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Recent advances in metal-family flame retardants: a review

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The use of polymer materials is inextricably linked to our manufacturing life. However, most of them are easily combusted in the air and the combustion process generates a large amount of toxic fumes and dangerous smoke. This can result in injuries and property damage, as well as limiting their use. It is essential to enhance the flame-retardant properties and smoke suppression performance by using multiple flame retardants. Metal-based flame retardants have a unique chemical composition. They are environmentally friendly flame retardants, which can impart good smoke suppression, flame retardancy to polymers and further reduce the production of toxic gases. The differences in the compounds formed between the transition metals and the main group metals make them act differently as flame retardants for polymers. As a result, this study presents the research progress and flame-retardant mechanism of flame-retardant polymers for flame retardants from different groups of metals in the periodic table of elements in a systematic manner. In view of the differences between the main group metals and transition metals, the mechanism of their application in flame retardant polymer materials is carefully detailed, as are their distinct advantages and disadvantages. And ultimately, prospects for the development of transition metals and main group metals are outlined. It is hoped that this paper will provide valuable references and insights for scholars in the field.

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1. Introduction

Synthetic and natural polymers have been widely used in many aspects of life as a result of technological advancement and rising productivity levels.^{1–5} Their molecular chains tend to break at high temperatures, producing various combustible gases. These polymers are highly susceptible to airborne combustion,^{6,7} which significantly limits their application. Furthermore, when polymers burn, a large amount of smoke



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and poisonous gases are released,^{8,9} making firefighting and rescue work difficult. Therefore, various flame retardants are typically added to the polymeric matrix to increase the fire safety of polymeric materials.^{10–13} Conventional flame retardants include halogen, phosphorus and nitrogen-based compounds. Halogen flame retardants produce persistent pollutants that cause irreversible and permanent pollution of the environment. And a lot of smoke and toxic gases will be released when a fire breaks out.^{14–16} Halogen-based flame retardants are increasingly being phased out due to the rising demand for environmental protection. There is a preference for more environmentally friendly non-halogen flame retardants,^{17,18} such as phosphorus and nitrogen-based. Although phosphorus¹⁹ and nitrogen-based flame retardants are effective,^{20,21} their combustion products are accompanied by a large volume of smoke.²² Consequently, more focus is being placed on creating environmentally acceptable flame retardants with excellent flame retardancy and they can also minimize the toxicity of smoke.

In recent years, numerous studies have been conducted on different flame retardants that are utilized to enhance the flame

retardancy and smoke suppression qualities of polymeric materials. Among these, metals and their compounds²³ are favored by researchers for their excellent smoke-suppression properties.^{24–26} This can be achieved by altering the thermal degradation pattern of the polymer to provide a physical barrier and cooling. It can also promote char formation by suppressing flames in the gas phase through thermal decomposition to produce non-combustible gas dilution.^{27,28} This increases flame-resistance of the polymer, and they can also reduce emission of smoke and hazardous gases during polymer burning.^{29–31} The earliest metal-based flame retardants developed were metal hydroxides, most commonly aluminum trihydroxide (ATH)^{32,33} and magnesium hydroxide (MH).^{34–36} Jiao *et al.* added MH to ethylene vinyl acetate (EVA) as a flame retardant to improve its fire and smoke suppression capabilities.³⁷ Meanwhile, the residual content of coke was also increased. In addition to the significant flame-retarding properties of metal hydroxides, metal oxides^{38,39} also offer outstanding performance.⁴⁰ They are often used as co-effectors,^{41,42} with literature reporting special effects of transition metal oxides such as copper oxide,^{43,44} nickel oxide⁴⁵ and so on. For example, Gogoi *et al.* synthesised a vegetable oil alkyd resin with epoxy resin (EP) as the primary raw material from *Jatropha curcas* oil.⁴⁶ On this basis, alkyd/epoxy/NiO nanocomposites with various NiO nanoparticle mass percentages were created using a physical stirring method. The results showed that NiO nanoparticles are helpful in thermal-stability, and fire-resistant characteristics. Gradually, it was discovered that most metal oxides and hydroxides, although widely used but poorly compatible with polymers, lead to severe deterioration of mechanical properties in direct blending. So people started to focus on metal salts⁴⁷ as flame retardants because they can access flame retardants by chemical bonding,^{48,49} thus overcoming the defects of deteriorating mechanical properties in a natural blending of hydroxides. It can also modify fabric materials to improve their thermal stability properties. For example, Zhang *et al.* prepared water-soluble fibres with water-soluble flame-retardant silk by using titanium sulfate, ferrous sulfate,⁵⁰ and casein phosphopeptide



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as the primary raw materials. The results showed that the treated fabric had strong charring qualities and high thermal stability, which enhanced the flame-retardant performance of the fabric. It is due to the fact that metal ions can be used as reaction units to gain access to the flame retardant or polymer matrix, and they can also operate better as catalysts for carbon cross-linking and dehydrogenation processes. In addition, partially metastable metal ions can be used as free radical trapping agents or oxidation catalysts in the gas phase flame retardant process.^{51,52} In the past few years, with the continuous research and exploration of metal flame retardants, a new type of metal flame retardant material called metal organic frameworks (MOFs)^{53,54} has been developed. This is a new type of porous material made by connecting inorganic metal nodes with organic ligands. People take advantage of its adjustable structure, good thermal stability, excellent adsorption and catalytic properties and organic-inorganic hybridization properties to prepare polymer/MOF flame retardant composites.^{55,56} Sai *et al.* synthesized a high-porosity zirconium-based metal organic skeletal material (Zr-BDC).⁵⁷ The results indicated that Zr-BDC has various effects such as catalytic oxidation, isomerization, and catalytic carbon formation of polycarbonate (PC) matrix, resulting in a dense, highly graphitized carbon layer. That means it is helpful for rescue and escapes in a real fire. As a result, metal-based flame retardants in flame retardancy and smoke suppression with low toxicity can play an excellent effect, keep developing more efficient flame retardants and smoke suppression and low toxicity of environmentally friendly flame-retardant additives are well worthy of being the focus of future research.

Based on the above, it is easy to find that different metal elements have different physical and chemical properties, and the compounds that can form flame retardants also differ. The electron layers of magnesium and aluminum, which are located in the main group metals of the periodic table. And they are basically in the occupied state, with fewer empty orbitals. The complexes they form are less stable and less diverse, so they generally form oxides or hydroxides for flame retardation of polymers. In contrast to the saturated state of the electronic layers of the main group elements, the electrons in the transition metals' second or penultimate third layer are unfilled and belong to an unstable structure. Since the formation of complexes requires sufficient empty orbitals to accommodate the lone pair of electrons of the ligand, the complexes formed by transition metals are much more stable than the main group metal complexes. The compounds formed are also more diverse, comprising stable oxides, hydroxides, and metal salts of different valence states. Therefore, both transition and main group metals can form corresponding stable compounds for flame and smoke suppression of polymers. In this review, based on the distribution of different metallic elements in the periodic table of elements, the differences in using different groups of metals as flame retardants are discussed and analyzed. And we hope to provide new ideas for further development of functional metal flame retardants with high efficiency, low smoke suppression and low toxicity in the future.

2. Flame-retardation mechanisms

Due to the specific chemical composition of the metal-based flame retardants themselves, this makes it possible to effectively enhance the flame retardancy and smoke suppressant properties of polymeric materials. When the polymer encounters heat and thermal decomposition, the metal oxide generated by the metal adheres to the surface of the matrix, playing a protective and physical barrier to prevent further combustion of the composite. Similarly, the thermal decomposition of metal hydroxides releases some non-combustible gases, such as H₂O, which can achieve the effect of diluting the concentration of various combustible gases generated by combustion. In particular, certain metals may further catalyse the carbonation process of the polymer, thereby preventing combustion and promoting the tight formation of the carbon layer may reduce heat release. The dense carbon layer greatly reduces the area of the polymer exposed to air, consequently limiting heat release and smoke generation.^{58–60} The flame-retardant mechanism of metal flame retardants in polymers has been extensively studied^{61,62} and can be summarized in the following four main aspects.

Metal-based flame retardants can catalyze a dense, intact carbon layer on the polymer matrix. It produces a highly graphitized structure that is thermally stable and prevents the release and diffusion of heat, while also providing a physical barrier against the spread of smoke. Peng *et al.* used solvent evaporation to prepare a series of metal oxides loaded on activated carbon (AC-MO) (Fe₂O₃, CuO, ZnO).⁶³ Additionally, the vulcanization, combustion, thermal stability, and ageing characteristics of AC-MO and the flame-retardant ethylene vinylacetate copolymer rubber made from ammonium polyphosphate/dipentaerythritol synergistically expanded were examined. Fe₂O₃ loaded on AC improved its catalytic charring effect and enhanced the integrity and densification of the flame-retardant ethylene vinylacetate copolymer rubber char residue. Li *et al.* reported the reaction of phosphomolybdic acid (PMA) anions with three different metal ions (Ni, Na and Zn) to generate phosphomolybdate (PMOs) for use as an enhanced flame retardant mechanism for polypropylene/intumescent flame retardants (PP/IFR).⁶⁴ The results showed that PMOs can facilitate the reaction between IFRs, slow down the exothermic rate during the burning process, and develop a charcoal layer with superior barrier effect. Yang *et al.* reported the use of tannic acid (TA)-Fe^{III} MPNs as an efficient green flame retardant designed for the flame retardant mechanism of coatings on polyurethane (PU) foam surfaces.⁶⁵ As can be seen from the Fig. 1, due to the excellent carbonization properties of Fe^{III}, the significant TA radical scavenging ability and the cohesive phase effect of the carbonization process during catalytic combustion. The encapsulated TA-Fe^{III} MPNs also successfully suppressed the heat release rate (HRR) and total flue gas volume, reducing the volatilization of harmful gases during combustion.

Secondly, the decomposition of metal hydroxides produces incombustible gases, which potentially reduce the concentration of combustible gases, thereby inhibiting the release of smoke.



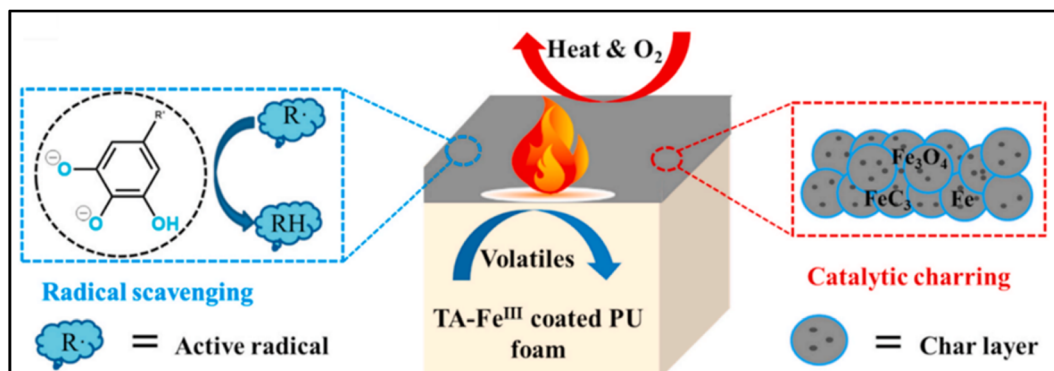


Fig. 1 Mechanism scheme of TA-Fe^{III} MPN flame retardant. Reproduced with permission from ref. 65. Copyright (2021) Elsevier.

Later, the metal hydroxides were further improved, and layered double hydroxide (LDH) was developed. Interestingly the layered structure also acts as a barrier, isolating the substrate from heat and preventing further combustion of the substrate. Ye *et al.* examined the cooperative effect of borosiloxane (BSiI) and magnesium hydroxide in EVA/MH blends of halogen-free flame retardants.⁶⁶ The mechanism of the synergistic effect of BSiI and MH can be described as BSiI promotes the formation of a dense burnt layer, prevents cracking of the burnt layer and actively defends the substrate polymer from further combustion. Jiang *et al.* successfully obtained Ni–Al LDH and used it as synergist to improve triazine-based IFR's flame retardancy and smoke suppression properties.²⁹ The flame-retardant mechanism is shown in Fig. 2. When NiAl-LDH is added to the PP/IFR system, the alkali metal can act as a cross-linking agent, effectively improving the graphitization and thermal stability of the

carbon slag and a significant increase in the residual amount of PP/IFR/Ni–Al LDH. Furthermore, the introduction of LDH and the introduction of non-combustible gases (NH₃ and H₂O *etc.*) from the decomposition of the composite effectively act as a dilution agent in the gas.

