Recent trends of phosphorus-containing flame retardants modified polypropylene composites processing

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Abstract

Polypropylene has been used for applications requiring high mechanical properties, good adhesion, chemical stability and insulation. Whereas, Polypropylene itself is flammable, and its limiting oxygen index (LOI) is low, which cannot pass the UL-94 combustion test. Therefore, extensive use will cause a serious threat to human life and property. With the wide application of thermoplastic polypropylene in industry, the development of environmentally friendly flame retardant materials has become an important research direction. For the past dozen years, researchers have been exploring flame retardants with high flame retardant efficiency, low toxicity, less smoke or other excellent performance flame retardants. This paper reviews the research progress of some phosphorus-containing flame retardants on the flame retardant properties of polypropylene in recent years. Phosphorus flame retardant is a flame retardant with high flame retardant efficiency, good stability and wide application. The types and flame retardant properties of phosphorus flame retardant will be introduced, and the future research of phosphorus flame retardant is summarized, direction and development opportunities.

1. Introduction

Thermoplastic polypropylene (PP) is one of the essential materials, because of its comprehensive mechanical properties, easy processing, good toughness, good shock absorption, high wear resistance, oil resistance, good acid and alkali resistance, etc. [1,2]. It has been widely used in construction, automotive, electrical, and electronic devices and other industrial/commercial fields. Therefore, it is an ideal material in our daily lives, bringing us great convenience [3]. Although thermoplastics are ubiquitous, their chemical properties are naturally flammable due to the carbon-based materials whose structure consists of carbon atom chains, limiting their application in some industrial fields [4]. Under the temperature (250 °C–450 °C), that will crack/decompose the carbon chain and the structure will be destroyed [5,6].

Fire light illuminates the world and promotes the progress of human civilization, but today, the fire incidents that have caused immeasurable losses to human life and irreparable damage to nature [7]. Thus, many industries have put forward strict flame retardant requirements for the materials used [8]. Toxic gases and smoke are released during combustion, which are harmful to human health and the natural environment [9]. In general, flame retardancy can be achieved in the gaseous and condensed phases of flammable polypropylene composites. Flame retardant is mainly performed in the gas phase by capturing combustion-free radicals, diluting combustible gases or combustion-supporting gases. In the condensed phase, the flame retardant is mainly achieved through heat absorption/dissipation, drip promotion and barrier protection. The method of improving the flame retardant of polymer materials is usually to carry out flame retardant modification on the bulk polymer matrix or the polymer surface [10]. Adding flame retardants (FRs) to the polymer matrix by physical blending, adding flame retardant monomer units to the polymer chains, and building a flame retardant layer on the polymer surfaces are basic flame retardant methods [11].

Traditionally, flame retardant materials have generally used halogen-containing FRs, particularly brominated FRs, which have good flame
With the development of society, some halogen-based FRs have been phased out due to environmental concerns, and thus promoting the development of halogen-free FRs in recent years [14, 15, 16]. Among all halogen-free FRs, P-containing FRs are widely used in PP due to their low toxicity, high efficiency, multiple FRs mechanism and diversity of molecular structure. Therefore, they may be one of the most promising FRs materials [17]. When the external heat source reaches a specific combustion temperature, in the presence of oxygen or air, the reaction of degrading combustibles maintains the combustion of the polymer. The combustion process of some polymers is caused by the participation of highly reactive hydrogen (H) and hydroxyl radicals (OH·), which are two critical radicals in the presence of flames. The combustion of the polymer itself also generates a large amount of combustion heat, which provides heat feedback to the underlying polymer to promote combustion [5]. And this system was understood as the fire triangle. Still, now it has been modified into a fire tetrahedron consisting of four key contributors: fuel, oxygen, heat and a chain reaction (Figure 1). (Figure 1a) Represents a schematic diagram of polymer combustion, and (Figure 1b) Represents a diagram of the mechanism of flame retardant properties of polymers by P-containing FRs [11,18] (Abbreviations of some compounds or test methods are shown in Table 1).

2. Additive-phosphorus flame retardant

2.1. Flame retardant mechanism of P-containing FRs in PP

Up to now, a variety of P-containing FRs has been widely used and studied. Overall, the flame retardancy mechanism of P-containing FRs. Phosphorus is a polyvalent element that can exist in any valence of –3, 0, +1, +3 and +5. It has now been demonstrated that the flame-retardant mechanism of flame-P-containing FRs generally depends on their oxidation state in the flame retardant. During the combustion process, oxidized phosphine plays a vital role in the gas phase, and phosphate plays a significant role in the condensed phase [19]. In high oxidation states (+3, +5), P-containing FRs particularly demonstrate a condensed phase mechanism, and P-containing FRs in low oxidation states (0, +1) mainly exhibit a gas-phase mechanism [20]. For P-containing FRs, gas phase and condensate phase mechanisms coexist and condensed phase mechanisms coexist and act as synergistic flame retardants. In addition, silicon (Si) or boron (B) containing can promote the formation of a compact and glassy char during combustion, thus underpinning the condensed-phase mechanism [21].

