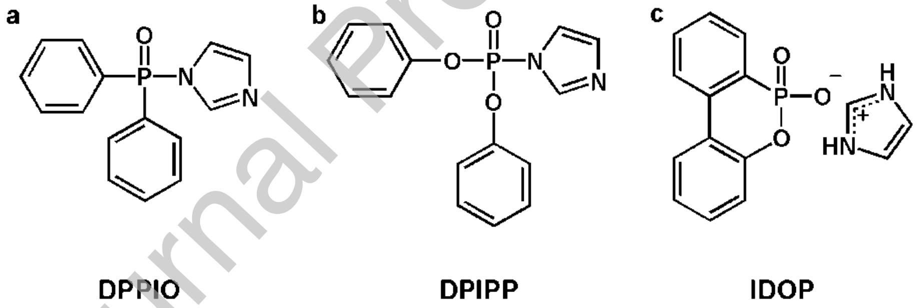

Fig. 15. Three typical P-modified imidazole curing agents: a) DPPIO, b) DPIPP and c) IDOP. a, b) [107], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.; and c) [108], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.

Very recently, Huo *et al.* [14, 109] have reported two P-containing imidazole derivatives, BICP and DA (see Figures 16a and 16d), which were applied to fabricate high-performance one-component EP thermosets. Both EP/BICP and EP/DA systems exhibit improved thermal latency due to the electron-withdrawing and steric hindrance effects of phosphorus-containing groups. As shown in Figures 16b and 16e, the cyclotriphosphazene group significantly increases the char yield of the EP thermosets, while the diphenylphosphinic group only shows a marginal effect. In addition, the introduction of cyclotriphosphazene or diphenylphosphinic group leads to obvious notable reductions in the PHRR value of the final EP thermosets under a heat flux of 50 kW/m^2 (see Figures 16c and 16f), indicating their strong flame-retardant effect. For instance, the PHRR of EP/BICP-12 thermoset decreases by ~70% relative to the reference the EP/BIM-10 thermoset, and that of the EP/DA-16 sample reduces by ~32% compared with the reference EP/AI sample. The flame-retardant mechanism analysis reveals that the cyclotriphosphazene group mainly functions in the condensed phase whereas the diphenylphosphinic group primarily acts in the gaseous phase during combustion. In addition to extraordinary flame retardancy, the resultant EP thermosets also present improved mechanical strength, indicating their promising market prospects. The P-modified imidazole curing agents have broad prospects in the fiber-reinforced epoxy prepregs, which are suitable for large-scale industrial production. However, besides the overall properties of flame-retardant EP thermosets, there is still no systematic study on resin-fiber wettability and the performance of the fiber-reinforced flame retardant epoxy composites.

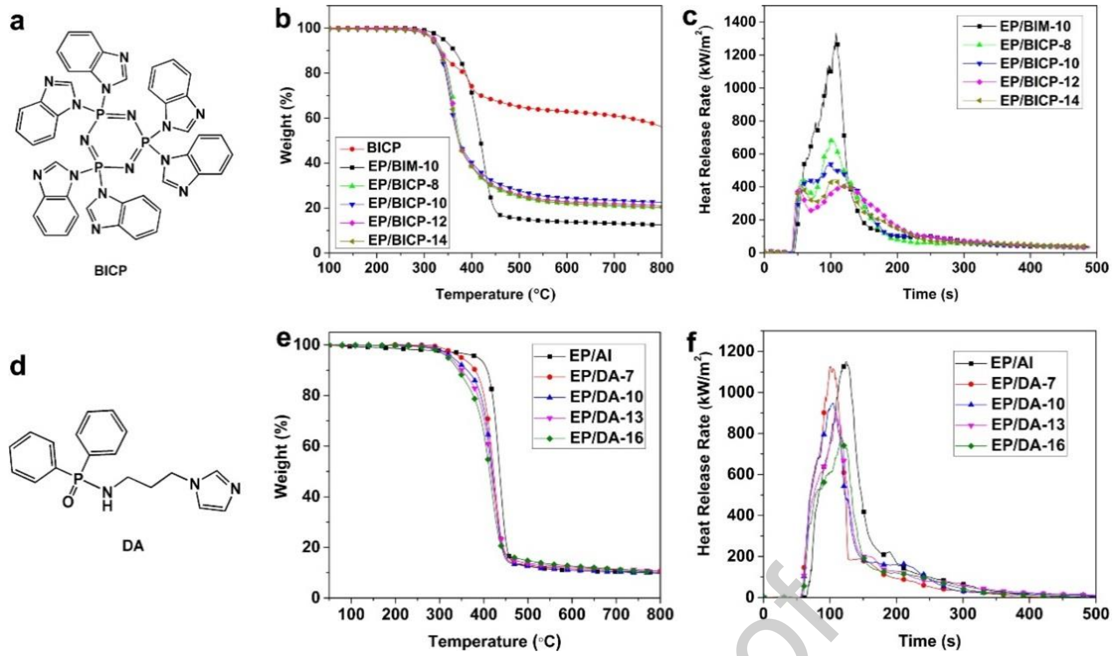

Fig. 16. Two P-modified imidazoles and their impact on the thermal and flame retardancy properties of EP thermosets. a) Chemical formula of BICP; b) TGA and c) HRR curves of EP/BICP thermosets; d) chemical formula of DA; and e) TGA and f) HRR curves of EP/DA thermosets. a-c) [14], Copyright 2019. Reproduced with permission from Elsevier Science Ltd.; and d-f) [109], Copyright 2019. Reproduced with permission from Elsevier Science Ltd.

4.2.5. Performance comparisons of P-modified curing agents

From the perspective of practical applications, it is essential to compare the overall properties of the flame retardant EP thermosets cured by P-based curing agents. Figure 17 presents the LOI values, relative PHRR reductions, and T_g differences (ΔT_g) of the reported flame-retardant EP thermosets with a UL-94 V-0 rating, with detailed data listed in Table 6. All the flame-retardant epoxy thermosets exhibit relatively high LOI values (≥ 29%) when their UL94 rating reaches up to V-0, demonstrating a good consistency of these two fire testing methods. Notably, the EP thermoset with BICP possesses a high LOI of 31.3% accompanied by a more significant reduction in the PHRR (~59.6%), thus indicating its superior flame-retardant effect of the cyclotriphosphazene group compared to other systems

[14].

Meanwhile, the impact of these flame-retardant curing agents on the T_g values of EP thermosets are shown in Figure 17b and Table 6. The P-modified Schiff bases and anhydrides are often used as co-curing agents of conventional curing agents, such as DDM and MeHHPA, for the EP. Generally, the P-modified Schiff-bases and anhydrides exhibit relatively complex chemical structures because of the introduction of P-containing groups, and thus they often suffer from lower curing activity than the common curing agents. Hence, the introduction of P-based co-curing agents usually leads to a reduced crosslinking density, thus decreasing the T_g value of the EP thermoset. For the P-modified aliphatic amines, their rigid phosphorus-containing groups restrict the motion of the EP chains to some extent, thus increasing the T_g value of the EP thermoset. Most P-modified imidazole curing agents, are likely to have a negative effect on the T_g of the EP thermoset. Unlike other P-modified imidazoles, the polyfunctional and rigid BICP improves the T_g value of EP thermoset. In comparison with other flame-retardant curing agents, the BICP leads to the largest increase in T_g, in addition to a high LOI value and significantly reduced PHRR of the EP.

In summary, most of the P-containing curing agents impart excellent flame retardancy to the EP thermoset at the expense of T_g value. Therefore, it remains a major challenge to address the trade-off between flame retardancy and heat resistance, which can determine the practical application of P-containing curing agents in the industry. Fortunately, the design of polyfunctional and rigid P-containing imidazole curing agents e.g., BICP, is one highly promising direction in the future.

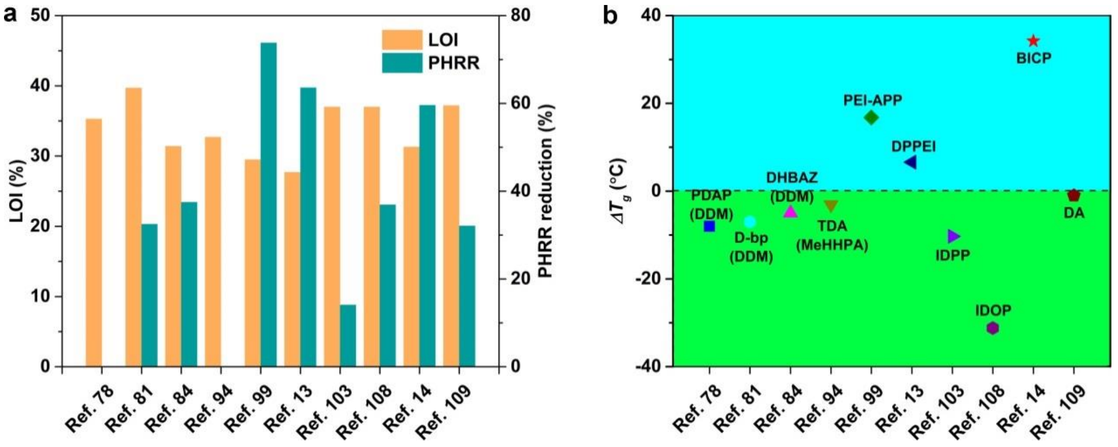

Fig. 17. The flame retardancy and thermal properties summary of the flame-retardant EP thermosets based on P-based curing agents with a UL-94 V-0 rating. a) LOI and PHRR reduction; and b) ΔT_g. (The T_g values are obtained from DMA test.)

Table 6. The overall performance of the flame-retardant epoxy thermosets based on P-based curing agents with a UL-94 V-0 rating.

Name of FR	P content [a] (wt%)	LOI (%)	Reduction (%)		ΔT_g (°C)	Other performances [d]	Ref.
			PHRR	THR			
PDAP	0.64	35.3	-	-	-8	$T_{5\%}$ reduces by 39.3 °C, the CY at 700 °C increases from 17.5% to 24.0%, and tensile strength increases by 11.2%.	[78]
D-bp	0.50	39.7	32.5 [b]	36.1 [b]	-7	$T_{5\%}$ reduces by 31.5 °C, and the CY at 700 °C increases from 15.7% to 26.9%.	[81]
DHBAZ	0.56	31.4	37.5 [b]	-	-5	$T_{5\%}$ reduces by 48.0 °C, and the CY at 800 °C decreases from 18.4% to 16.1%.	[84]
TDA	1.50	32.7	-	-	-3	$T_{5\%}$ reduces by 43.1 °C, and the CY at 700 °C increases from 3.9% to 18.1%.	[94]

PEI-APP	3.89	29.5	73.8 [b]	75.6 [b]	+16.8	$T_{5\%}$ increases by 0.2 ^{o}C, the CY at 700 ^{o}C increases from 11.0% to 33.9%, and TSP decreases by 70.3%.	[99]
DPPEI	1.65	27.7	63.6 [b]	69.5 [b]	+6.6	Tensile strength reduces by 2.1%, flexural strength decreases by 1.0%, impact strength reduces by 1.3%, and TSP decreases by 78.3%.	[13]
IDPP	1.62	37.0	14.1 [b]	43.1 [b]	-10.3	$T_{5\%}$ reduces by 20.2 ^{o}C, and the CY at 700 ^{o}C increases from 11.8% to 16.0%.	[103]
IDOP	1.55	37.0	36.9 [b]	38.0 [b]	-31.2	$T_{5\%}$ decreases by 3.4 ^{o}C, and the CY at 700 ^{o}C increases from 11.8% to 17.1%.	[108]
BICP	1.01	31.3	59.6 [c]	33.5 [c]	+34.2	$T_{5\%}$ decreases by 25.0 ^{o}C, the CY at 800 ^{o}C increases from 12.5% to 22.6%, tensile strength increases by 20.5%, flexural strength increases by 17.0%, and impact strength reduces by 7.4%.	[14]
DA	1.31	37.2	32.1% [c]	26.5% [c]	-1	$T_{5\%}$ decreases by 68 ^{o}C, the CY at 800 ^{o}C does not change, tensile strength increases by 5.2%, and flexural strength increases by 1.8%.	[109]

[a] P content in the cured EP;

[b, c] PHRR and THR are obtained from cone calorimeter test under a heat flux of 35 and 50 kW/m^2;

[d] $T_{5\%}$ and CY are obtained from TGA under N_2 flow.

5. Additive P-containing FRs

In comparison to reactive FRs, the additive FRs do not participate in the curing process of the EP resin, but their chemical structures and compositions are more flexible and thus of a greater variety. However, there are two major issues with additive phosphorus-containing FRs: (i) ease of migration or leaching out from the matrix, and (ii) the plasticization effect on the matrix. In order to mitigate the migration issue, attempts have been made to develop macromolecular or multi-group phosphorus-containing additives. Previous work [37, 43] has shown that the combination of P-containing and other flame-retardant (e.g., N-containing, B-containing, Si-containing) groups can further increase the effectiveness and reduce the overall required loading of FRs. In other words, the lower FR loading can mitigate their migration from the EP matrix to some extent. In order to address the plasticization effect, multifunctional P-containing additives have recently been developed and have simultaneously enhanced the flame retardancy and mechanical properties (e.g., elastic modulus) as well as Tg of the EP. Thus, this section will highlight the recent advance of multi-group and multifunctional phosphorus-containing additives.

5.1. Multi-group P-containing additives

The multi-group P-containing additives refer to a class of flame-retardant additives that combine a P-containing group and one or more other (e.g., P-, N-, B-, Si-containing) flame-retardant groups. They usually feature a high flame retardancy efficiency as a result of synergistic actions among different groups. This section reviews two classes of multi-group P-containing additives: bi-group and tri-group P-containing additives.

