Review Article

Nanoreinforcements of Two-Dimensional Nanomaterials for Flame Retardant Polymeric Composites: An Overview

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Polymer materials are ubiquitous in daily life. While polymers are often convenient and helpful, their properties often obscure the fire hazards they may pose. Therefore, it is of great significance in terms of safety to study the flame retardant properties of polymers while still maintaining their optimal performance. Current literature shows that although traditional flame retardants can satisfy the requirements of polymer flame retardancy, due to increases in product requirements in industry, including requirements for durability, mechanical properties, and environmental friendliness, it is imperative to develop a new generation of flame retardants. In recent years, the preparation of modified two-dimensional nanomaterials as flame retardants has attracted wide attention in the field. Due to their unique layered structures, two-dimensional nanomaterials can generally improve the mechanical properties of polymers via uniform dispersion, and they can form effective physical barriers in a matrix to improve the thermal stability of polymers. For polymer applications in specialized fields, different two-dimensional nanomaterials have potential conductivity, high thermal conductivity, catalytic activity, and antiultraviolet abilities, which can meet the flame retardant requirements of polymers and allow their use in specific applications. In this review, the current research status of two-dimensional nanomaterials as flame retardants is discussed, as well as a mechanism of how they can be applied for reducing the flammability of polymers.

1. Introduction

Polymer materials, due to the continuous development of science and technology, have been widely used in all aspects of humankind's basic life necessities [1]. Due to the environmental adaptability of polymer materials, they have been widely used in construction, transportation, agriculture, electronics and electrical systems, textile, and other major economic areas. However, most of polymer materials are highly flammable, with fast combustion propagation rates and are not easily extinguished. A large portion of annual fires worldwide are related to polymer materials. According to statistics, 237,000 fires were reported in China in 2018, resulting in 1407 deaths, 798 injuries, and direct property losses amounting to 3.675 billion RMB [2]. Therefore, it is critical to research and develop effective flame retardants so as to reduce the risks of accidental fires, costly damage to buildings materials, and to widespread health and safety [3].

Polymer flame retardants are mainly divided into halogen and halogen-free categories. However, halogen flame

retardants have limited use because they release toxic gases and corrosive smoke during combustion. Therefore, halogen-free compounds are currently being considered as promising flame retardants, based on their more environmentally friendly properties [4]. Numerous efforts have been made to find suitable halogen-free flame retardants polymers. Traditional inorganic flame retardants, including aluminium hydroxide [5, 6] and ammonium polyphosphate [7, 8], are usually added to polymers in large quantities, which can often lead to a decline in the processability and mechanical properties of these doped materials. Organic phosphorus flame retardants [9, 10] have high flame retardant efficiency, but most of these are liquids with poor heat resistance. In recent years, in addition to graphene, two-dimensional nanomaterials, such as hexagonal boron nitride (h-BN) [11–16], molybdenum disulfide (MoS_2) [17–20] and black phosphorus [21] (Figure 1), have also been developed, which has greatly expanded the properties and applications of two-dimensional materials in this realm. Notably, two-dimensional materials and their derivatives have been extensively studied as photocatalysts

FIGURE 1: Structure of some two-dimensional nanomaterials. (a) Molybdenum disulfide [52]. (b) α -zirconium phosphate [53]. (c) Hexagonal boron nitride [54]. (d) Layered double hydroxide [55]. (e) Black phosphorus [56]. (f) Graphene with (I) Zigzag and armchair edges, (II) Monovacancy, (III) Local structure of a curved graphene sheet [57].

[22, 23], sensors [24], drug delivery vehicles [25], transistors [26], lithium ion batteries [27], water treatment agents [28], ion exchange [29], fuel cells [30], nanofiltration membranes [31], conductive inks [32], quantum dots [33], adsorbents [34] and supercapacitors [35]. Moreover, two-dimensional nanomaterials/polymer composites have also been investigated. Lin et al. [36] realized the intercalation of polythiophene into MoS₂ could be achieved by means of in situ polymerization of intercalated monomers. This method has contributed to enhancing the conductivity of composites at ambient temperature. Wang et al. [37] prepared a high-performance thermal interface material based on exfoliated boron nitride nanosheets (BNNs) and polystyrene (PS) microspheres. Yan et al. [38] reported that g-C₃N₄-poly(3-hexylthiophene) polymer composites achieve enhanced hydrogen production using water as a substrate under visible light. Particularly, two-dimensional nanomaterials have attracted extensive attention in the field of flame retardant and smoke suppression due to their unique structure and properties [39].

Compared with zero-dimensional nanomaterials and one-dimensional nanomaterials, two-dimensional nanomaterials have emerged as a superior flame retardant option due to their layered structures, which have high thermal stability and can form a physical barrier in a polymer matrix [17, 40]. Additionally, homogeneous dispersion of a small amount of two-dimensional nanomaterials in polymers can effectively improve the mechanical properties of polymers [41, 42]. A well-dispersed layered structure in a polymer can not only greatly improve the thermal stability of a polymer [43, 44] but it can also further enhance the action of char residual in the inhibition of heat and mass transfer [39, 45]. It is believed that

the biggest obstacle to the application of two-dimensional nanomaterials as flame retardant additives is the high cost and the low yield of the peeled sheet structures [46]. Recently, as the number of publications related to these emerging two-dimensional nanomaterials has increased dramatically, a large number of studies on the large-scale production of two-dimensional nanosheets have paved the way for flame-retardant applications [47, 48]. Yao et al. [49] reported a facile and scalable method for the preparation of monolayer and few-layer of BN, MoS₂, and graphene using a combination of low-energy ball milling and sonication. These prepared 2D nanosheets could be well dispersed in high concentrations of aqueous solutions as 1.2 mg/ml (for BN), 0.8 mg/ml (for MoS₂) and 0.9 mg/ml (for graphene). These advantages make it possible to apply high performance 2D nanomaterials/polymers at low cost with great potential, which is beneficial to the application of such new 2D nanomaterials in the flame retardant field. If suitable two-dimensional nanomaterials are selected for the application of specific polymers and the functionally controllable two-dimensional nano flame retardants associated are prepared via a simple and versatile method, the multi-functional application challenges of polymers can be overcome. It is well known that nano-fillers can easily achieve good flame retardant effects (below 6 wt%) at low load, meaning that they have potential industrial prospects [50, 51].