2.1.1. Condensed-phase action

In the condensed phase, P-containing FRs act by promoting char formation. Specifically, at high temperatures, they generate phosphoric acid species during polymer combustion, which can promote the carbonization of the PP matrix through dehydration reactions [20]. For example, compounds such as APP [22], 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) [23], phosphate [24], and phosphine hydrogen compounds work together in the condensed and gas phases to act as flame retardants [25]. Thus, the flame retardancy of the material is enhanced.

2.1.2. Gas-phase action

In the gas phase, P-containing FRs decompose at high temperatures, releasing many P-containing groups, such as HPO2, HPO, PO2, PO, which can trap the highly reactive radicals H and HO· generated by substrate degradation [26, 27]. Thereby improving its flame retardancy. In addition, the introduction of synergistic flame retardant groups or elements has become an effective method to enhance the flame retardant mechanism of P-containing flame FRs [28]. For example, by adding nitrogen-containing groups such as triazine, triazole, triazine-trione, etc. Inert nitrogen-containing gas can be decomposed during the combustion process, and the gas-phase mechanism can be enhanced by diluting the concentration of O2 and fuel [29].

2.2. Effect of a single APP flame retardant on the flame retardant properties of PP

As one of the most important thermoplastic polymer materials, PP because of its excellent comprehensive performance, has been widely used [20]. However, its high flammability has a significant fire risk, the flame retardant performance of its research has been a hot topic, phosphorus expansive flame retardant because of its high toxicity, less smoke and flame retardant effect are good, so in recent years, its attention [30, 31]. APP is the acid source in Intumescent flame retardant (IFR) flame retardant, which decomposes into inorganic acid as a dehydrating agent when heated, and when the combustion temperature continues to rise, the dehydrating agent prompts the carbon source to generate ester compounds, which then dehydrate to form a carbon layer, and the resulting carbons form an expanded foam structural carbon layer when the gas source releases non-combustible gases. In addition, the foamed protective layer also has the ability to stop the diffusion of combustible gases, preventing not only the escape of gases generated by pyrolysis, but also the transfer of air and temperature from outside the material to the undecomposed material. The P-containing compound with flame retardant properties in PP can be an inorganic P-containing compound, an organic P-containing compound, or a combination of inorganic and organic P-containing compounds. P-containing materials usually act in the condensed phase, promoting coke formation on the surface, forming a physical barrier that further inhibits polymer re-decomposition combustion [32]. Different P-based substances are added to PP to make it flame retardant [2]. Table 2 shows the name and percentage content of APP FRs in PP.
The effect of APP and other FRs on the flame retardant performance of PP is shown in Table 3.

### 2.4. Microencapsulation of APP

In an IFR system, the acid source releases inorganic acid at a certain temperature to esterify the polyl and act as a dehydrating agent. The effects of different materials covered with APP on the flame retardant properties of PP are shown in Table 4. The esterification reaction occurs at higher temperature conditions and continues to produce melting behavior in the system. Then, some polyols and esters are dehydrated and carbonized at the same time, and the water vapor generated by the reaction and the non-combustible gas generated by the gas source cause the system to expand. Finally, the gel of the system is solidified, and a honeycomb-shaped porous carbon foam layer is formed inside. IFR mainly works in the solid phase, but at high temperatures, some gases are produced in the system that can combine with radicals and interrupt or terminate the chain reaction, and there is also gas phase flame retardation [46]. Some experiments have shown that the core-shell structure (microencapsulation) can significantly improve the mechanical properties and flame retardant properties of PP composites [47]. Huang et al. [48] the micro-coated core-shell structure of ammonium polyphosphate with melamine-formaldehyde resin and sodium silicate for flame retardancy of polypropylene. Technological process and existing flame retardant mechanism are shown in Figure 2. After testing, the UL-94 was reached V-0 and its mechanical properties were improved. When APP was microencapsulated by EP (EPAPP), the composite material had excellent compatibility with the PP matrix. After the polypropylene/EPAPP is treated with water, the surface will not have a hollow phenomenon, which is beneficial to improving flame retardancy [49].

### 2.5. Development of multifunctional P-containing hyperbranched FRs

The multifunctional P-containing additive is a P-containing flame retardant additive that can improve the flame retardancy and other properties of synthetic PP materials. In polymer processing, the amount of flame retardant and the ratio with other additives can be well controlled. It can be divided into hyperbranched P-containing FRs and nano-scale P-containing FRs.