Inorganic metal compounds formed by combining metals with organic acids can also exert a flame-retardant effect by decomposing to produce a corresponding metal oxide that covers the surface of the polymer matrix, protecting it from further combustion. Cheng *et al.* compounded melamine, melamine uric acid and polyphenylene ether with aluminum hypophosphite for flame retardant thermoplastic elastomers (blends of SEBS and polyolefin).⁶⁷ The TPE-S containing 16 wt% ATH, 20 wt% cyanuric acid melamine and 10 wt% poly (epoxy phenylene) passed the UL-94 test with V-0 rating and a limiting oxygen index (LOI) value of 28.2%. The flame-retardant

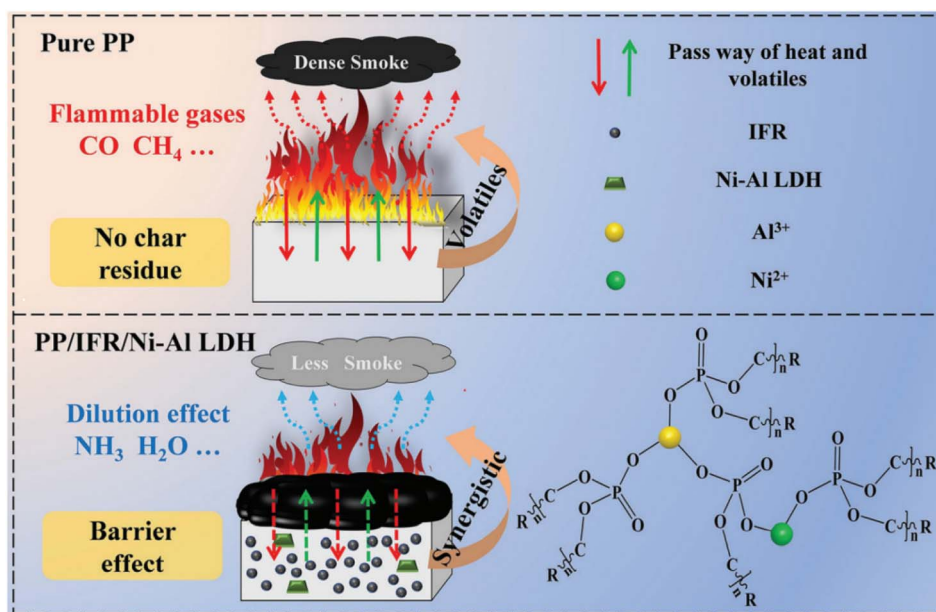


Fig. 2 Flame-retardant and smoke-suppression mechanism of PP flame retardant composites. Reproduced with permission from ref. 29. Copyright (2021) The Authors. Macromolecular Materials and Engineering published by Wiley-VCH GmbH.



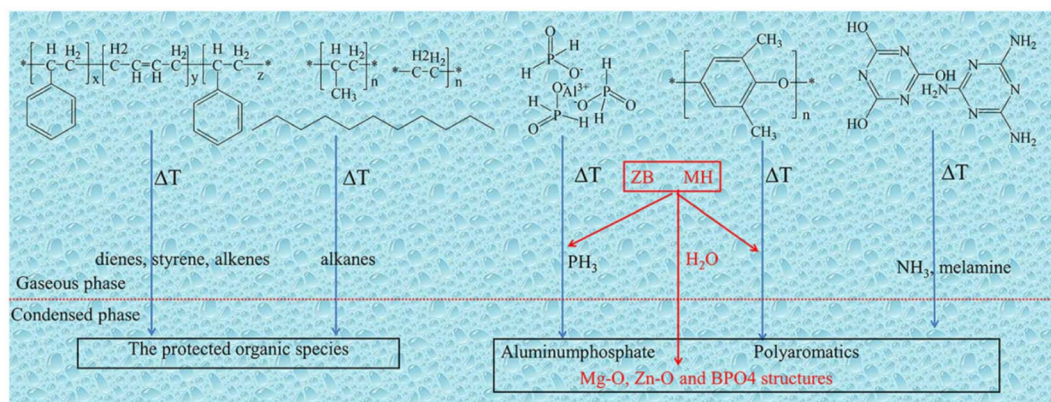


Fig. 3 Schematic diagram of proposed flame-retardant mechanism model of TPE-S/AHP/MCA/PPO composite with replacement of ZB and MH. Reproduced with permission from ref. 67. Copyright (2019) SAGE Publications.

mechanism model for the composite is shown in Fig. 3. When the temperature is raised to 445 °C, the polymer decomposes to form AlPO_4 . Then the melamine cyanurate (MCA) decomposes to melt and release NH_3 , diluting the internal combustible gases and forming an inorganic layer. Aluminum hypophosphite, MCA and polyphenylene oxide contribute to the formation of swelling coke, which is dense and continuous. The composite decomposes to form MgO , ZnO and borophosphate in addition to concentrated aluminium phosphate, which, combined with the water generated, further dilutes the concentration of combustible gases.

Finally, the emerging MOFs show great potential for flame retardant applications by exploiting the catalytic carbon formation of metals and the capture of free radicals by organic flame-retardant compounds. Huang *et al.* designed a novel MOF through the synergistic interaction of MOF ($\text{NH}_2\text{-MIL-101(Al)}$) and phosphorus-containing nitrogen ionic liquids ([DPP-NC(3) [PMO]) composite.⁶⁸ As the Fig. 4 shows, in the gas phase, the diphenylphosphine group in the imidazolium cation of ionic liquid (IL) containing phosphorus compounds reacts with the reactive radical to inhibit flame propagation. And the catalytic

oxidation of carbon monoxide (CO) by the metal cluster in $\text{NH}_2\text{-MIL-101(Al)}$ can effectively reduce the heat and CO release. In the coalescence phase, the imidazole cation and phosphomolybdate anion of IL act as catalysts to induce cross-linking, forming a stable char layer. These two effects give $\text{IL@NH}_2\text{-MIL-101(Al)}$ good refractoriness.

Therefore, in the burning process of polymers, all metal flame retardants can play a role in catalyzing the carbon generation of the matrix. It is worth noting that some metal hydroxides and inorganic metal compounds can also produce non-combustible gases by decomposition to dilute combustible gases and generate the corresponding metal oxide to cover the surface of the substrate and protect it from further combustion. At the same time, the metal-organic framework can also absorb some toxic gases because of its porous structure. The metal-organic framework can also adsorb some poisonous gases due to its porous structure. Overall, catalytic carbon formation of metal-based flame retardants plays a key role in enhancing flame retardancy and smoke inhibition. At the same time, it can also catalyze the conversion of CO, reducing the number of toxic gases released.

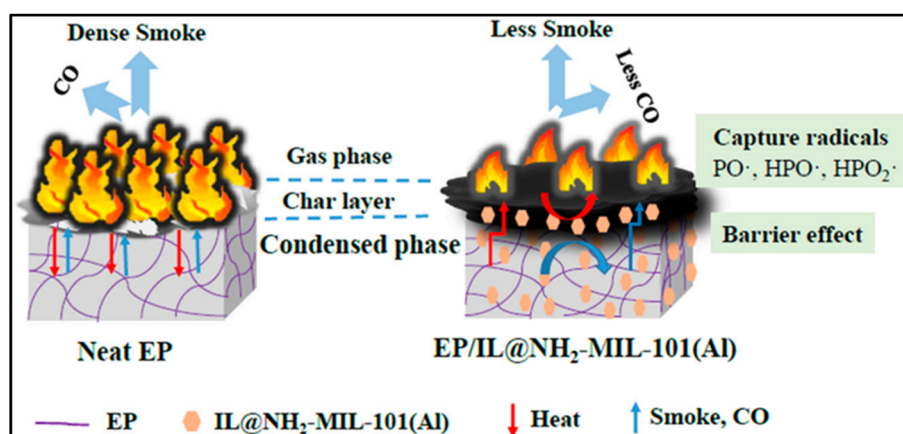


Fig. 4 Schematic illustration of the proposed mechanism of EP/IL@NH₂-MIL-101(Al). Reproduced with permission from ref. 68. Copyright (2019) Polymers.



3. Classification of metal-based flame retardants

In the periodic table of elements, metal elements commonly used in flame retardant research are divided into transition and main group metals. Different metal elements can form different metal compounds, which play different roles when used as flame retardants. Therefore, the metal-based flame retardants were divided into common transition metal flame retardants, rare transition metal flame retardants, main group metal flame retardants and multi-metal compound flame retardants. This way better investigates the similarities and differences between the different groups of metal elements in the periodic table of elements to form metal compounds used as flame retardants.

3.1. Common transition metal flame retardants

As transition elements in the periodic table, their electrons form chemical bonds when chemical reactions occur and can exhibit a wide range of oxidation states. Transition elements generally form ionic bonds when forming compounds in the low oxidation state and are prone to hydrate, and covalent bonds are formed when forming compounds in the high oxidation state. Transition elements have empty d orbitals that can be used for bonding and a high charge/radius ratio, readily forming stable coordination compounds with various ligands. For example, common iron, copper and zinc can be used with organic ligands to form metal complexes or MOFs for enhancing the flame retardancy of polymers. The performance of some transition metal-based flame retardants in different polymeric materials in recent years is listed in Table 1.

3.1.1. Manganese-based flame retardants. The chemical compounds of manganese are +2, +3, +4, +5, +6, +7, -1, -2 and -3 in valence states. Mn^{2+} is stable, not readily oxidized and not easily reduced, and can be applied as a functional flame retardant alone or as a booster to further increase the efficiency of other flame-retardant systems. It is often used in intumescent flame-retardant systems to catalyze the formation of carbon in the matrix and to enhance flame retardancy. For example,

intumescent flame-retardant coatings consisting of polyethyleneimine (PEI) and sodium polyphosphate have several drawbacks, including poor water durability, poor flame retardancy and high consumption of non-renewable raw materials. Zhang *et al.* developed a intumescent flame retardant coating that can be used with manganese ions on cotton fabric by the layered assembly technique.⁸¹ The thermal decomposition temperature of the fiber was gradually reduced by the catalytic action of manganese ions, and the carbon content produced increased. The specimen containing manganese have the largest LOI of 28.3% and a more complete and continuous carbon layer structure after combustion. The scanning electron microscopy (SEM) results showed that a large number of vacuoles and residual carbon existed on the surface of the manganese-treated cotton fabric. These results indicate that the coordination of manganese ions is responsible for the catalytic and synergistic effects. In addition, the coatings containing manganese still showed better water resistance after washing. The incorporation of manganese ions can improve the flame-retardant properties and water resistance of cotton fabrics effectively. Dong *et al.* designed and synthesized a novel Mn^{2+} -containing phosphate piperazine (HP-Mn) as carbon-forming agent for intumescent flame retardant systems.⁷⁸ SEM of HP-Mn are shown in the Fig. 5(b). The peak heat release rate (PHRR), total heat release (THR) (Fig. 5(a)) and smoke production rate (SPR) were reduced by 74%, 30% and 70%, respectively, compared to pure PP. As shown in Fig. 5(c) and (d), SEM analyses of the carbon residues showed that Mn^{2+} could catalyze the charring of the combustion material to form a continuous dense, highly graphitized carbon layer.

In future development, manganese-based flame retardants still have excellent growth potential. Using it as intumescent flame-retardant system as flame-retardant coating to cover the surface of the composite, it not only cooperates with the carbon forming agent to play flame retardant effect, but also can enhance the water resistance of cotton fabric related materials.

