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Synthesis of 3D Hollow Layered Double Hydroxide-Molybdenum Disulfide Hybrid Materials and Their Application in Flame Retardant Thermoplastic Polyurethane

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Abstract: The development of high-performance thermoplastic polyurethane (TPU) with high flame retardancy and low toxicity has always been the focus of its research. In this paper, the novel 3D hollow layered double hydroxide/molybdenum disulfide (LDH/MoS2) hybrid materials were synthesized by hydrothermal method using the MIL-88A as in situ sacrificial template and MoS2 as synergistic flame retardant. Among all TPU composites, the peak heat release rate, total heat release rate, and total smoke release rate of TPU/NiFeTb-LDH/MoS2 were reduced by 50.9%, 18.2%, and 35.8% compared with pure TPU, respectively. The results of the thermogravimetric infrared analysis demonstrated that the contents of combustible volatiles (hydrocarbons) and toxic volatiles (CO and HCN) emitted from TPU/LDH/MoS2 were significantly reduced, indicating that LDH/MoS2 hybrid materials can dramatically enhance the fire safety of TPU composites. Combined with the analysis of carbon residues and thermal stability of TPU composites, the enhanced flame retardancy and smoke suppression performances are primarily attributed to the catalytic carbonization of LDH and the physical barrier effect of MoS2.

Keywords: layered double hydroxide; molybdenum disulfide; thermoplastic polyurethane; flame retardant

1. Introduction

Thermoplastic polyurethane (TPU) is widely used in various fields such as food, medical, clothing, cables, automobiles, etc. owing to its excellent wear resistance, high stability, and mechanical performance [1–3]. Nevertheless, similar to most polymers, TPU is highly flammable and emits a great number of toxic gases and fumes during combustion, which dramatically limits its applications [4]. Consequently, flame retardant modifications of TPU composites are essential, especially in some fields with high requirements for fire resistance. Traditional halogen flame retardants have the advantages of high flame retardant efficiency, low addition amount and low cost. However, due to the generation of harmful gases such as dioxins during the combustion process, halogen flame retardants have been reduced or even banned in some areas [5]. In recent years, some new halogen-free flame retardants have been proved to improve the fire resistance and thermal stability of polymer, such as layered double hydroxide (LDH) [6], molybdenum disulfide (MoS2) [7], graphene oxide (GO) [8], etc.

Layered double hydroxide (LDH), also known as anionic clay, is a lamellar nanomaterial composed of positively charged layers and interlayer anions [9]. LDH has a wide range of applications in flame retardancy, adsorption and catalysis due to its high thermal stability, tunable chemical composition and high anion exchange capacity [10]. LDH endows polymer with good smoke suppression and flame retardancy properties mainly by generating protective carbon layers and diluting combustible gases during combustion.
It is well known that the flame retardancy of LDH is closely related to its good dispersion in polymer. Nonetheless, inorganic LDH is not well dispersed in hydrophobic polymer due to its hydrophilic surface [11]. Hence, it is necessary to develop a novel LDH that can make full use of the advantages of two-dimensional (2D) LDH while avoiding the self-stacking of 2D LDH. In recent years, the use of metal-organic frameworks (MOFs) as self-sacrificial templates to construct three-dimensional (3D) hollow LDH has attracted extensive attention. MOFs are porous, contain metal and organic components, and have weak physical and chemical stability, making MOFs particularly suitable for precursors or template materials [12]. After the unstable core of MOFs is etched, ultrathin LDH nanosheets are obtained by in-situ transformation and deposition, thus effectively avoiding the self-stacking of LDH [13]. In addition, the cavity can release the metal sites deeply hidden in the MOFs framework, which can effectively improve the utilization of metal sites. However, the only MOFs reported as precursors are ZIF-67, ZIF-8, and MIL-88A. For instance, Zhou et al. [14] synthesized 3D NiCo-LDH@PZS hollow dodecahedral structure using ZIF-67 as a precursor and in situ sacrificial template, and introduced it into epoxy resin (EP). The results showed that the peak heat release rate (PHRR) and the total heat release (THR) of EP/NiCo-LDH@PZS are reduced by 30.9% and 11.2%, respectively, compared with pure EP.