The research shows that the development direction of the synthesis of P-containing FRs is a P-containing hyperbranched structure. P-containing hyperbranched compounds have attracted extensive attention due to their low viscosity, multiple terminal functions, and good compatibility with polymer materials. Chen et al. [10] synthesized a polyphosphate with a novel structure (HBPPDA-Si), which improved the compatibility of APP in PP and produced a heat-resistant cross-linked substance during combustion. Because the polymer composed of triazine ring and P-containing compound usually has good carbon-forming ability and good thermal stability. Ye et al. [51] synthesized a polyphosphoric acid diester (PPBPPDA) containing a compound p-n, which has a branched structure and can be used as a blowing agent and a coking agent. When 25 wt% of flame retardant (APP: HBPPDA = 3:1) was added to the PP matrix, the PP composite achieved V-0 rating as measured by UL-94, the LOI value increased to 30.6%, and its PHRR and THR were reduced by 76.2% and 41.5%, respectively, in the CCT test. Figure 3 presents the development road map of P-containing FRs, and gives some representative chemical structures and that synthetic route (Figure 3a). A novel FRs, tetrakis (5, 5-dimethyl-1,3-dioxophosphoramid-2-oxo) neopentane (DOPNP), was synthesized. The TGA test results show that DOPNP has good carbon-forming ability. When IFR-PP is thermally decomposed in advance, the thermal decomposition rate of the PP matrix is reduced, the amount of coke is increased, and the flame retardant efficiency is improved [52] (Figure 3b). Through the reaction of melamine and phytic acid, a new type of flame retardant containing P and nitrogen is produced: phytate melamine (MPA). The TGA shows that MPA has a good high-temperature carbonization ability [53] (Figure 3c). Used 2-carboxy...
(phenyl) phosphonic acid (CEPFA) and tris (2-hydroxy) isocyanate (THEIC) as starting materials to generate a P/N-containing hyperbranched polymer (PN-HBP). In its UL-94 test, it has reached the V-0 level and has a good flame retardant effect. The PHRR of the PP composite material is significantly lower than that of pure PP [54] (Figure 3d). Using tris (2-hydroxyethyl) isocyanurate (THEIC), polyphosphoric acid, and melamine as synthetic raw materials, an intumescent flame retardant (TPM) was prepared, which was found to be more stable in PP than pure PP. After the flame retardant TPM was added to the composite, its HRR and TSP were significantly reduced [54] (Figure 3e). A novel structure of FRs containing phosphorus and (4-hydroxyphenyl) phosphonic acid (CEPPA) and tris (2-hydroxy) isocyanate (THEIC) as starting materials to generate a P/N-containing hyperbranched polymer (PN-HBP). In its UL-94 test, it has reached the V-0 level and has a good flame retardant effect. The PHRR of the PP composite material is significantly lower than that of pure PP [54] (Figure 3d). Using tris (2-hydroxyethyl) isocyanurate (THEIC), polyphosphoric acid, and melamine as synthetic raw materials, an intumescent flame retardant (TPM) was prepared, which was found to be more stable in PP than pure PP. After the flame retardant TPM was added to the composite, its HRR and TSP were significantly reduced [54] (Figure 3e). A novel structure of FRs containing phosphorus and (4-hydroxyphenyl) phosphonic acid (CEPPA) and tris (2-hydroxy) isocyanate (THEIC) as starting materials to generate a P/N-containing hyperbranched polymer (PN-HBP). In its UL-94 test, it has reached the V-0 level and has a good flame retardant effect. The PHRR of the PP composite material is significantly lower than that of pure PP [54] (Figure 3d).

### Table 2. Proportions of P-containing FRs in the table, and cone calorimetry (CCT) parameters (TTI, PHRR, THR), LOI and UL-94 values. The names and percentages of FRs are listed separately. And wt% represents the loading weight of FRs, while representing additive-free systems or neat PP.

| P-Containing FRs* | Wt% | TTI (s) | PHRR (kW.m⁻²) | THR (MJ.m⁻²) | LOI (%) | UL-94 | Ref. |
|-------------------|-----|--------|---------------|--------------|---------|-------|------|
| APP               | 20  | 40.0   | 787           | 92.0         | 20.5    | NR    | [33] |
| –                 | 66.0| 633    | 44.2          | 17           |         |       | [34] |
| APP               | 20  | 31.0   | 424           | 38.6         | 21      | NR    | [34] |
| –                 | –   | 606 ± 26| 78.0 ± 3.2    | 17.6 ± 0.2   |         |       | [29] |
| APP               | 25  | –      | 411 ± 14      | 73.2 ± 3.8   | 20.7 ± 0.2|         | [29] |
| –                 | 18  | 1457   | 156.0         | 19.0         |         | NR    | [35] |
| APP               | 25  | 20     | 1455          | 148.0        | 21.9    | V-2   | [35] |
| –                 | 21  | –      | 111           | 18.6         |         | NR    | [36] |
| APP               | 25  | 21     | –             | 107          | 21.7    | NR    | [36] |
| –                 | 33 ± 2| 1416 ± 55| 219 ± 4      | 17.0         |         | NR    | [37] |
| APP               | 25  | 19 ± 1 | 526 ± 17      | 180 ± 1      | 19.6    | NR    | [37] |
| –                 | 60 ± 1| 761.6  | 151.9         |              |         | NR    | [38] |
| APP               | 30  | 57 ± 1 | 373.4         | 127.1        |         | NR    | [38] |
| –                 | 44  | 831    | 158           | 17.5         |         | NR    | [39] |
| APP               | 30  | 30     | 432           | 114          | 22.0    | NR    | [39] |

3. Nanoscale P-containing additives

Due to the development of nanomaterials technology, various nanoscale additives have been developed due to their unique physical and chemical properties [57, 58, 59]. The discovery and preparation of some nanomaterials are used as gas barrier films [60], electromagnetic interference shielding materials [61] and protective polymer films [62], as well as energy storage materials [63], especially flame retardancy materials [64] and other applications. The field offers opportunities. For nanocomposites, polymer flammability can be significantly reduced at very low additions, such as reductions in heat release rate (HRR), total smoke release (TSR), and mass loss rate (MLR). This is due to the conformation of a thermally insulating and low-permeability carbon layer that acts as a shield against volatile burn products. In addition, due to its high surface energy, agglomeration easily occurs in the matrix. Most nanofillers do not perform well in limiting oxygen index (LOI) and UL-94 tests, which have a negative impact on the flame retardancy and mechanical properties of the matrix. To solve such problems, nanoscale materials are usually modified with P-based functional groups to enhance their dispersibility and flame retardancy in polymer matrices. Some of