Recent progress and future development trends in flame-retardant materials using two-dimensional materials were summarized above. This also highlighted the effects of two-dimensional nanomaterials and the unique flame retardant mechanisms of sulfur, phosphorus, nitrogen, silicon, layered double hydroxide, and carbon skeleton.

2. The Flame-Retardant Mechanism of Two-Dimensional Nanomaterials

The combustion of polymer materials involves the evolution of combustible volatiles through decomposition in an oxygen-rich atmosphere. No matter which flame retardant is used, its flame-retardant mechanism is through one of the following two processes (or occasionally a combination of the two): (i) condensed phase or (ii) gas phase [58]. Figure 2 shows three possible processes of flame retardant mechanisms.

2.1. Condensed-Phase Mechanism

2.1.1. Physical Barrier. Two-dimensional nano-layered flame retardants can function as an effective insulating barrier, to inhibit mass loss during the thermal degradation process.

Shi et al. [61] reported a ternary PS/g-C₃N₄/aMWCNT assembled system using LBL technology, which led to the improved thermal stability of the PS matrix, including $T_{-10\%}$, T_{-max} , and char residue increased by 11°C, 20.0°C and 6.5%, respectively. The generation of total gaseous products was also distinctly inhibited by the ternary assembled systems. Moreover, the ternary assembled systems showed outstanding improvements in flame retardancy; i.e., HRR and THR decreased by around 45% and 47%, respectively. These enhancements were attributed to the LBL assembly strategy being conducive to building extremely tight barriers.

Hu et al. [62] synthesized a functionalized graphene oxide (FGO) that was grafted by hyper-branching as a flame retardant to reduce the combustion and toxicity of PS. The addition of 0.1% FGO significantly increased the $T_{-5\%}$ of PS-FGO0.1 nanocomposites compared to that of pure PS. This effect was attributed to the combined effect of the physical barrier and the capture of oxygen molecules and free radicals by FGO layers under atmospheric air. This enhanced barrier effect was also demonstrated by a suppressed mass loss rate, implying the retardation of mass transfer from nanocomposites to the flame zone.

2.1.2. Formation of a Continuous Char Layer. During the combustion process, a compact and stable char layer is formed on the surface of a polymer, which acts as a thermal insulating barrier to heat and separates oxygen from burning materials, thus preventing mass and heat transfer, reducing the heat release rate and total amount of flammable volatile gases after the char layer is established.

Xie et al. [63] synthesized a ZrP-decorated macromolecular charring agent (ZrP-d-MCA), which was then introduced into polypropylene. A mechanistic study showed that ZrP-d-MCA/APP effectively involved PP incorporation into the charring reaction, forming a compact and firm intumescent char layer with outstanding barrier properties. ZrP first catalyzed the carbonization of MCA on its surface, forming closed micro-nano char-cages, which then trapped the degradation products of PP and further catalyzed them into a thermostable graphitized char.

Feng et al. [64] proposed a ternary thermal interface material based on epoxy resin (EP), silver nanowires (AgNWs), and a small amount of flame-retardant functionalized graphene (GP-DOPO). Char analysis confirmed that the char's

yield and quality (integrality and compact degree) were increased dramatically by incorporating GP-DOPO into EP/AgNWs, due to the strong catalytic charring effect. The increased organic chars not only protected the AgNWs from melting and wicking action but also connected the AgNWs network to form a protective char layer with a compact and robust structure, which acted as a barrier to prevent the transfer of heat, oxygen, and flammable volatile products between the inside and outside of the polymer melt, thus improving the flame retardancy of the EP/AgNWs/GP-DOPO composite.

2.2. Gas-Phase Mechanism

2.2.1. Dilution of Oxygen by Inert Gases. The gas dilution flame retardant mechanism is typified by a large amount of nonflammable gases being produced during the decomposition process of a flame retardant at high temperatures, and these nonflammable gases can prevent the combustion of a polymer by diluting the oxygen concentration.

Wang et al. [65] reported Cardanol-BS modified layered double hydroxide (M-LDH) being synthesized by a coprecipitation method, and its subsequent incorporation into EP at different loadings. The degradation gaseous products could be mainly divided into two categories: one was inflammable gases, such as water vapor and CO₂, and the other was flammable gases, such as carbonyl, aromatic compounds, and esters. The maximum absorbance intensity of inflammable volatiles for EP/LDH-6% and EP/m-LDH-6% composites was much higher than that for pure EP, which effectively diluted the concentration of flammable volatiles.

Xu et al. [66] reported a hybrid RGO-LDH/Mo system through RGO-LDH modified by heptaheptamolybdate (Mo₇O₂₄⁶⁻) via ion exchange method, and introduced it into polyurethane elastomer (PUE). Compared with pristine PUE, the pHRR of PUE1 was decreased by 36.4% because the LDH layer and carbon residue inhibited the volatilization of combustible gases produced during polymer decomposition, isolated oxygen, and reduced the thermal radiation of materials. At the same time, due to the generated water vapor, the temperature was lowered and the combustion process of the composites was delayed, so the heat was absorbed in the endothermic decomposition process of LDH.

2.2.2. Gas Phase Free Radical Inhibition. Flame retardants can also capture and annihilate active free radicals, thus preventing and inhibiting free radical chain reactions, reducing the flame burning rate and extinguishing a flame.