As a typical representative of layered metal sulfides, MoS$_2$ is a more commercially valuable 2D layered material with a similar structure to graphene [15]. Transition metal element Mo can promote the formation of carbon layer in the polymer matrix, thus improving the flame retardancy and smoke suppression properties of the polymer [16]. Compared with graphene, MoS$_2$ has lower thermal conductivity, which is not conducive to heat transport within the polymer matrix and thus can effectively delay thermal degradation [17]. However, the exfoliated MoS$_2$ nanosheets are easily aggregated in the polymer matrix due to the van der Waals force, so the satisfactory flame retardancy effect cannot be achieved by MoS$_2$ alone [18]. It has been reported that the compounding of MoS$_2$ with other conventional flame retardants can not only prevent the agglomeration of MoS$_2$ but also improve the thermal stability and flame retardancy of the polymer [16]. Till now, there are few studies on 3D hollow LDH/MoS$_2$ hybrid materials as flame retardant.

In this paper, rare earth ions (Ce$^{3+}$/Tb$^{3+}$) doped MIL-88A were synthesized. The introduction of Ce$^{3+}$/Tb$^{3+}$ can protect the outer structure of MIL-88A from the attack of alkaline media, while the inner structure with weak stability was selectively eroded under alkaline conditions, novel 3D hollow LDH was obtained. In addition, then 3D hollow LDH was hybridized with MoS$_2$ nanosheets to construct 3D hollow LDH/MoS$_2$ hybrid materials. and employed as nanofillers for TPU. The cone calorimeter and thermogravimetric-infrared results demonstrated that the flame retardancy and smoke suppression performances, thermal stability, and fire safety of TPU/LDH/MoS$_2$ were significantly enhanced. Combined with the carbon residues analysis of TPU composites, the enhanced flame retardancy properties are mainly attributed to the catalytic carbonization and physical barrier effects of LDH/MoS$_2$ hybrid materials.

2. Experimental

2.1. Materials

Iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, AR) was supplied by Aladdin Chemical Reagent Manufacturing Co. Ltd., Ontario, CA, USA. Cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, AR), urea (CH$_4$N$_2$O, AR) and fumaric acid (C$_4$H$_4$O$_4$, AR) were bought from McLean Chemical Reagent Co. Ltd., London, UK. Nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, AR) were supplied by Tianjin Dingshengxin Chemical Co. Ltd., Tianjin, China. Molybdenum disulfide (MoS$_2$) and n-butyllithium (C$_4$H$_9$Li, AR) were supplied by Sinopharm Group Chemical Reagent Co. Ltd., Shanghai, China. Thermoplastic polyurethane (TPU, 9380A) was purchased from Germany’s bayer. Deionized water was used during the experiments.
2.2. Synthesis of 3D Hollow NiFeCe-LDH and NiFeTb-LDH

The 3D hollow NiFeCe-LDH and NiFeTb-LDH were synthesized according to previous literature with modification [19]. Firstly, 0.348 g of fumaric acid and 1.44 g of urea were added into 60 mL of deionized water followed by stirring for 30 min at room temperature. Then Fe(NO₃)₃·9H₂O, Ce(NO₃)₃·6H₂O and Ni(NO₃)₂·6H₂O (2.835 g) were successively added to the above solution, and the total amount of Ce(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O is fixed at 3.25 mM. Then, the completely dissolved mixture was poured to the 100 mL Teflon-lined autoclave and reacted at 110 °C for 12 h. After the reaction, it was cooled to room temperature, and the obtained product was washed with deionized water and ethanol for three times. The washed precipitate was dried in a vacuum drying oven at 60 °C for 12 h to obtain 3D hollow NiFeCe-LDH and NiFeTb-LDH.

2.3. Synthesis of 3D Hollow NiFeCe-LDH/MoS₂ and NiFeTb-LDH/MoS₂ Hybrid Materials

The exfoliated MoS₂ nanosheets were prepared according to the previously reported method [20]. In addition, 3D hollow NiFeCe-LDH/MoS₂ and NiFeTb-LDH/MoS₂ hybrid materials were synthesized under the comparable experimental conditions as above. The mass fraction of MoS₂ in the obtained hybrid materials was fixed to 3 wt%. Figure 1 is the schematic diagram of the preparation process of the 3D hollow LDH/MoS₂ hybrid materials.

