Novel MoS$_2$–DOPO Hybrid for Effective Enhancements on Flame Retardancy and Smoke Suppression of Flexible Polyurethane Foams

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ABSTRACT: A novel MoS$_2$–DOPO hybrid has been successfully synthesized through the grafting of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) on the surface of MoS$_2$ nanosheets using allyl mercaptan as an intermediate. MoS$_2$–DOPO was used as a flame retardant additive to prepare flame-retardant flexible polyurethane foam (FPUF). The influence of MoS$_2$–DOPO on the mechanical, thermal stability, and flame retardancy properties of FPUF composites were systematically investigated. The incorporation of MoS$_2$–DOPO could not deteriorate greatly the tensile strength and 50% compression set of FPUF composites, but effectively improves the char residue. The cone calorimeter and smoke density tests results revealed that the peak heat release rate, total heat release, and the maximum smoke density of the MoS$_2$–DOPO/FPUF composite were reduced by 41.3, 27.7, and 40.5%, respectively, compared with those of pure FPUF. Furthermore, the char residue after cone calorimeter tests and pyrolysis gaseous products of the MoS$_2$–DOPO/FPUF composite were analyzed by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and thermogravimetric analysis/infrared spectrometry. The results suggested that the MoS$_2$–DOPO hybrid played a synergistic flame retardant effect of gas and condensed bi-phase action. In addition, a possible flame retardancy and smoke suppression mechanism of the MoS$_2$–DOPO/FPUF composite were proposed. This study provides a facile and promising strategy for the fabrication of polymer materials with excellent flame retardancy and smoke suppression properties.

INTRODUCTION

Polyurethane is a type of polymeric material containing many repetitive urethane groups in its chain structure, which is generally produced by the reaction of isocyanates and polyols. Flexible polyurethane foam (FPUF) is one of the main varieties of polyurethane materials, and widely used in vehicles, furniture, and cushions because of its vibration insulation, high resilience, low density, and good mechanical properties. Unfortunately, FPUF is highly flammable because of its large specific surface area and open-cell structure. Meanwhile, a large amount of heat, smoke, and toxic gas products is generated during the thermal degradation and combustion process, which greatly affects the escape and rescue of trapped humans. Consequently, in recent years, various methods for enhancing the flame retardancy of FPUF have been explored to meet its practical demands. Among them, the incorporation of flame retardants has been considered to be an effective strategy to enhance its fire safety properties.

Generally, halogenated, metal hydroxides and phosphorous flame retardants are usually used to achieve good flame retardancy. Halogenated flame retardants exhibit superior flame retardancy for FPUF. However, a massive amount of corrosive and toxic volatile compounds are released from halogenated flame retardants, which could do great harm to the ecological environment and human health. Thus, many researchers have been devoted to develop environment-friendly halogen-free flame retardants to reduce environmental problems and potential negative health effects, especially phosphorus-containing and metal hydroxide flame retardants. Previous studies have revealed that metal hydroxides, such as aluminium hydroxide and magnesium hydroxide, have obvious advantages in thermal stability, nontoxic, and smoke suppression properties. However, the high addition of metal hydroxides is needed to achieve satisfactory flame retardant efficiency, which usually damages the mechanical performance of the polymers. Recently, layer-by-layer assembly and sol–gel techniques have attracted increasing attention in the flame-retardant treatment of FPUs because of their high efficiency and environmentally friendly nature, but they usually exhibit poor durability under the influence of the physical damages, washing, and chemical etching.
MoS$_2$ is one of layered transition-metal dichalcogenides and composed of a three-layer sandwich structure (S–Mo–S) formed by van der Waals forces. The bulk MoS$_2$ can be peeled off into nanosheets by destroying the weak van der Waals interactions. MoS$_2$ nanosheets are expected as a promising filler to improve the flame retardancy of polymer matrices because of its excellent barrier effect, lower thermal conductivity, and smoke suppression properties. In recent years, MoS$_2$ nanosheets has been studied to enhance flame retardant properties of many polymers, such as polyurethane, polyethylene, and polypropylene. However, the exfoliated MoS$_2$ nanosheets cannot disperse well in polymer matrices because of its high specific surface area and van der Waals interactions, which could seriously affect its flame-retardant efficiency. Previous reports have shown that the dispersibility and flame-retardant efficiency of MoS$_2$ nanosheets can be obviously improved by surface modification with metal oxide, layered double hydroxide, POSS, and graphene. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) plays an obvious flame-retardant role in the gas phase and condensed phase simultaneously. Some studies have showed that the flame retardancy of polymer matrices has been greatly improved using DOPO grafted onto SiO$_2$ nanoparticles, graphene oxide, and POSS. As reported by the many previous literatures, some novel hybrid flame retardants show satisfactory flame-retardant efficiency. Qian et al. prepared flame-retardant polypropylene composites with a novel organic–inorganic hybrid char-forming agent (SCTCFA-ZnO), and the hybrid compounds showed high-efficiency flame retardancy and smoke suppression performance. Therefore, it is promising to obtain flame-retardant synergistic effect of MoS$_2$ nanosheets and DOPO by grafting MoS$_2$ nanosheets with DOPO.