5.1.1. Bi-group P-containing additives

On the basis of the synergistic effect between phosphorus-containing and other flame-retardant groups, including nitrogen-, phosphorus-, silicon-, iron-, and boron-containing groups, many bi-group phosphorus-containing additives have been recently designed for creating flame-retardant EP thermosets. For example, Qian *et al*. [110-114] synthesized a series of phosphaphenanthrene/triazine- and phosphaphenanthrene/triazine-trione-containing flame-retardant additives (see Figure 18). In these cases, the resultant EP thermosets exhibit much lower PHRR, AHRR, and THR values relative to the unmodified EP thermoset in the cone calorimeter test under an external heat flux of 50 kW/m^2. These flame-retardant EP samples show higher LOI values and UL-94 ratings than the control phosphaphenanthrene-modified EP sample at the same P content. This is mainly because the N-containing groups can strengthen the flame retardancy effect of the P-containing flame retardant. The study on flame-retardant mechanism reveals that phosphaphenanthrene and nitrogen-containing groups act in both the condensed and gaseous phases by prohibiting the combustion of the EP matrix. The combination effect has been also reported in the other bi-group flame-retardant additives that contain phosphorus- and nitrogen-based groups [115-119]. However, there is still a lack of comparative research in relation to the flame retardant efficiency of bi-group flame-retardant additives with different P-containing (e.g. DOPO, PEPA) and N-containing (e.g., triazine, triazine-trione, triazole) groups.

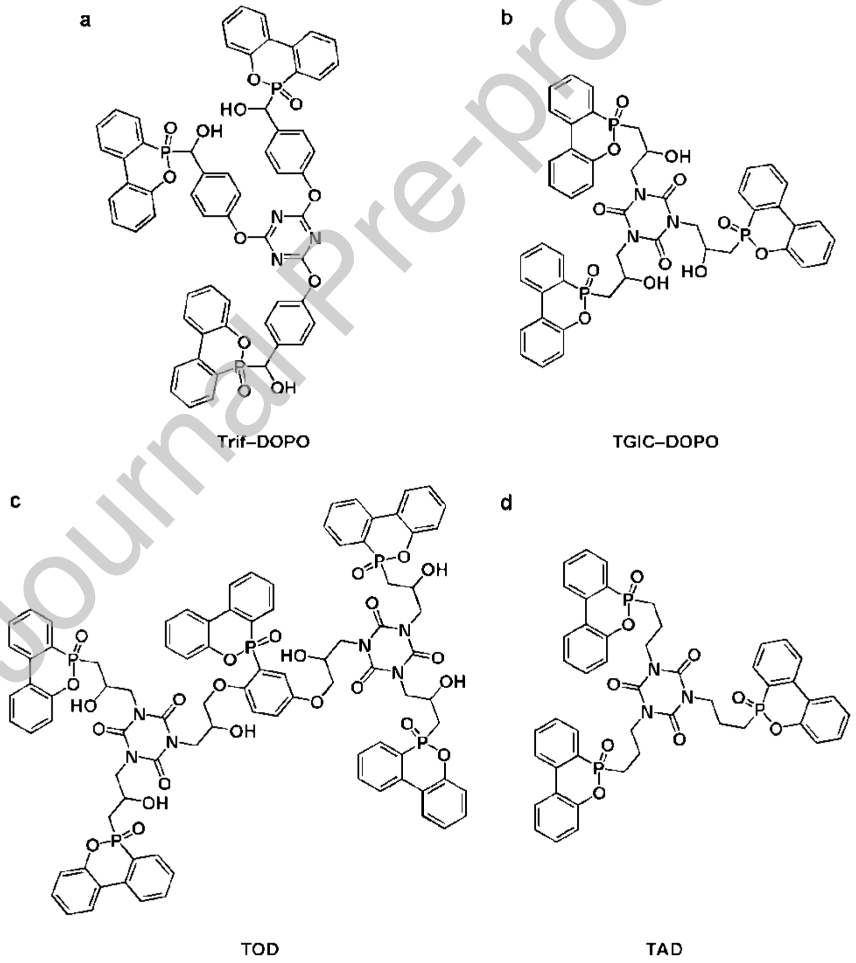

Fig. 18. Four typical phosphaphenanthrene/triazine- and phosphaphenanthrene/triazine-trione-containing flame-retardant additives: a) Trif-DOPO, b) TGIC-DOPO, c) TOD and d) TAD. a) [110], Copyright 2019. Reproduced with permission from

John Wiley & Sons Inc.; b) [111], Copyright 2014. Reproduced with permission from Elsevier Science Ltd.; c) [113], Copyright 2016. Reproduced with permission from Royal Society of Chemistry; and d) [114], Copyright 2016. Reproduced with permission from Elsevier Science Ltd.

In addition, some flame-retardant additives with two different phosphorus-based groups have been designed for flame-retardant EP thermosets [9, 120, 121]. For instance, Wang *et al.* [120] synthesized a highly effective FR with two different phosphorus-based groups (D-P, see Figure 19a) *via* an Atherton-Todd reaction between DOPO and PEPA, and investigated their synergistic effect. As shown in Figures 19b and 19c, the PHRR and THR under a 35 kW/m^2 external heat flux for the EP thermoset with D-P respectively decrease from 1291 to 595 kW/m^2 (~54% reduction) and 87.2 to 45.9 MJ/m^2 (~47.4% reduction) as compared with the unmodified EP thermoset. Notably, when the FR content is 9.1 wt%, the D-P-flame-retarding EP thermoset exhibits a much better flame-retardant performance in comparison to the EP thermosets containing DOPO or PEPA, with its LOI value and UL-94 rating reaching 35.0% and V-0, respectively, indicating a synergistic effect between DOPO and PEPA. The synergistic effect between DOPO and PEPA might be attributed to their different oxidation states. Meanwhile, the synergy is mainly reflected by the formation of a continuous and compact char layer, which suppresses the combustion of the underlying matrix and thus significantly enhances the flame retardancy.

Very recently, Ran *et al.* [120] also reported one bio-based additive flame retardant with two different P-containing groups (EHPP and PA), namely EHPP@PA (see Figure 19d). As presented in Figures 19e and 19f, the EHPP@PA can simultaneously reduce the heat release and smoke emission of the EP thermoset. For instance, the addition of 10 wt% of EHPP@PA reduces the PHRR and TSP of the EP by~64% and ~21%, respectively, under a heat flux of 35 kW/m^2. The results reveal that the EHPP mainly acts in the gaseous phase to inhibit the combustion reaction *via* capturing active H· and OH· free radicals; meanwhile, the PA primarily functions in the condensed phase by promoting the formation of P-rich intumescent char during combustion (see Figure 19g). This indicates that the EHPP@PA features a bi-phase flame retardant effect, which is also ascribed to the combination of phosphorus-derived groups with two different valances.

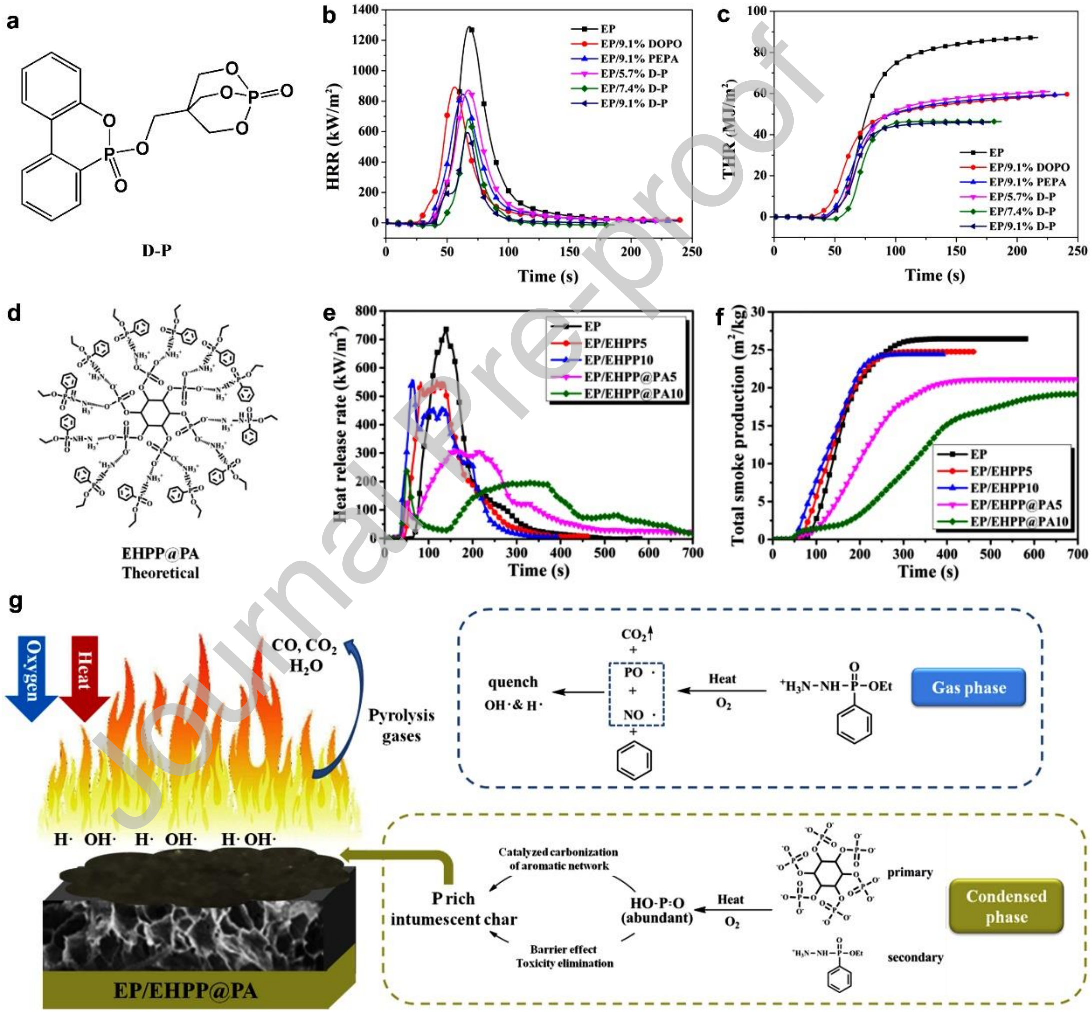

Fig. 19. Two P/P-containing flame-retardant additives and their impacts on the flame retardancy of EP thermosets. a) Chemical structure of D-P; b) HRR and c) THR curves of EP thermosets with D-P; d) theoretical chemical structure of EHPP@PA; e) HRR and f) TSP curves of EP thermosets with EHPP@PA; and g) flame retardant mechanism of EHPP@PA. a-c) [120], Copyright 2017.

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In addition, Tao *et al.* [122] reported the synthesis of two phosphaphenanthrene/siloxane-containing compounds (DOPO-TMDS and DOPO-DMDP) as flame-retardant additives for *o*-cresol novolac EP thermosets cured by PN. The influences of the two FRs on the heat resistance, mechanical and flame-retardant properties of EP thermoset were evaluated. The results show that the addition of 20 wt% of DOPO-TMDS enables the EP thermoset to achieve a LOI value of 33% and a UL-94 V-0 rating. In comparison, 24 wt% of DOPO-DMDP is required to enable the EP thermoset to attain a LOI value of 32% and a UL-94 V-0 rating. Meanwhile, both the DOPO-TMDS and DOPO-DMDP bring about enhancements in the mechanical strength of the EP thermoset, mainly because of the homogeneity between additives and the matrix, and the toughening effect arising from their siloxane-containing structures. The introduction of a soft siloxane structure, however, leads to certain reductions in the T_gs of the final EP thermosets.

Hu *et al.* synthesized a phosphaphenanthrene/ferrocene-containing flame retardant additive (PFDCHQ) combining a smoke suppression function [123]. The addition of only 5 wt% of PFDCHQ enables the EP thermoset to acquire a LOI value of 32.0% and a UL-94 V-0 rating. According to previous works, the DOPO-containing EP thermoset with similar FR content can only pass the V-1 rating in the UL-94 test [53, 86]. Such results demonstrate the higher flame retardant efficiency of PFDCHQ due to the introduction of ferrocene. Additionally, a significant reduction in the SPR is also observed during cone calorimeter tests under an incident heat flux of 35 kW/m^2, indicating the smoke suppression effect of the PFDCHQ. PFDCHQ functions in a bi-phase flame-retardant manner, similar to the majority of other bi-group FRs.

Unfortunately, one issue with PFDCHQ is that its addition slightly reduces the mechanical strength of the EP thermoset. Meanwhile, Liu *et al.* reported a cyclotriphosphazene/organoboron-containing flame-retardant additive (CP-6B) for the EP thermoset [124]. In this case, the presence of only 7 wt% of CP-6B increases the LOI value and UL-94 rating of the resultant EP to 32.3% and V-0, respectively. Meanwhile, the PHRR and THR of the final EP composites reduce by ~65% and ~35%, respectively relative to the control EP, under an incident flux of 50 kW/m^2. Such significantly improved flame retardancy is probably attributed to the fact that during the combustion, the cyclotriphosphazene and organoboron units promote the formation of an intumescent and dense char layer in the condensed phase, and inhibit the combustion in the gaseous phase by capturing active free radicals and releasing inert gaseous products to dilute the concentration of the combustion mixture. However, the T_gs of the flame-retardant EP samples gradually decrease with the increasing content of CP-6B, which has also been widely reported for other P-based flame-retardant additives [125-127].

5.1.2. Tri-group P-containing additives

Besides bi-group phosphorus-containing FRs, some tri-group additives have also been synthesized and applied in flame-retardant EP thermosets. In the light of good high-temperature stability of maleimide derivatives, two highly effective tri-group flame-retardant additives containing the maleimide group, namely DOPO-TMT and DMT have been recently designed for the EP by Huo *et al.* [128, 129] (see Figures 20a and 20d). In addition to maleimide, the phosphaphenanthrene and triazine serve as flame-retardant groups in the DOPO-TMT, the phosphaphenanthrene and triazine-trione groups in the DMT. The EP thermoset cured by DDS is used as the reference sample and named as EP in these works. With only 1.0 wt% loading of phosphorus, the EP/DOPO-TMT-1.0 sample exhibits a LOI value as high as 36.5%, with UL-94 V-0 rating, and the EP/DMT-1.0 system shows a comparable flame retardancy (LOI: 35.8%, and UL-94 rating: V-0). Meanwhile, the PHRR, THR and AHRR values of both the EP/DOPO-TMT and EP/DMT samples are found to gradually decrease with the increasing content of phosphorus under a heat flux of 50 kW/m^2. Specifically, compared with the reference EP, the PHRR of EP/DOPO-TMT-1.0 significantly decreases from 1208 to 776 kW/m^2 (a ~36% reduction), and that of the EP/DMT-1.0 sample declines from 1208 to 506 kW/m^2 (a ~58% reduction), indicative of high flame-retardant efficiency, as shown in Figures 20b and 20e. The enhanced flame retardancy is largely because both DOPO-TMT and DMT simultaneously function in the condensed and gaseous phases during combustion. In the condensed phase, DOPO-containing group cooperates with N-containing groups (maleimide and triazine or triazine-trione) to promote the formation of an intumescent and compact char acting as a fire shield (see Figures 20c and 20f). In the gaseous phase, the DOPO-containing group mainly inhibits the combustion by quenching free radicals, and the N-containing groups release inert gaseous fragments to dilute the combustible gases.