3.1.2. Iron-based flame retardants. Iron is a relatively active metal, ranking ahead of hydrogen in the metal order of activity table, and has moderately active chemical properties. It can

Table 1 The fire behaviors of transition metals flame retardants in polymers

| Sample | Polymers | Adding amount (%) | UL-94 | LOI (%) | pHRR reduction (%) | THR ($MJ m^{-2}$) | Reference |
|---|----------|-------------------|-------|---------|--------------------|---------------------|-----------|
| Fe_2O_3 (MMT- Fe_2O_3) | PVC | — | — | — | 56.6 | 27.5 | 69 |
| FeP(FeP@APP@CS) | APP | 0.4 | 0 | 28.5 | 57.2 | — | 70 |
| FeP(FeP/APP) | PEI | 45 | 0 | 31.8 | 71.8 | 74.2 | 71 |
| MIL-100(Fe)/MA | PA6 | 5 | — | — | 73.0 | 22.5 | 72 |
| Fe-OMT/MPP | | 2 | 0 | 31.0 | 46.1 | 41.7 | 73 |
| Fe-MOF | PS | 2 | — | — | 14.4 | 4.0 | 74 |
| Co-MOF | | 2 | — | — | 28.0 | 17.6 | 74 |
| ZIF-67/RGO-B | | 2 | 0 | 26.4 | 65.1 | 41.4 | 75 |
| NiO/APP/CSi-MCA | PLA | 3 | 0 | 34.1 | — | — | 76 |
| Ni(OH) ₂ (FGO2/PP) | PP | 2 | — | — | 32.6 | 19.0 | 77 |
| ZnSO ₄ ·7H ₂ O/IFR/PP | | 1 | 0 | 32.7 | 65.0 | 26.9 | 48 |
| HP-Mn | | 12.5 | 0 | 30.7 | 74.2 | 35.8 | 78 |
| MOF-Cu/APP | TPU | 0.125 | 0 | 27.0 | 74.5 | 69.8 | 79 |
| ZnO@MOF@PZS | PUA | 3 | 0 | 22.8 | 28.3 | 19.6 | 80 |



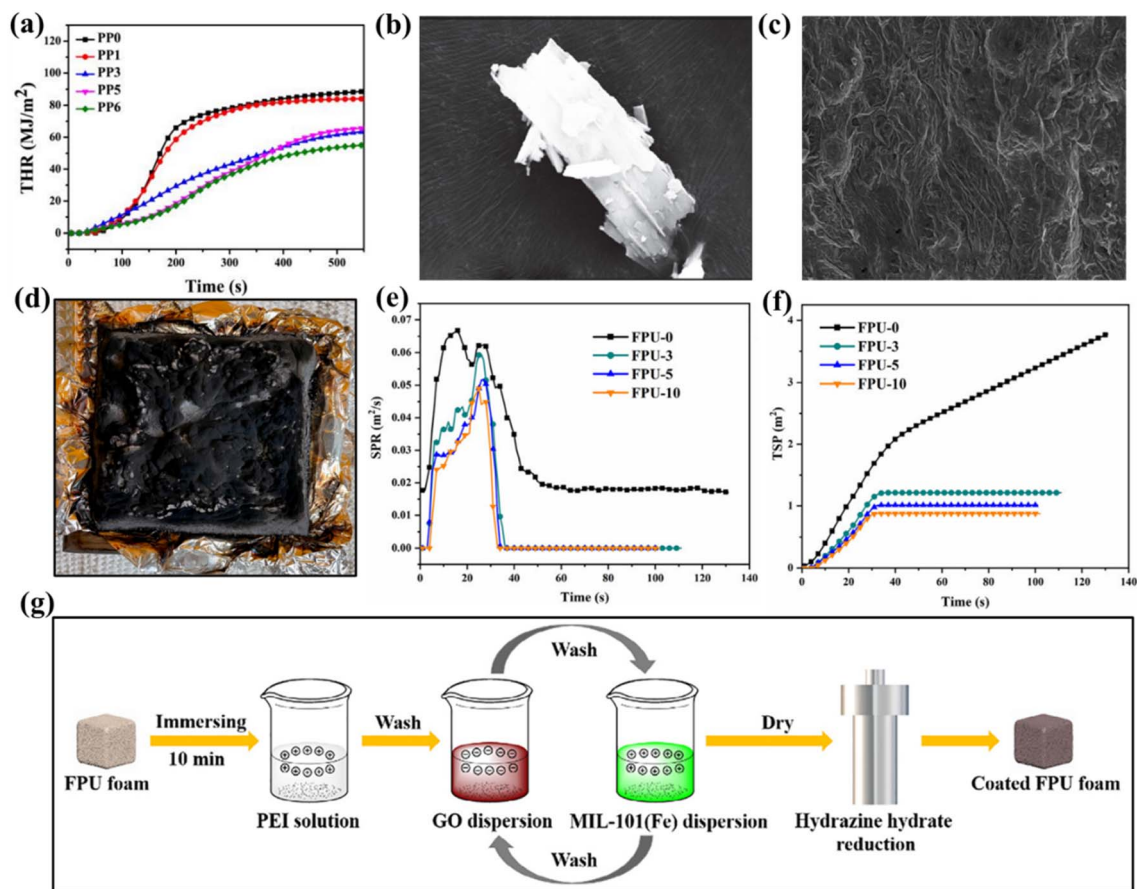


Fig. 5 (a) THR curves of samples during the combustion in CCT; (b) SEM images of HP-Mn; (c) SEM images of the char residue obtained after CCT for PP3; (d) digital photographs of the char residue of PP3. Reproduced with permission from ref. 78. Copyright (2021) Materials; (e) SPR, (f) TSP and curves of FPU-0 and coated FPU foams; (g) preparation schematic of coated FPU foams via LBL self-assembly technology. Reproduced with permission from ref. 85. Copyright (2021) Elsevier.

exert excellent flame retardant and smoke suppressing effects, whether as a single metal ion or combined with other substances to form compounds and the formation of MOFs. MOFs are new porous materials that link inorganic metal nodes with organic ligands. Their adjustable structures, excellent thermal stability, superior adsorption and catalytic properties, and organic-inorganic hybridization properties have been used to prepare polymer/MOF flame retardant composites.⁸²⁻⁸⁴ Huang *et al.* modified flexible polyurethane (FPU) foams by using reduced graphene oxide and iron-based metal organic frameworks to improve their smoke suppression and oil absorption properties (the preparation diagram is shown in Fig. 5(g)).⁸⁵ As shown in Fig. 5(e) and (f), the results of cone calorimeter testing (CCT) showed that the peak smoke production and total smoke production (TSP) of the modified FPU foam were significantly reduced by assembling a nano-coating on the bubble surface. At the same time, oil adsorption experiments showed that the foams of the coating had a relatively high adsorption capacity and maintained their adsorption capacity even after 10 cycles. This work provides a new strategy for solving the problem of FPU foam generating large amounts of toxic fumes during combustion.

Due to the risk of phosphate mine depletion and increasing costs, there is a growing demand for low phosphorus or eco-phosphorus based flame retardants and materials containing iron⁸⁶ exhibit excellent flame retardant properties. In chemistry, the common organic ligand bound to iron is carboxylic acid.⁸⁷ However, most carboxylic acid mixtures do not have flame retardant elements, and when iron and carboxylic acid compounds with no flame-retardant effect form complexes, the flame-retardant effect is not satisfactory. To address these limitations, Jiang *et al.* used transition metal iron and phosphorus to form an iron@ phosphorus complex (Fe-PMC) complex,⁸⁸ aiming to prepare a new flame retardant with iron-phosphorus interaction and using it to replace pure phosphorus flame retardants. The synthetic route is shown in the Fig. 6(a) and the appearance of synthesized MIL-53 is shown in Fig. 6(b). The results show that Fe-PMC has a higher flame suppression capacity than the iron-only MIL-53 and that Fe-PMC reduces the laminar flame speed of cellulose and dramatically reduces the flame temperature.

In summary, it is not difficult to find that in addition to forming complexes for flame retardancy, iron can also be used to build the recently emerging iron-metal organic frameworks,

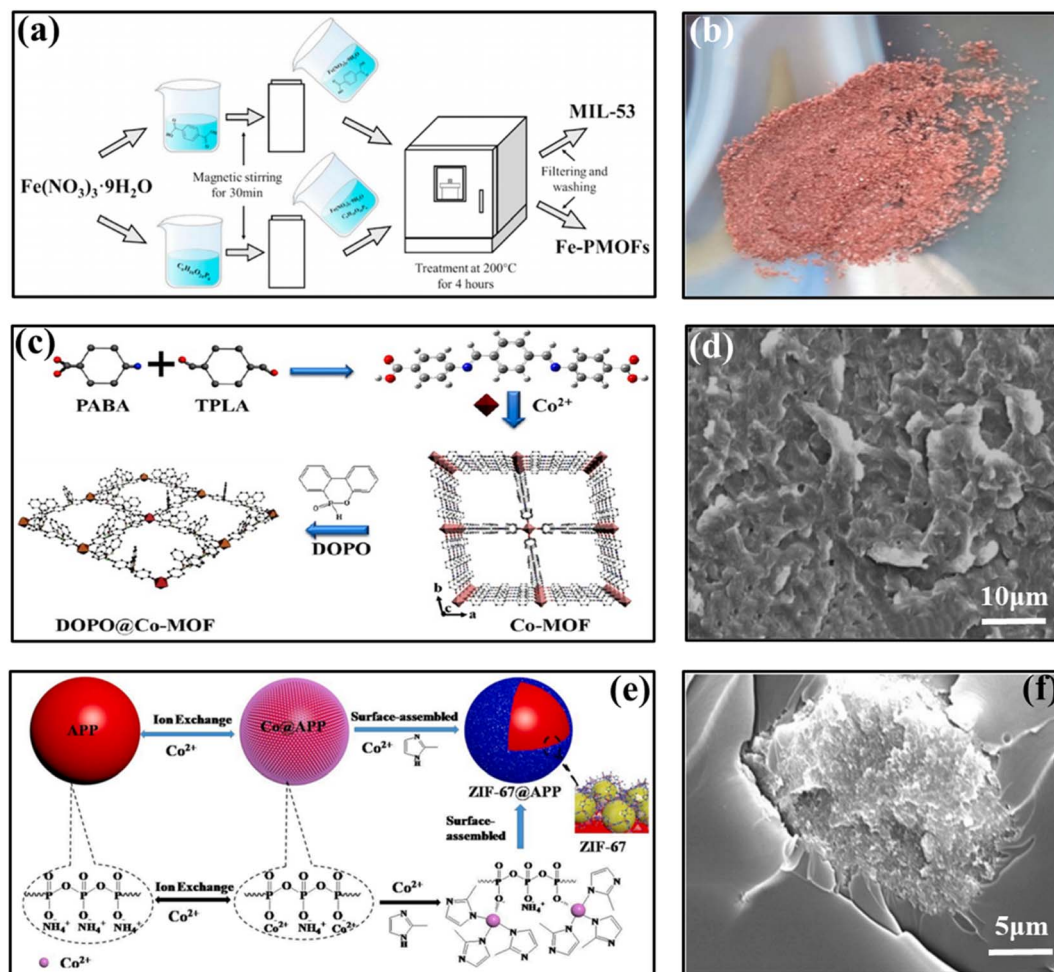


Fig. 6 (a) Illustration of preparation of MIL-53 and Fe-PMC; (b) appearance of synthesized MIL-53 (reddish brown crystals). Reproduced with permission from ref. 88. Copyright (2022) Elsevier; (c) schematic illustration of preparation process of DOPO@Co-MOF hybrids; (d) SEM images of fractured surfaces of PLA/DOPO@Co-MOF. Reproduced with permission from ref. 90. Copyright (2018) ACS Publications; (e) the synthetic route of ZIF-67@APP; (f) the fractured morphology of 5ZIF-67@APP/EP. Reproduced with permission from Ref. 92. Copyright (2021) Elsevier.

attractive new porous materials with different potential and easily customizable structures. In future developments, iron will continue to have an unshakable “place” in enhancing flame retardancy in composites.