### Table 3. CCT parameters (TTI, PHRR, THR), LOI and UL-94 values. The names and percentages of FRs are listed separately. And wt% represents the loading weight of FRs. NP is a no phosphorus flame retardant, P is a P-containing flame retardant, and P:NP is the ratio of the mass of P-containing flame retardant to that of the added no phosphorus substance.

| Name                        | Wt% | Type of FR | TTI (s) | PHRR (kW.m⁻²) | THR (MJ.m⁻²) | LOI (%) | UL-94 | Ref. |
|-----------------------------|-----|------------|--------|---------------|--------------|---------|-------|------|
| APP/PER                     | 25  | P:NP = 2:1 | 25     | 1239          | 123.6        | 18.5    | NR    | [42] |
| –                           | –   | –          | 25     | 1239          | 123.6        | 18.5    | NR    | [42] |
| APP/PER                     | 25  | P:NP = 1:1 | 34     | 1727          | 112          | 18.0    | NR    | [43] |
| –                           | –   | –          | 34     | 1727          | 112          | 18.0    | NR    | [43] |
| The polypropylene (PP)/modified APP with piperazine (MAPP)/ATPIP | 25  | P       | 47     | 718.3         | 57.3         | 17      | NR    | [44] |
| (MAPP/ATPIP)                | 25  | P:NP = 2:1 | 41     | 593.9         | 41.3         | 22      | V-2   | [44] |
| (MAPP/ATPIP)                | 25  | P:NP = 3:1 | 30     | 186.7         | 40.9         | 27      | V-1   | [44] |
| (APP/DPER)                  | 25  | P:NP = 2:1 | 40     | 158.8         | 39.3         | 30      | V-0   | [44] |
| DPER/AIPo₄                 | 25  | P:NP = 2:1 | 30     | 247.1         | 104          | 26.4    | V-1   | [45] |
| –                           | –   | –          | 27     | 262           | 97           | 28.5    | V-1   | [45] |
| APP/DPER/AIPo₄             | 25  | P:NP = 5:2:1| 26     | 831           | 112          | 24.1    | NR    | [45] |
these typical nanoscale additive materials, such as Polyhedral oligomeric silsesquioxane (POSS), Carbon nanotube (CNT), Montmorillonite (MMT), LDH, and GO, etc.

### 3.1. P-containing POSS

Polyhedral oligosiloxane (POSS) is an organic-inorganic hybrid material whose structure consists of nano-cage hybrid molecules composed of silicon and oxygen elements \[65, 66\]. Since the residual POSS aggregates after combustion generally only form loose and porous chars, they cannot effectively prevent the combustion of the underlying polymer. Therefore, modifying such organic-inorganic hybrid materials to increase their dispersibility can reduce the problem of poor interfacial compatibility between additive materials and the matrix, and even act as plasticizers for polymer materials \[67\]. Therefore, POSS and its derivatives are applied to thermoplastics and thermosetting polymers through physical blending or chemical reactions to improve the mechanical and flame retardant properties of the polymer matrix \[68\]. It has been reported that POSS nanoparticles and their derivatives can impart some flame retardancy to many thermoplastic polymers, such as incorporation into polycarbonate (PC) (about 45% reduction in PHRR) \[69\] and PP materials (about 43% reduction in PHRR). POSS can act as a flame retardant or a reinforcing agent in PP polymer materials and has good smoke suppression and flame retardant properties for PP \[70\]. Yang et al. \[71\] studied a novel one-component intumescent flame retardant (IFR) RMAPP and octa-vinyl polyhedral oligomeric silsesquioxane (OV-POSS) as a synergist and compatibilizer and reported to be highly efficient flame retardant poly. As shown in Figure 4, Figure 4a represents the structure of octavinyl-POSS. Figure 4b and 4c represent the synthesis process of RMAPP and the mechanism diagram of RMAPP/OV-POSS composites, respectively. In Figure 5, Heat release rate-time curve of HRR (Figure 5a), THR (Figure 5b), SPR (Figure 5c) and TSP (Figure 5d) of pure PP, PP/RMAPP (75/25) and PP/RMAPP/POSS (75/24/1) composites shows that pure PP is highly flammable with a peak exothermic rate of 1023 kW/m² and a PHRR of 66 kW/m² for the addition of 1 wt% of POSS and 24 wt% of RMAPP composites. The CCT test results show that there is a good synergistic effect between RMAPP and OV-POSS. In addition, its HRR, THR, TSP and SPR were clearly reduced. Its flame-retardant

![Figure 2. Technological process and the mechanism of action of FRs in PP \[48\].](image-url)
mechanism is shown in Figure 6. The addition of modified POSS significantly improved the dispersion and compatibility of IFR in the matrix, and considerably enhanced the flame retardancy and mechanical performance of PP composites. Under the synergistic effect of P–Si, people have gradually developed a variety of P-containing POSS additives that can improve flame retardant efficiency [5,71,72].