In this work, we develop a novel strategy to design the DOPO-functionalized MoS$_2$ nanosheets. Generally, it is difficult to realize the one-step grafting of DOPO onto MoS$_2$ nanosheets because of the lack of functional groups on the surface of MoS$_2$ nanosheets. To obtain MoS$_2$ nanosheets with more defects, MoS$_2$ powders is exfoliated by the ultrasonication-assisted method in a N-methyl-2-pyrrolidinone (NMP)/H$_2$O$_2$ mixed solvent. Allyl mercaptan (AM) is innovatively selected for the preliminary modification of MoS$_2$ nanosheets, and stably attached on the surface of MoS$_2$ through covalent interaction. Then, the addition reaction between −C=O groups of AM and P–H bonds of DOPO molecules happens using a solvothermal method, and the DOPO group-functionalized MoS$_2$ nanosheets (MoS$_2$–DOPO) hybrid is obtained. The synthesis route of the MoS$_2$–DOPO hybrid is illustrated in the Scheme 1. Subsequently, the MoS$_2$–DOPO hybrid is introduced into the FPUF matrix to reduce its fire hazards, and the formations of pure and flame-retardant FPUF composites are listed in Table 1. The introduced DOPO organic molecules could improve the dispersibility of MoS$_2$ nanosheets in the FPUF matrix. The microstructure, thermal stability, and flame-retardant properties of FPUFs are investigated by a scanning electron microscope.
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**RESULTS AND DISCUSSION**

Characterization of the MoS\(_2\)–DOPO Hybrid.** Atomic force microscopy (AFM) is used to estimate the thickness of MoS\(_2\) nanosheets and the data are displayed in Figure 1. As shown in Figure 1a, the two-dimensional MoS\(_2\) nanosheets have the lateral size of several hundred nanometers. Figure 1b presents the corresponding height profile of the AFM image, and the thickness of the MoS\(_2\) nanosheets is about 4.43 nm. Previous reports have shown that the thickness of an exfoliated MoS\(_2\) monolayer is about 1.0 nm,\(^{34,35}\) so the prepared MoS\(_2\) nanosheets comprises only 3–5 layers of the MoS\(_2\) monolayer, suggesting the successful exfoliation of bulk MoS\(_2\) into few-layer nanosheets.

Fourier transform infrared (FTIR) spectra of the MoS\(_2\) nanosheets, MoS\(_2\)–AM, DOPO, and MoS\(_2\)–DOPO are displayed in Figure 2. In the FTIR spectrum of MoS\(_2\) nanosheets, the absorption peaks at 1623 cm\(^{-1}\) belong to the characteristic O–H bending vibration band of the adsorbed water on the MoS\(_2\) nanosheets.\(^{36}\) In addition, the peak at about 469 cm\(^{-1}\) is assigned to Mo–S stretching vibration.\(^{37}\) In comparison with the FTIR spectrum of MoS\(_2\) nanosheets, new absorption peaks at 728 and 671 cm\(^{-1}\) can be emerged in the spectrum of MoS\(_2\)–AM, which are derived from the C–S bond,\(^{38}\) and the band at 1642 cm\(^{-1}\) is derived from CH\(_2\) stretching vibration.\(^{39}\) This indicates that AM is grafted onto the surface of MoS\(_2\) nanosheets. These peaks at 1449, 1226, and 754 cm\(^{-1}\) are assigned to the P–Ph, P=O, and P–O–Ph stretching vibration, respectively.\(^{40}\) Moreover, the disappearance of P–H stretching vibration (2362 cm\(^{-1}\)) and CH=CH\(_2\) stretching vibration (1642 cm\(^{-1}\)) suggests the occurrence of the addition reaction between MoS\(_2\)–AM and DOPO. The FTIR results confirm the successful grafting of DOPO onto MoS\(_2\) nanosheets through the addition reaction of the P–H group with the CH=CH\(_2\) group using AM as an intermediate.

Transmission electron microscopy (TEM) measurements were used for investigating the morphologies of the MoS\(_2\) nanosheets and MoS\(_2\)–DOPO and the corresponding results are exhibited in Figure 3. Figure 3 shows the TEM images of MoS\(_2\) nanosheets and MoS\(_2\)–DOPO, and the energy-dispersive X-ray spectroscopy (EDX) spectrum of MoS\(_2\)–DOPO, respectively. It can be clearly seen from Figure 3a that MoS\(_2\) nanosheets exhibit a typical sheet-like morphology and uniform and smooth surfaces. As shown in Figure 3b, a lattice distance of 0.27 nm is consistent with the space of the (100) lattice plane hexagonal MoS\(_2\).\(^{41}\) Composed with MoS\(_2\) nanosheets, MoS\(_2\)–DOPO has a much rougher surface (Figure 3c), and some pellet-like DOPO nanoparticles with diameters of approximately 15–20 nm are distributed randomly on the surfaces of MoS\(_2\) nanosheets, indicating that DOPO molecules are successfully covalently attached on the surface of MoS\(_2\) nanosheets. According to a previous literature, the MoS\(_2\) nanosheets modified with organic components show better dispersibility and compatibility in the polymer matrix, which contributes to the improvement of flame-retardant efficiency.\(^{42,43}\) Therefore, with the aid of DOPO molecules, the dispersibility and compatibility of MoS\(_2\)–DOPO in the FPUF matrix may be improved. In addition, the elemental compositions of MoS\(_2\)–DOPO were also examined by EDX spectroscopy and the results are shown Figure 3d. The elements Mo, S, C, O, and P are detected in the EDX spectrum. This result also implies that DOPO molecules are successfully grafted onto the surfaces of MoS\(_2\) nanosheets.