3.1.3. Cobalt-based flame retardants. Cobalt is usually valuable for applications to enhance the flame retardancy of composites, either in ionic form or by forming a cobalt metal-organic framework. For example, Yang *et al.* synthesized a phosphonate and triazole-containing dicarboxylic acid ligand *via* an azide-alkyne reaction.⁸⁹ They ligated it with cobalt to form a metal-organic backbone (PN-MOF) containing phosphorus and nitrogen. The *av*-HRR, PHRR, THR and TSP of the EP/PN-MOF composites were reduced by 52.9%, 44.6%, 44.0% and 36.2%, respectively, when added to EP at 6 wt%. The LOI was increased from 24.3% to 29.8%. The flame-retardant mechanism is as follows: PN-MOF can act as flame retardant in both the gas and condensed phases. Large amounts of phosphorus and cobalt-containing compounds promote the formation of dense carbon layer that inhibits flame spread, heat, pyrolytic volatiles and oxygen transfer, thereby protecting

the underlying EP substrate and reducing smoke release. In high temperature environments, PN-MOF can produce non-combustible gases, reducing the concentration of combustible gases and oxygen in the gas phase. In addition, PN-MOF and its pyrolysis products have good catalytic oxidation and porous adsorption properties for CO, significantly reducing flue gas toxicity. Cobalt-based metal-organic backbone (Co-MOF) nanosheets were successfully synthesized by Hou *et al.*,⁹⁰ and they using organic ligands with Schiff base structures. The preparation process of DOPO@Co-MOF blends is shown in Fig. 6(c) and the SEM images of fractured surfaces of PLA/DOPO@Co-MOF is shown in Fig. 6(d). Interestingly, the composites outperformed the single material in terms of improving the thermal stability and flame retardancy of the poly (lactic acid) (PLA) matrix and suppressing smoke and CO emissions. This suggests that DOPO and Co-MOF synergistically improve the fire safety of PLA. As shown in Fig. 7(a) and (b), the results show that the enhanced fire safety of PLA composites is confirmed by the significant reduction in PHRR (27%), TSP (56%) and total CO production (20%). In addition, as shown in



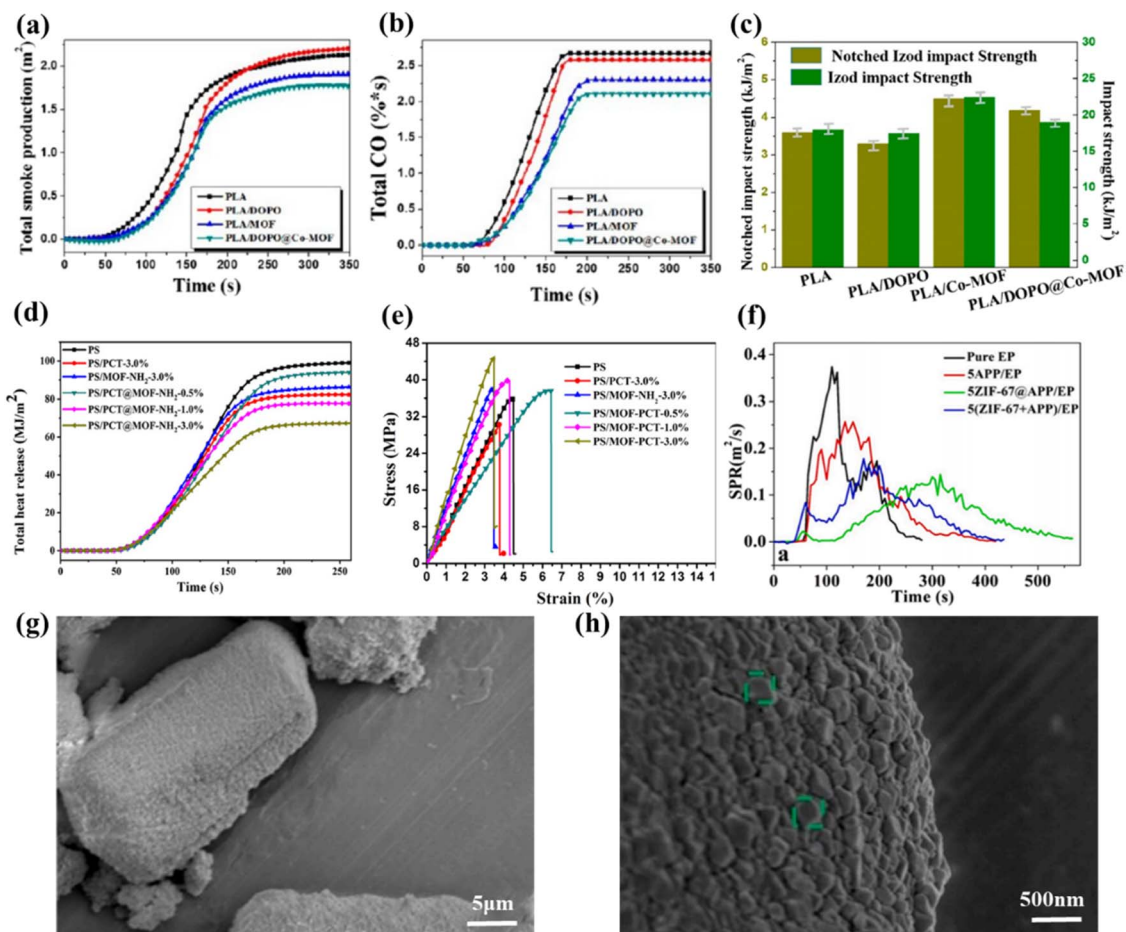


Fig. 7 (a) TSP, and (b) total CO release curves of PLA and its assembly systems; (c) impact strength results of PLA and its composites. Reproduced with permission from ref. 90. Copyright (2018) ACS Publications; (d) THR curves of PS and its composites at a heat flux of 35 kW m⁻²; (e) results of tensile test for PS and its composites. Reproduced with permission from Ref. 91. Copyright (2020) Elsevier; (f) the SPR curves of pure EP, 5APP/EP, 5ZIF-67@APP/EP and 5(ZIF-67 + APP)/EP; (g and h) the morphology of ZIF-67@APP. Reproduced with permission from Ref. 92. Copyright (2021) Elsevier.

Fig. 7(c), incorporating DOPO@Co-MOF has a positive effect on mechanical properties, including tensile properties and impact resistance. Xu *et al.* prepared a flame retardant named PCT@MOF-NH₂ by modifying cobalt-based MOF-71-NH₂ with phosphonitrilic chloride trimer (PCT),⁹¹ which can improve the flame retardant performance of polystyrene (PS). Compared to pure PS, the addition of 3 wt% of PCT@MOF-NH₂ and the values of PHRR and THR (Fig. 7(d)) were reduced by 40% and 31%, respectively. The results of tensile test for PS and its composites are shown in Fig. 7(e). The flame-retardant mechanism of PS composites is mainly the carbon formation catalyzed by PCT@MOF-NH₂, which lays the foundation for the study of flame-retardant mechanism of PS composites.

Of course, in addition to the common cobalt metal-organic frameworks, cobalt ions are often coordinated or modified with other phosphorus and nitrogen organic compounds to enhance the flame-retardant properties of polymers further. Shao *et al.* performed a coordination reaction using ZIF-67@APP to distribute it more uniformly on ammonium polyphosphate (APP).⁹² The synthesis route of ZIF-67@APP is shown in the Fig. 6(e) and the fractured morphology of 5ZIF-67@APP/EP is

shown in Fig. 6(f). The morphology of ZIF-67@APP is shown in Fig. 7(g) and (h). The LOI value of EP was 28.5% at 5 wt% loading, and its PHRR decreased by 67.4% and SPR (Fig. 7(f)) decreased by 46.2%. In addition, ZIF-67@APP/EP exhibits better mechanical properties. Its tensile and flexural strengths are significantly improved. It can form dense and stable expanded carbon layer, which can isolate the transmission of oxygen and heat and therefore has a high fire safety. Zhou *et al.* synthesized cobalt oxide nanoparticles adsorbed on graphene nanosheets by a hydrothermal method.⁹³ The mixture was introduced into the thermoplastic polyurethane (TPU) matrix as a reinforcing agent. The mixture was well scattered in the TPU and no significant aggregation occurred. Compared to pure PU, nanocomposites offer remarkable performance improvements in terms of thermal stability, flame retardancy and mechanical properties. These significant improvements in performance are mainly attributed to the “bent path” effect of graphene nanosheets.

In general, cobalt can exist in many forms to exert flame retardant effects, such as cobalt ions, cobalt metal-organic framework, *etc.* However, cobalt resources are less abundant



and more expensive than iron. In the future, compounding with other metals can be considered to meet the cost reduction and further enhance the flame-retardant effect.

3.1.4. Nickel-based flame retardants. Nickel is also very abundant in the earth's crust. In terms of flame retardancy, oxides and hydroxides of nickel metal, whether used alone or as synergists, can show unique efficacy in flame and smoke suppression by catalyzing the formation of carbon from the matrix. For example, Gao *et al.* incorporated nickel oxide nanoparticles (NiO) as synergists into PLA/APP/Si-mca polymer char composites.⁷⁶ SEM images from PLA3 after CCT is shown in Fig. 8(a). The results showed that the synergistic flame-retardant effect of NiO was evident, with the prepared PLA composites having LOI after the addition of 3 wt% NiO values as high as 34.1%, UL-94 reached V-0 level, and PHRR values decreased by 63.2%. The possible mechanism of occurrence is that the char layer contains APP and silicon-containing (Si-mca) by esterification and cross-linking reaction to char and PLA matrix by Si-mca and NiO catalysis to char. Two layers of carbon are closely stacked to create more continuous and dense carbon layer, which can effectively reduce the heat transfer rate and thus protect the base material from further combustion. Yuan *et al.* artificially improved graphene oxide's dispersion and flame retardant.⁷⁷ To improve the dispersion and flame-retardant efficiency of graphene oxide (GO), and modified GO with hexachlorocyclotriphosphonitrile and *p*-phenylenediamine to obtain a functionalized graphene oxide flame retardant (FGO1) and the Transmission Electron Microscope (TEM) images of FGO1 is shown in Fig. 8(b). On this basis, Ni(OH)₂ was used to modify FGO1 further to obtain a doubly modified flame retardant (FGO2). The addition of FGO1 and FGO2 significantly

improved the flame retardancy of PP. The graphitization of the residual carbon was determined by Raman spectroscopy, and the test results showed that the residual carbon of FGO1/PP and FGO2/PP was significantly better than that of GO/PP. FGO2 showed further reductions in total smoke release (TSR), THR and PHRR of 12.0%, 18.5% and 14.3% based on FGO1. At the same time, the flame growth index was also reduced, fully demonstrating the synergistic effect of Ni(OH)₂.

In addition to nickel oxides and hydroxides, nickel ions can also form metal ionic compounds to enhance flame retardancy, catalyzing carbon formation from the substrate and reducing heat transfer. Sui *et al.* obtained a new green flame retardant (Ni@SiO₂-PA) (SEM images of Ni@SiO₂-PA is Fig. 8(c) and (d)) by aggregating nickel phytate as shell on amination-modified silica through electrostatic interactions.⁹⁴ The synthetic route is shown in the Fig. 8(e). After adding the Ni@SiO₂-PA with a core-shell structure to EP, the flame retardancy and stability of EP composites thermally were significantly improved. The flame-retardant mechanism was also speculated, and Ni@SiO₂-PA initially formed a net-like structure to prevent further decomposition. The nitrogen-phosphorus synergistic flame-retardant system generated gas inhibition body and phosphorus-rich expanded carbon layer. In addition, the heat and exchange between the oxygen and the substrate are prevented by introducing Ni²⁺ catalyzed carbon layer. As shown in the Fig. 8(f), the mechanical properties of the composites were also improved after the addition of flame retardants. Gong *et al.* prepared phytic acid nickel (PA-Ni) by reacting phytic acid with nickel acetate in water and then compounded PA-Ni with pentaerythritol and APP as a flame retardant into PLA.⁹⁵ The PLA composites prepared under 4 wt% PA-Ni and 11 wt% IFR could

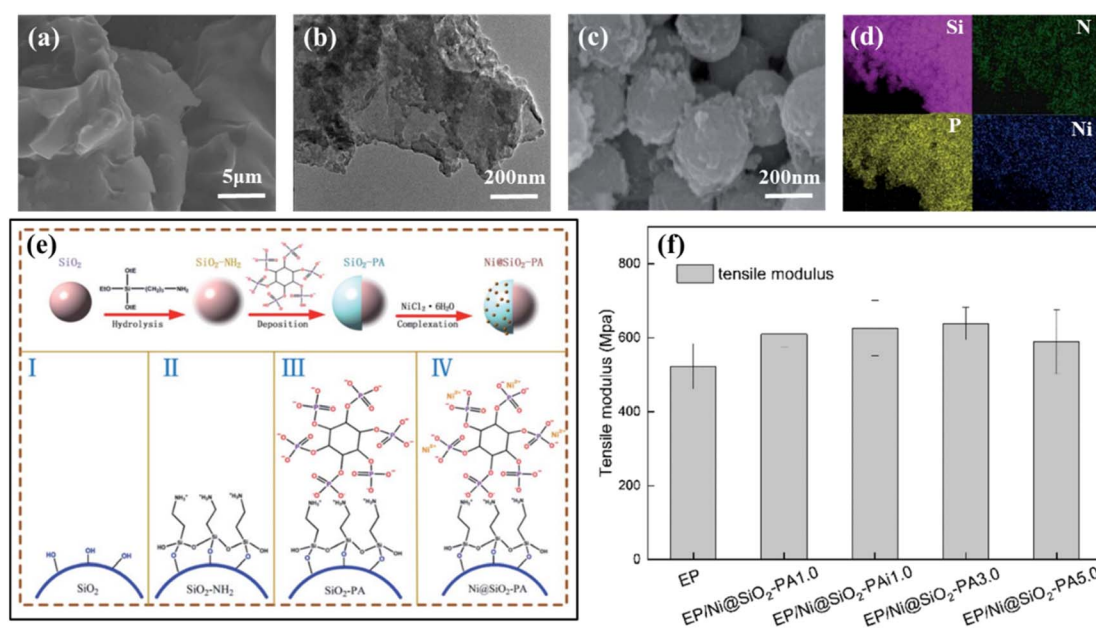


Fig. 8 (a) SEM images from PLA3 after cone calorimeter test. Reproduced with permission from ref. 76. Copyright (2019) Elsevier; (b) TEM images of FGO1. Reproduced with permission from ref. 77. Copyright (2017) Elsevier; (c) SEM images of Ni@SiO₂-PA; (d) SEM image of Ni@SiO₂-PA with elemental mapping of Si, N, P, and Ni; (e) synthesis route of the nanostructure Ni@SiO₂-PA; (f) tensile modulus of pure EP and its composites. Reproduced with permission from ref. 94. Copyright (2020) RSC Advances.



achieve UL-94 test rating of V-0. The PHRR of the PLA/11IFR/4PA-Ni composite was 62.3% lower than the original PLA, and the carbon residue was 12.5% higher.