Yang et al. [67] used organophilic α -zirconium phosphate (α -ZRP, OZRP) as a synergistic agent with aluminium hydroxide (ATH), and introduced it into low-density polyethylene and ethylene-vinyl acetate (LDPE/EVA) blends. As LDPE/EVA/(ATH, OZRP) hybrids burned, ATH first decomposed rapidly with the release of hydration water. This endothermic decomposition lowers the temperature of the reaction, and the released water vapor dilutes flammable volatile gasses. Second, a small amount of phosphorus monoxide (PO•) produced by the combustion of OZRP can quench active radicals produced by the burning of the gas phase, while the exfoliated OZRP layers can efficiently promote the formation of compact

FIGURE 2: Flame retardant mechanisms of partial two-dimensional materials. (a) The free radicals of PP chain scission are inhibited, and then a coherent, thermally stable, and tough swollen char is formed under the catalysis of solid acid sites on the surface of α -zrp core [59]. (b) LDHs catalyze the formation of a thick char layer on the surface of EP [60]. (c) A MoS_2 -CNT hybrid acts as a physical barrier in an EP [19].

FIGURE 3: (a) Illustration of the preparation of MoS_2 -LDH nanohybrids via a self-assembly method. (b) Intensity of characteristic peaks for pyrolysis products of EP and EP/2% NiFe-LDH- MoS_2 composites. (c) The TSP and THR of EP and EP composites. Adapted from [39].

charred layers in the condensed phase and hinder the diffusion of oxygen and flammable volatile products.

Ren et al. [68] prepared black phosphorene/graphene (BP/G) composites by high-pressure nano-homogenizer machine (HNHM) and distributed them uniformly in WPU. The addition of graphene could reduce pHRR by 21.2%, and the addition of BP/G could reduce pHRR by 48.18% when compared with the pristine WPU. This was because the special layered structure of graphene and BP had barrier effects during degradation process, which could prevent materials from oxygen and heat transfer. In addition, BP could form $\text{PO}\cdot$ free radicals, diffuse in surrounding gases, and react with $\text{H}\cdot$ or $\text{OH}\cdot$ free radicals produced by polymer under combustion, hence reducing the flame.

3. Research Progress on Polymer/Two-Dimensional Nanomaterial Flame Retardant Composites

3.1. Sulfur-Containing Compounds. Various 2D nanosheets, such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), have attracted tremendous attention due to the unusual properties associated with their ultrathin nanosheet structures. MoS_2 is composed of three stacked atomic layers (S-Mo-S) held together by van der Waals forces [17]. Mechanically exfoliated atomically thin sheets of WS_2 have been shown to exhibit high in-plane carrier mobility and electrostatic modulation of conductance similar to MoS_2 [69]. These have been extensively studied in the field of polymer flame retardation because of their outstanding mechanical properties, which can be attributed to their small size, typically in the range of 40–180 nm, and their chemical inertness [70].

On the one hand, MoS_2 has been used for enhancing the thermal, flame-retardant, and mechanical properties of polymer composites [18–20, 71–83] due to its small size and high thermal stability. For instance, cellulose nanofibers (CNFs) were nano-wrapped with ultrathin 1T phase MoS_2 nanosheets via chemical crosslinking to produce an aerogel. Thermal and combustion characterization revealed highly desirable properties (thermal conductivity $k = 28.09 \text{ mW m}^{-1} \text{ K}^{-1}$, insulation R value = 5.2, limit oxygen index (LOI) = 34.7%, total heat release = 0.4 MJ m^{-2}). Considering the inherently low density of this material, there was significant opportunity for its use in a number of insulating applications [72]. Wang et al. reported the synthesis of MoS_2 nanosheets via a “thiol-ene” click reaction between defect-rich MoS_2 nanosheets with sulfydryl groups and ene-terminated hyperbranched polyphosphate acrylate (HPA), and characterized these nanosheets by FTIR and XPS to confirm their covalent functionalization through C–S bonds. The combustion behavior of unsaturated polyester resin (UPR) composites was also investigated, demonstrating an obvious reduction of 43.2% and 39.6% in Peak Heat Release Rate (pHRR) and Total Heat Release (THR), respectively [74]. To solve the problem of homogeneous dispersion of MoS_2 nanosheets in a polymer matrix and exact interface control, hierarchical polystyrene@ MoS_2 core-shell structures were constructed by combining latex technology and self-assembly of oppositely charged MoS_2 nanosheets onto

the surface of PS spheres. This method proved to be an efficient and facile approach to fabricate polymer/ MoS_2 nanocomposites with good dispersion and improved properties [75].

On the other hand, MoS_2 and its derivatives have been used for smoke suppression of various polymers, including polystyrene [17, 84], polyvinyl alcohol [85], epoxy [86–89], polyurethane [90], and polyamide 6 [91]. For example, Zhou et al. [86] reported LDH/ MoS_2 hybrids were facilely prepared by self-assembly of exfoliated MoS_2 nanosheets and LDH via electrostatic forces. This approach endowed excellent fire resistance to an epoxy matrix, which was reflected by the significantly reduced peak heat release rate, total heat release, and total smoke production (Figure 3). Qiu et al. [88] showed that polyphosphazene nanoparticles (PPN) functionalized with MoS_2 nanosheets have been successfully fabricated, followed by high temperature polymerization. The incorporation of P and N atoms efficiently reduced the stacking of MoS_2 nanolayers and formed a large number of active sites. It was also demonstrated that the introduction of MoS_2 @PPN nanohybrids significantly improved the flame retardancy of EP. Feng et al. [91] used supramolecular self-assembly to prepare sandwich-like melamine cyanurate/ MoS_2 sheets as hybrid flame retardants for PA6. The introduction of MoS_2 sheets functioned not only as a template to induce the formation of two-dimensional melamine cyanurate capping layers, but also as a synergist to generate integrated flame-retarding effects in the hybrid sheets, in addition to a high-performance smoke suppressor to reduce the fire hazards of PA6 materials.

WS_2 is one of the most commonly used compounds in semiconductor TMS's. In recent years, materials such as WS_2 have attracted increased attention in the field of nanocomposite fillers, due to their high thermal and mechanical properties [69, 92]. Díez-Pascual et al. prepared an inorganic fullerene-like tungsten disulfide (IF- WS_2) lubricant, and then used this to manufacture PPS/IF- WS_2 /CF laminates via melt-blending and hot-press processing. These multiscale laminates exhibited higher ignition points and notably reduced pHRR compared to PPS/CF alone. The coexistence of micro- and nano-scale fillers resulted in synergistic effects that enhanced the stiffness, strength, thermal conductivity, and flame retardancy of the matrix [70]. Wenelska et al. reported WS_2 functionalized with metal oxides (iron oxide and nickel oxide) as a filler for PEs. This showed that composites can provide a certain physical barrier and inhibit the diffusion of heat and gaseous products during combustion [69].