3.2. P-containing CNTs

Carbon nanotubes (CNTs) are one-dimensional nanomaterials that have good thermal stability [73]. It is considered a promising nanoscale flame retardant additive, which includes: multi-wall and single-wall carbon nanotubes (MWNT and SWNT) [74, 75]. The flame retardancy of PP/MWNT nanocomposites during combustion in PP mixtures depends mainly on the residual carbon structure formed during combustion. When the CNTs content reaches a certain value, a three-dimensional network structure will be formed, forming a protective continuous carbon layer, isolating most of the flammable gas and air circulation interchange, reducing heat generation. According to the latest research, CNTs are combined with phosphorus-based FRs, and a synergistic effect can be obtained by decorating P-containing groups on CNTs [76]. It has been reported that the combination of CNTs with DOPO, antimony oxide and organophosphorus FRs can significantly improve the performance [77, 78, 79]. However, Du et al. [80] showed an antagonism between CNTs and P-containing IFR tested in PP, and the addition of CNTs increased the viscosity of the molten polymer to some extent and hindered the expansion of IFR to a certain extent, thereby weakening the thermal barrier of the Carbon layer structure. For example, the PHRR values between CNTs and organophosphorus FRs were increased compared to the composites without CNTs added [81]. Therefore, there is a suitable ratio between IFR and carbon nanotubes to improve flame retardancy, which can achieve a balance between the two mechanisms. Yang et al. [82] reported that carbon nanotubes (CNTs) were packaged and functionalized with covalently bonded polypropylene maleic anhydride (PPMA) to generate dense carbon layered structures. The resulting PP/functionalized CNT (FCNT) composites obviously improved the flame retardancy and mechanical performance of the composites. Figure 7 shows the FR mechanism and mechanical properties of typical P/N-containing IFRs-modified CNTs on PP [82]. Introducing P-containing groups on the surface of carbon nanotubes is an effective way to enhance the flame retardant properties of carbon nanotubes. The combination of different FRs and carbon nanotubes will help to form a dense carbon layer when the polymer material is burned, and suppress the generation of smoke, improve the flame retardant properties of the material.

3.3. P-containing MMT

Montmorillonite (MMT) is a two-dimensional nanomaterial, due to its green environmental protection, low price, layered structure, high aspect
ratio and special mechanical properties. More importantly, MMT is also a promising flame retardant synergist to improve the flame retardancy of polymer matrices [83, 84]. It has been shown that P-containing groups can be introduced into organoclays to prepare novel halogen-free FRs with good synergistic flame retardant properties. Unfortunately, some organic intercalators have high flammability, which has a certain negative impact on the flame retardancy of nanocomposites. In order to achieve better flame retardancy, organically modified MMT (OMMT) was combined with P-containing compounds such as Resorcinol Bis(diphenyl phosphate) (RDP) and triphenyl phosphate (TPP) [85]. After adding the organoclay containing FRs, its tensile strength and elastic modulus were significantly improved [86]. Du et al. [87] also investigated the effect of OMMT on the flame retardancy and mechanical performance of PP composites using IFRs. In addition, the addition of OMMT to PP/IFR can also enhance the mechanical strength and modulus. Yuan et al. [88] synthesized a novel linear polymer carbonizer (PEPAPC) by a

Figure 4. The component structure of OV-POSS and the process of synthesizing FRs. (a) The structure of OV-POSS. (b) The schematic diagram for synthesizing product RMAPP. (c) Schematic representation of the interaction of RMAPP/OV-POSS composite with PP matrix [71].

Figure 5. Heat release rate-time curve of (a) HRR, (b) THR, (c) SPR and (d) TSP of pure PP, PP/RMAPP (75/25) and PP/RMAPP/POSS (75/24/1) composites [71].
nucleophilic substitution reaction. Unfortunately, due to the poor compatibility of IFR with the polymer matrix, a new type of linear polymer carbonizer was prepared by melt intercalation technique. Flame retardant PP/IFR/OMMT nanocomposites using branched PP as compatibilizer. As shown in Figure 8, Figure 8a presents schematic diagram of the PP/IFR/OMMT composite structure. HRR (Figure 8b), THR (Figure 8c) and flame retardancy mechanism of OMMT in PP/IFR composite system (Figure 8d) when 2 wt% OMMT with good dispersibility was added, the PHRR and THR were reduced by 90.5 and 62.7%, respectively, compared with pristine PP, thus, OMMT possessed a nano-barrier and catalytic carbonization effect. In addition, OMMT has a significant impact on tobacco toxicity inhibition, toughening and strengthening of PP/IFR system. This method may provide a solution for the synthesis of high-performance polymer materials on organic/inorganic hybrid nanocomposites, thereby effectively reducing the fire risk. In recent years, the combination of MMT and new FRs has also become the research direction of flame retardant materials.

3.4. P-containing LDH

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite, are an important type of layered double hydroxide, similar to MMTs due to their excellent physicochemical properties, and LDHs act synergistically with conventional FRs to improve the flame retardancy of the material due to their high-performance polymer materials on organic/inorganic hybrid nanocomposites, thereby effectively reducing the fire risk. In recent years, the combination of MMT and new FRs has also become the research direction of flame retardant materials.