Morphology Analysis. Generally, the morphologies of FPUs are mainly their cellular structure. The cellular structures of pure FPUF and flame-retardant FPUs were investigated by scanning electron microscopy (SEM) analysis and the SEM micrographs are shown in Figure 4. It can be seen from Figure 4a,b that pure FPUF displays a smooth surface and porous network with the cellular size of about several hundred micrometers. However, the cellular size of MoS\(_2\)/FPUF is obviously increased compared with that of pure FPUF (Figure 4c). Moreover, many agglomerated MoS\(_2\) nanosheets can be also observed on the surface of FPUF from Figure 4d. From Figure 4e,f, the cellular structures of DOPO/FPUF tend to collapse, which is due to the fact that...
DOPO would damage the cellular structure by affecting the bubble nucleation and bubble growth in the foaming process.\textsuperscript{44} In contrast, it can be observed from Figure 4g that MoS$_2$−DOPO/FPUF exhibited similar cellular structures and cell size to pure FPUF, and hardly had any cracks, suggesting that the good incompatibility between the MoS$_2$−DOPO particles and the FPUF matrix. In addition, it can be seen from Figure 4h that the MoS$_2$−DOPO nanoparticles are uniformly distributed in the FPUF matrix, suggesting a better dispersion in the FPUF matrix and stronger interfacial interaction with the matrix than MoS$_2$ nanosheets. This result is consistent with the aforementioned TEM analysis.

**Physical and Mechanical Properties.** As shown in Table 2, the densities of pure and flame-retardant FPUFs are in the range of 26−28 kg/m$^3$, which are in the density range of FPUFs.\textsuperscript{45} The densities of FPUFs increase slightly with the addition of MoS$_2$, DOPO, and MoS$_2$−DOPO. The mechanical properties of FPUF are mainly determined by their composition and cellular structures.\textsuperscript{46} Table 2 also shows their tensile strength, elongation at break, and 50% compression set. When MoS$_2$ nanosheets (6 wt %) are added, the tensile strength and the elongation at the break of MoS$_2$/FPUF decrease compared with those of the pure FPUF, and it can be ascribed to that MoS$_2$ nanosheets leads to deterioration of the cellular structures and further results in the decrease of tensile strength and elongation at the break. In particular, the tensile strength of DOPO/FPUF is slightly higher than that of pure and other flame-retardant FPUFs, which should be attributed to the nucleophilic addition reaction between DOPO and toluene diisocynate (TDI). The incorporation of DOPO slightly deteriorates the elongation at the break and 50% compression set of FPUF. Unsurprisingly, compared with MoS$_2$/FPUF and DOPO/FPUF, MoS$_2$−DOPO/FPUF has relatively moderate mechanical properties. The tensile strength and elongation at the break were 78 kPa and 124%, respectively. The deterioration of the 50% compression set may be ascribed to that MoS$_2$−DOPO increased the stiffness of FPUF. These results show that the incorporation of MoS$_2$−DOPO could not greatly reduce the mechanical properties of FPUF.

**Figure 3.** (a) TEM and (b) high-resolution TEM images of MoS$_2$ nanosheets, (c) TEM image, and (d) EDX spectrum of MoS$_2$−DOPO.

**Figure 4.** SEM micrographs of the fracture surface of (a,b) pure FPUF, (c,d) MoS$_2$/FPUF, (e,f) DOPO/FPUF, and (g,h) MoS$_2$−DOPO/FPUF.

**Table 2.** Densities and Mechanical Properties of Pure and Flame-Retardant FPUFs

| sample            | density (kg/m$^3$) | tensile strength (kPa) | elongation at break (%) | 50% compression set (%) |
|-------------------|--------------------|------------------------|-------------------------|-------------------------|
| pure FPUF         | 26.8               | 83                     | 147                     | 2.6                     |
| MoS$_2$/FPUF      | 27.3               | 62                     | 86                      | 4.5                     |
| DOPO/FPUF         | 27.7               | 85                     | 135                     | 3.3                     |
| MoS$_2$−DOPO/FPUF | 27.8               | 78                     | 124                     | 4.1                     |
Thermal Stability Properties. TG analysis was employed to assess the thermal stability and char-forming ability of pure and flame-retardant FPUFs. TG and differential thermogravimetry (DTG) curves of pure and flame-retardant FPUFs under a N₂ atmosphere are shown in Figure 5, and the correlative data are summarized in Table 3. It is observed in Figure 5a,b that all the FPUFs present similar two decomposition stages, and there are two DTG peaks between 220 and 470 °C. In the first stage, many volatile gases are released because of the breaking of the bonds between TDI-derived moieties. The second stage is ascribed to the degradation of the soft segments. For pure FPUF, the initial degradation temperature (T₅%) was at 255 °C, while the first maximum weight loss temperature (Tₘ₅₁) and the second maximum weight loss temperature (Tₘ₅₂) are at 284 and 381 °C, respectively. In comparison with pure FPUF, the T₅%, Tₘ₅₁, and Tₘ₅₂ of the flame-retardant FPUFs decrease slightly, especially for the MoS₂−DOPO/FPUF composite. Moreover, the char residue at 700 °C was only 0.3 wt % for pure FPUF. The incorporation of MoS₂ or DOPO could improve the charring ability of the flame-retardant FPUFs at high temperature, and the corresponding residues at 700 °C for MoS₂/FPUF and DOPO/FPUF were 5.9 and 9.3%, respectively. This phenomenon may be attributed to MoS₂ and DOPO which act as catalysts to promote char formation during degradation. On the contrary, MoS₂−DOPO/FPUF has a higher char residue value, up to 12.0%, indicating a synergistic effect between MoS₂ nanosheets and DOPO. These char residues can act as a thermal isolated physical barrier to prevent the transfer of heat, oxygen, and flammable gases, which enhances the flame retardancy and smoke suppression of FPUF. These results demonstrate that MoS₂−DOPO can significantly improve the thermal stability and char residue of FPUF.