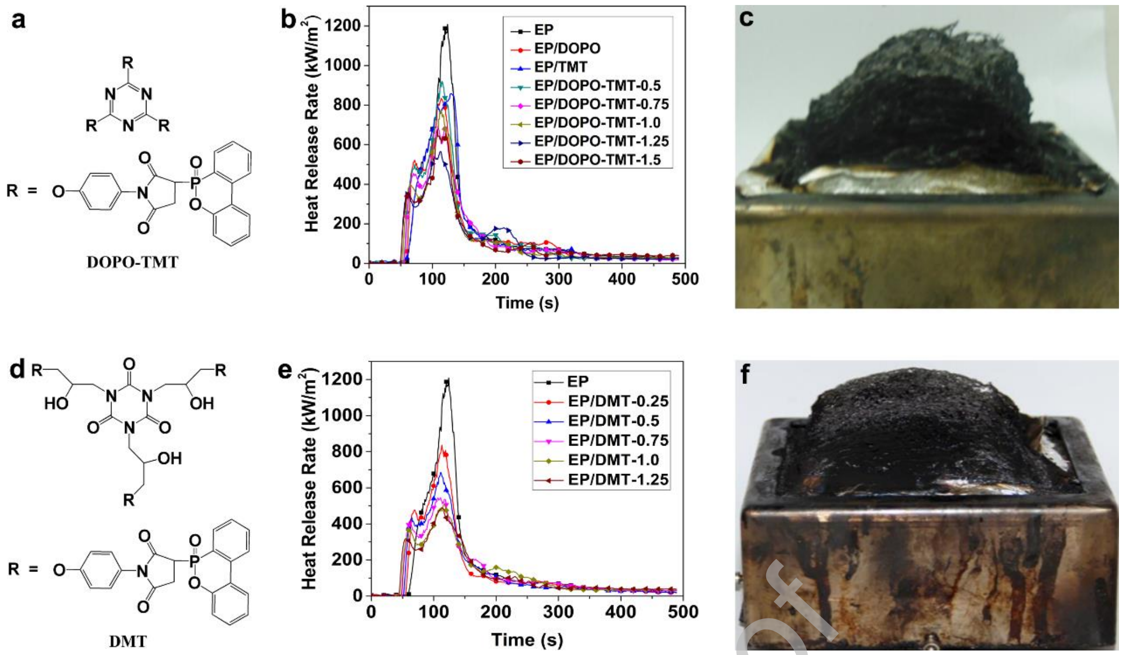

Fig. 20. Two tri-group P-based additives and their impacts on the flame retardancy of EP thermosets. a) Chemical structure of DOPO-TMT; b) HRR curves of EP and EP/DOPO-TMT thermosets; c) digital image of char residue of EP/DOPO-TMT-1.0 thermoset; d) chemical structure of DMT; e) HRR curves of EP and EP/DMT thermosets; and f) digital image of char residue of EP/DMT-1.0 thermoset. a-c) [128], Copyright 2015. Reproduced with permission from American Chemical Society; and d-f) [129], Copyright 2016. Reproduced with permission from Elsevier Science Ltd.

Recently, Zhang *et al.* [130, 131] reported two highly effective flame-retardant additives (DTB and BNP, see Figures 21a and 21b) with phosphorus-, nitrogen- and boron-based groups. The DTB-containing EP thermoset exhibits a high LOI value of 35.6% and a UL-94 V-0 rating, when the phosphorus content is only 0.81 wt%. Comparably, the BNP-containing EP thermoset containing 0.9 wt% of phosphorus also shows a moderately lower LOI value of 33.3%, despite a UL-94 V-0 rating achieved. In addition to the high flame retardancy efficiency of both DTB and BNP, they can also serve as excellent smoke suppressants for the EP. For example, the DTB-containing EP thermoset presents a 35.5% reduction in the TSP, whereas the BNP-containing counterpart displays a 41.7% reduction as compared with the control

EP sample, under an incident flux of 50 kW/m^2. Such remarkable enhancements in the flame retardancy and smoke suppression are realized through the collaboration of three flame-retardant groups in the condensed phase, leading to the formation of an intumescent and glassy char layer providing effective thermal protection effect during combustion.

Afterwards, Hu *et al.* [132] used their as-synthesized tri-group flame-retardant additive (PPAP, see Figure 21c) containing phosphonate, phosphate and piperazine for creating flame retardant EP thermosets. With the addition of 20 wt% of PPAP, the PHRR, AHRR and THR for the resultant EP thermoset decreases by ~72.5%, ~61.5% and ~61.6%, respectively, relative to the control EP thermoset under a heat flux of 35 kW/m^2. Moreover, a LOI value of 35.0% and a UL-94 V-0 rating are also achieved, suggesting good flame-retardant performances. The formation of a phosphorus-rich and dense char layer is considered to account for the significant improvement in the flame-retardant performance. In addition, the T_g of the EP thermoset steadily increases with the increasing content of PPAP because of their strong interfacial compatibility. Similar to other additive phosphorus-containing FRs [133-135], the PPAP has a certain negative affect on the thermal stability of the EP thermoset.

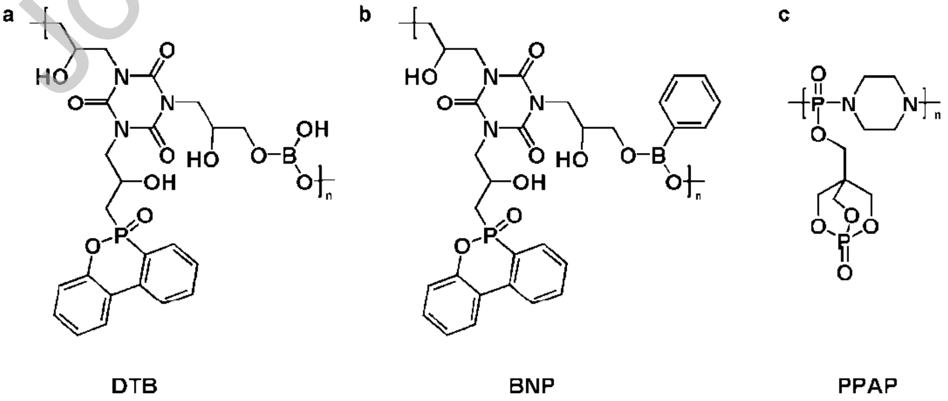

Fig. 21. Three typical tri-group P-containing additives: a) DTB, b) BNP and c) PPAP. a) [130], Copyright 2016. Reproduced with permission from Elsevier Science Ltd.; b) [131], Copyright

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5.1.3. Performance comparisons of Multi-group P-containing additives

In order to comprehensively evaluate the flame retardant efficiency of as-reported multi-group flame-retardant additives, the LOI value as a function of required flame retardant content for the EP thermosets with a UL-94 V-0 rating is plotted in Figure 22a. Their relative PHRR and THR reductions are also compared in Figure 22b. For better comparisons, the PHRR reductions and the LOI value of all the reported multi-group flame-retardant EPs containing 1.0 wt% of P are also plotted in Figure 22c. Their detailed flame retardant and thermal properties are summarized in Table 7.

Overall, most multi-group flame-retardant additives are capable of endowing the EP with a desirable flame retardancy (LOI ≥ 30.0% and UL-94 V-0) at a relatively low loading level (≤ 20 wt%), as shown in Figure 22a and Table 7. Meanwhile, all the EP thermosets show reduced initial decomposition temperatures ($T_{2\%}$, $T_{5\%}$, and $T_{10\%}$) and increased CYs because the P-based FRs catalyze the thermal decomposition and promote the carbonization of the EP matrix at elevated temperatures. Interestingly, in order to reach a UL94 V-0 rating, the required loading levels of FRs of the flame-retardant EP/DDM systems is lower than those of the flame-retardant EP/DDS and the EP/PN systems, as presented in Figure 22a, which is probably because of the relatively high flame retardancy of the control EP/DDM system that already exhibits an LOI of ~26.0%. In addition, the EP/TOD/DDM system exhibits a much higher LOI value relative to other flame-retardant EP/DDM systems when the FR content is comparable, clearly indicating a higher flame retardancy efficiency of TOD than other FRs due to the P-N synergy.

As shown in Figure 22b and Table 7, the PHRR and THR reductions of EP/TOD/DDM system are also greater than other flame-retardant EP/DDM systems, further demonstrating the better synergy between phosphorus and nitrogen. Meanwhile, Trif-DOPO with triazine and phosphaphenanthrene groups performs better in reducing PHRR of the EP/DDS thermoset compared with other bi-group flame-retardant additives (CTP-DOPO and TGIC-DOPO), mainly because triazine groups with a bi-phase effect can simultaneously strengthen the gas- and condensed-phase mechanisms of the phosphorus-containing group. Therefore, the combination of triazine and P-containing groups is an effective way to create high-efficiency P/N-containing FRs. In addition, the tri-group flame-retardant EP (EP/DMT/DDS and EP/DTB/DDS) systems show more significant PHRR reductions relative to the bi-group flame-retardant EP/DDS systems in addition to comparable LOI values, suggesting that synthesizing flame-retardant additives based on tri-group synergy is another promising strategy to enhance the flame retardancy efficiency.

Similar results can also be observed when the P content of the multi-group flame-retardant EP thermosets is around 1.0 wt% (see Figure 22c). The multi-group flame-retardant additives (e.g., Trfi-DOPO, DTB and DMT) based on the P-N or tri-group synergy exhibit higher flame-retardant efficiency than other flame-retardant counterparts. In summary, to develop highly efficient P-containing FRs for the EP thermoset, more attention should be paid to the design of multi-group flame-retardant additives based on the P-N synergy (e.g., P-triazine), or tri-group synergy (e.g., P-N-Si and P-N-B).

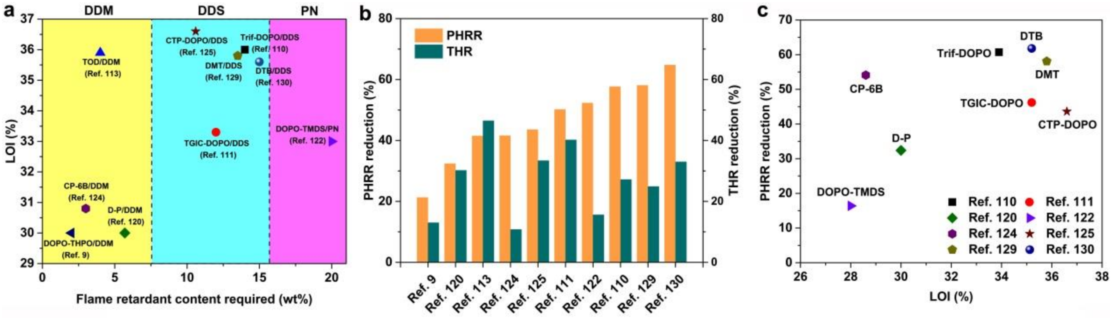

Fig. 22. The flame retardancy summary of the multi-group flame-retardant EP thermosets. a) The required flame retardant contents and LOI values; b) the PHRR and THR reductions of the multi-group flame-retardant EP thermosets with UL-94 V-0 ratings; and c) LOI values and PHRR reductions of the multi-group flame-retardant EP thermosets with ~1.0 wt% of P.

Table 7. Flame retardancy and thermal properties of the multi-group flame-retardant EP thermosets with UL-94 V-0 ratings.

Name of FR	FR content (wt%)	P content [a] (wt%)	LOI (%)	Reduction (%)		Thermal properties [d]	Ref.
				PHRR	THR		
Trif-DOPO	14.0	1.20	36.0	57.7 [b]	27.2 [b]	$T_{5\%}$ significantly reduces and CY obviously increases.	[110]
TGIC-DOPO	12.2	1.18	33.3	50.2 [b]	40.2 [b]	T_g decreases to 176 °C by 15 °C, $T_{2\%}$ reduces by 44 °C and the CY at 700 °C increases from 12.3% to 18.8%.	[111]
TOD	4.0	0.35	35.9	41.5 [b]	46.5 [b]	$T_{10\%}$ decreases by 14 °C, and the CY at 700 °C increases from 13.2% to 15.2%.	[113]
D-P	5.7	0.90	30.0	32.4 [c]	30.2 [c]	$T_{5\%}$ decreases by 34.4 °C, and the CY at 800 °C increases from 10.8% to 17.5%.	[120]
DOPO-THPO	2.0	0.33	30.0	21.3 [c]	13.0 [c]	T_g increases to 155 °C by 8 °C, $T_{5\%}$ decreases by 25 °C, and the CY at 735 °C increases from 16.2% to 18.1%.	[9]

DOPO-TMDS	20	2.0	33.0	52.3 [b]	15.6 [b]	T_g decreases to 141 °C by 36 °C, $T_{5\%}$ is unchanged, and the CY at 700 °C increases from 24.1% to 31.6%.	[122]
CP-6B	3.0	0.29	30.8	41.6 [b]	10.8 [b]	T_g decreases to 139 °C by 16.7 °C, $T_{5\%}$ decreases by 39.4 °C, and the CY at 800 °C increases from 9.7% to 18.0%.	[124]
CTP-DOPO	10.6	1.1	36.6	43.6 [b]	33.4 [b]	$T_{5\%}$ decreases by 35.4 °C, and the CY at 700 °C increases from 14.1% to 29.1%.	[125]
DMT	13.5	1.0	35.8	58.1 [b]	24.9 [b]	$T_{5\%}$ decreases by 69 °C, and the CY at 800 °C increases from 17.3% to 23.3%.	[129]
DTB	15.0	0.81	35.6	64.8% [b]	33.0% [b]	$T_{5\%}$ decreases by 38 °C, and the CY at 800 °C increases from 17.3% to 28.7%.	[130]

[a] P content in the cured EP;

[b, c] PHRR and THR are determined by cone calorimeter test at a heat flux of 50 and 35 kW/m^2;

[d] $T_{2\%}$, $T_{5\%}$, $T_{10\%}$ and CY are obtained from TGA under N_2 flow.