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Considering the incompatibility between LDH and PP, modification of LDH is a common measure to improve the dispersibility of LDH in PP, and the adsorption method mainly uses surfactants to modify the surface of LDH to enhance the adhesion of LDH in PP and Improve the flame retardant properties of PP polymer materials [94]. The interlayer method is to add some modifiers [95, 96], or some chemicals to the interlayer of LDH [97], thereby enhancing its synergistic flame retardant effect in PP. At present, the main focus of research on LDH has been on its modification by intercalation. Liu et al. [98] prepared ammonium APP with flame-retardant properties and acid red 88 (AR88) with UV-absorbing properties to be embedded in the LDH interlayer to improve the flame-retardant properties and UV-absorbing properties of PP. Xu et al. [99] successfully prepared P₃O₁₀⁻ intercalated Mg/Al hydrotalcite (LDH-P) by impregnation-reconstruction method. LDH-P is used as a flame retardant for the PP matrix. The resulting test shows that the introduction of LDH-P increases the amount of residual carbon in the PP polymer and increases the denseness of the residual carbon, which provides a compact and folded structural form that protects the underlying material more effectively. Wang et al. [100] prepared multifunctional...
PP/LDH composites by introducing suitable metal ions on LDH, the flame retardant effect of the PP blend is enhanced and the UV resistance of the PP blend is also improved. Hu et al. [96] used a novel bio-based adenosine triphosphate (ATP) pillared magnesium-aluminum layered double hydroxide (LDHs-ATP) was prepared. As shown in Figure 9, Figure 9a presents the diagram of LDHs-ATP synthesis process. Figure 9b–e illustrate SEM, TRR, THR and TSR of Neat PP, PP/LDHs-C, PP/LDHs/ATP and PP/LDHs-ATP during CCT tests. The flame retardant was added to the PP matrix, and the SEM test results showed that LDHs-ATP promoted the uniform dispersion and thermal stability of the material. The LOI value of the PP/LDHs-ATP composite reaches 29.1% and reaches V-0 with only 20 wt% LDHs-ATP loading. The CCT showed that the THR and TSR of the PP/LDHs-ATP composite were notably reduced.

Therefore, the investigators prepared P-containing compounds as modifiers of LDHs [101]. The dispersion of the modified LDHs in the matrix is improved and the flame retardant performance are significantly improved. The phenomenon suggests that organically modification of LDHs may provide new opportunities for the design of flame retardant polymer/LDHs nanocomposites. The results indicate that in the next few years, designing P-containing LDHs FRs will be flame retardant and contain other effects.

3.5. P-containing GO

As a two-dimensional nanomaterial, graphene has a large surface area, high aspect ratio, excellent mechanical properties, and good
thermochemical stability [5, 102, 103]. Due to these properties, gra-
phene and its derivatives have been developed for capacitors, microwave
absorption, mechanical sensing, and thermally conductive composites
[104, 105, 106, 107]. Graphene Oxide (GO), whose structure contains
more graphene with oxygen-containing functional groups, is more active
[108, 109]. Cao et al. [110] prepared graphene oxide (GO/HCPA) with a
network structure by introducing polynamine molecules with triple roles
(crosslinking agent, FRs agent, and reducing agent). As shown in
Figure 10. It has good mechanical toughness, excellent expansion effect
and ultra-sensitive fire alarm response. So far, studies have found that
graphene oxide flakes exhibit hydrophilic and hydrophobic amphiphi-
llicity from edge to center. Making graphene oxide an efficient synergist,
showing excellent flame retardancy in PP composites [111].

It has been found that graphene can significantly reduce the HRR of
polymeric blends, outperforming layered silicates and CNTs [112, 113,
114]. The surface area of the nanoparticles (particle morphology) also
affects the dispersion and flame retardancy of the nanomaterials in the
polymer matrix [115]. Due to the π–π superposition effect, graphene
nanosheets have a strong solid tendency to overlap and agglomerate,
which makes it difficult to uniformly disperse in the polymer matrix,
which will hinder its flame-retardant and mechanical strengthening
[116]. Therefore, P-functionalized graphene or graphene oxide, or mixed
with other FRs, which make them have a synergistic flame-retardant
effect, form a dense and uniform carbon layer structure, and improve
its mechanical strength [117, 118, 119]. Studies have shown that
phosphorus-functionalized graphene nanomaterials generally exhibit

Figure 9. (a) The diagram of LDHs-ATP synthesis process. (b) SEM (c) TRR (d) THR and (e) TSR of Neat PP, PP/LDHs-C, PP/LDHs/ATP and PP/LDHs-ATP during CCT
tests [96].