Table 3. TG Data for Pure FPUF, MoS₂/FPUF, DOPO/FPUF, and MoS₂−DOPO/FPUF

| sample       | T₅% (°C) | Tₘ₅₁ (°C) | Tₘ₅₂ (°C) | char residue at 700 °C (%) |
|--------------|----------|-----------|-----------|---------------------------|
| pure FPUF   | 255      | 284       | 381       | 0.3                       |
| MoS₂/FPUF   | 249      | 276       | 372       | 5.9                       |
| DOPO/FPUF   | 250      | 279       | 378       | 9.3                       |
| MoS₂−DOPO/FPUF | 254     | 281       | 380       | 12.0                      |

Flame Retardancy Analysis. Cone calorimetry measurements were conducted to investigate the flammability of pure and flame-retardant FPUFs. A heat flux of 35 kW/m² is usual for testing FPUFs because the foams with the open-cell structure cannot withstand a high heat flux. The cone calorimeter gives quantitative analysis to their flammability by investigating several important parameters, such as time to ignition (TTI), heat release rate (HRR), total heat release (THR), average effective heat of combustion (Av-EHC), smoke production rate (SPR), and CO production rate.
Figure 6 gives the HRR, THR, SPR, and CO production rate curves of pure FPUF, MoS2/FPUF, DOPO/FPUF, and MoS2−DOPO/FPUF samples. The corresponding cone calorimetry data are illustrated in Table 4.

From Figure 6a, it has been demonstrated that pure FPUF displays a rapid heat release, and a high peak HRR (pHRR) value of 356 kW/m² is achieved at 35 s. The addition of the flame retardant decreases significantly the pHRR value and increase the time to pHRR of the FPUF samples. Specifically, the pHRR of the MoS2−DOPO/FPUF composite is reduced to 209 kW/m² (41.3% reduction), and the time to pHRR is prolonged by 20 s. As shown in Figure 6b, all the FPUFs display very low TTI (≤7 s) because of their open cellular structure. The pure FPUF releases heat very quickly after ignition and the THR value reaches 21.3 MJ/m² at the end of the combustion process. The THR value of MoS2/FPUF and DOPO/FPUF composites drop to 19.2 and 16.1 MJ/m², respectively, much lower than that of pure FPUF. It is worth noting that the THR value of the MoS2−DOPO/FPUF composite is remarkably reduced to 15.4 MJ/m², with a decrease of 27.7% compared with that of pure FPUF, which indicates that the flame spread slows down and the fire heat hazards reduce. The obtained THR reduction is higher than those previously reported values of 17.7% for FPUF containing 10 php additive flame-retardant55 and 17.4% for FPUF containing 6.3 wt % inherent flame-retardant.56 As depicted in Table 4, the addition of DOPO and MoS2−DOPO brings about an obvious reduction in the Av-EHC values of FPUF composites, suggesting the lower heat released from the volatile thermal decomposition products. The lower Av-EHC values meant that the gaseous-phase flame retardant effects of DOPO and MoS2−DOPO in DOPO/FPUF and MoS2−DOPO/FPUF composites.57

**Smoke Suppression Property.** SPR and total smoke production (TSP) are considered to be important parameters to evaluate smoke hazards. The lower peak of SPR (pSPR) and TSP suggests lower smoke hazards and longer escape times for humans in a fire.57 As seen in Figure 6c and Table 4, the incorporation of MoS2 and MoS2−DOPO would obviously reduce the pSPR and TSP values of FPUFs. However, the addition of DOPO leads to an increase in the pSPR and TSP values, probably due to less complete combustion of the DOPO/FPUF composite. Compared with pure FPUF, the pSPR and TSP values of the MoS2/FPUF composite are decreased by 36.7 and 19.2%, respectively. In addition, the MoS2−DOPO/FPUF composite has great reductions of pSPR (33.7%) and TSP (25.5%), which exhibits superior smoke suppression efficiency of MoS2−DOPO. Furthermore, the time for pSPR for MoS2−DOPO/FPUF (55 s) displays a great delay as compared to that for pure FPUF (35 s) and MoS2/FPUF (40 s). The smoke suppression properties are probably ascribed to the physical barrier effect of a compact char layer for reducing the volatilized pyrolysis products release during the combustion.