Along with aluminium, copper, lead and zinc, nickel is the most economically valuable of the common metals. Strength, formability, and improved corrosion resistance are known properties of nickel, making nickel-containing materials necessary in harsh environments and at very high temperatures. Therefore, nickel metal flame retardants will have a broader range of applications.

3.1.5. Copper-based flame retardants. The excellent flame retardancy and smoke suppression exhibited by copper in polymeric materials have been confirmed by numerous studies. Copper is abundant in nature, has excellent properties and is easy to process. It is second only to aluminum in consuming non-ferrous materials in China. It is widely used in electrical and mechanical manufacturing, construction, transport and other areas. Numerous studies have shown that copper and its compounds in polymers can play a good role in suppressing smoke release and reducing smoke toxicity, so it is also widely used to enhance the fire safety of composite materials.

Riyazuddin *et al.* synthesized polymeric flame retardants (ETPMP) by nucleophilic substitution reactions using ethanolamine, piperazine, and melamine, as raw materials.⁹⁶ ETPMP, APP and CuO were used in various ratios to prepare intumescent flame retardants (IFR and IFR/CuO). Flame retardant and

smoke suppression tests were conducted and the results showed that the addition of a small amount of CuO significantly improved the LOI results and the UL-94 to V-0 level and the strength analysis results of epoxy, EP/IFR, and EP/IFR/CuO-5% sample charred layers is shown in Fig. 9(a). Analysis of the TGA results revealed that the addition of CuO significantly increased the residual carbon content and altered the thermal degradation behaviour. SEM testing of the residual carbon after CCT (Fig. 9(b) and (c)) showed that the EP/IFR/CuO-5 wt% residual carbon was significantly smoother than the EP/IFR composite, indicating that the addition of CuO can have strong synergistic effect with IFR, forming dense carbon layer without pores and cracks, effectively blocking the flow of heat and oxygen. Jia *et al.* modified graphene with CuO as a co-effector for PU flame retardancy,⁹⁷ and experimentally demonstrated that CuO has good smoke and toxic gas suppression effect while significantly reducing PHRR and THR. It also showed excellent synergistic effect on improving the amount and denseness of residual carbon formation. In addition to forming copper oxide for flame retardation, it is often used, as is iron, to construct MOFs for flame and smoke suppression in polymeric materials. For example, Chen *et al.* synthesized a copper metal-organic backbone (MOF-Cu),⁷⁹ and added it to TPU matrix in synergy with APP to prepare high-performance TPU composite. The synthetic route is shown in the Fig. 9(d) and the SEM images of TPU/APP/Cu0.0625 is shown in Fig. 9(e). It was found that the PHRR and

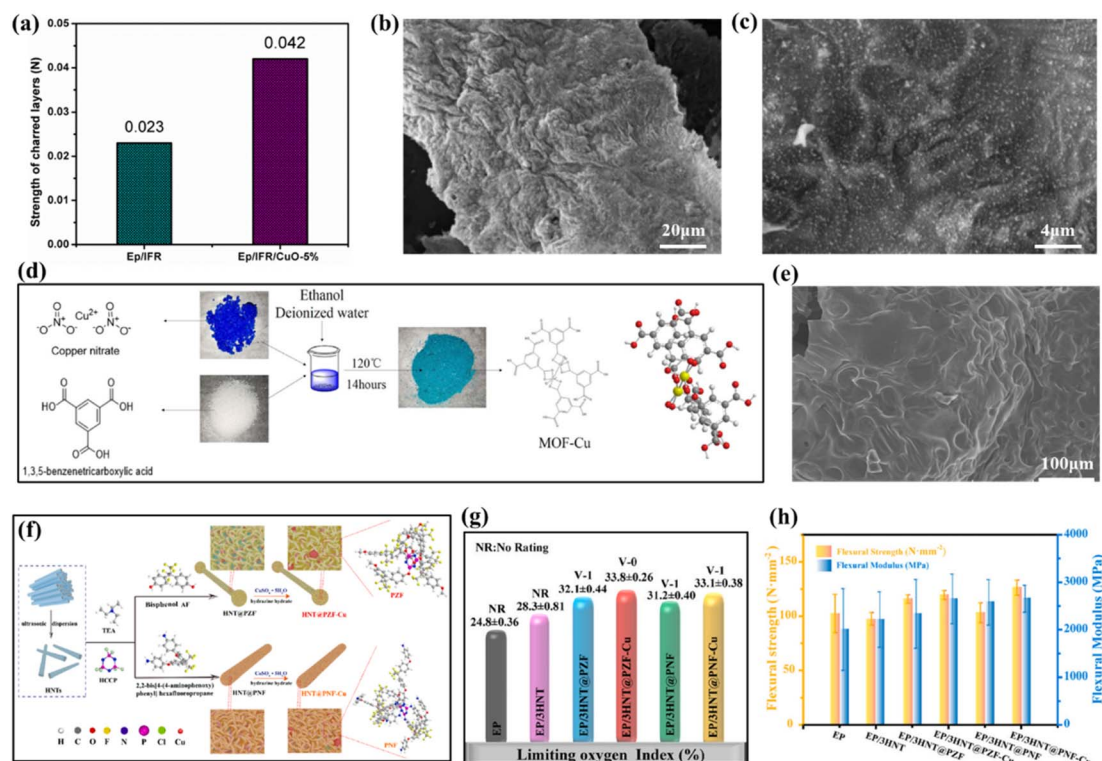


Fig. 9 (a) Strength analysis results of epoxy, EP/IFR, and EP/IFR/CuO-5% sample charred layers; (b and c) SEM images of EP/IFR/CuO-5% charred layers with different amplifications. Reproduced with permission from ref. 96. Copyright (2020) Molecules; (d) schematic representation for the preparation of MOF-Cu; (e) SEM images of TPU/APP/Cu0.0625. Reproduced with permission from ref. 79. Copyright (2021) Polymers for Advanced Technologies; (f) schematic illustration for the synthesis process of HNT@PZF-Cu and HNT@PNF-Cu; (g) UL-94 vertical burning and LOI values; (h) flexural strength and modulus of EP nanocomposites. Reproduced with permission from ref. 99. Copyright (2021) Elsevier.



THR of TPU/Cu0.0625 wt% were reduced by 26.0% and 1.3%, respectively, compared to the pure TPU samples, while the PHRR and THR values of TPU/APP samples were reduced by 70.3% and 15.8%, respectively, compared to the pure TPU samples. And the PHRR and THR values of TPU/APP/Cu0.0625 wt% samples were further reduced by 19.2% and 63.4%, in addition, TPU/APP/Cu0.125 wt% reduced the TSR by 23.4% compared to TPU/APP. This indicates that MOF-Cu has significant flame-retardant effect and that APP shows a better synergistic flame-retardant effect with MOF-Cu.

Copper still achieves excellent flame retardancy when forming the complexes while also reducing the impact on the mechanical properties of the composites themselves. For example, Abd El-Wahab *et al.* synthesized a Schiff base sulphamide ligand and its copper metal complexes, which were coated onto TPU surfaces at 0.5 wt% addition.⁹⁸ The test results showed that the LOI increased from 20% to 45% when the TPU was blank and increased by 7% compared to the ligand alone as flame retardant, indicating that the metal complex had better flame-retardant properties than the ligand. It is worth mentioning that the complexes did not show significant damage to the mechanical properties of the substrate while improving the flame-retardant effect. Hong *et al.* coated the surface of kaolinite nanotubes (HNT) with amino-terminated (PNF) and hydroxyl-terminated (PZF) polyphosphonitrile, respectively.⁹⁹ While copper nanoparticles (2.6 ± 0.8 nm) were

immobilized on the surface of these two core-shell structures, the flame retardants were named HNT@PZF-Cu and HNT@PNF-Cu, respectively. The synthetic route is shown in the Fig. 9(f). The results showed that HNT@PZF-Cu exhibited better smoke suppression and flame retardancy against EP. This is because HNT@PZF-Cu promotes the rapid carbonization of EP nanocomposites, resulting in the formation of structurally stable carbon slag. Meanwhile, copper nanoparticles can effectively reduce the release of toxic fumes and volatile organic compounds (VOCs) during catalytic combustion. The UL-94 vertical burning and LOI values is shown in Fig. 9(g). Flexural strength and modulus of EP nanocomposites is shown in Fig. 9(h), compared to pure EP, EP materials with both flame retardants are improved.

In summary, both copper oxides and hydroxides, metal ligands and nanoparticles are equally effective in enhancing flame retardancy, but the addition of oxides or hydroxides have certain degree of impact on the mechanics of the composite, whereas metal ligands or metal ionic compounds have less impact on its mechanical properties and are a major trend for future development.

3.1.6. Zinc-based flame retardants. Zinc metal has good ductility, wear resistance, corrosion resistance, castability and good room temperature mechanical properties, and it can be alloyed with a variety of metals with excellent properties. Similarly, due to its inherently active nature, zinc can form various

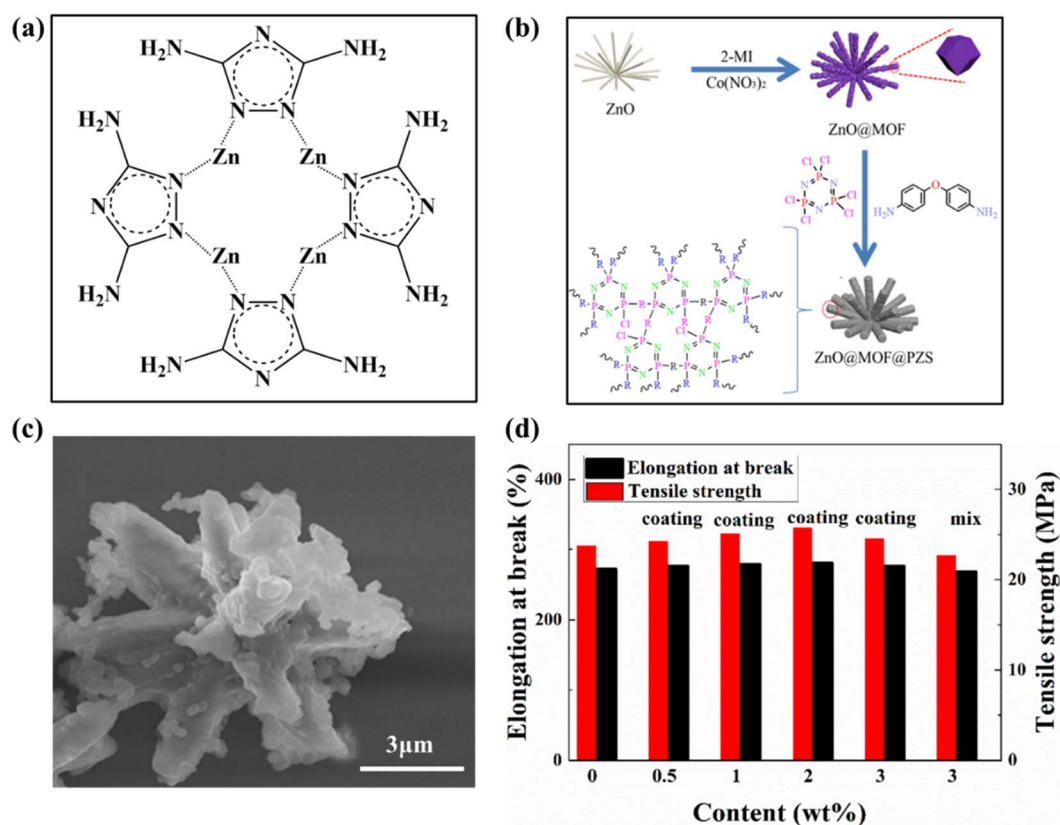


Fig. 10 (a) Proposed molecular structure of zinc-triazole complex. Reproduced with permission from ref. 100. Copyright (2021) Elsevier; (b) schematic diagram of the synthetic route of ZnO@MOF@PZS; (c) SEM images of ZnO@MOF@PZS; (d) mechanical property curves of PUA and its composites. Reproduced with permission from ref. 80. Copyright (2021) Polymers for Advanced Technologies.