![Figure 1. Schematic Diagram of 3D hollow LDH/MoS₂.](image)

2.4. Synthesis of TPU Composites

Preparation of TPU composites via melt blending method. Under the conditions of an internal mixing temperature of 180 °C and rotating speed of 30 rpm, TPU and the prepared flame retardants (the additional amount of flame retardants is 2 wt%) were mixed in an internal mixer in a certain proportion until they are completely mixed. Then, the TPU composites were hot-pressed for 10 min and cold-pressed for 3 min at 180 °C and 10 MPa. Finally, the pressed TPU composites were cut to the appropriate size (100 × 100 × 3 mm³) for subsequent testing.

2.5. Characterization

X-ray diffraction (XRD) patterns were conducted on a Philips X’Pert Panalytical diffractometer using Cu-Kα radiation (λ = 0.1542 nm). Fourier transform infrared spectroscopy (FTIR) spectra were made with an IRAffinity-1 FTIR spectrophotometer (PerkinElmer, Waltham, MA, USA) with a test range of 400–4000 cm⁻¹. X-ray Photoelectron Spectroscopy (XPS) performed by AXIS SUPRA Spectrometer (Kratos, London, UK). The Brunauer-Emmett-Teller (BET) specific surface area was measured by N₂ adsorption-desorption method on an ASAP2020 system. Scanning electron microscope (SEM) images were acquired using a JSM-6700F instrument with a parameter condition of 5 kV. Transmission
Electron Microscopy-Energy Dispersion (TEM-EDS) measurements were performed using a JEOL-2010 instrument. The TPU composites were determined by the JCZ-2 cone calorimeter according to ISO 5660 standard. The TPU composites with a size of 100 × 100 × 3 mm³ were wrapped in aluminum foil, placed horizontally on the sample rack and heated with an external heat source of 50 kW/m². Thermogravimetric analysis-infrared spectrometry (TG-FTIR) was performed on a DT-50 instrument at a heating rate of 20 °C/min (N₂ atmosphere), and the temperature range was 40–800 °C.

3. Results and Discussion
3.1. Characterization of 3D Hollow LDH and Its Hybrid Materials

The crystallinity of MIL-88A, MoS₂, MIL-88A derived LDH and LDH/MoS₂ hybrid materials were investigated by XRD, as shown in Figure 2. It can be seen from Figure 2a that the diffraction peak of exfoliated MoS₂ at 2θ = 14.2° corresponds to the (002) plane [18]. The diffraction peaks of the as-synthesized MIL-88A are in good agreement with the results reported in the previous literature [21]. The (003), (006), (012) and (110) planes occurring in LDH correspond to the typical characteristic peaks of LDH, indicating that NiFeCe-LDH and NiFeTb-LDH have been successfully synthesized [19]. Meanwhile, there are no diffraction peaks corresponding to MIL-88A in the obtained LDH materials, indicating that MIL-88A is completely transformed into LDH. It is worth noting that NiFeCe-LDH and NiFeTb-LDH have broad diffraction peaks, which may be due to the fact that the ionic radii of Ce³⁺ (102 pm) and Tb³⁺ (92.3 pm) are much larger than that of Fe³⁺ (55 pm), causing lattice distortion of LDH. The XRD patterns of LDH/MoS₂ and LDH have similar peaks, corresponding to the characteristic peaks of LDH. This is mainly due to the fact that the LDH nanosheets grown on the surface of MoS₂ destroy the face-to-face stacking structure of MoS₂ nanosheets, which can effectively inhibit the restacking of the MoS₂ nanosheets [22].

![Figure 2. XRD patterns of MIL-88A, MoS₂ (a) and NiFeCe-LDH, NiFeTb-LDH, NiFeCe-LDH/MoS₂, NiFeTb-LDH/MoS₂ (b).](image_url)