Besides the heat and smoke hazards, the toxicity of the generated gases in a fire is an important factor affecting the survival and escape of humans. Figure 6d shows the CO production rate compared with the pure FPUF and MoS2−FPUF. The total CO production values of MoS2/FPUF and MoS2−DOPO/FPUF are as low as 0.58 and 0.47 g, respectively, decreased by 21.6 and 36.5% of those of pure FPUF. Hence, the reduction in total CO production is tremendously helpful for reducing the risk of asphyxiation during the evacuation and rescue process.

The smoke density test is another effective method to investigate the smoke suppression properties of polymer materials.59 The maximum smoke density is an important parameter to estimate the smoke suppression ability of flame retardants. Generally, the lower the maximum smoke density is, the better for evacuation and fire extinguishing in a fire.60 Figure 7 gives the smoke density curves of pure and flame-retardant FPUFs. Pure FPUF can easily produce a lot of black and toxic smoke during combustion. The smoke density quickly increases in the first 150 s, tends to be stable after 200 s, and its maximum value reaches to 390. However, the smoke density of DOPO/FPUF shows an initially faster increase trend than that of pure FPUF, attains the maximum value (394) at 350 s, and then there is a slow decrease. DOPO plays a role of the flame retardant in the gas phase by capturing free radicals at the early stage of combustion, resulting in an increase of smoke density. Because it also could promote the char formation in the condensed phase, the char residue layer may reduce the smoke production at a later stage of combustion. For the MoS2/FPUF composite, it can be observed that the smoke density is lower than that of pure FPUF, and gets a maximum smoke density of 264 at 250 s, indicating that MoS2 nanosheets have an obvious smoke suppression effect. Compared with the MoS2−DOPO/FPUF composite, the maximum smoke density of the MoS2−DOPO/FPUF composite is further decreased to 232 at 300 s, which is significantly reduced by 40.5% as compared with that of pure

### Table 4. LOI and Cone Calorimeter Tests Data for Pure and Flame-Retardant FPUFs

| Sample       | LOI (%) | TTI (s) | pHRR (kW/m²) | THR (MJ/m²) | Av-EHC (MJ/kg) | pSPR (m²/s) | TSP (m²) | Total CO (g) | Char Yield (%) |
|--------------|---------|---------|--------------|-------------|---------------|--------------|----------|--------------|----------------|
| Pure FPUF    | 17.3    | 5       | 356          | 21.3        | 32.8          | 0.098        | 5.93     | 0.74         | 3.2            |
| MoS2/FPUF    | 21.6    | 5       | 248          | 19.2        | 31.2          | 0.062        | 4.79     | 0.58         | 9.3            |
| DOPO/FPUF    | 23.2    | 5       | 279          | 16.1        | 26.4          | 0.121        | 6.28     | 0.59         | 11.5           |
| MoS2−DOPO/FPUF | 23.9  | 7       | 209          | 15.4        | 26.7          | 0.065        | 4.42     | 0.47         | 15.6           |

Figure 7. Smoke density curves of pure and flame-retardant FPUFs.
FPUF. The smoke density results further confirm that there may exist a synergistic effect of smoke suppression between MoS$_2$ nanosheets and DOPO in the MoS$_2$–DOPO/FPUF composite.

Char Residue Analysis after Cone Calorimeter Tests.
In order to study the effects of flame-retardant additives on the char formation of flame-retardant FPUFs, the morphologies of the char residues after cone calorimetric tests were investigated by SEM analysis. Figure 8 presents the photographs and SEM images of the char residue for the pure and flame-retardant FPUFs after cone calorimeter tests. As shown in Figure 8a,b, there is almost no residual char left in the pure FPUF, and a very small amount of the residual char exhibits an obvious broken structure with abundant cracks and holes, which cannot effectively prevent the inner matrix from further combustion.$^{61}$ These cracks and holes result from the emission of the volatile gas during thermal decomposition and combustion.$^{62}$ As for MoS$_2$/FPUF (Figure 8c,d), the charred layers has a uniform and compact surface, but a few small holes and flaws are also observed on its surface, suggesting the fragile structure of the char residue caused by inhomogeneous dispersion of MoS$_2$ nanosheets. As a comparison, a more compact and intact char layer is formed for DOPO/FPUF (Figure 8e,f). In addition, from Figure 8g,h, it is seen that the charred layer becomes more continuous and integrated by the incorporation of MoS$_2$–DOPO into FPUF, indicating a good synergistic effect of MoS$_2$ nanosheets and DOPO during the char formation process. This continuous and compact char layer can effectively prevent the emission of combustible volatiles and heat feedback from the flame, resulting in the inhibition on its combustion.$^{63}$