compounds for use as flame retardants in polymeric materials. For example, new zinc–triazole complex was synthesised by Nabipour *et al.*,¹⁰⁰ and they using co-precipitation method and the proposed molecular structure of zinc–triazole complex (ZTC) is shown in Fig. 10(a). The results show that the addition of 4 wt% ZTC had little effect on the thermal stability of the EP matrix, whereas the addition of 4 wt% 3,5-diamino-1,2,4-triazole deteriorated its thermal stability. The EP composites containing 4 wt% ZTC passed the UL-94 V-0 test, while the EP composites containing 4% 3,5-diamino-1,2,4-triazole complexes passed the V-1 test. Compared to the pure EP, the EP composites with 4 wt% zinc–triazole complex had 72.9%, 86.0% and 73.8% lower PHRR, THR and SPR, respectively. When the mass fraction of the ZTC was 4%, the glass transition temperature (T_g) and tensile strength of the composites were significantly increased. This can be attributed to the increased crosslink density and structural stiffness of ZTC. The zinc–triazole mixture promotes the formation of heat-stable coke layer containing zinc oxide. The coke layer acts as physical barrier to protect the underlying polymer from combustion. ZTC are ideal for high performance epoxy thermosets that offer both improved flame retardancy, smoke suppression and mechanical properties, making them a promising polymer with high fire safety. Wang *et al.* prepared ZnO@MOF@PZS by hydrothermal method and polycondensation method.⁸⁰ The synthetic route is shown in the Fig. 10(b). ZnO nanoflowers acted as template in the growth of MOF@PZS and the formation of the ZnO source of MOF and the SEM images of ZnO@MOF@PZS is shown in Fig. 10(c). Mechanical property curves of PUA and its composites is shown in Fig. 10(d). Subsequently, the obtained ZnO@MOF@PZS was blended into polyurea (PUA) to study its flame retardancy and toxicity inhibition properties. CCT showed that ZnO@MOF@PZS significantly improved the flame retardancy of the PUA composites. The addition of 3 wt% ZnO@MOF@PZS in PUA resulted in PHRR, THR and total CO yield of 28.30%, 19.59% and 36.65%, respectively. It is worth noting that the improved flame retardancy of the PUA composites is mainly attributed to the formation of dense carbon slag promoted by ZnO@MOF@PZS.

It is well known, zinc is also commonly used to coat and protect steel from corrosion, so zinc metal flame retardants can be used in the future as a fire and corrosion resistant coating in production life, both to ensure the flame-retardant properties of the base material can also enhance its corrosion resistant properties.

3.2. Rare transition metal flame retardants

Rare metals are usually referred to as metals that are less abundant or sparsely distributed in nature. They are difficult to extract from raw materials and also late in industrial preparation and application. Rare metal mineral resources have a wide range of uses, especially in astronautics, atomic energy, electronics, the defense industry and other high-tech technology applications. With the continuous development of science and technology, some rare metals can also serve as efficient flame retardants in polymers.

3.2.1. Titanium-based flame retardants. We all know that titanium is a healthy and environmentally friendly metal, and it is a non-magnetic metal that will not be magnetized. Therefore, titanium metal flame retardant can also be used as green flame retardant, it has certain degree of corrosion resistance, as well as zinc, can also be used as the fireproof coating.

Titanium is referred to as the “space metal” due to its stable chemical characteristics, good resistance to extreme cold and heat, potent acids and bases, high strength, and low density. As a rare metal element, titanium has been studied relatively little in flame retardant research, but it can be used as co-effector in combination with certain other flame retardants to show substantial flame resistant effects. For example, Zhou *et al.* synthesized a diblock polymer containing DOPO.¹⁰¹ Through the Schiff base reaction, it continued to react with titanium-hybridized aminopropyl-polyhedral oligomeric sesquioxane (Ti-POSS), resulting in the creation of the novel graft copolymer PolyTi, which was then employed to modify EP materials as polymeric flame retardant. The findings indicated that, in comparison to pure EP, the T_g , LOI, coke graphitization, and mechanical properties of the EP/PolyTi composites were all improved by the addition of PolyTi. Additionally, compared to the EP/PolyTi composites, the phosphorus portion of the EP/DOPO composites migrated more readily. Apparently, the large molecule flame retardant-modified EP/PolyTi composites showed better thermal stability, flame retardancy, and migration resistance compared with the small molecule flame retardant-modified EP. Wei *et al.* utilized tetrabutyl titanate, tetraethyl orthosilicate, and diphenylphosphonic acid as raw ingredients by hydrothermally reaction to create a new hybrid nanorod called OPTS.¹⁰² And it contains organophosphorus-titanium-silicon (P-Ti-Si) and the synthetic route is shown in the Fig. 11(a). Based on the structural properties of OPTS, it is used to manufacture PC with high flame-retardant properties and its CCT values are shown in the Fig. 11(b–d). Just 0.1 wt% OPTS received PC 29.7% LOI value and UL-94 V-0 rating. When OPTS content was increased to 0.1 wt%, the tensile strength and elongation at break of flame-retardant PC increased to 8.0 and 8.3%, respectively.

3.2.2. Zirconium-based flame retardants. Zirconium, as a rare insoluble metal with high melting point, is mainly used in ceramics and refractory materials in the form of zirconium silicate and zirconium oxide. Zirconium is generally used as organometallic compound in flame retardant studies of various polymers. For example, Xu *et al.* explored the effect of the layered two-dimensional material α -zirconium phosphate (α -ZrP) on the flame retardant properties of plywood.¹⁰³ In order to create flame-retardant modified poplar veneer for use, the positively charged PEI and negatively charged APP were adsorbed on the surface of poplar veneer using layer-by-layer self-assembly process, and composite adhesive of urea-formaldehyde (UF) resin with α -ZrP different mass fractions was prepared. The synthesis process is shown in the Fig. 11(e) and the FE-SEM images of α -ZrP is shown in Fig. 11(f). The results indicated that the PHRR of the plywood was lowered by 41.8% and the THR was lowered by 22.9% when the flame-



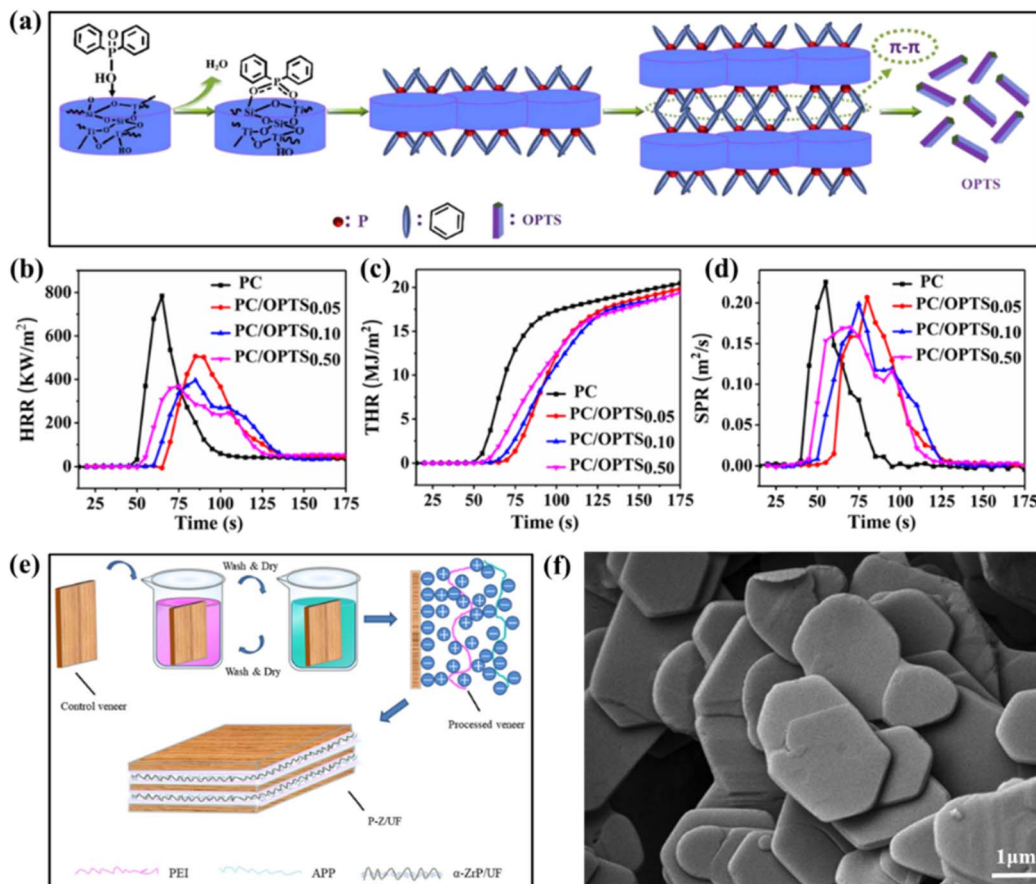


Fig. 11 (a) Formation process of OPTS nanorods; (b) HRR, (c) THR and (d) SPR results of pure PC and PC/OPTS nanocomposites during a CCT. Reproduced with permission from ref. 102. Copyright (2019) ACS Publications; (e) preparation process of P-Z/UF flame-retardant plywood (plywood was prepared by flame-retardant processed veneers and α -ZrP/UF composite adhesive); (f) FE-SEM images of α -ZrP. Reproduced with permission from ref. 103. Copyright (2021) Elsevier.

retardant veneer was used together with the composite adhesive, which represented significant improvement in the ability to suppress heat. Moreover, the introduction of α -ZrP resulted in a significant reduction in total smoke generation and toxic gas CO concentration, which reflected the good synergistic flame retardant performance of α -ZrP on poplar plywood when used in combination with APP. Shao *et al.* prepared an organozirconium complex with inorganic phosphorus named PTA-Zr@APP for flame retardant EP.¹⁰⁴ When the PTA-Zr@APP content reached 3 wt%, the EP composite showed UL-94 V-0 level with large reduction in heat release, proving its excellent flame-retardant effect. And the composites produce more gaseous non-combustible substances such as aromatic compounds during the combustion process. Therefore, PTA-Zr@APP has satisfactory flame retardant and fire retardant properties of EP based on good catalytic carbonization and excellent gas dilution for synergistic effect. Wang *et al.* embedded two-dimensional zirconium phosphate (ZrP) in reduced graphene oxide (RGO) interlayers to produce layered hybrids (ZrP-RGO).¹⁰⁵ These hybrids were combined with APP to create automatic screen-printed IFR coatings on cotton fabrics. According to experimental findings, when cotton materials were

subjected to butane flames, they displayed exceptional self-extinguishing qualities. Specifically, compared to those of regular cotton materials, the PHRR and THR during combustion were much lower by 92.1% and 61.8%, respectively. Additionally, the flame-resistant cotton fabric has UV protection index of 215.1, which results in exceptional UV-blocking ability. The coated cotton fabric maintains excellent flame retardancy and UV-blocking performance even after wear and tear. This study offers a straightforward and workable method for creating versatile fabrics.

In recent years, there has been less research into the application of zirconium in flame retardancy. As a new rare metal flame retardant, zirconium has amazing corrosion resistance, high melting point, and ultra-high hardness and strength, so there is much to explore in the future for zirconium in flame retardancy.