5.2. Multifunctional P-containing additives

The multifunctional P-containing additives represent a class of P-containing flame-retardant additives that can enhance simultaneously the flame retardancy and other properties (e.g., elastic modulus, T_g) of the resultant EP composites. This section mainly focuses on two classes of multifunctional P-containing additives: hyperbranched and nanoscale P-containing additives.

5.2.1. Hyperbranched P-containing additives

Hyperbranched polymers have gained increasing attention because of their facile synthesis, low viscosity, multifunctional terminals, good miscibility and compatibility with other polymeric materials [136-142]. In recent years, many hyperbranched phosphorus-containing additives have been utilized as multifunctional flame-retardant additives for the EP thermoset because they can simultaneously improve the flame retardancy and the mechanical properties.

For example, Hu *et al.* [143] synthesized a hyperbranched phosphorus-containing additive (HPUPO, see Figure 23a) from 4,4’-diphenylmethane diisocyanate and trihydroxymethylphosphine oxide. The introduction of HPUPO results in a significant improvement in the flame-retardant performance of the EP thermoset. The resultant EP thermoset with 4.0 wt% of HPUPO shows a LOI value of 30.5% and a UL-94 V-0 rating, and the PHRR and THR decrease from 1795 to 1035 kW/m^2 with a ~42.3% reduction, and from 67.5 to 42.7 MJ/m^2 with a ~36.7% reduction, respectively, compared with the unmodified EP thermoset under an external heat flux of 35 kW/m^2. The char data reveal that during combustion, the HPUPO can increase the CY of the EP matrix to form a protective char layer in the condensed phase, thus giving rise to enhanced flame retardancy. Moreover, the HPUPO maintains the high T_g and improves the toughness of the EP matrix because of its hyperbranched structure.

In another work, Qian *et al.* [144] have recently prepared a phosphaphenanthrene/borate-containing hyperbranched FR (ODOPB-Borate, see Figure 23b) for EP thermoset. The ODOPB-Borate serves as a multifunctional additive to simultaneously enhance the flame retardancy, T_g and impact strength of the EP thermoset. Specifically, with 6.0 wt% of ODOPB-Borate, the LOI value and UL-94 rating of the final EP sample reach 31.6% and V-0, respectively. Additionally, a ~24.0% reduction in the PHRR and a ~13.7% reduction in the THR are observed under an external heat flux of 50 kW/m^2. The phosphaphenanthrene and borate groups work cooperatively in both the condensed and gaseous phases, thus suppressing the combustion of the EP matrix. Notably, in comparison to the unmodified EP sample, the T_g for the ODOPB-Borate-modified EP sample increases from 194.2 °C to 196.4 °C, and the impact strength increases from 9.72 to 21.92 kJ/m^2 with ~55.7% enhancement. This indicates that the ODOPB-Borate is superior to some bi-group flame-retardant additives [115, 116] because of its multifunctional characteristics.

Recently, Zhang *et al.* [145] developed a hyperbranched bio-based phosphorus-containing additive (DOPO-HBP, see Figure 24a) from DOPO, diisopropanolamine and renewable itaconic anhydride. In this work, the DOPO-HBP simultaneously enhances the flame retardancy, smoke suppression and mechanical properties of the EP thermoset at low phosphorus content. Typically, the EP thermoset with the DOPO-HBP exhibits a LOI value of 36.4% in addition to a UL-94 V-0 rating when the phosphorus content is as low as only 0.26 wt%. Additionally, with the incorporation of 10.64 wt% DOPO-HBP (0.72 wt% phosphorus), the PHRR (see Figure 24b) and TSR of the resultant EP thermoset decrease by ~21.3% and ~16.0%, respectively, relative to the unmodified EP thermoset under a heat flux of 35 kW/m^2. Such improved flame retardancy is primarily because the DOPO-HBP inhibits the combustion of the EP matrix *via* generating phosphorus-based free radicals to interrupt the combustion in the gas phase, and forms a phosphorus-rich layer in the condensed phases, which is similar to most DOPO-based FRs [28, 146-149]. In addition, the DOPO-HBP possesses a strong effect on the tensile strength and toughness of EP thermoset. As shown in Figure 24c, the introduction of 10 wt% of DOPO-HBP also leads to a prominent increase in both the tensile strength by 37.8% and the impact strength by 133.2% of the EP thermoset. Unfortunately, the DOPO-HBP shows a plasticization effect on the EP, as reflected by the reduced T_g because of its flexible aliphatic segment.

Very recently, Schartel *et al.* [150-154] synthesized several different kinds of multifunctional hyperbranched phosphorus-containing FRs for the EP. For instance, they fabricated a hyperbranched poly(phosphoester) (hbPPE, see Figure 23c) and compared its flame-retardant effect with that of the commercial BDP in EP [150]. The EP with hbPPE exhibits a much lower THE and a higher LOI than the EP with the same loading level of BDP, indicating a better flame-retardant performance of hbPPE. Specifically, the EP with 10wt% BDP shows a THE of 83 MJ/m^2, while the EP with 10wt% hbPPE gives a THE of only 62 MJ/m^2. Both hbPPE and BDP act in the condensed and gaseous phases, but the former is more effective in increasing the char yield, which might be the main reason for its better performance. In addition, for different hyperbranched FRs, the overlap of the decomposition temperatures between them and the EP matrix are found to play an important role in the flame retardancy. This means that a matched decomposition temperature of the FRs with the polymer matrix can help give rise to a better flame retardancy in the polymer.

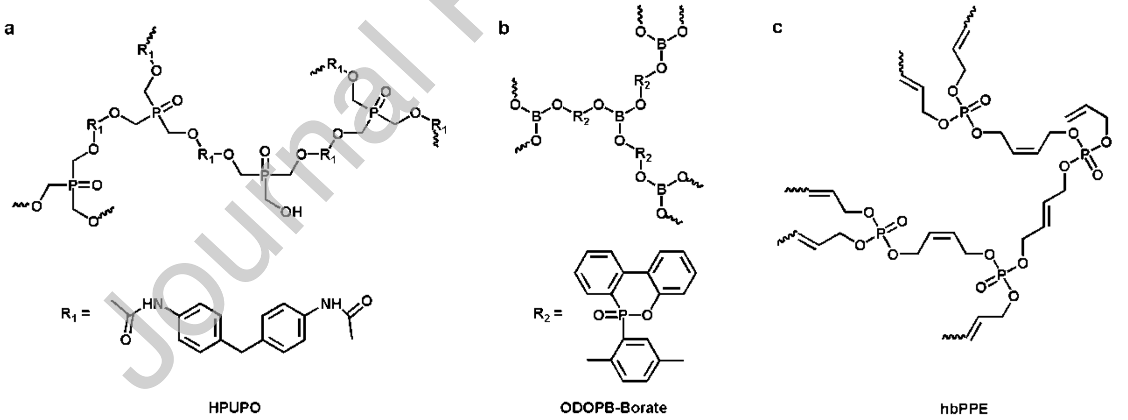

Fig. 23. Three typical hyperbranched P-containing additives: a) HPUPO, b) ODOPB-Borate and c) hbPPE. a) [143], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.; b) [144], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.; and c) [150], Copyright 2014. Reproduced with permission from Royal Society of Chemistry.

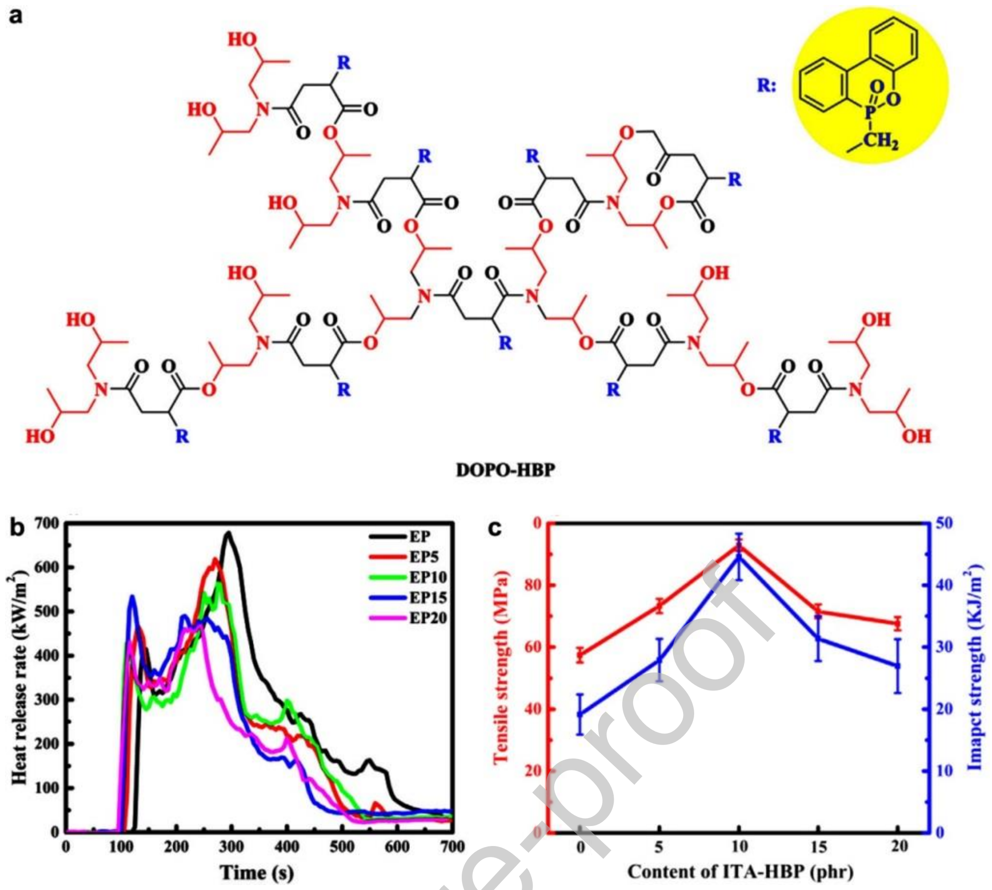

Fig. 24. DOPO-HBP and its impact on the properties of EP thermosets. a) Chemical structure of DOPO-HBP; b) HRR curves of EP thermoset as a function of time; and c) tensile strength and impact strength of EP thermosets. [145], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

5.2.2. Nanoscale P-containing additives

With the rapid development of nanotechnology, various nanoscale additives are exploited as functional additives for creating high-performance polymeric materials because of their unique physical and chemical properties [155-159]. In recent years, nanoscale additives have been extensively applied in flame-retardant EP thermosets because of their superior thermal stability and flame retardancy properties [160-164]. Apart from flame retardancy, nanoscale additives can often improve other performances, such as the mechanical and electrical properties of the EP matrix. Although the resultant EP nanocomposites show a remarkable reduction in the combustion intensity (HRR and THR) during cone calorimeter tests, they often fail conventional fire safety tests, such as LOI and UL-94. In addition, high aspect ratios of nanomaterials tend to agglomerate within the polymer matrix due to high surface energy, which can significantly undermine their flame retardancy and mechanical reinforcement effects on the polymer. To better address these two issues, various phosphorus-based functional groups have been used to modify nanoscale additives to further improve their dispersion within the polymer matrix and flame-retardant efficiency. This section will focus on the development of some typical nanoscale additives including POSS, CNT, MMT, LDH, GO or rGO, MoS_2, and h-BN.

5.2.2.1. P-containing POSS

POSS, as a class of inorganic-organic hybrid nanomaterials comprising silicon and oxygen, has attracted tremendous interest in the field of flame retardancy because of its environmental neutrality, exceptional heat resistance, and thermoxidative stability [165-167]. Several phosphorus-containing POSS additives with improved flame-retardant efficiency have been developed based on a P-Si synergism [168-170]. In addition, most of these P-modified POSS additives exhibit multiple functions: simultaneously enhancing the flame retardancy, thermal stability, and mechanical properties of the EP thermoset. For instance, Dai *et al.* [169] synthesized a DOPO-containing POSS (see Figure 25a) *via* a Kabachnik-Fields reaction and prepared flame-retardant EP nanocomposites based on POSS-bisDOPO. The resultant EP/POSS-bisDOPO nanocomposite exhibits simultaneous enhancements in the flame-retardant, charring capability and mechanical properties. With 20 wt% of POSS-bisDOPO, the LOI value of the EP thermoset attains 34.5% (see Figure 25b). Additionally, with the same FR addition (herein, 5 wt%), the EP sample containing POSS-bisDOPO shows a higher LOI value than that containing POSS or DOPO, indicating the higher flame retardancy efficiency of POSS-bisDOPO due to the synergy of POSS and DOPO and better dispersibility. Meanwhile, the flame-retardant EP nanocomposite shows a ~11.7% increase in the flexural strength relative to the bulk EP. The char analysis shows that in the combustion process, the POSS-bisDOPO can give rise to an intumescent and compact char layer to protect the underlying matrix, accounting for the improved flame retardancy. Analogous mode of actions were also reported for the phosphorus-containing POSSs by Yang *et al.* [170, 171].

In another work, Zeng *et al.* [172] reported a phosphaphenanthrene/triazine/POSS-containing multifunctional nanoscale FR (PDT, see Figure 25c), and found that all the EP thermosets with PDT exhibited a single T_g but higher than that of the neat EP thermoset, resulting from the uniform dispersion of rigid PDT. The addition of 7 wt% of PDT enables the EP thermoset to gain a LOI value of 32.5% and a UL-94 V-0 rating, in addition to a 12.0% reduction in the PHRR relative to the unmodified EP in the MCC test (see Figure 25d). Similar to the POSS-bisDOPO [169], the PDT shows a better flame-retardant performance, in terms of LOI values and UL-94 ratings than DOPO and POSS at the same content. The PDT improves the flame retardancy by promoting the matrix to form a protective char in the condensed phase, and by releasing phosphorus/nitrogen-containing free radicals to quench the H·, O· and OH· free radicals in the gaseous phase during combustion. Moreover, the PDT shows a mechanical reinforcement effect, leading to improved flexural modulus and impact strength of the EP thermoset, probably because it self-assembles into dandelion-shaped nanoparticles in the EP matrix, leading to a toughening effect. This indicates that the PDT is a multifunctional flame-retardant additive for the EP.