EDX analysis was carried out to investigate the elemental composition of char residues, and the EDX spectra of the residual char for pure FPUF and MoS$_2$–DOPO/FPUF after cone tests are presented in Figure 9. In the Figure 9a, the main compositions of the residual char are C and O elements for the pure FPUF, and Mo (2.31 at. %) and S (0.73 at. %) signals in the char residues of the MoS$_2$–DOPO/FPUF composite (Figure 9b), indicating that some MoS$_2$ nanosheets are oxidized to MoO$_3$ during combustion.$^{64}$ MoS$_2$ nanosheets are very helpful to the improvement of smoke suppression and catalytic oxidation of CO,$^{65}$ leading to the reduction in the release of harmful smoke and CO. The existence of MoO$_3$ in the char residues could
further enhance the thermal oxidation resistance of the char residue effectively. Moreover, 1.13 at. % of the P element is also detected in the char layers because of the formation of phosphorus-containing compounds. The char residues of pure FPUF and MoS$_2$−DOPO/FPUF composites after cone calorimeter tests were surveyed by X-ray diffraction (XRD) analysis. As presented in Figure 10a, the XRD pattern of pure FPUF displays a broad band centered at approximately 23°, which is ascribed to the (002) diffraction peak of graphite. For the XRD pattern of the MoS$_2$−DOPO/FPUF composite (Figure 10b), a broad and weak band at around 23° reveals the formation of graphitized carbon. Besides, the sharp peaks at 12.6, 32.8, 33.8, 39.1, 46.3, 49.3, and 52.7° are attributed to the (020), (101), (111), (060), (210), (002), and (211) diffraction peaks of MoO$_3$, which is probably due to the oxidation of MoS$_2$ nanosheets with the presence of oxygen and oxygen-containing pyrolysis products. This is consistent with the many crystal particles observed on the char residue of the MoS$_2$−DOPO/FPUF composite. Hence, MoS$_2$ nanosheets not only serve as an effective barrier to inhibit oxygen and heat transfer between the gas phase and condensed phase, and the release of combustible gases from the underlying materials during thermal decomposition and combustion, but also can be oxidized to MoO$_3$ that can effectively suppress the generation of smoke particles.

**Gaseous Products Analysis by TG Analysis/IR Spectrometry Measurements.** TG analysis/IR spectrometry technique was usually used to study the volatilized pyrolysis products in the gaseous phase during the thermal decomposition process of flame-retardant FPUFs, which provides a new method for further study of the flame retardant mechanism. Figure 11 shows the FTIR spectra of the pyrolysis products evolved from pure FPUF and MoS$_2$−DOPO/FPUF at $T_{5\%}$, $T_{max1}$, and $T_{max2}$ during TG-IR measurements. As shown in Figure 11a, at $T_{5\%}$ and $T_{max1}$, the band at 2314 and 2351 cm$^{-1}$ are attributed to the vibration absorption −NCO groups and CO$_2$, respectively. This is probably due to the degradation of urethane groups (−NHCOO−) in the polyurethane chains during the heating process. However, it can be seen from Figure 11b that MoS$_2$−DOPO/FPUF also releases many compounds containing P=O groups (1238 cm$^{-1}$) at the $T_{5\%}$ (254 °C) and $T_{max1}$ (281 °C), indicating the cleavage of P−C bonds and the formation of PO$^*$ radicals. The PO$^*$ radicals can act as free-radical scavengers to capture the H$^*$ and OH$^*$ radicals in the gaseous phase during the combustion process. When the temperature increased to $T_{max2}$, pure FPUF and MoS$_2$−DOPO/FPUF show the same absorption peaks at around 3600, 2900, 2350, 1730, 1610, 1460, and 1100 cm$^{-1}$, corresponding to the characteristic absorption of water, C−H groups in saturated hydrocarbons, carbon dioxide, carbonyl, aromatic compounds, amide, and C−O groups, respectively.

![Figure 11](https://dx.doi.org/10.1021/acsomega.9b03346)

**Figure 11.** FTIR spectra of the volatilized pyrolysis products emitted from (a) pure FPUF and (b) MoS$_2$−DOPO/FPUF at $T_{5\%}$, $T_{max1}$, and $T_{max2}$ during TG-IR measurements.

![Figure 12](https://dx.doi.org/10.1021/acsomega.9b03346)

**Figure 12.** Absorbance intensity of pyrolysis products for pure FPUF and MoS$_2$−DOPO/FPUF vs temperature: (a) total, (b) hydrocarbons, (c) aromatic compounds, and (d) amide.

![Figure 13](https://dx.doi.org/10.1021/acsomega.9b03346)

**Figure 13.** Absorbance intensity of pyrolysis products for pure FPUF and MoS$_2$−DOPO/FPUF vs temperature: (a) total, (b) hydrocarbons, (c) aromatic compounds, and (d) amide.
This suggests that the urethane groups are further decomposed into macromolecular scission products.

Furthermore, the TG-IR technique was also carried out to investigate the smoke suppression effect of the MoS2−DOPO hybrid on reducing volatilized pyrolysis products. Figure 12a–d displays the absorbance intensity of volatilized pyrolysis products for pure FPUF and MoS2−DOPO/FPUF versus temperature, including total, hydrocarbons (2980 cm⁻¹), aromatic compounds (1610 cm⁻¹), and amide (1460 cm⁻¹). As can be seen, the absorbance intensities of pyrolysis products evolved from MoS2−DOPO/FPUF are significantly lower than that for pure FPUF, especially aromatic compounds and amide compounds. Because the pyrolysis molecules would further condense and aggregate to form smoke particles, the reduction of these pyrolysis products could lead to the suppression of smoke. This is consistent with the results of the reduction of smoke production in the cone calorimetric tests.