3.2. Phosphorus-Containing Compounds. Phosphorus-containing compounds, including α -zirconium phosphate (α -ZrP), black phosphorus (BP), and vanadium dehydrated phosphate (VOPO_4), may replace halogenated variants that are still widely used in flame retardants. Phosphorous flame retardants can play a role in both the gas phase and condensed phase extinguishing mechanisms during a fire [3]. In the following, different P-containing flame retardants are explored in detail.

3.2.1. α -Zirconium Phosphate. α -ZrP is a type of solid acid, which represents a wide range of chemical substances that are able to accept electrons and create coordinate bonds. The

dehydrogenation of a polymer occurs and these unsaturated sites then lead to crosslinking and ultimately graphitization. Therefore, solid acid-type α -ZrP can play an effective role as a crosslinking catalyst through the catalysis of carbonization of the polymer itself during thermal decomposition [93]. However, two main subjects have to be addressed before their further applications as flame retardants: the inherent agglomeration of nano-sized α -ZrP and their incompatibility with polymers [59, 63, 67, 93–114].

Planar-like α -ZrP particles have been modified with a kind of cyclophosphazene derivative (named HAC) by a three-step hybridization method [113]. The combination of (intumescent flame retardant) IFR and HAC can significantly improve the yield and graphitization of these residues, make them more stable, compact, and continuous, and allowing the inhibition of the thermo-oxygen contact of the underlying poly (vinyl alcohol) (PVA). In addition, the mechanical properties of such composites could be enhanced and toughened by specific HAC content.

Xie et al. [63] reported a macromolecular charring agent (MCA) decorated with zirconium phosphate nanosheets. This was then combined with ammonium polyphosphate (APP) to reduce the flammability of polypropylene. The limiting oxygen index (LOI) of PP/ZrP-d-MCA/APP reached 32.5% and a UL-94-V0 rating when the content of ZrP-d-MCA and APP was 5%wt and 15%wt, respectively. The flame-retardant mechanism of ZrP-d-MCA/APP was further studied. It was shown that a ZrP nanosheet could effectively catalyze the carbonization reaction of MCA to form a closed micro-nano carbon cage during the combustion process.

Fu et al. [114] reported the synthesis of a hybrid cardanol-derived zirconium phosphate (CZrP) from the renewable resource cardanol. Their results showed that the enlarged interlayer spacing of CZrP facilitated the homogeneous dispersion of the nano-additive in an epoxy resin. The suppressed fire hazards of EP were attributed to the physical barrier effect induced by the 2D-CZrP. In addition, the tensile strength and the elongation at break were enhanced simultaneously due to the reinforcing effect of the inorganic platelet and the plasticizing effect of the long alkyl chains in this unique hybrid.

3.2.2. Black Phosphorus and Dehydrated Vanadyl Phosphate. Mono or multi-layer BP is a two-dimensional nanomaterial with distinct physical/chemical properties due to dimensionality effects [21, 68]. BP can catalyze the formation of char and capture free radicals, and its unique layered structure can also serve as a physical barrier for insulation from heat and oxygen during the combustion process [115]. For example, Qiu et al. [115] reported a stable cross-linked polyphosphazene-functionalized BP (BP-PZN) synthesized in the presence of air. The BP-PZN was developed with abundant $-NH_2$ groups via a one-pot polycondensation of 4,4'-diaminodiphenyl ether and hexachlorocyclotriphosphazene on the surface of BP nanosheets. Results demonstrated that the introduction of 2 wt% BP-PZN distinctly improved the flame-retardant properties of EP. For instance, there was a 59.4% decrease in pHRR and a 63.6% reduction in THR. The diffusion of pyrolysis products from an EP during combustion

was obviously suppressed after incorporating BP-PZN nanosheets. Digital photos, SEM, and Raman spectra of char residue from such an EP are shown in Figure 4.

VOPO₄ is a new two-dimensional graphene material with a typical layered structure where VOPO₄ has been formed by connecting VO₆ octahedra with vertex-sharing with phosphate PO₄ tetrahedra. An ultrathin VOPO₄ nanosheet is expected to improve the thermal stability, flame retardancy, and mechanical properties of a polymer. In addition, VOPO₄ nanosheets can also catalyze the dehydrogenation of a polymer and promote the carbonization of a polymer [116]. For example, a VOPO₄ ultrathin nanosheet was synthesized by a simple refluxing method and then modified with typical organic surfactants (VOP) [117]. Afterwards, this nanosheet was incorporated into PS for reducing fire hazards. With a loading of 1 wt% of modified VOP, $T_{5\%}$, $T_{10\%}$, $T_{50\%}$, and T_{max} values increased 15, 22, 29, and 33°C, respectively. Furthermore, the presence of VOP nano-sheet reduced the decomposition rate of PS and increased the char residue.

3.3. Nitrogen-Containing Compounds. As a structural analogue of graphene, monolayer 2D hexagonal boron nitride (h-BN), with the alternate use of boron and nitrogen atoms instead of carbon atoms in the 2D conjugate layers, has attracted increased attention due to its high-temperature stability, excellent thermal conductivity, superior chemical inertness, and low friction coefficients [16, 118]. Considering the ionic properties of the B–N bond in the boron nitride layer, which is different from the covalent C–C bond of graphene, boron nitride nanosheets have outstanding resistance to oxidation (the degradation temperature in air is 840°C) and corrosion [119]. Most notably, boron nitride with a 2D morphology and high thermal resistance can be used as an effective nano flame retardant to improve the thermal stability, thermal conductivity, and flame retardancy of a polymer.