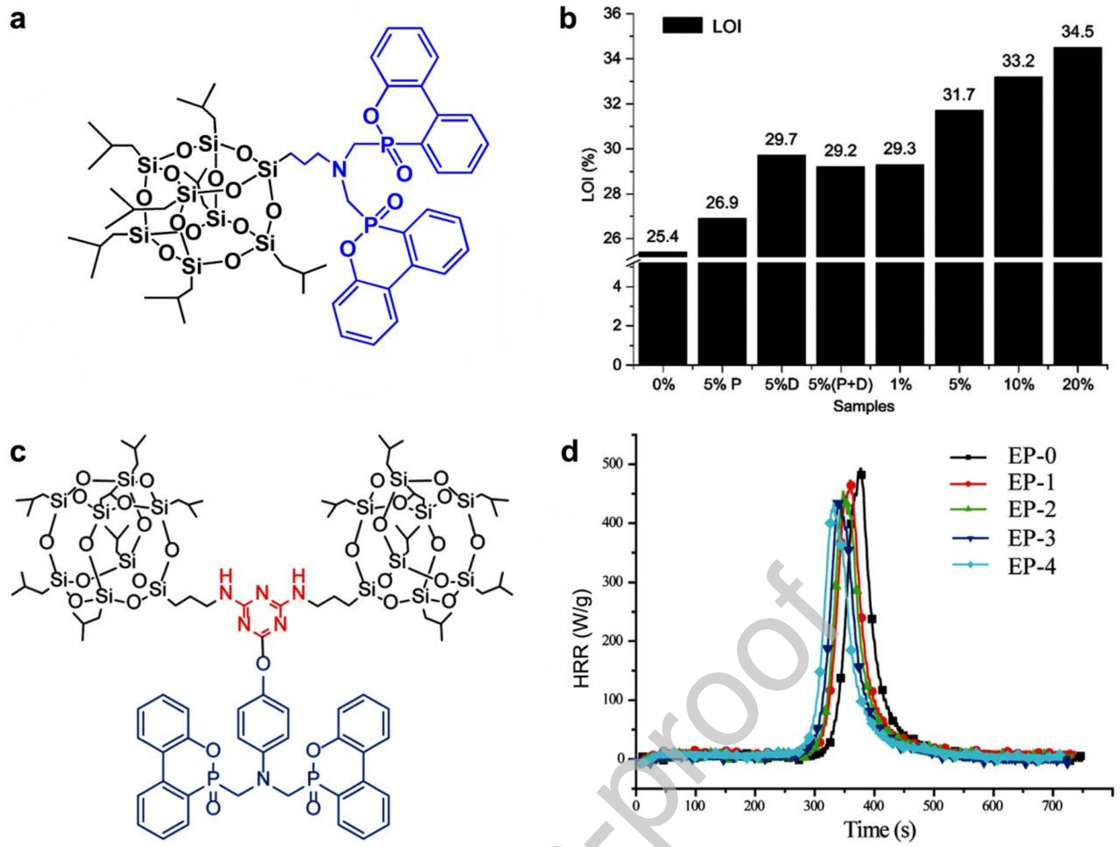

Fig. 25. Two typical P-containing POSSs and their impacts on the flame retardancy of EP nanocomposites. a) Chemical structure of POSS-bisDOPO; b) LOI values of EP samples with POSS-bisDOPO and the control samples; c) chemical structure of PDT; and d) HRR curves of EP sample with and without PDT. a, b) [169], Copyright 2016. Reproduced with permission from American Chemical Society; and c, d) [172], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.

5.2.2.2. P-containing CNTs

CNTs have been considered to be promising flame-retardant nanoscale additives for EP thermosets because of their high length-diameter ratio, outstanding mechanical and electrical properties [163, 173-175]. Recently, the combination of CNTs and phosphorus-based flame retardants has been reported to create flame-retardant EP nanocomposites by decorating CNTs with phosphorus-containing groups [176-178] . Generally, the resultant EP nanocomposites with phosphorus-containing CNTs normally exhibit improved flame retardancy and mechanical properties. Fei *et al.* [176]

prepared a phosphorus/nitrogen-containing polymer wrapped carbon nanotubes (CNT-PD, see Figure 26a) *via* strong π-π stacking interactions. The CNT-PD was found to significantly improve the flame-retardant performances of the EP thermoset at a low loading level. For example, 2 wt% of CNT-PD increases the LOI value from 26.3% of the neat EP to 33.6%. Moreover, under an external heat flux of 50 kW/m^2, the PHRR of the EP with 2 wt% of CNT is 963 kW/m^2, and the 2 wt% of CNT-PD decreases the PHRR to 754 kW/m^2 (see Figure 26b), indicating the combined effect of phosphorus/nitrogen-containing polymer and the 3D CNT network. Specifically, in the gaseous phase, the phosphorus/nitrogen-containing polymer decomposes to generate PO_2· and PO· free radicals that can quench the active H• and HO• free radicals in the flame to inhibit the combustion. In the condensed phase, the phosphorus/nitrogen-containing polymer and CNTs promotes the formation of an intumescent char layer reinforced by the CNT network, which significantly suppresses the thermal degradation of the underlying EP matrix by preventing the heat feedback. Following this work, Fei *et al.* [177] introduced phosphaphenanthrene groups onto the surface of CNTs to prepare another phosphorus-containing flame-retardant CNTs, namely PDAP-CNT. In this case, a very low loading level of PDAP-CNT also causes significant improvements in the LOI value and the UL-94 rating of the EP thermoset, and a prominent reduction in the PHRR, THR and TSR. The two works demonstrate that introducing phosphorus-containing groups onto the CNTs surface is an effective way to strengthen the flame-retardant efficiency of CNTs.

Meanwhile, Ma *et al.* [178] reported a functionalized multiwalled carbon nanotube with cyclotriphosphazene groups (MWNT-HCPCP, see Figure 26c), which was used to improve the flame retardancy and mechanical properties of the EP thermoset. In comparison to the EP nanocomposite with 5 wt% of MWNT, the addition of 5 wt% of MWNT-HCPCP further increases the LOI value of the EP from 22.2% to 23.8%, and further decreases the SDR value from 89.3% to 83.3%, indicating an improved flame retardancy and smoke suppression effect. More impressively, the introduction of MWNT-HCPCP enhances the tensile strength and elastic modulus of the EP thermoset (see Figure 26d), resulting from the homogeneous dispersion of MWNT-HCPCP in the EP matrix. Thus, the grafting of cyclotriphosphazene-containing unit can improve the dispersion of CNTs within the polymer host, and the flame-retardant efficiency of CNTs. Such simultaneous improved flame retardancy and mechanical performances have also been observed in other EP nanocomposites based on P-containing CNTs [179-181].

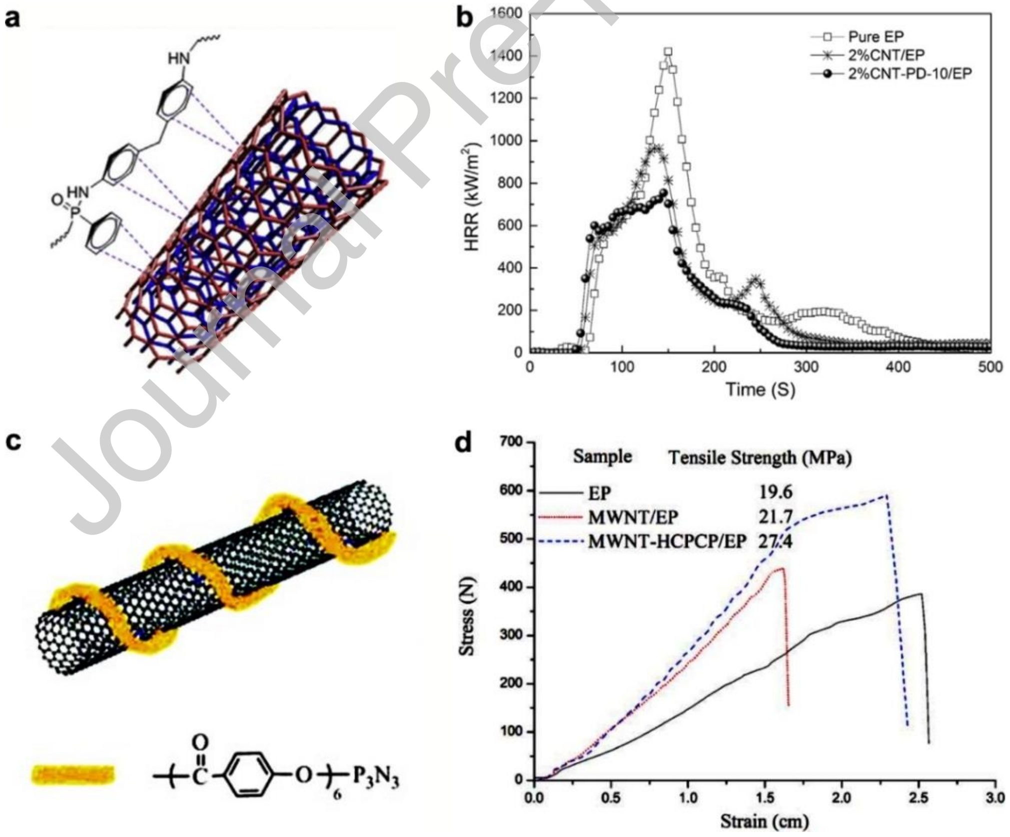

Fig. 26. Two P-containing carbon nanotubes and their impacts on the properties of EP nanocomposites. a) Schematic illustration of the structure of CNT-PD; b) HRR curves of EP samples and EP nanocomposite with CNT-PD; c) schematic illustration of the structure of

MWNT-HCPCP; and b) stress-strain curves of EP samples and EP nanocomposite with MWNT-HCPCP. a, b) [176], Copyright 2016. Reproduced with permission from Elsevier Science Ltd.; and c, d) [178], Copyright 2014. Reproduced with permission from John Wiley & Sons Inc.

5.2.2.3. P-containing MMT

Nanoscale montmorillonite (MMT) possesses a crystal structure comprising a central octahedral alumina sheet sandwiched between two tetrahedral silica sheets [182-184]. It has been widely used to create flame-retardant polymer nanocomposites showing increased char yield and reduced heat release rate due to its physical barrier effect [185-187]. For the EP/MMT nanocomposites, their thermodynamic incompatibility and the poor dispersion of MMT within the EP matrix often results in unsatisfactory flame retardancy and mechanical properties. Hence, it is essential to address these two issues for the creation of high-performance EP/MMT nanocomposites.

Recently, Zhang *et al.* [188-190] demonstrated an effective method to promote the dispersion of MMT layers in the EP matrix by modifying the MMT with P-containing flame retardants. Typically, they prepared DOPO-modified montmorillonite (DOPO-MMT) *via* high-speed stirring and ultrasonication (see Figure 27a) and used the DOPO-MMT to fabricate flame-retardant EP nanocomposite (EP/DOPO-MMT) [189]. Meanwhile, the unmodified EP thermoset, the EP thermoset with MMT, the EP thermoset with DOPO and the EP thermoset with DOPO and MMT, namely EP, EP/MMT, EP/DOPO and EP/DOPO+MMT, are also prepared as the reference samples. The resultant EP/DOPO-MMT system exhibits better flame retardancy than other reference samples, e.g., a LOI value of 33.4%, a UL-94 V-0 rating, and a 53.7% reduction in PHRR relative to the neat EP (see Figure 27b) due to (i) the improved dispersion of DOPO-MMT and (ii) the synergy between DOPO and

MMT. Using high-speed stirring and ultrasonication, DOPO molecules diffuse into the gallery of MMT to enlarge the interlayer spacing, which facilitates the dispersion of MMT layers in the EP matrix. Meanwhile, the well-dispersed MMT layers cooperate with DOPO to form a continuous and firm MMT-containing char barrier which can suppress the combustion of the EP. Similar phenomena were also observed in the other two reports by Zhang *et al.* [188, 190]. However, the introduction of DOPO-MMT decreased the T_g value by 16 ^{o}C, probably due to the reduced crosslinking density of the resultant EP as a result of the end-capping reaction between DOPO and epoxy groups. In brief, it remains a huge challenge to design phosphorus-containing MMT for creating high-performance EP thermosets with enhanced flame retardancy without reducing the T_g of the EP.

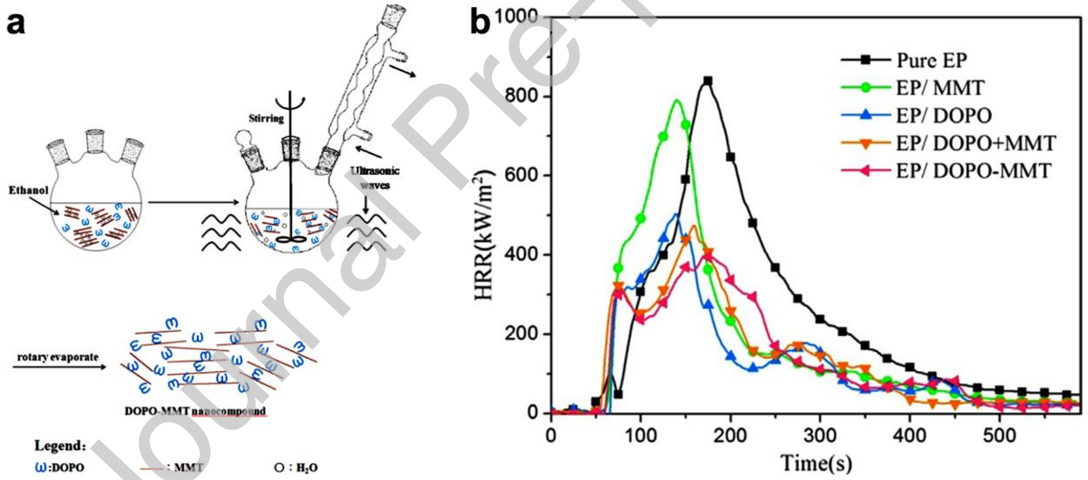

Fig. 27. DOPO-MMT and its impact on the flame retardancy of EP nanocomposites. a) Schematic illustration of the preparation process of DOPO-MMT; and b) HRR curves of EP samples as a function of time. [189], Copyright 2017. Reproduced with permission from Elsevier Science Ltd.