Probable Flame Retardancy and Smoke Suppression Mechanism. Based on the above analysis, a possible flame retardant mechanism of MoS2−DOPO in the FPUF composite is proposed, and displayed in Figure 13. During the thermal decomposition and combustion process, FPUF liberates a variety of volatilized pyrolysis products, such as hydrocarbons, aromatic compounds, amide, and so on. These pyrolysis products can react with the surrounding oxygen and releases a large amount of heat. Meanwhile, hydrocarbons and aromatic compounds tend to aggregate into small smoke particles, which increase the risk of fire and human casualties.

Three possible reasons may be responsible for the effective enhancements on flame retardancy and smoke suppression of the MoS2−DOPO/FPUF composite. First, with the encapsulation of DOPO organic molecules, MoS2−DOPO could be well dispersed in the FPUF matrix by strong interface interaction. The well-dispersed state favorably exerts the synergistic flame retardant effect between MoS2 nanosheets and DOPO. Second, the two-dimensional MoS2 nanosheets can adsorb and capture hydrocarbons and aromatic compounds via weak van der Waals interaction, resulting in the effective physiosorptions and chemisorptions. Moreover, the excellent physical barrier effect of MoS2 nanosheets retards the release of combustible pyrolysis products and the permeation of heat and oxygen. This absorption and barrier dual-effect is very helpful for the aggregation of smoke particles to form char residues on the surfaces of MoS2 nanosheets. MoS2 is oxidized into MoO3 by the reactive oxygen species decomposed from the oxygen-containing pyrolysis products. MoO3 nanoparticles improves the thermal oxidation resistance of the char residues. Third, DOPO can play a crucial flame retardant role in the gas phase and condensed phase simultaneously. PO radicals released from DOPO are able to scavenge the highly active H⁺ and OH⁻ radicals in the flame zone and intercept the radical chain reactions in the flame zone, resulting in an incomplete combustion and a decrease of the heat production. The catalytic char-forming function is another important role of DOPO. Part of the DOPO molecules is decomposed to oxygen-containing phosphorus acids, which promotes dehydration and charring of the hydroxyl-containing compounds to form the phosphocarbonaceous structure. Therefore, MoS2 nanosheets plays an important flame retardancy role in the condensed phase, while DOPO plays an important free radical quenching effect in the gas phase and the char-forming enhancement in the condensed phase. As a result, MoS2−DOPO can significantly improve the flame retardancy and smoke suppression properties of FPUF composite through a synergistic effect of gas and condensed bi-phase action from MoS2 and DOPO.

CONCLUSIONS

In this work, a novel MoS2−DOPO hybrid was successfully synthesized using a facile two-step reaction approach. The structure of the MoS2−DOPO hybrid was analyzed by the FTIR, TEM, and EDX measurements. Subsequently, the synthesized MoS2−DOPO hybrid was used as an additive flame retardant to reduce the fire hazards of FPUFs. SEM photographs of MoS2−DOPO/FPUF confirmed the well-dispersed MoS2−DOPO in the FPUF matrix and good compatibility between the MoS2−DOPO nanoparticles and the FPUF matrix. The incorporation of MoS2−DOPO did not reduce significantly the mechanical properties of FPUF. The MoS2−DOPO/FPUF composite exhibited an obvious en-
hancement in thermal stability, flame retardancy, and smoke suppression properties, compared with those of pure FPUF and flame-retardant FPUF composites with a single MoS2 or DOPO. Particularly, the THR and maximum smoke density of MoS2−DOPO/FPUF were decreased by 27.7 and 40.5%, respectively, as a comparison with pure FPUF. Furthermore, the char residue analysis manifested that the addition of MoS2−DOPO promoted char formation in the condensed phase and MoS2 was oxidized to MoO3 with excellent thermal oxidation resistance. Moreover, the amount of volatilized pyrolysis products from FPUF decomposition was significantly decreased. The enhanced flame retardancy and smoke suppression of MoS2−DOPO/FPUF could be generally attributed to the synergistic effect of MoS2 and DOPO, including adsorption and physical barrier effects of MoS2, nanosheets, catalytic char-forming function, and free radical quenching of DOPO. This study provides a new insight into fabricating organic−inorganic hybrid flame retardants for halogen-free flame retarding polymer composites.

■ EXPERIMENTAL SECTION

Materials. Pristine MoS2 powder was supplied by Tianjin Chemical Reagent 4th Factory Kaida Chemical Plant (Tianjin, China). NMP and 30% hydrogen peroxide (H2O2) were obtained from by Changdu Kelong Chemicals Co., Ltd (Sichuan, China). DOPO was purchased by Guangdong Wengjiang Chemical Reagent Co., Ltd (Guangdong, China). Polyether polyols (jmdyc-3000, number average molecular weight of 3000, OH content of 56 mg of KOH/g), TDI, triethylenediamine (A-33), and silicone oil (L-580) were obtained from Jining Huakai Resin Co., Ltd (Shandong, China). AM and tin 2-ethylhexanoate (purity 95%) were obtained from Jining Huakai Resin Co., Ltd (Shandong, China). DOPO was purchased by Guangdong Wengjiang Chemical Reagent Co., Ltd (Guangdong, China). AM and tin 2-ethylhexanoate (purity 95%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). All the reagents were analytical grade and used as received without further purification.