Figure 10. Scheme for preparing the GO/HCPA paper nanocomposites via a simple water evaporation-induced self-assembly strategy [110].
multifunctional properties. Nie et al. [111] found that organophosphorus zirconium-modified graphene oxide can reduce the flammability of PP nanocomposites. Yuan et al. [120] investigated a new type of halogen-free FRs, namely ternary graft product of silsesquioxane, graphene oxide and DOPO (PMGO), whose graphene oxide layer structure was modified, and synthesized phosphorus, various elements of nitrogen and silicon, which are combined with conventional IFR to form an excellent intumescent carbon layer with high mechanical strength and thermal stability. As shown in Figure 11a-d, the experimental results show that introducing 5 wt% PMGO and 20 wt% IFR, the peak exothermic rate and total exotherm of the composites are decreased by 61.5% and 40.2%, respectively, compared with pure PP. Ji et al. [121] used a covalent modification method to synthesise a novel functionalised graphene oxide (F-GO). LOI of flame retardant epoxy resin (FREP) increased from 19.9% to 30.8 % when F-GO content was 1wt, and the THR and PHR decreased by 44.0% and 55.5%, respectively.

In summary, Graphene is combined with P-containing compounds by physical or chemical modifications, when added to PP polymers will promote the formation of carbon layer in the matrix, effectively inhibiting the generation of heat and the release of combustible gas energy. At the same time, it prolongs the ignition time of the polymer, inhibits the droplet phenomenon generated during the combustion of the polymer, slows down the flame spread, and improves the mechanical properties of PP to some extent.

4. Trends and the future of phosphorus-based FRs

Phosphorus chemistry, one of the oldest areas of chemistry, is a potent and versatile element for FRs to replace halogens, which are still widely used today. Generally, compounds containing phosphorus are usually extracted and manufactured from “phosphate rock” [20]. The process synthesis routes of some P-containing FRs are shown in Figure 12. Such as ammonium polyphosphate, phosphazene [25] and DOPO and other development and synthetic routes, proved the complex diversity of phosphorus-based FRs. Meanwhile, PCl3 is an intermediate for the synthesis of organophosphorus FRs. As phosphate rock is a limited resource, it is a non-renewable resource and will be used up in the future. With the development of society, as halogen FRs are more harmful to humans, animals and plants and are gradually being replaced, people are paying more and more attention to the development of healthy, green and sustainable FRs [122, 123, 124]. To ensure the sustainable application of P-containing fertilizers and phosphorus chemistry, there has been a strong effort to develop renewable phosphorus fertilizers. For example, plant extracts, bio-based P-containing FRs or P extraction from human urine and feces can be part of sustainable phosphorus chemistry.

4.1. Organophosphorus FRs (OPFRs)

Organophosphorus FRs (OPFRs) have flame retardant and plasticizing functions and can replace halogen-based FRs. The production and use of some halogenated FRs have been banned in some countries and regions due to their persistence, bioaccumulation and toxicity (PBT) [125, 126]. Therefore, the advance of other non-brominated alternatives has been promoted. OPFRs are represented by phosphate, phosphorus compounds, heterocyclic phosphorus compounds, phosphorous acid, etc., and have high flame retardant efficiency in both the gas phase and condensed phase [20]. The release of PO radicals in the gas phase interrupts the combustion process, and the dehydration of the polymer into char in the condensed phase shows excellent flame retardant efficiency. Due to their biodegradability [127], OPFRs can also be used as plasticizers and defoamers, so OPFRs have developed rapidly [128]. In most cases, the first step in degradation is the hydrolysis of phosphate groups catalyzed by enzymes called organophosphorus hydrolases or phospho- triesterases [129]. In addition, compounds containing nitrogen, silicon or
intumescent FRs can also be used as synergistic flame retardant additives. OPFRs are currently one of currently the research topics, and multi-element synergistic FRs are one of the important development directions of future OPFRs. However, the presence of organophosphorus FRs or compounds will produce bioaccumulation and biomagnification effects in animals, plants, humans, and ecosystems [130, 131, 132]. Therefore, it is necessary to increase research efforts to produce reasonable, efficient and environmentally friendly OPFRs.

4.2. Renewable P-containing bio-flame retardant

In recent years, due to the increasing use of fossil raw materials, people have a deeper understanding of resource issues. To promote sustainability, some renewable biological sources can be used to replace non-renewable resources. Therefore, renewable resources FRs Development gets more attention [133]. From renewable P-containing flame retardant materials such as deoxyribonucleic acid (DNA), phytic acid, casein and hydrophobin, etc. Among them, DNA is considered a potential green and renewable FR biomacromolecule because of its unique chemical structure, and each unit contains phosphorus and nitrogen elements. The components in DNA include phosphate group, deoxyribose sugar and base pair, which satisfy the conditions of expanding FRs, namely acid source, carbon source and foaming agent. Alongi et al. [134] also applied DNA to various polymeric substrate coatings such as EVA, PP, ABS and polyamide 6 (PA6), etc. As shown in Figure 13. The protective carbon layer is formed by the surface coating of the DNA-containing, which reduces the amount of heat release and has good flame retardancy.