5.2.2.4. P-containing LDH

Layered double hydroxides (LDHs) are also ionic nanoclays, which comprise positively-charged metal hydroxide layers intercalated with anions and water [191-193], and Mg-Al LDH and Co-Al LDH are two typical LDHs [194-196]. Similar to MMT, LDHs are widely used in flame-retardant EP thermosets because of their large amount of interlayer water and a synergy with conventional FRs [197-199]. However, strong interlayer interactions and polarity make it difficult to disperse well, thus leading to inadequate flame-retardant performances and mechanical reinforcement. Hence, various intercalating agents, including sulfonates [200, 201] and fatty acid salts [202], have been employed to promote the dispersion of LDHs within the EP matrix.

Recently, Wang *et al.* [203] reported an effective approach to improve the dispersion and flame-retardant efficiency of LDHs through the design of a multifunctional Mg-Al LDH, SIEPDP-LDH (see Figure 28a), by using an as-synthesized P/Si-containing intercalating agent. The SIEPDP-LDH can enhance the flame retardancy and mechanical properties for the EP thermoset at a low loading level. Compared with the unmodified LDH (NLDH), the SIEPDP-LDH presents a higher flame retardancy efficiency at the same loading level. With the FR addition of 8 wt%, the EP thermoset with SIEPDP-LDH exhibits a UL-94 V-0 rating, while the EP thermoset with NLDH fails (see Figure 28b). In addition, the PHRR of the EP thermoset with SIEPDP-LDH is only 658 kW/m^2, much lower than that of the EP thermoset with NLDH (835 kW/m^2) under a heat flow of 50 kW/m^2 when the FR content is 4wt%. Moreover, the presence of SIEPDP-LDH improves the impact strength of the EP whereas the incorporation of NLDH reduces the impact strength, as shown in Figure 28c. Such performance enhancements in flame retardancy and impact toughness are due to the improved dispersion of LDH, and the additional flame retardancy effect of the P/Si-containing the intercalating agent. Following this work, they prepared another modified LDH with phosphorous-containing intercalating agent, which also exhibited multifunctionality in the EP thermoset [204]. These results demonstrate that the design of P-containing intercalating agents for LDHs presents a promising strategy for developing multifunctional LDHs as highly effective flame retardants of EP thermosets.

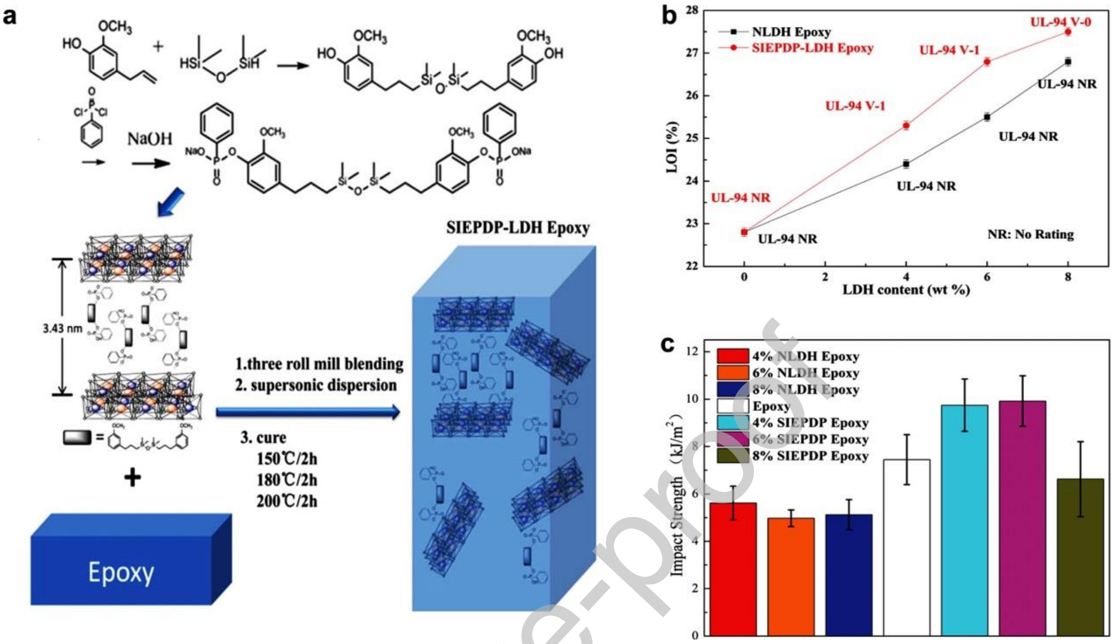

Fig. 28. SIEPDP-LDH and its impact on the properties of EP nanocomposites. a) Schematic illustration of the preparation procedure of EP nanocomposite with SIEPDP-LDH; b) LOI values and UL-94 ratings of EP nanocomposites; and c) impact strength of EP nanocomposites. [203], Copyright 2015. Reproduced with permission from American Chemical Society.

5.2.2.5. P-containing GO or rGO

As a two-dimensional atom-thick nanomaterial, graphene features a large surface area, high aspect ratios, exceptional mechanical properties, and good thermal and chemical stability [205-207]. Because of these merits, graphene and its derivatives have been exploited for possible applications as capacitors, sensors, microwave absorptions, and thermally-conductive composites [208-212]. They have recently demonstrated an excellent flame retardant effect in EP thermosets because high aspect ratios enable them to serve as physical barriers during the combustion of polymers [213-215].

However, the graphene nanosheets exhibit a strong tendency to restack and re-agglomerate due to strong π-π stacking interactions, which makes it difficult to uniformly disperse graphene within the polymer matrix, thus restricting their flame-retardant and mechanical reinforcement effects. For this reason, the graphene needs to be functionalized for addressing this issue. A promising strategy is functionalizing graphene with phosphorus-containing groups or compounds because this enables a synergistic flame-retardant effect between them, and improved dispersion of graphene sheets within the polymer matrix, which is promoted by the phosphorus-containing modifiers on the graphene surface [216-218]. As a result, the phosphorus-functionalized graphene nanomaterials often exhibit multifunctional characteristics. For instance, Hu *et al.* [219] reported the use of DOPO/silicon-containing graphene (FRs-rGO) for flame-retardant EP nanocomposites. An *in-situ* sol-gel method is used to exfoliate the majority of graphene nanosheets into the DOPO/silicon-containing organic matrix, which facilitates the dispersion of graphene nanosheets in the EP matrix. The flame retardancy measurements show that in addition to a 35% reduction in the PHRR under a heat flux of 35 kW/m^2, a LOI value of 29.5% and a UL-94 V-0 rating are achieved for the resultant EP nanocomposites with an inclusion of 5 wt% FRs-rGO, as compared with a LOI value of 21.0% and no UL-94 ratings for the neat EP sample. Such an improved flame-retardant performance may be due to the free radical quenching effect of DOPO, the char-reinforcing effect of silicon, and the barrier effect of graphene nanosheets. Moreover, the presence of FRs-rGO improves the T_g and storage modulus of the resultant EP nanocomposite because of the restricting effect of homogeneously-dispersed graphene nanosheets on the EP segments and their mechanical reinforcement effects, respectively.

In addition, Ye *et al.* [220] also reported the covalent functionalization of graphene by using a P/N/Si-containing flame retardant. Upon the addition of 3 wt% of FRGO, the PHRR, THR and TSP of the EP decrease by 34%, 14% and 30%, respectively, compared with the neat EP, under an external heat flux of 35 kW/m^2.Furthermore, when the FR content is 1.0 wt%, the rGO-containing EP sample just displays a LOI value of 24.3% and no rating during the UL-94 test. In contrast, the FRGO-containing EP system exhibits a higher LOI value of 26.3% and reaches a UL-94 V-2 rating. The improved flame-retardant efficiency is attributed to the synergistic effect between P/N/Si-containing flame retardant and rGO. Moreover, the presence of FRGO nanosheets leads to increased storage modulus of the EP nanocomposite. In addition, Yu *et al.* [221] have very recently prepared functionalized graphene (f-rGO) by chemically bonding DOPO-phosphonamidate onto the graphene nanosheets (see Figure 29a). Upon the chemical functionalization, the f-rGO shows improved interfacial interactions with the EP matrix. With the same addition (1 wt%), the f-rGO/EP1.0 sample shows a ~11% reduction in PHRR (see Figure 29b), ~19% reduction in THR and ~11% reduction in TSR compared to the reference GO/EP1.0 sample, under a heat flux of 35 kW/m^2. The improved flame retardancy and smoke suppression result from DOPO-phosphonamidate cooperation with rGO nanosheets to facilitate the formation of a thermally insulating char layer as a shield for both heat and smoke. Meanwhile, f-rGO also improves the CY at 800 °C, the storage moduli, and the T_g of the EP nanocomposite. Moreover, many other similar covalently functionalized phosphorus-containing graphene nanosheets have also been developed for the fabrication of high-performance flame-retardant EP nanocomposites so far [214, 222-224].

In addition to covalent functionalization, many functionalized GOs based on physical interactions have also recently been reported [225, 226]. Typically, Song *et al.* [225, 226] prepared a phytic acid/piperazine-functionalized graphene oxide (PPGO) *via* simple hydrogen-bonding self-assembly in water. The EP/PPGO nanocomposite exhibits remarkably improved flame retardancy, smoke suppression, thermal stability, and thermo-mechanical properties. Compared with the EP nanocomposite with 3 wt% of GO, the addition of 3 wt% of PPGO reduces the PHRR by ~37%, the THR by ~19%, and the TSP by ~19%, respectively, under a heat flux of 35 kW/m^2. This is largely because of the charring effect of the phytic acid, the gas dilution effect of piperazine, and the creation of a tortuous path caused by GO layers that can slow the diffusion of small degradation products during the burning of EP. Moreover, the PPGO is also capable of dramatically increasing the T_g, initial decomposition temperatures, and the char yield at 700 °C of the EP nanocomposite. Subsequently, Zhang *et al.* [227] reported a similar functionalized graphene oxide (f-GO, see Figure 29c) by using a phosphorus/nitrogen-containing flame retardant. With the addition of 2 wt% f-GO, the final EP nanocomposite achieves a LOI value of 31.5% in addition to 29.3% and 73% reductions in the PHRR and TSP relative to the neat EP sample under a heat flux of 35 kW/m^2 (see Figure 29d), respectively, due to a similar flame-retardant mode of action to PPGO.

In summary, functionalizing graphene with phosphorus-containing compounds through chemical or physical approaches represents a highly promising and effective strategy to develop multifunctional phosphorus-containing graphene as high-performance flame retardant additives for EP thermosets.

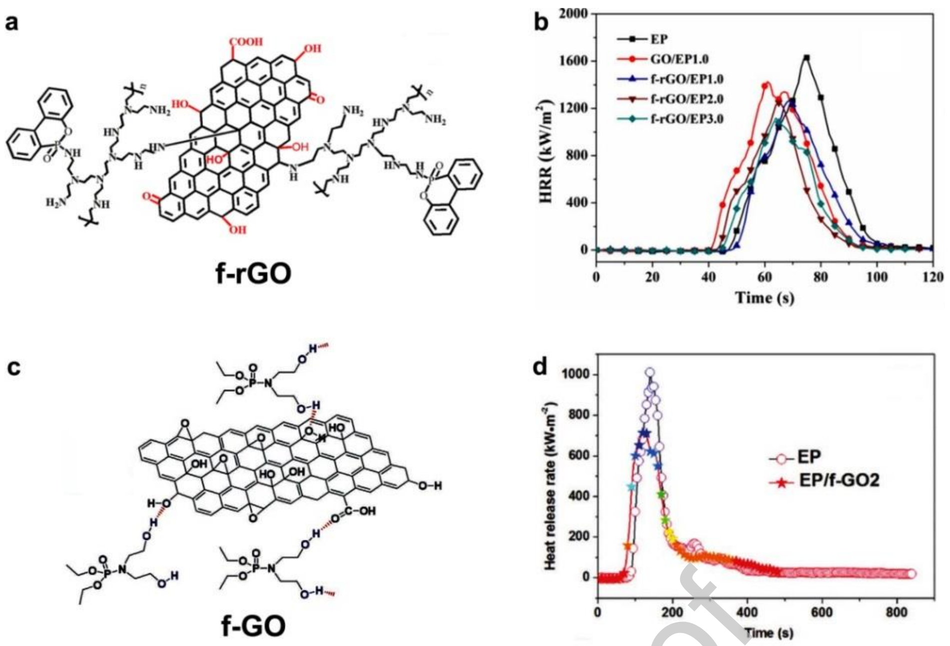

Fig. 29. Two P-containing graphenes and their impacts on the flame retardancy of EP nanocomposites. a) Schematic illustration of the structure of f-rGO; b) HRR curves of pure EP sample and EP nanocomposites with GO or f-rGO as a function of time; c) schematic illustration of the structure of f-GO; and d) HRR curves of the neat EP sample and EP nanocomposite with 2 wt% f-GO as a function of time. a, b) [221], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.; and c, d) [227], Copyright 2019. Reproduced with permission from John Wiley & Sons Inc.

5.2.2.6. P-containing MoS_2

Molybdenum disulfide (MoS_2) is a class of rising 2D layered nanomaterials, formed by a stack of honeycomb layers of Mo atoms sandwiched between adjacent layers of S atoms *via* van der Waals interactions [228-230]. Similar to other 2D aforementioned nanomaterials, MoS_2 has also been exploited to improve the thermal stability and flame retardancy of EP thermosets in recent years [231-233]. Likewise, the inclusion of MoS_2 nanosheets can also enhance the mechanical properties of the EP thermosets because of their nanosized thickness, high specific surface area and exceptional mechanical properties [234]. However, its flame-retardant efficiency is inadequate if used alone for EP, and meanwhile the uniform dispersion of MoS_2

within the EP matrix is another challenge, which can further weaken its flame-retardant efficiency.

To improve the dispersion of MoS_2 and its flame-retardant efficiency, organic phosphorus-based flame retardants are used to functionalize the MoS_2 nanosheets [235, 236]. For instance, Xing *et al.* [235] fabricated a polyphosphazene nanoparticle (PPN) functionalized MoS_2 nanosheet (MoS_2@PPN) *via* a facile ball-milling approach (see Figure 30a). The inclusion of 2 wt% of MoS_2 into the EP leads to a 19.6% reduction in PHRR, whereas 2 wt% of MoS_2@PPN leads to a 30.7% reduction in PHRR (see Figure 30b) because of a higher flame-retardant efficiency. Moreover, the MoS_2@PPN also exhibits a good smoke suppressive effect on the EP. The performance enhancements in flame retardancy and smoke suppression are mainly attributed to the catalytic charring effect of polyphosphazene nanoparticles, and the physical barrier effect of 2D MoS_2 nanosheets. In addition, the MoS_2@PPN is also found to noticeably improve the mechanical and tribological performances of the resultant EP nanocomposite.