3.2.3. Molybdenum-based flame retardants. Despite being a scarce metal element, molybdenum is frequently employed as a synergistic flame retardant in various polymeric compositions. Yang *et al.* synthesized a new IFR by using APP, benzoxazine of trialkoxysilane (BA-a-Si), melamine (MEL) and MoS₂ as synergists for flame retardant paraformaldehyde (POM).¹⁰⁶



According to experimental findings, MoS₂ and IFR work well together. Only a small amount of MoS₂ (0.8 wt%) is required to synergise with IFR, and flame-retardant POM composites (FR-POM) can achieve UL-94 V-0 rating with LOI of 62.5%, 25.3% reduction in exotherm rate and 29.5% reduction in total smoke emission. Additionally, it was discovered through the mechanical property research that while nano-scale MoS₂ (N80) was more beneficial in enhancing the lubricating characteristics, micro-scale MoS₂ (M2) could better improve the flexural and tensile properties of FR-POM composites. He *et al.* designed and prepared BP@MoS₂ hybrids to improve the fire safety and mechanical properties of WPU, and BP@MoS₂ had a novel cactus-like structure.¹⁰⁷ BP@MoS₂ was prepared using chemical vapour phase transfer method for the preparation of black phosphorus flakes and *in situ* growth of molybdenum disulphide (MoS₂) for the preparation of BP@MoS₂. The addition of 2.0 wt% BP@MoS₂ increased the tensile strength by 57.7% and fracture strength of composites by 36.5%. The PHRR and TSP were reduced by 50.3% and 52.0%, demonstrating that the mechanical and fire properties were effectively improved. Meanwhile, BP@MoS₂ has flame retardant effect on WPU in condensed phase and gas phase. In the condensed phase, the residual carbon has physical barrier. In the gas phase, BP@MoS₂ can inhibit the production of flammable volatiles such as aromatic and aliphatic compounds during the combustion of composites, thus suppressing the exothermic and smoke-emitting behavior.

Molybdenum also is a refractory metal, although less research has been done on the use of molybdenum as flame retardant than has been done with zirconium, molybdenum exhibits good synergy in the formation of compounds to enhance the flame-retardant properties of polymers. More research is required to determine whether molybdenum can be used widely as flame retardant in polymers.

3.3. Main group metal flame retardants

In addition to transition metals, main group elements also contain many metal elements. The main group metals, such as magnesium and aluminum, are often used in flame retardant studies. They are generally used to form metal oxides and hydroxides rather than metal-ion complexes as flame retardants. Aluminum can also form organic acid compounds to strengthen the fire resistance of polymers. The performance of some main group metal-based flame retardants in different polymeric materials in recent years is listed in Table 2.

3.3.1. Magnesium-based flame retardants. Magnesium makes up around 2 wt% in the Earth crust, making it the eighth most plentiful element on the planet. The research and use of MH flame retardants are more common in some countries. The United States is the largest producer of MH and the largest variety of countries. China has huge reserves of magnesium resources, so China is also committed to the development and application of MH flame retardant. MH has a high decomposition temperature and the ability to absorb heat but also has low smoke emission and non-toxic energy. It is known that dense carbon layer can effectively prevent heat and oxygen from entering the composite system, thus enhancing flame retardancy.¹¹¹ MH is flame-retardant by decomposing to produce MgO and H₂O, generating stable carbon layer and producing non-combustible gases.

Tang *et al.* applied layered MH to flame-retardant thermoplastic elastomers (TPE).³⁴ When the MH content was 35 wt%, the TPE/Mg(OH)₂ composites had the best flame retardant capabilities, with delay in the ignition when compared to samples without MH addition. The TSP, HRR, THR, and mass loss rate were reduced by 56%, 31.4%, 35.6%, and 34.2%, respectively. He *et al.* employed organic magnesium hydroxide (OMH) (the SEM image at the same scale magnifications for OMH is shown in Fig. 12(b)) and expandable graphite (EG) as raw materials to create environmentally friendly flame-retardant unsaturated polyester resin (UPR) material.¹¹⁰ Instead of the conventional direct addition of MH to the UPR matrix, OMH participated in the polycondensation process of UPR as reactive monomer, which considerably increased the compatibility of the flame retardant with the substrate. Interestingly, the flame retardant UPR composites demonstrated more adequate flame retardancy when 8 wt% EG was added to the UPR/OMH matrix, with increasing in LOI from 21.7% to 28.5% and a V-0 rating in UL-94 testing. This was owing to the synergistic impact between OMH and EG. Zhao *et al.* created a new organic-inorganic hybrid flame retardant (DMMH) (the synthesis process is shown in the Fig. 12(a) and the SEM images of DMMH is shown in Fig. 12(d) and (e)) by neutralizing the addition reaction of maleic acid with MH and DOPO, which was then mixed with APP to create an IFR system.¹¹² With 1.7% DMMH and 5.3% APP added, EP-7 received UL-94 V-0 rating with LOI of 26.0%. In comparison to pure EP, the samples' THR and smoke emission decreased by 54.5% and 43.6%, respectively. And the mechanical properties of the EP were unaffected by the addition of DMMH (Fig. 12(c)). Liu *et al.* used

Table 2 The fire behaviors of main group metal-based flame retardants in polymers

| Sample | Polymers | Adding amount (%) | UL-94 | LOI (%) | pHRR reduction (%) | THR (MJ m ⁻²) | Reference |
|--|----------|-------------------|-------|---------|--------------------|---------------------------|-----------|
| Fe ₂ O ₃ /AlPi/IO | E-PHBV | 8 | — | — | 31.4 | 13.3 | 41 |
| Sb ₂ O ₃ (AlPi/AO) | | 8 | — | — | 45.0 | 20.0 | 41 |
| ZIF-67@MgAl-LDH | EP | 2 | 1 | 25.5 | 62.3 | 39.3 | 108 |
| Mg(OH) ₂ (MH-O-SEBS-PP) | PP | 70 | 0 | 38.3 | 90.7 | 45.1 | 109 |
| OMH | UPR | 1 | — | 26.4 | 67.3 | 31.7 | 110 |



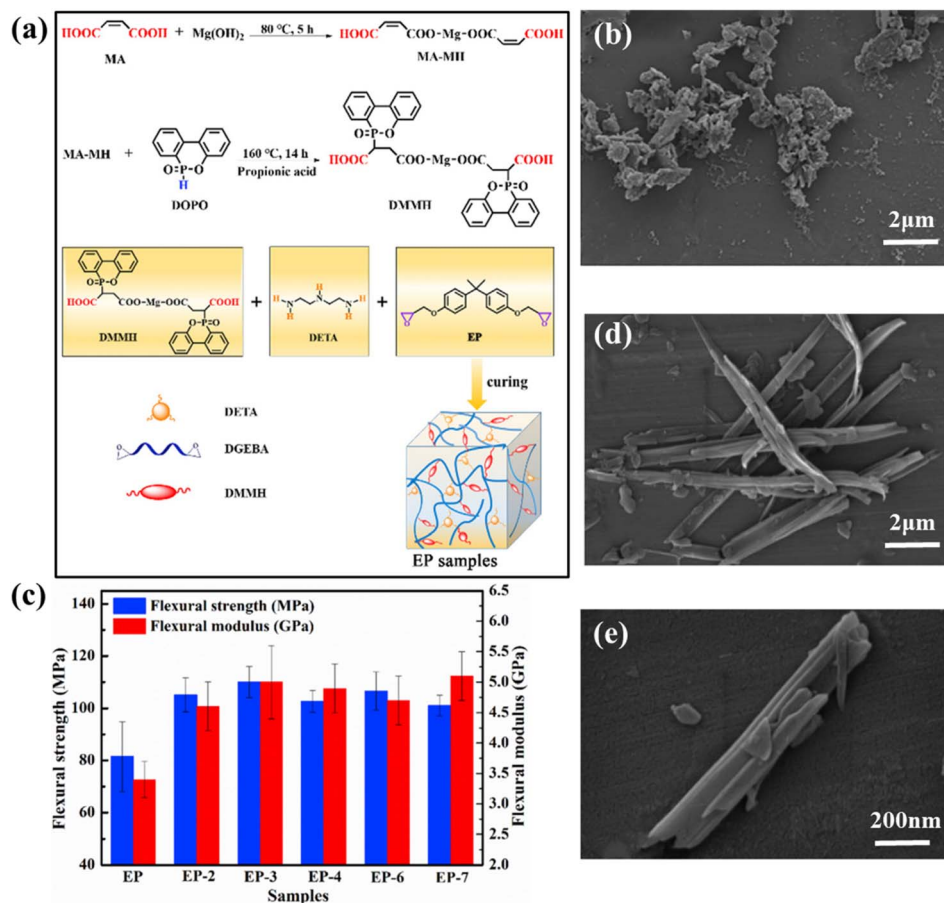


Fig. 12 (a) Synthesis of DMMH and schematic diagram of the curing process of the EP samples. Reproduced with permission from ref. 112. Copyright (2021) Elsevier; (b) SEM image at the same scale magnifications for OMH. Reproduced with permission from ref. 110. Copyright (2019) Wiley; (c) effect of the mechanical properties of flame retardant UPR composites; (d and e) SEM images of DMMH. Reproduced with permission from ref. 112. Copyright (2021) Elsevier.

triethoxysilane and polymethylvinyl silicone rubber for modified MH to prepare flame-retardant composites.¹⁰⁹ A water contact angle of 141 demonstrates the outstanding hydrophobicity of the modified MH (MMH). When the loading of MH or MMH was 70 wt%, the sample (1.6 mm) passed the UL-94 V-0 rating, indicating that its modification had no adverse effects on the flame-retardant qualities of MH. Comparing MH-O-SEBS-PP composites to MMH-O-SEBS-PP composites, the tensile strength and elongation at break of the latter improved by 20.4% and 88.9%, respectively. The mechanical properties were enhanced by the better interfacial compatibility of the flame retardant with the matrix. Additionally, after 168 hours of water treatment at 70 °C, the mechanical and flame-retardant properties of the MMH-O-SEBS-PP composites were still intact.

In recent years, due to the traditional MH flame retardant on the mechanics of polymer materials, people are more committed to the study of LDH and found that the introduction of magnesium into LDH can better play the efficacy of flame retardants, which is the future of magnesium-based flame-retardant development trend.

3.3.2. Aluminum-based flame retardants. Aluminum, as a main group metal, can also play an excellent role in flame retardant research, of which ATH flame retardants are the most

common. ATH has an initial decomposition temperature of about 205 °C. Also the ATH flame retardants can release large amounts of water vapor when heated, which can store heat and reduce the number of combustible gases in polymers, and also can form incombustible barrier between the ignition source and the substrate material, thus achieving flame retardancy.

Ai *et al.* used ATH to synthesize an organic-inorganic synergistic flame retardant.³² The LOI was 27.0% and the UL-94 rating was V-0 for PE/20% ATH/20% CP-6B. In comparison to pure PE, the PHRR of PE/20% ATH/20% CP-6B was 33.7% higher. In addition to its improved flame retardancy, ATH also has suppressive effect on the smoke and toxicity released by burning polymers. Li *et al.* have similarly concluded in their flame retardant study on bitumen that ATH has high flame retardant qualities and can reduce the generation of CO and aldehyde fumes.³³ In addition to the excellent flame retardancy of the hydroxide formed by aluminum, compounds formed with other flame-retardant elements are also effective in enhancing the flame retardancy of polymers. For example, Wang *et al.* prepared flame retardant EP materials using aluminum diethyl hypophosphonate (ADP), melamine (MEL) and pentaerythritol (PER).¹¹³ The data showed that the LOI was 29.5% when ADP was only 15%, and the material passed the UL-94 V-0 rating. In



the thermogravimetric test, a residual of 13.10% was achieved. When the total of 10% flame retardant was supplied, the EP-4 compound system and the EP-5 composite system both displayed outstanding flame retardancy, demonstrating that ADP, MEL, and PER have a good synergistic flame retardancy effect. A low amount of flame-retardant additive still has good flame-retardant effect when PER is present, which can accelerate the carbonization of the sample and successfully reduce smoke production. Hu *et al.* prepared PU elastomers based on monomethyl aluminum hypophosphonate (MeP-Al).¹¹⁴ The outcomes demonstrated that adding MeP-Al gave the PU the desirable flame retardancy and anti-drip qualities. With LOI value of 29.6%, samples containing 20 wt% MeP-Al passed the UL-94 V-0 rating and did not leak when burning. Additionally, there is a considerable reduction in both the heat released after burning and the organic volatilization from PU degradation. The effective action of MeP-Al in the gas and condensing phases is responsible for the good flame retardancy, anti-drip capabilities, and the significantly reduced emission of heat and organic compounds. MeP-Al breaks down into monomethylphosphonic acid in the gas phase, which dampens heat release and flames. MeP-Al transforms into tough aluminum pyrophosphonate in the condensed phase, where it interacts with PU to encourage the synthesis of stable carbonaceous coke from PU.