It is believed that H–BN can be used as a rigid barrier for the transfer of decomposed fragments due to its highly thermal stability via its layered structure, thus improving the fire safety of polymers [11–16, 42, 51, 118–133]. Zhang et al. [16] reported a multifunctional CPBN that was successfully prepared via the wrapping of a phytic acid doped polypyrrole shell, followed by the adsorption of copper ions. The significant suppression of CO and HCN release could be observed from a TG-IR test. Tensile tests showed that the addition of CPBN was beneficial to the mechanical properties of TPU.

Additionally, super paramagnetic zinc ferrite (ZF) has been used to modify the surface of boron nitride nanosheets (BNN) via a typical solvothermal method [133]. The prepared ZF-BNNS nanofiller was then loaded in an EP and placed in a weak magnetic field (0.05 T) to achieve an orderly orientation of the EP matrix. Results showed that this weak magnetic field could adjust the orderly arrangement of ZF-BNNS nanofillers in an EP matrix, and well-ordered ZF-BNNS nanofillers were superior to randomly distributed ZF-BNNS nano-fillers in enhancing EP fire resistance.

With the rapid development of electronic devices, there is an increasing demand for high heat-dissipation polymers [13, 118, 126, 129]. We found that a high thermal conductivity (TC) is also an important factor for the high flame retardancy

(a)

(b)

FIGURE 4: (a) Micrographs of external residues from a top and side view for EP and its nanocomposites. (b) SEM images and Raman spectra of external and interior char residues for (I) EP, (II) EP/BP-Bulk2.0, and (III) EP/BP-PZN2.0 nanocomposites. Adapted from [115].

FIGURE 5: (a) Schematic illustration of thermal conduction and flame retardation mechanisms of EP/ILFR-fBNNS nanocomposites. (b) Thermal conductivity of EP/h-BN, EP/BNNS, and EP/ILFR-fBNNS composites. (c) The HRR, THR, TSP, and mass loss versus time curves of neat EP, EP/ILFR, EP/BNNS 12.1% vol and EP/ILFR-fBNNS 12.1% vol samples obtained from cone calorimeter tests. Adapted from [118].

of boron nitride nanosheets. Non covalent ionic liquid flame retardant-functionalized boron nitride nanosheets (ILFR-fBNNSs) were used as a multifunctional nano-additive for

fabricating EP-based nanocomposites with both superior TC and flame retardancy [118]. These ILFR-fBNNS trigger resin crosslinking at a given temperature, while conferring

TABLE 1: Formulations and flammability test results of TPU composites [45].

Sample	TPU [g]	APP [g]	CS [g]	ACS [g]	OMMT [g]	LOI [%]	UL-94 rating
TPU	100	0	0	0	0	20.8 ± 0.3	None
TPU/APP/CS	90	5	5	0	0	26.6 ± 0.2	None
TPU/APP/ACS	90	5	0	5	0	28.6 ± 0.1	V-2
TPU/APP/ACS/OMMT	90	4.5	0	4.5	1	29.0 ± 0.1	V-0

TABLE 2: Burning parameters of two-dimensional nanomaterials/polymer composites.

Polymer matrix	Recipes	pHRR	THR	TSR	Year and reference
EP	2 wt% MoS ₂ @PPN	-30.7%	-23.6%	-43.0%	2018 [88]
PE	2 wt% WS ₂ /Ni ₂ O ₃	-34.9%	-17.0%	/	2018 [69]
EP	6 wt% MCPA-ZrP	-42.2%	-21.4%	/	2018 [114]
EP	2 wt% BP-PZN	-59.4%	-63.6%	-32.0%	2019 [115]
PS	3 wt% C-VOP	-48.3%	-43.6%	/	2017 [117]
EP	3 wt% ZF-BNNS	-48.5%	/	-6.5%	2019 [133]
PP	4 wt% Co-OMt/19 wt%IFR	-63.8%	-17.6%	/	2017 [143]
EP	7 wt% fCD-DBS-Ph-LDH	-72.3%	/	-63.7%	2016 [180]
EP	2 wt% RGO-LDH/CuMoO ₄	-47.6%	-28.5%	-38.0%	2018 [191]
PS	4 wt% g-C ₃ N ₄ /DAHPi	-42.8%	-20.8%	/	2017 [233]
EP	2 wt% ZIF-67/RGO-B	-65.1%	-41.4%	-37.6%	2019 [223]
EP	2 wt% MoS ₂ -CNTs	-26.4%	-31.3%	/	2015 [19]

improvements in the dispersion and interfacial adhesion, thereby forming a thermally conductive network with reduced interfacial phonon scattering and a high-efficiency nano-barrier network acting synergistically with ILFR-induced char residues during thermal degradation. Figure 5 shows the relationship between thermal conductivity and flame retardancy.

Liu et al. [13] demonstrated the use of exfoliated h-BN nanosheets as a high-performance, binder-free fire-resistant coating for wood. The surface of a wood substrate remained intact after exposure to fire. The anisotropic thermal conductivity and low thermal diffusivity and effusivity of h-BN make it an excellent wood protection coating.

3.4. Silicon-Containing Compounds. Among nanofillers, layered silicates are the most widely used for preparing polymer nanocomposites because they are readily available and well characterized. Montmorillonite (MMT) is a crystalline 2:1 layered clay mineral where a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets, and it has been shown to be safe in animals or humans [134, 135].

There are various methods that have been used to realize flame-retardant polymer/montmorillonite nanocomposites, including intercalation, synergy, organic modification, hybridization, layer-by-layer assembly, and self-assembly [134–152]. Inspired by nacre, Xie et al. [151] developed a super-efficient fire-safe nanocoating based on carboxymethyl chitosan and modified MMT via one-step self-assembly. The nanocoating possessed a well-arranged nacre-like hierarchical microstructure, exhibiting high transparency and specific nacre-like iridescence. Most importantly, the peak heat release rate, total

heat release, peak smoke production rate, and total smoke production of polyurethane foam were decreased by 84.1%, 89.4%, 84.4%, and 95.2%, respectively. A polyimide (PI) composite aerogel was also prepared by freeze-drying with graphene and MMT as additives [141]. Through the strong interaction between the two components, GO/MMT complexes could be synergistically dispersed in water and have good dispersion in a PI matrix, thus endowing the composite aerogel with enhanced mechanical, thermal, and flame-retardant properties. In order to improve the flame retardant performance of IFR/PP composites, OMMT intercalation cobalt compounds (Co-OMt) have been prepared and modified using acidified chitosan to further expand the interlayer spacing of MMT [143]. CO-OMT/IFR/PP nanocomposites have been prepared by a melt blending method. With addition of 4% mass Co-OMt, 4% mass Co-OMt/IFR/PP nanocomposites have surpassed a UL-94 V-0 rating, with an LOI value as high as 32.1%.