Additionally, Zhou *et al.* [236] recently synthesized another MoS_2 hybrid, i.e., TPP-MoS_2, *via* electrostatic interactions of exfoliated MoS_2 nanosheets and TPP. In this work, TPP was combined with MoS_2 to achieve superior flame retardancy in the EP nanocomposite. With the incorporation of 2 wt% TPP-MoS_2, the PHRR (see Figure 30c), THR and TSR of the final EP nanocomposite reduces by 26%, 17% and 21%, respectively, relative to the pure EP thermoset under a heat flux of 35 kW/m^2 because of an improved char quality retarding the heat release and smoke emission (see Figure 30e). Meanwhile, the TPP-MoS_2 also improves the char yield and T_g of the EP nanocomposite, e.g., 2 wt% of TPP-MoS_2 increasing the T_g value from 128 °C for the EP to 159 °C, as shown in Figure 30d.

Therefore, the phosphorus-containing MoS_2 nanomaterials can also be a class of highly effective flame retardants for EP thermosets. However, a high loading level is required to enable the final EP to meet the fire retardancy requirement, e.g., a UL-94 V-0 rating in the industry. In addition, a major challenge remains relating to optimizing the combination of MoS_2 and phosphorus-containing FRs to maximize the flame retardancy efficiency.

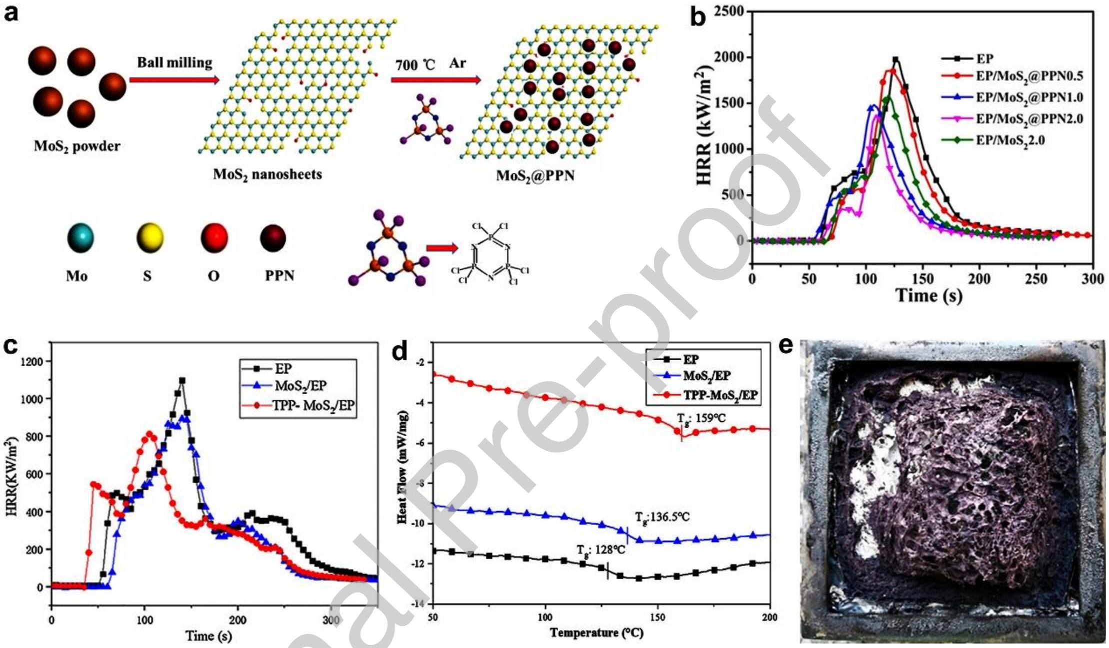

Fig. 30. Two P-containing MoS_2 and their impacts on the properties of EP nanocomposites. a) Schematic illustration of the preparation procedure of MoS_2@PPN; b) HRR plots of pure EP sample and EP nanocomposites with MoS_2 or MoS_2@PPN as a function of time; c) HRR curves of pure EP sample and EP nanocomposites with MoS_2 or TPP-MoS_2 as a function of time; d) T_g of pure EP sample and EP nanocomposites with MoS_2 or TPP-MoS_2; and e) digital photograph of char residue of EP nanocomposite with TPP-MoS_2. a, b) [235], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.; and c-e) [236], Copyright 2019. Reproduced with permission from Elsevier Science Ltd.

5.2.2.7. P-containing h-BN

In addition, hexagonal boron nitride (h-BN), structurally analogous to graphene, is a thermally- and chemically-resistant 2D material comprising boron and nitrogen

[237-239]. Because of the 2D structure and high thermal stability, h-BN is considered to be a potential nanoscale additive to improve thermal stability, thermal conductivity, mechanical properties and flame retardancy of EP thermosets [240-243].

Phosphorus-modified h-BN exhibits a similar multiple effect to other phosphorus-modified 2D nanomaterials. For instance, a poly(phosphazene-co-bisphenol A)-coated boron nitride, defined as PCB-BN, was synthesized by Qu *et al.* [244] and used as a multifunctional flame retardant additive for EP thermosets. The incorporation of 20 wt% of PCB-BN leads to 11.4% and 24.5% reductions in the PHRR and THR values of the EP thermoset in the MCC test, respectively, but fails to make the EP pass a V-0 rating. Additionally, the thermal conductivity of the final EP nanocomposite increases to 0.708 W m^{-1} K^{-1}, which is 3.7 times higher than that of the neat EP thermoset. Moreover, the resultant EP/PCB-BN nanocomposite exhibits improved electrical insulation and thermal stability, thus holding great promise for thermal management and microelectronic encapsulation applications.

5.2.2.8. Performance comparisons of P-containing nanomaterials

The PHRR and THR reductions and the detailed performances of the reported phosphorus-containing EP nanocomposites are presented in Figure 31 and Table 8 respectively. On the whole, the nanoscale phosphorus-containing additives can significantly reduce the PHRR and THR values at low loading levels mainly because of the combination effect of P-containing components and nanomaterials during combustion. As shown in Figure 31, as compared with other nanoscale phosphorus-containing flame retardant additives, fCD-Ph-DBS-LDH [204], APP-MMT [188], and DOPO-MMT [189] lead to more significant reductions in both PHRR and THR of the resultant EP nanocomposites, whereas the PCB-BN [244] and

PDT [172] result in relatively smaller reductions in the PHRR and THR relative to the control EP thermosets. The different reductions in both PHRR and THR are most likely due to the relatively low thermal conductivity of both 2D LDH and MMT than 2D h-BN and their better physical barrier effects than those of 0D POSS particles.

As shown in Table 8, most P-containing nanomaterials significantly increase the char yields of EP thermosets, indicating that nanomaterials primarily function in the condensed phase. In addition to flame retardancy, some P-containing nanomaterials (e.g., POSS-bisDOPO, PDT, MWNT-HCPCP, MPCNT, SIEPDP-LDH, FRs-rGO, PPGO and TPP-MoS_2) simultaneously improve the T_g values and mechanical properties because of the restricting effect of evenly-dispersed nanostructures on the EP segments and their mechanical reinforcement effect. Impressively, most reported 2D P-containing nanomaterials, especially APP-MMT, fCD-Ph-DBS-LDH and f-GO, feature an obvious smoke suppressing effect due to their outstanding physical barrier effects, which makes them superior to many other 0D and 1D P-based nanomaterials.

In summary, most P-containing nanomaterials can remarkably reduce the flammability of EP thermosets; they are, however, often involved in complicated preparation procedures, such as chemical functionalization and separation, and high costs, such as graphene, h-BN and MoS_2 nanosheets, all of which significantly restrict their industrial application. In addition, there is a color issue with some nanomaterials, including black CNTs and graphene. In comparison, inexpensive MMT represents a relatively more promising candidate to develop highly effective nanoscale P-containing flame retardant additives for EP thermosets in the future. However, much more work needs to be carried out to maximize their comprehensive performances, such as flame retardancy efficiency and mechanical reinforcement effects by carefully tailoring the combination of P-containing compounds and nanomaterials.

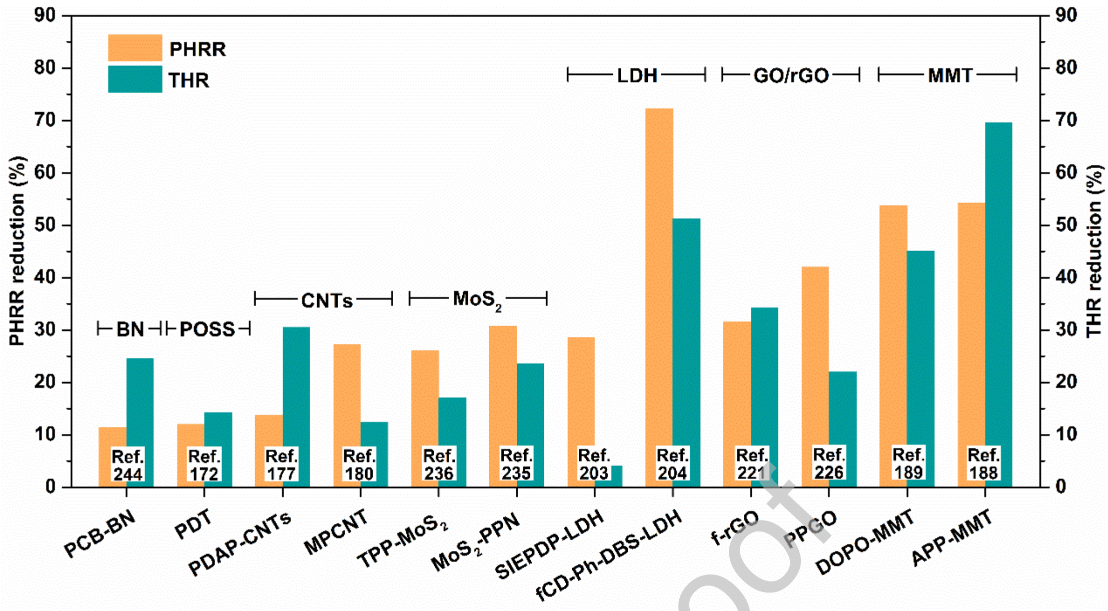

Fig. 31. The PHRR and THR reductions of the reported P-containing flame-retardant EP nanocomposites.

Table 8. Performance comparisons of the reported P-containing flame-retardant EP nanocomposites.

Name of nanomaterial	Content of nanomaterial (wt%)	LOI (%)	UL-94 rating	Reduction (%) PHRR	Reduction (%) THR	Other highlights ^{d}	Ref.
POSS-bisDOPO	20	34.5	-	-	-	The CY at 800 °C increases from 0.91% to 11.53%, and flexural strength increases by ~11%.	[169]
PDT	7	32.5	V-0	12.0 ^{a}	14.3 ^{a}	The CY at 800 °C increases from 16.3% to 22.0%, flexural and storage moduli increase by 22.4% and 34.9%.	[172]
PDAP-CNTs	5	31.8	V-0	13.7 ^{b}	30.5 ^{b}	The CY at 700 °C increases from 15.7% to 27.9%, and TSR decreases by 26.9%.	[177]

MWNT-HCPCP	5	23.8	-	-	-	SDR decreases by 11.8%, and tensile strength increases by 39.8%.	[178]
MPCNT	4	-	-	27.2[c]	12.4[c]	The CY at 750 °C increases from 13.4% to 19.1%, TTI increases from 55 s to 57 s, storage modulus and T_g increase by 25.8% and 5 °C.	[180]
APP-MMT	10	30.0	V-0	54.3[b]	69.6[b]	TSR decreases by 63.6%, and the CY at 800 °C increases from 10.6% to 30.6%.	[188]
DOPO-MMT	6	33.4	V-0	53.7[b]	45.1[b]	TTI value increases from 50 s to 59 s.	[189]
SIEPDP-LDH	4	25.3	V-1	28.5[b]	4.0[b]	TSP decreases by 14.3%, impact strength and T_g increase by 31.0% and 2 °C.	[203]
fCD-Ph-DBS-LDH	7	26.5	V-0	72.3[b]	51.2[b]	TSP decreases by 63.7%, and the CY at 750 °C increases from 14.5% to 19.6%.	[204]
FRs-rGO	5	29.5	V-0	35[c]	-	The CY at 700 °C increases from 14.2% to 19.6%, T_g and storage modulus increase by 6 °C and 22.0%.	[219]
FRGO	3	28.2	V-1	33.8[c]	13.8[c]	TSP decreases by 30.4%, the CY at 650 °C increases from 7.5% to 18.0%, TTI increases from 67 s to 72 s, storage modulus increases by 25.9%.	[220]
f-rGO	3	-	-	31[c]	34.3[c]	TSR decreases by 9.5%, storage modulus increases by 38.0%, and the CY at 800 °C increases from 8.6% to 12.9%.	[221]
PPGO	3	-	-	42[c]	22[c]	TSP decreases by 24.3%, the CY at 700 °C increases from 5.8% to 11.5%, T_g, $T_{5\%}$, and storage modulus increase by 8 °C, 33 °C and 20.4%.	[226]

f-GO	2	31.5	-	29.3^{c}	10.5^{c}	TSP decreases by 73%, and the CY at 800 °C increases from 14.3% to 23.8%.	[227]
MoS_2@PPN	2	-	-	30.7	23.6	Storage modulus increases by 32.3%, TSR, friction coefficient value and volume wear rate significantly decrease.	[235]
TPP-MoS_2	2	-	-	26^{c}	17^{c}	The CY at 700 °C increases from 13.0% to 19.0%, T_g increases by 31 °C, TSP and TSR decrease by 24% and 21%.	[236]
PCB-BN	20	-	-	11.4^{a}	24.5^{a}	The CY at 800 °C increases from 3.7% to 29.7%, $T_{10\%}$ and thermal conductivity increase by 8 °C and 3.7 times.	[244]

[a] PHRR and THR are obtained from MCC;

[b, c] PHRR and THR are determined by cone calorimeter test at a heat flux of 50 and 35 kW/m^2, respectively.