The FTIR spectra of NiFeCe-LDH/MoS₂ and NiFeTb-LDH/MoS₂ hybrid materials together with MoS₂, NiFeCe-LDH and NiFeTb-LDH are depicted in Figure 3a. It can be seen from Figure 3a that all five materials show absorption peaks at 3446 cm⁻¹ and 1626 cm⁻¹, which are related to the stretching vibration of the -OH group and the bending vibration of the water molecules in the middle layer. As for NiFeCe-LDH and NiFeTb-LDH, the positions of their absorption peaks are basically the same. For instance, the
absorption peak at 1382 cm\(^{-1}\) is attributed to the stretching vibration of NO\(_3^-\) as interlayer anion, and the absorption peaks below 700 cm\(^{-1}\) correspond to the stretching vibration of metal-OH in the LDH structure, which further proves that the prepared materials are metal hydroxides [23]. In addition, it is worth noting that the positions of the absorption peaks of NiFeCe-LDH/MoS\(_2\) and NiFeTb-LDH/MoS\(_2\) are similar with those of NiFeCe-LDH and NiFeTb-LDH, which is consistent with the analysis results of XRD. The thermal decomposition behaviors of MoS\(_2\), NiFeTb-LDH, and NiFeTb-LDH/MoS\(_2\) under N\(_2\) atmosphere were investigated by TGA, and the TG results are shown in Figure 3b. It can be seen from Figure 3b that the MoS\(_2\) nanosheets have high thermal stability with a mass loss of only 6.9%. In contrast, NiFeTb-LDH presents three decomposition stages: the first mass loss stage of NiFeTb-LDH occurs in the range of 50 °C and 200 °C corresponding to the loss of interlayer water; the second mass loss stage appears between 250 °C and 370 °C, which is related to the decomposition of metal hydroxides; the third mass loss stage occurs between 450 °C and 550 °C, which can be attributed to the collapse of metal organic frameworks [24]. At 800 °C, the char yield of NiFeTb-LDH is 65.3%. For NiFeTb-LDH/MoS\(_2\), it has a similar thermal decomposition trend to NiFeTb-LDH, which might be ascribed to the higher content of NiFeTb-LDH in the NiFeTb-LDH/MoS\(_2\) hybrid material. The char yield of NiFeTb-LDH/MoS\(_2\) at 800 °C is 61.6%, which is only slightly lower than that of NiFeTb-LDH.

The morphologies of MIL-88A, NiFeCe-LDH, NiFeTb-LDH, NiFeCe-LDH/MoS\(_2\), and NiFeTb-LDH/MoS\(_2\)/LDH were characterized by SEM. It can be observed from Figure 4a that the precursor MIL-88A presents a hexagonal micro rod structure with a uniform size (about 2 µm in length and 500 nm in width) and a smooth surface. As revealed in Figure 4b–e, NiFeCe-LDH and NiFeTb-LDH still maintain the hexagonal microrod structure of precursor, but their surfaces are rougher, indicating that LDH nanosheets are successfully synthesized on the surface of nano frame. As shown in Figure 4f,g, it is a failure to find MoS\(_2\) nanosheets in the SEM images of NiFeCe-LDH/MoS\(_2\) and NiFeTb-LDH/MoS\(_2\) hybrid materials, which may be caused by the exfoliated MoS\(_2\) nanosheets completely covered by LDH [25]. In order to investigate the distribution of elements, plan scan image and EDS spectrum analysis were performed on NiFeCe-LDH/MoS\(_2\) and NiFeTb-LDH/MoS\(_2\)/LDH hybrid materials. As shown in Figure S1a,c, we can clearly see that Fe, Ni, and Ce/Tb elements are uniformly distributed throughout the nano frame, which proves that the composition of LDH is

**Figure 3.** FTIR spectra of MoS\(_2\), NiFeCe-LDH, NiFeCe-LDH/MoS\(_2\), NiFeTb-LDH and NiFeTb-LDH/MoS\(_2\) (a); TG curves of MoS\(_2\), NiFeTb-LDH and NiFeTb-LDH/MoS\(_2\) (b).
ternarily doped. Meanwhile, the detected Mo elements also corroborate the presence of MoS$_2$, indicating the successful preparation of LDH/MoS$_2$ hybrid materials.

Figure 4. SEM images of MIL-88A (a), NiFeCe-LDH (b,d), NiFeTb-LDH (c,e), NiFeCe-LDH/MoS$_2$ (f) and NiFeTb-LDH/MoS$_2$ (g).

The structural features of MoS$_2$, MIL-88A, NiFeCe-LDH, and NiFeTb-LDH were further characterized by TEM. It can be seen from Figure 5a that the exfoliated MoS$_2$ nanosheets present typical two-dimensional sheet-like morphology with a size of about 200 nm. However, MoS$_2$ nanosheets exhibit different degrees of restacking in some areas due to van der Waals forces. From Figure 5b, we can observe that the precursor MIL-88A is a solid structure. As shown in Figure 5c,d, NiFeCe-LDH and NiFeTb-LDH possess distinct hollow structures with an average length of about 1 µm. The ultrathin and uniform LDH nanosheets are mainly inserted vertically on the surface of the hollow nano frame, which effectively inhibits the aggregation of LDH nanosheets. In addition, the loose stacking of LDH nanosheets on the precursor surface forms a highly porous structure, thus NiFeCe-LDH and NiFeTb-LDH have high specific surface areas of 98.2047 m$^2$/g and 100.7177 m$^2$/g, respectively (Figure S2).