There is a wide range of main group metal elements, the most traditional and earliest development of MH and ATH flame retardants are the most widely used. However, as transition metals are increasingly used in flame retardant research and play outstanding smoke-suppression and flame-retardant capabilities, MH and ATH flame retardants are facing serious challenge to their status.

3.4. Multi-metal composite flame retardants

Flame retardants or synergists containing single metal element have been confirmed to be effective by abundance of research. But the different metal elements have different chemical properties and the different roles played in catalyzing the composite matrix into carbon or inhibiting smoke toxicity, and the price of different metals is also somewhat different. Therefore, some studies have shown that multi-metal collaboration can make use of the advantages between different metal elements to complement each other. This includes both transition metals and transition metals, as well as transition metals and main group metals, which can achieve better flame-retardant smoke suppression effect.

Liu *et al.* prepared a flame retardant ($\text{MnO}_2@ZHS$) consisting of two-dimensional manganese dioxide nanosheets and stereo-hydroxyzine stannate (ZHS) binary hybrid, and the synthesis

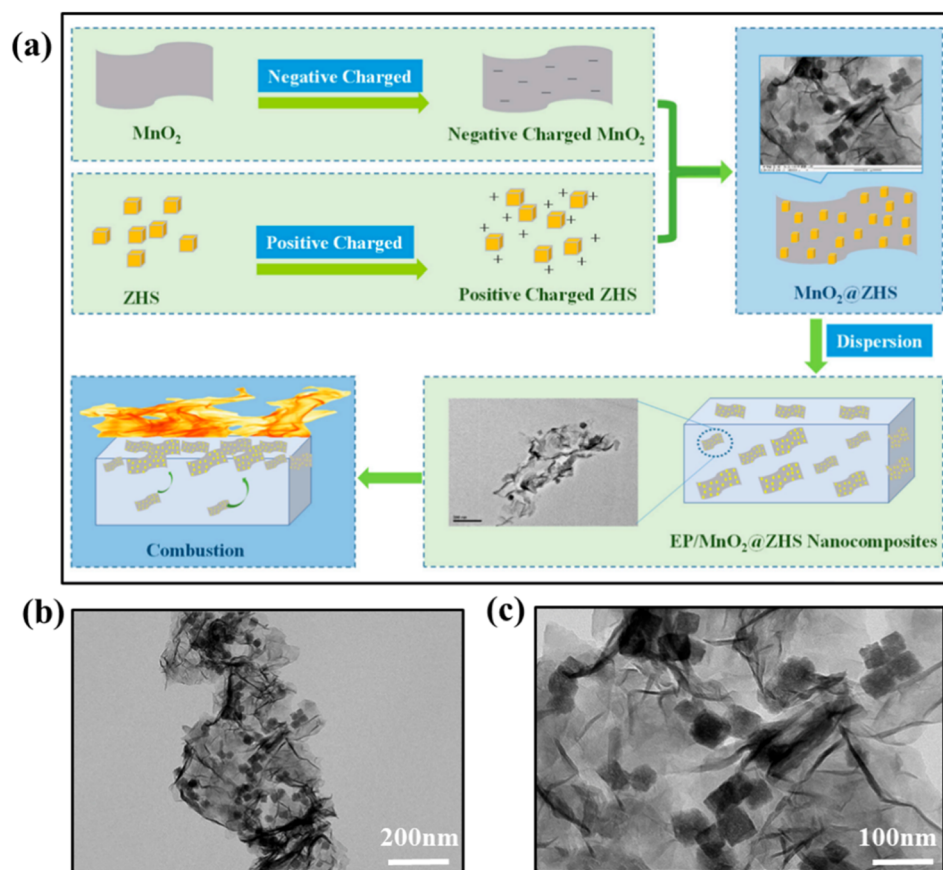


Fig. 13 (a) Synthesis of $\text{MnO}_2@ZHS$ hybrids and flame retardancy mechanism in epoxy; (b and c) TEM images of $\text{MnO}_2@ZHS$ hybrid. Reproduced with permission from ref. 115. Copyright (2019) Polymers.



process is shown in the Fig. 13(a).¹¹⁵ The microstructural analysis showed that $\text{MnO}_2\text{@ZHS}$ was successfully prepared and was morphologically and structurally intact and the TEM images of $\text{MnO}_2\text{@ZHS}$ hybrid is shown in Fig. 13(b) and (c). The $\text{MnO}_2\text{@ZHS}$ binary hybrid efficiently suppressed the PHRR of EP composites, according to CCT findings. At 2 wt% loading, the THR of EP/ $\text{MnO}_2\text{@ZHS}$ may be lowered by nearly 40% compared to the control EP, which is better than that of ZHS alone. The $\text{MnO}_2\text{@ZHS}$ binary hybridization improved the density and graphitization of the residual carbon, successfully preventing oxygen and flammable gases from escaping. Shao *et al.* created a flame retardants, which used the Fe/Zn-LDH to modify the APP.¹¹⁶ The outcomes revealed that the EP containing 4 wt% Fe/Zn-LDH@APP had the greatest LOI of 29.4% and passed the UL-94 V-0 class. The fire growth rate, peak smoke production rate and PHRR were reduced by 80.7%, 48.4% and 66.4% compared to pure EP. This is due to the LDH and APP in Fe/Zn-LDH@APP may better accelerate the conversion of aliphatic molecules to aromatic or polyaromatic compounds, thereby reducing the emission of smoke and heat. Li *et al.* inserted ferrocene molecules into the nanocavities of the sulfonated cyclodextrins of the layered hydroxide (LDH-CD) *via* host-guest chemistry, the LDH-CD-Ferr formed a more homogeneous dispersion than LDH-CD in the EP matrix.¹¹⁷ The peak and total smoke generation rates of the EP matrix were lowered by 43 and 42% when added 6 wt% of LDH-CD-Ferr, while the LOI and PHRR were reduced by 5% and 36%, respectively. A higher quality carbonaceous layer was constructed by the catalytic charring of retained ferrocene, and oxidative degradation of fume intermediates was promoted by the delayed release of ferrocene. Chen *et al.* synthesized iron-based flame retardant enhancers using a hydrothermal method with iron sulfate $\text{Fe}_2(\text{SO}_4)_3$ and urea as raw materials.¹¹⁸ The outcomes demonstrated that a modest quantity of FeOOH might significantly increase the compound's flame retardancy. The compound's LOI value increased to 30.8% when FeOOH was added at 1.5

phr, and the UL-94 vertical flame-retardant test grade reached V-0.

Transition metals and main group metals are not completely separated from each other. On the contrary, they are inextricably linked to each other. In future research on transition metals and main group metal flame retardants, the compounding of multiple metals is also major research hotspot. However, the problems of complex operation and preparation difficulties when compounding different metals are still major challenge for the future.

In summary, combined with the research on metal-based flame retardants in recent years, as shown in Fig. 14, the main group metal elements mainly exist in the form of oxides and hydroxides for flame retardant, for example, MH can dilute the concentration of combustible gases through the water and magnesium oxide produced by thermal decomposition, thus providing a flame-retardant effect. It is worth noting that they can also form LDH to flame retardant, mainly through the formation of a layered structure to play a physical barrier role to isolate combustible gases to achieve flame retardant effect. In contrast to the more homogeneous forms of compounds formed by the main group metal elements, the transition metal elements can form many different types of compounds, for example, iron can form +2 and +3 valence compounds, while manganese has +2, +3, +4, +5, +6, +7, -1, -2 and -3 valence states. Some of the transition metal elements can form a variety of valence compounds in addition, they can also and a variety of organic flame-retardant elements to form the corresponding complexes and organic framework, *etc.* The common metal organic framework are IRMOF series, ZIF series, MIL series, UIO series and PCN series. Transition metals can not only use the catalytic process of the metal matrix into carbon but also catalyze the conversion of toxic gases to achieve a flame retardant and low smoke and low toxicity effect. At the same time, the synthesized organometallic compounds can also combine the flame-retardant effect of organic flame-retardant elements to

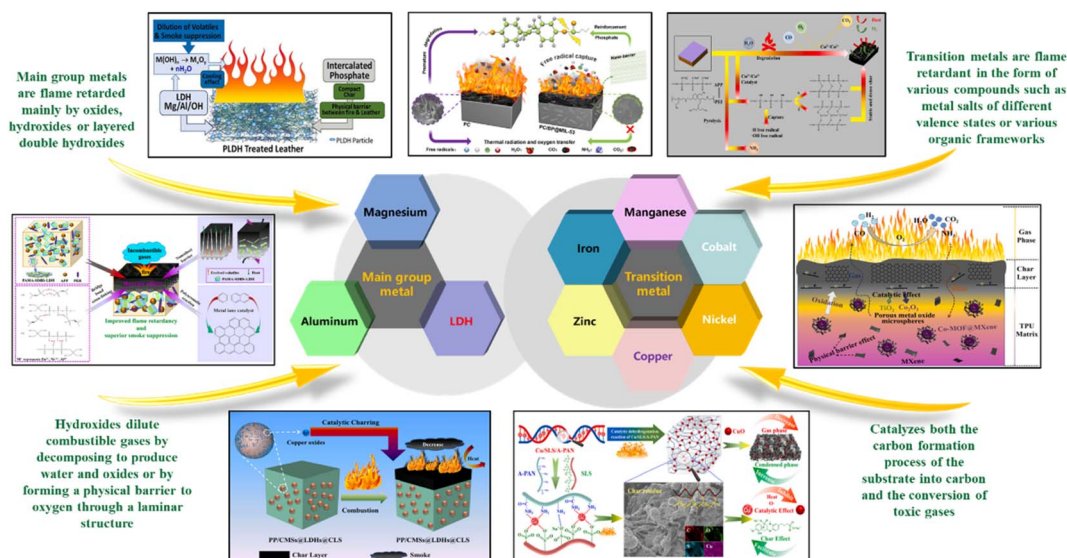


Fig. 14 Differences between main group metals and transition metal flame retardants.



further enhance the flame-retardant effect of polymers. In future metal flame retardant research, transition metal flame retardants, due to their superiority, form a wider variety of compounds and can be developed in a broader range of aspects. The limitations of the main group metal flame retardants lead to their future development needs to be combined with transition metal elements in order to play a better role. Therefore, the composite of multiple metal elements is a major research trend in the future, using multiple metal elements for synergy, and then combined with organic flame-retardant elements such as phosphorus and nitrogen, to achieve a highly efficient flame retardant and low smoke and low toxicity effect.

4. Conclusion and prospect

This paper reviews the progress of research on flame retardants of different metallic elements to provide various synergistic additives to strengthen the flame retardancy of polymers. The primary methods by which metal flame retardants work as well as the many forms of various metals used to construct flame retardant complexes to improve the flame retardancy of polymers are described. Most studies demonstrate that metals can catalyze the carbon formation process in composites to generate dense carbon layer that serves as useful physical barrier by reducing heat transmission, containing flammable gas egress, and preventing further matrix combustion. Additionally, the gases produced during burning may help dilute the oxygen and other combustible gases. According to the current literature, most metals and their compounds cannot be used alone to give polymers excellent LOI values or UL-94 vertical combustion behavior. Instead, they must act chemically modified or in synergy with other organic flame-retardant compounds and carbon formers. Moreover, some metal compounds tend to congregate within the polymer matrix and cannot be entirely disseminated, failing to achieve the maximum enhancement effect in the manufactured polymer composites, which might negatively affect the mechanical properties of the polymer itself.

In general, at present, various metal flame retardants have various problems while achieving an efficient flame retardant and smoke suppression, such as how to uniformly disperse in the polymer material, certain impact on the mechanical properties of the base material and the preparation process is complicated and difficult. Therefore, in the future development stage, the research of metal flame retardants is more inclined to combine the main group metals and transition metals or a variety of transition metal elements, while introducing organic flame-retardant elements such as phosphorus, nitrogen, silicon, *etc.* So as to further enhance the flame retardancy of polymer engineering materials by using the catalytic carbon formation effect of metal elements and reducing the smoke and toxicity on the one hand, and combining the gas phase and condensed phase flame retardancy of organic flame-retardant elements on the other. In addition, when combining metal elements and organic flame-retardant elements, the introduction method of metal elements should be considered, and the introduction in the

form of ions can effectively reduce the mechanical impact on the base material and better dispersion in the base material, which are the areas that need to be focused on when studying metal flame retardants in the future. In a word, metal flame-retardant have excellent functions of catalytic matrix carbon formation and smoke emission inhibition, making them a promising class of environmentally friendly flame retardants and smoke suppressants that are considered to have promising industrial applications in polymers.

Conflicts of interest

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.

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