[d] $T_{10\%}$ and CY are obtained from TGA under N_2 flow.

6. Applications of P-containing flame-retardant EP thermosets

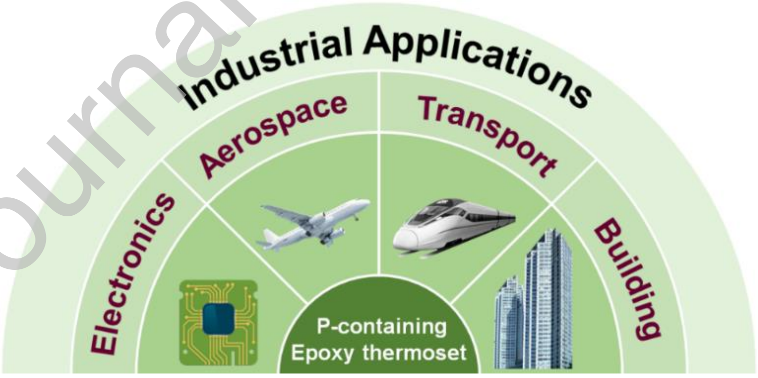

Fig. 32. Industrial applications of P-containing flame-retardant EP thermosets.

Because of their outstanding flame retardancy and other intrinsic merits, phosphorus-containing flame retardant EP thermosets have been expanding their applications in the fields of electronics [245, 246], aerospace [247-249], transport [250, 251] and building [252, 253] (see Figure 32), with detailed discussions below.

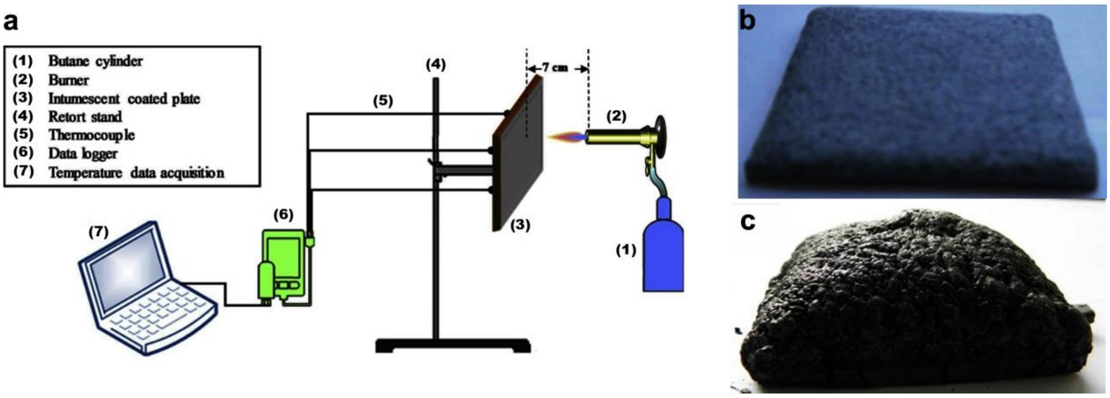

Fig. 33. P-containing flame-retardant EP coatings. a) Schematic diagram of a lab-scale fire retardant test; and the intumescent fire-retardant coating b) before and c) after a fire test. a) [252], Copyright 2019. Reproduced with permission from Elsevier Science Ltd.; and b, c) [253], Copyright 2017. Reproduced with permission from Elsevier Science Ltd.

Phosphorus-containing fire-retardant EP coatings have been widely applied in the building and construction industry. For instance, Ahmad *et al.* [252-255] prepared phosphorus-containing intumescent fire retardant EP coatings for the fire protection of structural steels as load-bearing building materials. In general, these coatings comprise the EP binder and IFRs. The IFRs contain ammonium polyphosphate, expandable graphite, melamine, and boric acid, with some inorganic additives as synergistic agents. The fire resistance of these EP coatings is investigated *via* a lab-scale test according to the ASTM E119 standard (see Figure 33a). Without the coating, the backside temperature of the steel reaches above 550 °C within 5 min, causing a dramatic reduction in the mechanical strength of the steel at this temperature. In contrast, with the intumescent fire-retardant EP coatings, the backside temperature of the steel significantly reduces. In most cases, the coated steel exhibits a backside temperature of only ~200 °C even exposure to fire for 60 min, indicating excellent fire resistance. This is because at elevated temperatures the IFRs can form an intumescent char layer with a thermal shielding effect on the structural steel (see Figures 33b and 33c), thus preventing the transfer of heat from the combustion zone to the underlying steel, and thus maintaining the mechanical strength of structural steels.

In order to mitigate the potential fire hazards of flammable plywood, transparent intumescent fire-resistant EP coatings were fabricated by Wang *et al.* [256, 257], comprising P-containing EP and melamine-formaldehyde resins. The fire resistance of the coatings was also evaluated by using the above-mentioned lab-scale test, where the uncoated plywood board exhibits a backside temperature of 220 °C upon exposure to external flame for only ~100 s. In contrast, the as-used EP coatings significantly prohibit the heat transfer while protecting the underlying plywood board. In some cases, the backside temperature of the coated board will not reach 220 °C for about 19 min. Thus, the P-containing intumescent fire-resistant EP coatings hold great promise for extensive use as building materials.

Phosphorus-containing flame-retardant EP thermosets are often used as the matrix of fibre-reinforced composites widely used in transport and aerospace fields. Schartel *et al.* [258] reported the use of two DOPO-containing flame-retardant EP matrices in a carbon fiber-reinforced composite. For these carbon-fiber-reinforced flame-retardant EP composites, their LOI values are as high as 40%, manifesting their exceptional flame retardancy levels, in addition to high interlaminar shear strength of around 60 MPa. Because of the combination of exceptional flame retardant and mechanical performances, these carbon-fiber-reinforced flame retardant EP composites [248, 259-261] will find more widespread applications as advanced materials for automotive and aviation industries and high-speed trains, because of the more demanding performance requirements.

7. Conclusions, challenges and opportunities

7.1. Conclusions

This review summarizes the state-of-the-art understanding of reactive and additive phosphorus-containing flame retardants for EP thermosets and focuses on their impact on the flame retardancy, thermal stability and mechanical properties of the resultant EP thermosets. For the reactive P-containing flame retardant, both P-containing EP monomers and curing agents can endow EP thermosets with inherent flame retardancy, thus having broad prospects in practical applications. From the perspective of practical applications, the P-containing EP monomers cannot fully replace the common epoxy resins because of their relatively poor processability and high costs. In comparison, the use of P-containing curing agents seems a more feasible strategy and has recently becoming increasingly popular. However, most of the currently-reported P-containing curing agents often suffer low curing activities and exhibit an undesired adverse impact on T_g, which should be satisfactorily addressed prior to their practical applications. In regard to the additive P-containing flame retardants, multi-group P-containing additives can endow EP thermosets with excellent flame retardancy at relatively low addition, and hyperbranched and nanoscale P-containing additives usually exhibit multiple functions. Compared with the other two P-containing additives, the additive that is hyperbranched has received more attention over the past few years because of its positive impact on mechanical properties and relatively simple synthesis process. However, for industrial applications, the hyperbranched P-containing additive still requires further improvements in flame retardancy and smoke suppression.

The phosphorus-containing FRs usually suppress the combustion of the EP matrix *via* the free-radical-capturing effect and the promoting-charring effect. Their flame-retardant efficiency can be improved through the combination and even synergistic effects, such as the combined effect of the element P and other flame-retardant element/groups, and that of P-containing FRs and nanomaterials. Because of enhanced flame retardancy and sometimes improved thermal resistance and mechanical properties, phosphorus-containing flame-retardant EP thermosets are expected to find wider applications in many industrial fields, such as aerospace, building, transport and electronics.

7.2. Key challenges and opportunities

Although phosphorus-containing FRs have shown significant advances in recent years, several challenges remain unsolved. First, concerns regarding sustainability. The majority of reported P-based FRs are derived from petroleum-based resources, and thus their widespread use can raise sustainability concerns in the long run. Also, their synthesis often involves the abundant use of organic solvents, which can lead to high production costs and potential environmental issues, thus restricting their practical applications in industry. Finally, the environmental and human toxicity of phosphorus-containing FRs need to be carefully evaluated.

A second concern is the lack of efficiency optimization. Although high flame retardancy efficiency is achieved for many multi-group or multifunctional P-containing FRs, there has been a lack of optimization of their flame-retardant efficiency. In general, the maximum efficiency of the P-containing flame retardants is strongly dependent on the mole or mass ratio of different flame-retardant groups or components. However, current work mainly focuses on a fixed ratio of different flame-retardant groups or components of the P-containing flame retardants, which significantly restricts their flame retardant efficiency in the EP host. In addition, the interfacial compatibility of FRs with the EP matrix determines the flame retardancy performances, which is normally neglected during the design of P-containing flame retardants.

A third concern involves the recyclability and reconfigurability of P-based EP thermosets. The recyclability and reconfigurability are considered two key issues of EP thermosets. Likewise, the P-containing ones are also unable to be recycled or reconfigured once cured, thus leading to the same challenging issues.

In response to the major challenges to phosphorus-containing flame retardants above, some possible opportunities are proposed in the following:

First, the use of bioderived resources as sustainable building blocks. In general, biobased raw materials for designing P-based flame retardants are multitudinous. For instance, Zhang *et al.* [48] have recently developed a biobased cyclotriphosphazene-containing epoxy monomer (HEP) from eugenol. Compared with the common DGEBA/D230 sample, the HEP/D230 sample exhibits superior flame retardancy and smoke suppression because of the presence of cyclotriphosphazene. Specifically, its PHRR and TSP are reduced by 66% and 78% respectively relative to the control DGEBA/D230 sample. Meanwhile, Qian *et al.* [262] used bioderived cinnamaldehyde to synthesize a P-modified Schiff-base curing agent (DCAD) for EP. Moreover, the DCAD can improve the impact strength of the EP thermoset because two C=C bonds in the DCAD structure form an elastomer-like crosslink during curing, leading to a toughening effect. Moreover, green solvent or solvent-free preparation methods are preferred in the production of flame retardants. Thus, in the future, more efforts should be made to develop bio-derived P-containing flame retardants in a more sustainable way for EP. In addition, the evaluation of environmental toxicity and biodegradation of P-containing flame retardants represents a new and interesting research opportunity in the future.

A second opportunity is the optimization of synthesis to maximize the flame retardant efficiency. One research opportunity is the optimized synthesis of P/N/Si-, P/N/B-, or P/Si/B-containing flame retardants that can work simultaneously in the condensed and gaseous phases. In addition, the optimized preparation of P-containing nanomaterials represents another strategy to achieve more efficient flame retardants. High-throughput synthesis and screening facilitate the optimized synthesis of the P-containing flame retardants. In addition, the computer-aided design represents a highly efficient means for the optimized synthesis of flame retardants.

A third opportunity concerns the design of recyclable flame-retardant EP thermosets. The design of epoxy vitrimers based on dynamic covalent chemistry has been proven to be a promising approach to create recyclable and reconfigurable epoxy resins [263, 264]. The epoxy vitrimers can rearrange their structure under stimuli *via* the reversible or exchange reactions of dynamic covalent bonds. Therefore, the molecular design of phosphorus-containing epoxy monomers or curing agents that consists of dynamic bonds (e.g., imine, carboxylate ester and disulfide bonds) offers many other promising opportunities for creating high-performance flame-retardant recyclable EP thermosets.

In addition to the flammability issue, the EP thermosets normally suffer great brittleness due to high crosslinking density. Hence, the development of mechanically tough and flame retardant EP thermosets by developing hyperbranched P-containing flame retardants represents another promising research direction in the future, given the increasing performance requirements in the aerospace and transport field. In addition to research into the flame-retardant properties, urgent research into the potential health impacts of P-containing flame retardants on both humans and the environment will be needed in the future.

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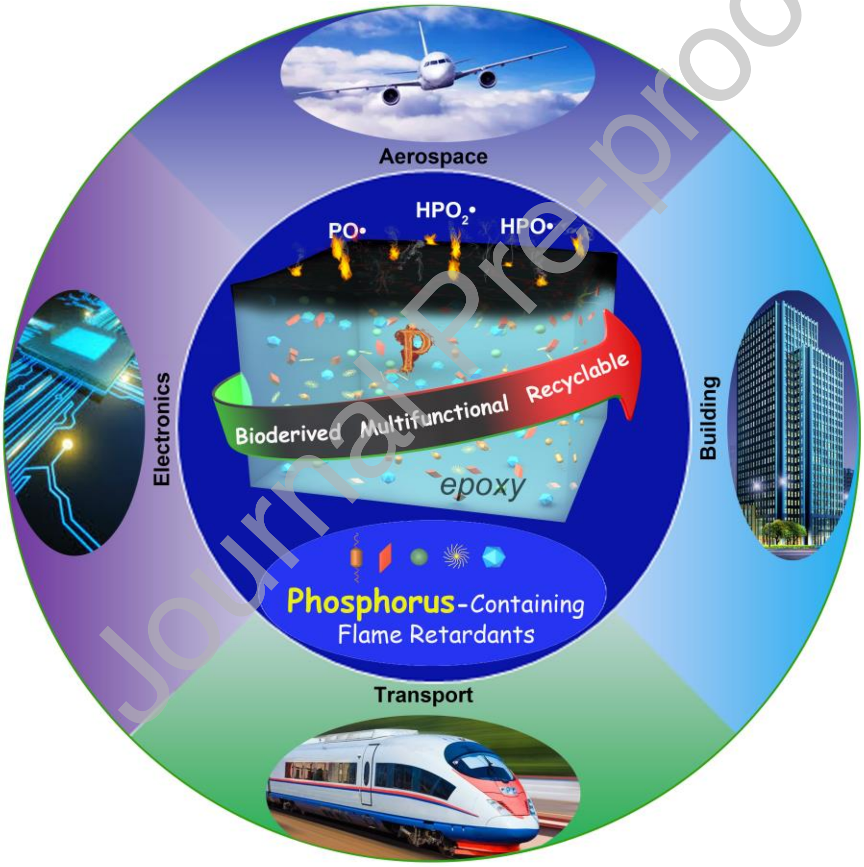
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract



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