To further confirm the chemical composition of LDH/MoS$_2$ hybrid materials, the XPS characterization was carried, and the results are shown in Figure S3. XPS results show that LDH/MoS$_2$ hybrid materials are composed of C, O, Fe, Ni, Ce/Tb and Mo elements, which also corresponds to the EDS results of LDH/MoS$_2$ hybrid materials. The peak signal of Mo is lower due to the small amount of MoS$_2$ added in the LDH/MoS$_2$ hybrid materials. In the high-resolution Fe 2p spectrum, there are two typical peaks located at 712.5 eV and 725.1 eV, which indicate that Fe mainly exists in the positive trivalent state in the LDH/MoS$_2$ hybrid materials. Ni, Ce/Tb and Mo perform divalent, trivalent and tetravalent states in LDH/MoS$_2$ hybrid materials, respectively.
3.2. CCT Tests of TPU Composites

Cone calorimeter based on the principle of oxygen consumption has been widely used to evaluate the combustion performance of materials, which can obtain important physical parameters related to heat and smoke [26]. Table 1 shows the specific data of the cone calorimeter test (CCT).

**Table 1.** Cone calorimeter data of TPU composites.

| Sample Code        | PHRR kW/m² | THR MJ/m² | PSPR m²/s | TSP m² |
|--------------------|------------|-----------|-----------|--------|
| TPU                | 1135       | 118.8     | 0.113     | 12.3   |
| TPU/MoS₂           | 804        | 104.6     | 0.103     | 11.9   |
| TPU/NiFeCe-LDH     | 710        | 108.5     | 0.065     | 8.1    |
| TPU/NiFeTb-LDH     | 652        | 114.6     | 0.049     | 9.5    |
| TPU/NiFeCe-LDH/MoS₂| 581        | 98.4      | 0.050     | 7.4    |
| TPU/NiFeTb-LDH/MoS₂| 557        | 97.2      | 0.045     | 7.9    |

Heat release rate (HRR) is an important parameter to evaluate the fire risk level of materials. It can be used to predict the size and spread rate of fire [26]. As can be seen from Figure 6, the pure TPU is highly flammable and reaches the peak heat release rate (PHRR) with a value of 1135 kW/m² at around 175 s. Compared with pure TPU, the HRR curves of MoS₂, NiFeCe-LDH and NiFeTb-LDH filled TPU are relatively flat, and the PHRR decreases from 1135 kW/m² to 804 kW/m², 710 kW/m², and 652 kW/m², corresponding to 29.2%, 37.4%, and 42.6% decrement, respectively. This can be attributed to the fact that the physical layered structure of MoS₂ and LDH can play a role of sheet barrier during TPU combustion. In addition, the decomposition of LDH at high temperature can release water vapor and absorb heat, thereby reducing the combustion rate of the TPU matrix. It is interesting to note that the PHRR values of TPU filled with NiFeCe-LDH/MoS₂ and NiFeTb-LDH/MoS₂ hybrid materials further decreased to 581 kW/m² and 557 kW/m², which decreased by 18.2% and 14.6% compared with that of TPU/NiFeCe-LDH and TPU/NiFeTb-LDH, respectively. This indicates that MoS₂ and LDH have a good synergistic effect in improving the flame retardancy of TPU. On the one hand, metal oxides formed by thermal decomposition of LDH can promote the formation of a protective carbon layer on TPU
matrix, which can prevent the heat transfer of the system and reduce the concentration of combustible gas in the system [27]. On the other hand, MoS2 nanosheets have large contact area, which can prevent the penetration of external heat and oxygen, suppress the release of combustible pyrolysis products, and then promote the carbonization of TPU matrix [28]. As can be seen from Figure 6, the ignition time of TPU composites containing MoS2 is slightly prolonged than that of TPU composites without MoS2, which may be related to the fact that the two-dimensional structure of MoS2 nanosheets inhibits the release of combustible gases during the ignition phase.