The use of MMT as a synergic additive to flame retardants for designing polymers with better flame-retardant properties has already been extensively studied [45, 153–166]. The effect of APP/zinc borate (ZB) for making highly efficient flame retardants and ceramics of ethylene-vinyl acetate/mica powder/organic modified montmorillonite (EVA/MP/OMMT) composites has been shown [166]. In a fire test, the EVA/MP/OMMT/APP/ZB system displayed obvious flame-retardant features, showing a much lower THR and TSR than pure EVA. Zhang et al., [45] reported a flame retardant (ACS) prepared by crosslinking chitosan with bis-(4-formylphenyl)-phenyl-phosphonate. Flame-retardant TPU composites were then prepared by melt blending of ACS, APP, and OMMT. For TPU

FIGURE 6: (a) SEM images of the surfaces residues of (I) neat TPU, (II) TPU/APP/CS, (III) TPU/APP/ACS, and (IV) TPU/APP/ACS/OMMT. (b) TGA curves of TPU composites in air. (c) Screenshots from UL-94 test videos of TPU and TPU/APP/ACS/OMMT samples. Adapted from [45].

samples containing 10% flame retardant, the LOI increased from 20.8 to 29.0, the UL-94 rating increased from no to V-0, and the pHRR decreased from 1090 to 284 kW/m², respectively. The test results for added OMMT and non-added samples are shown in Figure 6 and Table 1.

3.5. Layered Double Hydroxides. Layered double hydroxides (LDH) are a kind of synthetic anionic clay with host and guest nano-layered materials, which contain positively charged metal hydroxide nanosheets, intercalated anions, and water molecules [167]. LDHs can be represented by the chemical

formula $[M_{1-x}^{2+} M_x^{3+}(\text{OH})_2]^{x+} \cdot [A_{x/n}^{n-} \cdot y\text{H}_2\text{O}]^{x-}$, where M^{2+} , M^{3+} , and A^{n-} represent divalent metal cations, trivalent metal cations, and an inorganic or organic anion with negative charge n , respectively [168]. When used as flame retardant for polymer materials, it has been shown that the flame-retardant mechanism of LDHs are via the “barrier effect” of nano-layers, inert gas dilution of oxygen and the formation of ceramic-like materials [169].

LDHs can be directly used as flame retardant additives because of their unique chemical properties and layered structures [170–177]. For example, flexible polyurethane foam with

FIGURE 7: (a) The preparation process of PWA-LDH. (b) The LOI and UL-94 results of PLA composites. (c) Digital photos of (I) PLA, (II) PLA/IFR, (III) PLA/IFR/2.0LDH, and (IV) PLA/IFR/2.0PWA-LDH samples after cone calorimeter tests. Adapted from [167].

FIGURE 8: Schematic illustration of PN-rGO improving oxidation resistance of the char layer and catalytic carbonization capacity for EP chains. Adapted from [214].

FIGURE 9: (a) The preparation process of CNAPP. (b) The HRR and THR curves of PS and its composites. (c) TG and DTG curves of PS and its composites. Adapted from [232].

FIGURE 10: Digital photos of char residues of (a) PS, (b) PS/APP, (c) PS/CNAPP5, (d) PS/CNAPP10, (e) PS/CNAPP20, and (f) PS/CNAPP30 after the cone calorimetry measurement. Adapted from [232].

a density of $40 \pm 2 \text{ kg m}^{-3}$ was prepared by combining LDH and kraft lignin (a byproduct of the pulp and paper industry) with phosphorous polyol (E560) [175]. The effects of fillers on the mechanical properties and combustion properties of fibers were then studied. The presence of such low amounts of lignin by itself did not increase the flame retardancy of FPF, but the addition of E560 increased the charring efficiency, while the addition of LDH contributed to reinforcing the char layer, yielding a more cohesive protective layer that decreased the pHRR to 47% as compared with an unfilled foam OE. Wang et al. [176] investigated the synergistic effects of trace amounts of chloride on char formation and flame retardancy of linear low density polyethylene (LLDPE) filled with NiAl-LDHs. Their results showed that the char yield of 20% LDH/LLDPE (20 wt% NiAl-LDH) increased from 10.4% to 49.6% with the addition of 0.5 wt% NH_4Cl .

Moreover, the modification of LDHs via the intercalation of some flame-retardant molecules has been shown to be very effective in improving their compatibility with polymer matrices and flame retardants [44, 60, 65, 66, 167, 168, 178–185]. Zhang et al., prepared MgAl-LDH intercalated with phosphotungstic acid (PWA-LDH) by a reconstruction method and melted it with IFR and poly (lactic acid) (PLA) to prepare a flame-retardant biodegradable resin. Their studies showed that the maximum LOI value of composite materials

containing 18.0 wt% IFR and 2.0 wt% PWA-LDH was 48.3%, passed the UL-94 V-0 rating, and the pHRR of pure PLA was significantly reduced from 306.3 kW/m^2 to 40.1 kW/m^2 [167]. As shown in Figure 7, the introduction of LDH into PLA/IFR composites significantly improved the flame retardancy of the condensed phase. By designing composite multi-modifiers with varied functions, multifunctional intercalation of LDHs has been developed, including functionalized hydroxypropyl-sulfobutyl-beta-cyclodextrin (sCD), phytic acid (Ph), sodium dodecylbenzenesulfonate (SDBS), and chalcone, and these functions have been transferred to epoxy materials using nanocarriers [180]. Studies have shown that at only 7 wt% fCD-DBS-Ph-LDH, the resultant EP nanocomposites passed the UL-94 V-0 rating. Compared with a pure epoxy resin, the pHRR ($\sim 72\%$) in a cone calorimeter test decreased significantly.