Synthesis of MoS2−DOPO Hybrid. The synthetic route of the MoS2−DOPO is illustrated in Scheme 1. The exfoliated MoS2 nanosheets were prepared by ultrasonication-assisted exfoliation method in a mixed solvent. Briefly, 1.0 g of pristine MoS2 was dispersed in a 160 mL of the mixed solvent containing of NMP and 30% H2O2 (volume ration: 15:1) and exfoliated by ultrasonication-assisted method at a power of 600 W for 60 min. Subsequently, the black suspension was centrifuged at 6000 rpm for 15 min to collect MoS2 sediments. The MoS2 sediments were washed three times with deionized water and dried in a vacuum drying oven at 50 °C overnight to obtain MoS2 nanosheets.

Then, 0.5 g of MoS2 nanosheets was dispersed in 300 mL of NMP by an ultrasonic wave for 20 min. AM (1.0 mL) was added into the stable MoS2 dispersion under continuous mechanical stirring 24 h. The obtained MoS2−allyl mercaptan (MoS2−AM) was collected by centrifugation at 5000 rpm, repeatedly washed with ethanol, and dried under a vacuum at 50 °C for 10 h. The MoS2−DOPO hybrid was prepared by a solvolithapy method. The detailed process is as follows. MoS2−AM (0.5 g) and 0.2 g of DOPO were mixed in 100 mL of anhydrous ethanol and sonicated for 30 min in an ultrasonic bath. Then, the mixture was loaded into a 200 mL Teflon-lined autoclave and maintained at 100 °C for 12 h. Afterward, the resulting products were filtered and washed with ethanol to remove the residual DOPO. Lastly, the black MoS2−DOPO hybrid was dried at 50 °C overnight in a vacuum oven.

Preparation of the MoS2−DOPO/FPUF Composite. Pure FPUF and the flame retardant FPUF composites were prepared using a conventional one-pot and free-rising method. MoS2−DOPO/FPUF was prepared by the following approach. Briefly, polymer polyols, chain extender (tin 2-ethylhexanoate), catalyst (A-33), surfactant (L-580), blowing agent (distilled water), and flame retardant (MoS2−DOPO) were first mixed in a 1 L plastic beaker through vigorous mechanical stirring for 3 min. TDI was immediately added into the mixture with vigorous stirring at 1000 rpm for 5 s. The mixture was rapidly poured into an open plastic mold for free-rising of foam. The foam was cured in an oven for 24 h at 50 °C, and taken out of the mold. The formulations of the FPUFs are displayed in Table 1. The isocyanate index (NCO/OH in mol) was 1.05. The pure FPUF, MoS2/FPU, and DOPO/FPUF were also fabricated using a similar process, respectively.

Characterization. AFM was employed on a Bruker Multimode 8 in the tapping mode to analyze the thickness of MoS2 nanosheets, and the sample was prepared by spinning coating on a freshly cleaved mica surface. FTIR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer over the wavenumber range from 4000 to 400 cm⁻¹ using the KBr disk. TEM analyses were carried out using a JEM-2100 electron microscope integrated with an EDX to investigate the morphology and the elemental analysis of the samples, and the samples were prepared by one drop casting on carbon-coated copper grids. The morphologies of FPUFs and their char residues obtained from cone calorimeter tests were investigated by a Zeiss EVO MA15 TEM, and the samples were coated with a thin gold layer before observation. The elemental analysis of the char residues obtained from cone calorimeter tests was analyzed by an EDX (Oxford INCA 350). The densities of the FPUFs were measured according to the ISO 845:2006 standard test method. The size of each specimen was at least 100 cm³. The tensile strength and the elongation at the break of the FPUFs were determined by tensile measurements on an Instron 566 instrument following ISO 1798:2008 standard method. The 50% compression set test was examined in accordance with the standard method ISO 1856:2000 (22 h, 70 °C) at 50% deformation, and the dimensions of the sample were 50 × 50 × 25 mm². TG analysis was carried out on a Netzsch 209 F1 thermal analyzer (Netzsch, Germany) at a heating rate of 10 °C/min in the nitrogen atmosphere range from room temperature to 700 °C. Limiting oxygen index (LOI) values were obtained using a HC-2C oxygen index instrument according to ISO 4589-1:1996 with sheet dimensions of 150 × 10 × 10 mm³. The cone calorimeter test was performed with a cone calorimeter (Fire Testing Technology, U.K.) following the ISO 5660-1 standard. The samples were wrapped in aluminum foil and irradiated at a heat flux of 35 kW/m². The size of each specimen was 100 × 100 × 25 mm³. Smoke density tests were performed on a JQM-2 smoke density chamber (Jianqiao Co, China) according to ISO 5659-2 standard procedures. Samples with a size of 75 × 75 × 3 mm³ were wrapped in aluminum foil and irradiated horizontally under an external heat flux of 25 kW/m² with an additional pilot burner. Two tests were carried out for each sample. XRD measurements were carried out with a Bruker D8 ADVANCE powder diffractometer equipped with a Cu Kα radiation tube (λ = 0.1542 nm) at room temperature. The scanning range was from 5 to 60°. TG-IR measurements were conducted using a TGA Q5000 IR TG analyzer connected to a Nicolet 6700 FTIR spectrophotometer. Each
sample specimen was heated from room temperature to 700 °C at a heating rate of 20 °C/min under a nitrogen flow of 30 mL/min.

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Notes
The authors declare no competing financial interest.

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