![Figure 6. HRR curves of pure TPU and TPU composites (a,b).](image)

The total heat release (THR) curves of pure TPU and TPU composites are shown in Figure 7. As can be seen from Figure 7, the THR value of pure TPU is the largest, reaching 118.8 MJ/m². Compared with pure TPU, the THR values of TPU/MoS2, TPU/NiFeCe-LDH and TPU/NiFeTb-LDH decreased to 104.6 MJ/m², 108.5 MJ/m² and 114.6 MJ/m², respectively. Notably, compared with TPU composites filled with single MoS2 or LDH, TPU composites with the introduction of NiFeCe-LDH/MoS2 and NiFeTb-LDH/MoS2 hybrid materials have lower THR values of 98.4 MJ/m² and 97.2 MJ/m², respectively. This is mainly attributed to the better catalytic carbonization effect of the LDH/MoS2 hybrid materials during the combustion process. As a protective barrier, char can prevent the outflow of pyrolysis products from the decomposition zone, so as to slow down the spread of fire and reduce the total heat release [29]. At the same time, the CO₂ produced by the organic ligand fumaric acid during the combustion process will dilute the combustible gas, which can inhibit the further combustion of the TPU to a certain extent.

The hazard of smoke from polymer combustion is another important lethal factor in addition to thermal hazard. Therefore, flame retardants must keep smoke generation to a minimum to reduce fire hazards [14]. The smoke production rate (SPR) curves of pure TPU and TPU composites are illustrated in Figure 8. As can be seen from Figure 8, the peak smoke production rate (PSPR) of pure TPU is as high as 0.113 m²/s. Compared with pure TPU, the PSPR value of the TPU/MoS2 is only reduced by 9.7%, indicating that the smoke suppression effect of single MoS2 is not ideal. In contrast, the PSPR values of TPU/NiFeCe-LDH and TPU/NiFeTb-LDH are lower by 42.5% and 56.7%, respectively. This is mainly explained by metal oxides produced by LDH in the process of thermal degradation can adsorb incompletely burned carbon particles [30]. In the meantime, the water vapor and CO₂ produced during the thermal decomposition of LDH can dilute part of the flue gas. It can be clearly found that after adding NiFeCe-LDH/MoS2 and NiFeTb-LDH/MoS2 hybrid materials, the PSPR values of TPU composites are further reduced and the SPR curves are relatively flat, demonstrating that MoS2 nanosheets and LDH have a remarkable synergistic
smoke suppression effect. On the one hand, MoO$_3$ particles produced by the oxidation of MoS$_2$ have an efficient smoke suppression effect; on the other hand, the transition metal element Mo plays a catalytic role in TPU composites, and the generated carbon layer can delay the release of smoke particles.

![Figure 7. THR curves of pure TPU and TPU composites (a,b).](image)

![Figure 8. SPR curves of pure TPU and TPU composites.](image)

The total smoke production (TSP) curves of pure TPU and TPU composites are illustrated in Figure 9. It can be observed that pure TPU has the highest TSP with a value of 12.19 m$^2$. Nonetheless, the addition of MoS$_2$ has little effect on the TSP value, which can be explained by the poor dispersion of MoS$_2$ nanosheets due to the existence of the van der Waals force, so that MoS$_2$ nanosheets can’t give full play to the nano barrier effect. In comparison with the pure TPU, the TSP values of TPU/NiFeCe-LDH and TPU/NiFeTb-LDH decreased by 33.2% and 22.1%, respectively. This is mainly due to the fact that LDH would help to promote charring. The formation of carbon layer increases the difficulty of escaping combustible, which can further reduce combustible gas and smoke-forming materials in the gas phase [31]. Compared with TPU/MoS$_2$ and TPU/LDH, the TSP values of LDH/MoS$_2$ filled TPU are further reduced. This is mainly owing to the fact that organic volatiles mainly stay in the condensed phase, which is the main source of smoke particles [32].
The total smoke production (TSP) curves of pure TPU and TPU composites are illustrated in Figure 9. It can be observed that pure TPU has the highest TSP with a value of 12.19 m². Nonetheless, the addition of MoS₂ has little effect on the TSP value, which can be attributed to the poor dispersion of MoS₂ nanosheets due to the existence of the van der Waals force, so that MoS₂ nanosheets can’t give full play to the nano barrier effect. In comparison, the TSP values of TPU/MoS₂ and TPU/LDH are lower than those of pure TPU, indicating that the incorporation of MoS₂ and LDH leads to the forward of the initial decomposition temperature, which is consistent with the results of CCT analysis. In addition, compared with the single MoS₂ or LDH filled TPU and pure TPU, the LDH/MoS₂ hybrid materials filled TPU have higher char yield. At 800 °C, the char yield of TPU/NiFeCe-LDH/MoS₂ and TPU/NiFeTb-LDH/MoS₂ reach up to 10.11% and 13.74%, respectively, attributing to the better catalytic carbonization of hybrid materials, and the carbon layer can protect the unburned TPU matrix [22].