Lastly, the modification of LDHs via the covering surfaces with hydrophobic flame-retardant molecules is also generally believed to be very effective in improving their compatibility with other polymer matrices for flame retardation [40, 44, 66, 179, 186–194]. DBS intercalated LDH (LDH-DBS) nanosheets have been surface-assembled by an ultrafine $\text{Ni}(\text{OH})_2$ nanocatalyst via circular coordination-induced growth, with the aim of imbuing EP with high-efficient fire retardant properties [193]. An LDH-DBS@ $\text{Ni}(\text{OH})_2$ material was designed to

exploit a spatial-dependent catalytic strategy to improve the interfacial structure between LDH nanosheets and an EP matrix during dynamic charring. The results showed that 3 wt% LDH-DBS@Ni(OH)₂ led to an EP matrix with a UL-94 V-0 rating. Xu et al. [191] synthesized a hybrid compound containing MgAl-LDH loaded graphene (RGO-LDH) by a co-precipitation method. An RGO-LDH/CuMoO₄ hybrid was then prepared by introducing CuMoO₄ onto the surface of RGO-LDH. Their results illustrated that the pHRR and THR of an EP composite with RGO-LDH/CuMoO₄ added were decreased significantly. The reason was that the Cu₂O and MoO₃ generated from RGO-LDH/CuMoO₄ in the combustion process helped to increase the yield of char residue and the compactness of the char layer.

3.6. Carbon Skeleton. Graphene is one of the most classic flame retardant C-skeleton two-dimensional nanosheets. In recent years, g-C₃N₄ and organic frameworks have also been studied in the field of flame retardant polymers.

3.6.1. Graphene. Graphene is a single-layer carbon plate with high thermal conductivity, excellent mechanical strength, and superior electronic conductivity [195–199]. It has been shown that modified graphene has excellent fire resistance even when exposed to flame [200]. In order to obtain improved flame retardant performance, functionalization of graphene or loading of synergistic flame retardants should effectively improve the flame retardant efficiency of graphene.

Various functional treatments or synergistic addition of flame retardants have been performed on graphene surfaces, including the incorporation of P, N, or Si [201–212]. Hu et al., [62] synthesized a functionalized graphene oxide (FGO) grafted to a hyper-branched flame retardant based on N-aminoethyl piperazine and a phosphonate derivative to reduce the flammability and toxic gas release of polystyrene (PS). The authors attributed the function of this to the homogeneous dispersion of FGO in a PS matrix and enhanced physical barrier effects. Yu et al. [212] successfully prepared functionalized reduced graphene oxide (FRGO) wrapped with P-N flame retardants by a one-pot method, and then covalently incorporated them into EP. The glass transition temperature of FRGO/EP nanocomposites remarkably increased by 29.6°C under 4 wt% loading. The pHRR of EP nanocomposites containing 2 wt% FRGO decreased by 43.0%. Jing et al., [213] reported UL-94 V-0 rating flame retardant PLA composites with a total content of only 3 wt% using bio-based polyphosphonate (BPPT) and polyethyleneimine-modified graphene oxide (M-GO) as flame retardants. Feng et al., [64] used a “branch-like” strategy with a graphene polymer as the backbone and a flame retardant as the branch to functionalize reduced graphene oxide (RGO) to improve the flame retardant grafting rate and compatibility of RGO in a polymer matrix, and then introduced the resulting GP-DOPO into EP/AgNW composites in situ. Phosphorus-nitrogen co-doped rGO (PN-rGO) was also prepared by a scalable hydrothermal and microwave process to improve the flame retardancy of an EP [214]. Figure 8 shows the schematic illustration of the flame retardation mechanism for EP/PN-rGO. Pethsangave et al. [215] reported that functionalized polyaniline (PANI)- and

polypyrrole (PPy)-supported graphene nanocomposites were effective flame retardants. These synthesized nanocomposites showed excellent flame-retardant properties when coated on cotton fabric and wood. Li et al. [216] synthesized a hybrid flame retardant (GO-MD-MP) containing methacryloisobutyl polyhedral oligomeric silsesquioxane (POSSMA), reactive glycidyl methacrylate (GMA), bis-9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide methacrylate (bisDOPOMA) and its derivative functionalized graphene oxide (GO) via a one-step grafting method. Their results showed that the LOI of EP increased to 31.1% after adding 4 wt% GO-MD-MP, and it easily reached a UL-94 V-0 rating.

Graphene incorporated with metal oxides have also been realized for use as flame retardants [217]. CeO₂/RGO [218] hybrids and graphene-zinc stannate (G-ZS) [219] hybrids have been synthesized by hydrothermal methods. They can effectively reduce toxic gases released from the combustion process of polymers. Yuan et al. [220] used an ingenious method to decorate Ni(OH)₂ nanosheets onto the surface of GO via the strong affinity of Ni²⁺ with NH₂ groups. Their experiments showed that the addition of functionalized graphene oxide (FGO) reduced the pHRR, THR, and TSP of polypropylene (PP) during combustion. Wang et al. [221] synthesized a series of nitrogenous resorcinol formaldehyde/graphene oxide composite aerogels by using a self-assembly copolymerization strategy. The materials featured with multiple functions, e.g., thermal insulation, ultra light, anti-corrosion, mechanical resilient, high flame-retardant capability.