In addition, phytic acid (PA) is a P-containing biomass that is the main storage form of certain plant seeds, grains or legumes. It contains six phosphate groups and is therefore a more desirable flame retardant. Zhang et al. [135] prepared a novel polyelectrolyte composite (PEC) by reacting PA with polyethyleneimine (PEI), which formed a dense carbon layer structure during combustion and improved the thermal oxidation stability and flame retardancy of pristine PP. Gao et al. [136] prepared a new bio-based phytic acid PHYPI by the salt reaction of phytic acid and piperazine. After adding PHYPI to PP, PP showed high flame retardant efficiency in combustion tests. The LOI at 18.0 wt% of PHYPI increased by 38.9% compared to the LOI value of 18.0% for pure PP. Sacristán et al. [137] reported a new route to extract active P-containing vegetable oil derivatives or fatty acids from vegetable oils to improve the LOI value of the material. Shang et al. [138] used supramolecular self-assembly technology to form melamine phytate (MEL-PA) nanosheets based on MEL and PA. The addition of 2 wt% of MEL-PA reduced the peak exothermic rate from 756 to 608 kW/m² compared to pure polypropylene. MEL-PA improved the char formation rate of PP, analyzed the chemical structure and graphitization degree of the residual coke, and revealed its flame retardant mechanism.

Liu et al. [139] prepared a lignin-based flame retardant, wood-plastic composite (WPC) with abundant reactive functional groups and high carbon content, to which phosphorus, nitrogen and copper elements were chemically grafted, which could be used as a functional additive to WPC, and the PP composite exothermic rate and total smoke emission were significantly reduced. Recently, Zheng et al. [53] synthesized new phosphorus and N-containing flame retardant phytate melanine (MPA) by reacting melamine with PA, and it was added into halogen-free intumescent flame retardant system for flame retardant PP composites, and its LOI reached 28.5%. At the same time, bio-based FRs have better recycling opportunities and are also biodegradable, thus reducing their environmental impact and harm to humans compared to halogenated FRs. However, since the cost of halogen-free flame retardant plastics is higher than that of halogenated plastics, it is necessary to increase
research and development efforts to propose better solutions. Sustainable renewable resources will also serve as a bridge between economic growth, health and environmental safety.

5. Conclusion and perspectives

5.1. Conclusion

This paper reviews the application strategies and flame retardant methods of P-containing FRs in PP materials and introduces the relevant research progress in this field. The results show that the flame retardant method mainly exerts the flame retardant effect by forming a dense carbon layer structure through the solid-phase mechanism. In addition, there are other mechanisms of flame suppression, namely the generation of non-flammable gases, dilution, and cooling mechanisms and termination of the chain reaction. In terms of flame retardant compounds, because traditional halogenated FRs pollute the environment and negatively impact animals, plants, human bodies and ecosystems, P-containing FRs with less harm are used. Among them, the multi-group P-containing additives can make PP have good flame retardancy under the condition of low addition amount, and the hyperbranched and nano-scale P-containing additives usually show various functions. In most cases, the incorporation of FRs affects the mechanical properties of the PP matrix. Therefore, to address the compatibility of the PP matrix with FRs to enhance the adhesion between them, strategies have been adopted, including filler materials or blocking the surface modification of flammable compounds, as well as microencapsulation of P-containing compounds, and through the synergistic effect of various compounds to improve the mechanical performance, and improve the flame retardancy. Due to limited resources, further research and development of renewable P-containing compound FRs are required to achieve green and sustainable development. The renewable P-containing bio-based compounds FRs and their good flame retardant properties are also introduced. However, the research on renewable P-containing bio-based is in the early stage of development, and the realization of industrialization and commercialization still faces great challenges.

5.2. Challenge and future perspectives

In recent years, great progress has been made in the study of P-containing FRs, but there are still some problems that need to be solved. First, most organic and inorganic/organic P-containing FRs are non-renewable resources because most of the organic and inorganic/organic P-containing FRs extract phosphorus compounds from "phosphate rock" rather than renewable P-containing bio-based compounds. In addition, the synthesis of FRs often involves the use of a large number of organic solvents, which leads to production costs and potential environmental problems. In addition, P-containing FRs present certain hazards to the environment and human health, which will limit their industrial or commercial use. Second, due to the lack of perfect recycling measures and the company's lack of technology in this field, the recycling of P-containing flame-retardant plastics is challenging, so plastics such as P-containing flame retardant PP cannot be recycled or reconfigured for use. The third is the flame retardant efficiency and mechanical performance of P-containing FRs. The addition of FRs gives the PP polymer a better flame retardant effect. However, due to the poor compatibility of
some FRs with PP matrix, it will affect the mechanical properties of the matrix. In order to achieve V-0 grade, it is also necessary to consider the problem between its flame retardancy and its mechanical properties.

Some possible research directions will be explored for the above mentioned problems. In the production of FRs, green and renewable P-containing FRs are the first choice, followed by non-toxic solvents or solvent-free preparation methods. In addition, the organic P-containing FRs are treated in a biodegradable manner. For the recycling of flame retardant materials, Relevant recycling policies should be introduced. For the problem of poor compatibility of P-containing FRs with the matrix, the development of hyperbranched P-containing FRs can improve mechanical toughness and flame retardant performance. In addition, according to sustainable development, green and environmentally friendly renewable flame-retardant resources will be vigorously developed in the future, such as plant juices, eggshells and fruit wastes that can catalyze the formation of charcoal or release incombustible gas. Because of its low price, abundant output and environmental safety, it has great potential for development.

Declarations

Author contribution statement

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Data availability statement

Data will be made available on request.

Declaration of interest’s statement

The authors declare no conflict of interest.

Additional information

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