Table 2. Thermogravimetry data of TPU composites.

| Sample Code               | T_{5\%} (°C) | T_{max} (°C) | Char Yield (%) |
|---------------------------|--------------|--------------|----------------|
| TPU                       | 333          | 454          | 5.85           |
| TPU/MoS₂                  | 317          | 432          | 7.93           |
| TPU/NiFeCe-LDH            | 302          | 385          | 7.58           |
| TPU/NiFeTb-LDH            | 308          | 382          | 9.05           |
| TPU/NiFeCe-LDH/MoS₂       | 316          | 376          | 10.11          |
| TPU/NiFeTb-LDH/MoS₂       | 316          | 394          | 13.74          |

It is easy to see from the DTG curves that TPU/LDH composites have a similar thermal decomposition process to TPU/LDH/MoS₂. This can be explained by the low content of MoS₂ in the TPU/LDH/MoS₂, which makes MoS₂ unable to efficiently participate in the carbonization process of TPU.
3.4. Char Residues Analysis of TPU Composites

To profoundly understand the flame retardant mechanism in the condensed phase, the carbon residues of TPU composites were further analyzed. Figure S4 gives the digital photos of char residues. Figure S4a displays the exposed aluminum foil, and the pure TPU is completely burned. In Figure S4b, TPU/MoS$_2$ presents incomplete and fragile carbon residues after combustion, which also leads to the unsatisfactory flame retardancy and smoke suppression effects of the TPU. Although the carbon residues of TPU/LDH after combustion cover the entire aluminum foil, the carbon residues are relatively loose and there are hollows in the middle of the carbon residues. With the addition of LDH/MoS$_2$ hybrid materials, the carbon residues of TPU/LDH/MoS$_2$ are more complete and denser and the number of carbon residues increases significantly, which indicates that the LDH/MoS$_2$ hybrid materials have a better catalytic carbonization effect.

The microstructure of carbon residues was further studied by SEM, as shown in Figure 11. It can be seen from Figure 11a that the carbon layer formed by TPU/MoS$_2$ is discontinuous and the surface of the carbon layer is porous, which is not conducive to blocking heat, oxygen and combustible gases. For TPU added with NiFeTb-LDH, the morphology of carbon layer is relatively complete, but there are holes and cracks on the surface of the carbon layer. The holes can release the pyrolysis products from the underlying TPU matrix, thus reducing PHRR during combustion, but the reduction of THR is not obvious. As regards the carbon layer of TPU/ NiFeTb-LDH/MoS$_2$, the carbon layer has fewer holes, compact appearance and smooth surface. The dense carbon layer can act as physical barrier to inhibit the further combustion of the TPU matrix, thereby improving the flame retardancy of the TPU [35].

The carbon residues of TPU composites were further studied by XRD, and the results are shown in Figure 12. As shown in Figure 12a, there are diffraction peaks of MoS$_2$ and MoO$_3$ in the XRD pattern of the carbon residues of the TPU/MoS$_2$. However, the carbon residues of TPU/MoS$_2$ have a low degree of graphitization, which also leads to a low carbon formation rate, poor flame retardancy and smoke suppression effects of
TPU/MoS₂ in the combustion process. For the XRD patterns of the carbon residues of TPU/NiFeCe-LDH/MoS₂ (b) and TPU/NiFeTb-LDH/MoS₂ (c), there are not only the diffraction peaks of MoO₃ and graphite microcrystals, but also the diffraction peaks of metal oxides such as Fe₂O₃, NiO, Ni₂O₃ and Ce₂O₃/Tb₂O₃. The metal oxides help to form structurally stable carbon layers, which effectively limit the diffusion of oxygen and heat into the polymer interior.