Graphene has also been incorporated with other inorganic fillers [50, 222–226]. Chen et al. [226] ingeniously prepared a smart fire alarm wallpaper based on ultralong hydroxyapatite nanowires (HNs) and GO thermosensitive sensors. The thermosensitive sensor exhibited a low responsive temperature (126.9°C), fast response (2 s), long working time in flame (at least 5 min), and could be processed into various shapes, dyed with different colors, and printed with the commercial printer. It had broad application prospects in high-security interior decoration of houses. Nanosilica/graphene oxide (m-SGO) hybrids have been prepared by sol-gel and surface treatment processes on a large number of non-flammable silicas on the surface of graphene oxide [41]. These hybrids significantly improved the flame retardancy, mechanical properties, and thermal stability of an EP, endowing the EP resin with high thermal conductivity, low dielectric loss, and high dielectric constants. Zuo et al. [227] prepared polyimide (PI) composite aerogels with enhanced flame retardancy via an eco-friendly freeze-drying method, followed by a thermal imidization process with graphene and MMT as additives. Guo et al. [228] studied the mechanical and flame retardant properties of four composites, EVA with aluminum hydroxide (ATH), EVA with ATH and MoS₂, EVA with ATH and graphene nanoplatelets (GNPs), and EVA with all three components.

3.6.2. g-C₃N₄ and Organic Framework Nanosheets. Analogous to graphene, g-C₃N₄ also has stacked two-dimensional structure [229]. Because of its excellent thermal stability, chemical stability, and catalytic performance [230], it has attracted increased attention in the field of flame retardant and smoke suppression. For example, it

has been used for the improvement of the thermal stability and flame retardancy of polymers. Shi et al. [231] prepared polypropylene-grafted maleic anhydride (PP-g-MA)/g-C₃N₄ nanocomposites via a solvent mixing strategy. Their results showed that the T_{-10} and T_{-50} (temperature at 10% and 50% weight loss, respectively) of the composites increased by 14.6°C and 27.7°C, respectively. Additionally, a flame retardant CNAPP containing g-C₃N₄ wrapped ammonium polyphosphate (APP) was prepared and then incorporated into PS [232]. Experimental results show that the main reason for the improvement in flame retardancy of the resulting composites was that the POC and PCN structures formed after combustion significantly improved the stability of the char layer. When the content of g-C₃N₄ in CNAPP was 20%, the best flame retardant effect was obtained (Figures 9 and 10). g-C₃N₄/organic aluminum diethylhypophosphites (CDAHPI) hybrids have also been synthesized by salification reactions [233]. PS composites were then prepared by a melt blending method. Compared with pure PS, PS/CDAHPI showed additional advantages in terms of inhibiting pyrolysis gas release while reducing HRR and THR of the composite.

Smoke suppression in polymer combustion. The spinel copper cobaltate (CuCo₂O₄)/g-C₃N₄ (named C-CuCo₂O₄) nanohybrids were synthesized by hydrothermal method, and then incorporate with TPU by a master batch-melt compounding approach [234]. The number of pyrolysis gas products (including combustible volatiles and CO) decreased significantly, while the number of noncombustible gases (CO₂) increased. The g-C₃N₄/organic aluminum hypophosphites hybrid CPDCAHPI and CBODAHPI [235] were synthesized by esterification and salification reactions, and introduced into PS. The release of flammable aromatic compounds was reduced by introducing these hybrids, which was attributed to the synergy of gas phase action and physical barrier effect in condensed phase. The g-C₃N₄/carbon sphere/Cu (CSACS-C) nanohybrid [236] were prepared by metal ions-induced gel reaction as green template, and the amount of pyrolysis gaseous products; generation and pHRR of TPU/CSACS-C composites were significantly reduced.

Recently, organic frameworks, including covalent organic frameworks and metal organic frameworks, have also begun to be used as flame retardants in polymers [237–239]. Hou et al. [237] synthesized iron-based and cobalt-based metal-organic frameworks (MOFs) by solvothermal method and prepared PS/MOF composites. Compared with pure PS, the pHRR of PS/Fe-MOF and PS/Co-MOF decreased by 14% and 28%, respectively, indicating that MOF has flame retardant effect in polymer. Subsequently, DOPO was used to modify Co-MOF and introduced to PLA to improve the fire safety and mechanical properties of the composites [238]. Mu et al. [239] prepared the original phosphorus-containing flame retardant wrapped covalent organic frameworks (FCOFs) nanosheets and introduced it to EP by in-situ polymerization, which had a positive impact on the flame retardancy, toxic volatiles and the quality of char residue of the composites. Recently, the flame retardant properties of various two-dimensional materials/polymers have been extensively studied. The results are listed in Table 2.

4. Conclusion

Clarifying the special properties of various two-dimensional nanomaterials is pivotal for being able to fully exploit their flame-retardant properties. With increased awareness of the structure and properties of two-dimensional nanomaterials, researchers will be able to realize the potential of two-dimensional nanomaterials for fulfilling required flame-retardant effects under low load conditions. Based on the specific properties of different two-dimensional nanomaterials, they can be reasonably used as additives or reactive components in the design of polymer flame-retardant materials. With additional research, two-dimensional nanomaterials/polymers will be more suitable for specific applications. Although two-dimensional nanomaterials are widely used to prepare fireproofing materials in the laboratory because of their high efficiency and environmental friendliness, many challenges still remain. First is the challenge of the large-scale application of two-dimensional nanomaterials. New two-dimensional nanomaterials, including g-C₃N₄ and black phosphorus, have not been prepared at industrial as of yet. Moreover, the uniform dispersion of many two-dimensional nanomaterials in a polymer matrix depends on their efficient exfoliation and surface modification. The application of hydrophobic technology of two-dimensional nanomaterials in industry is promising. Second is finding suitable flame retardant applications for two-dimensional nanomaterials. In specific applications, polymer materials not only need to meet flame retardant requirements, but also need to face meet requirements for heat dissipation, dielectric properties, etc. In some special cases, appropriate multifunctional nanosheets can be designed to meet specific design challenges according to the molecular components and structure of the two-dimensional nanomaterial. For example, in highly integrated small electronic devices, h-BN nanosheets are a reasonable choice.

The authors are confident that the above-mentioned challenges will be gradually overcome through the continuous development and innovation of two-dimensional nanomaterials due to their intrinsic advantages over other materials. The thorough survey of the current literature presented here offers useful information for realizing the potential of two-dimensional nanomaterials/polymer and should help in guiding the design of novel high-performance flame-retardant composites.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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