**Figure 11.** SEM images of carbon residues of TPU/MoS₂ (a), TPU/NiFeTb-LDH (b) and TPU/NiFeTb-LDH/MoS₂ (c).

**Figure 12.** XRD patterns of carbon residues of TPU/MoS₂ (a), TPU/NiFeCe-LDH/MoS₂ (b) and TPU/NiFeTb-LDH/MoS₂ (c).
3.5. Gas Analysis

Thermogravimetric analysis-infrared spectrometry (TG-FTIR) is an efficient approach for the dynamic analysis of gaseous products during combustion processes [36]. Figure S5 presents the 3D TG-FTIR spectra of pure TPU and TPU/NiFeTb-LDH/MoS$_2$. As can be seen in Figure S5, the thermal decomposition process of TPU/NiFeTb-LDH/MoS$_2$ is analogous to that of pure TPU, indicating that the addition of NiFeTb-LDH/MoS$_2$ hybrid material does not change the pyrolysis products of TPU. The peaks of thermal decomposition products for TPU and TPU/NiFeTb-LDH/MoS$_2$ are mainly distributed in the ranges of 3500–4000 cm$^{-1}$, 2700–3000 cm$^{-1}$, 2200–2500 cm$^{-1}$, 1600–1800 cm$^{-1}$ and 1300–1600 cm$^{-1}$, which are consistent with previous literature [37].

Figure 13 presents the FTIR spectra of pure TPU and TPU/NiFeTb-LDH/MoS$_2$ under the maximal decomposition rate. The absorption peak at 2980 cm$^{-1}$ corresponds to the stretching vibration of the -CH$_3$ or -CH$_2$ group in hydrocarbons. The absorption peaks of HCN, CO$_2$ and H$_2$O are located at 673 cm$^{-1}$, 2360 cm$^{-1}$ and 3548 cm$^{-1}$, respectively. In addition, the peaks at 1510 cm$^{-1}$ and 1766 cm$^{-1}$ correspond to the typical absorption peaks of aromatic hydrocarbons and carbonyl compounds, respectively.

![FTIR spectra of TPU and TPU/NiFeTb-LDH/MoS$_2$ pyrolysis products at maximum decomposition rate.](image)

In order to explicitly understand the difference of pyrolysis products between pure TPU and TPU/NiFeTb-LDH/MoS$_2$, the main volatile pyrolysis products versus temperature were investigated, as depicted in Figure 14. It can be seen from Figure 14a that the absorbance intensity of the hydrocarbons of pure TPU is remarkably high compared to that of TPU/NiFeTb-LDH/MoS$_2$. The decrement of hydrocarbons can further reduce the generation of smoke and increase fire scene visibility, which reduces fire rescue difficulties [38]. At the same time, the reduction of combustible hydrocarbons is beneficial to suppress HRR, which is consistent with the results of cone calorimetry. The CO and HCN are typical asphyxiating gases that can cause heavy casualties. In the presence of NiFeTb-LDH/MoS$_2$, the release of CO and HCN from TPU is significantly lower than that of pure TPU, indicating that NiFeTb-LDH/MoS$_2$ can effectively inhibit the release of toxic volatiles. In summary, NiFeTb-LDH/MoS$_2$ endows TPU with better fire safety, which is the result of the catalytic effect of NiFeTb-LDH/MoS$_2$ and the dense carbon layer as a physical barrier.
3.6. Flame Retardant Mechanism

Combining the condensed phase-gas phase analysis and flame retardant performance results of TPU/LDH/MoS₂, a rational flame retardant mechanism is proposed, as shown in Figure 15. The flame retardant mechanism of TPU composites in the condensed phase can be summarized as the following points: (1) The MoS₂ nanosheets act as physical barriers during the combustion process of TPU, inhibiting the release of flammable and toxic gases from the underlying TPU composite. At the same time, MoO₃ generated by the oxidation of MoS₂ has a high-efficiency smoke suppression effect. (2) In the combustion process, the metal oxides formed by LDH can catalyze the polymer to form a carbon layer and absorb part of flue gas [22]. (3) The LDH/MoS₂ hybrid materials improve the degree of graphitization and compactness of the carbon residues, and the protective carbon layer can act as a barrier between the combustion zone and the substrate to protect the unburned substrate. The flame retardant mechanism of TPU composites in the gas phase is mainly attributed to the fact that the water vapor generated by the thermal decomposition of LDH can effectively dilute flammable gases such as oxygen. Overall, the addition of LDH/MoS₂ hybrid materials enhances the flame retardancy of TPU.
Figure 15. Illustration of the flame retardant mechanism of TPU/LDH/MoS$_2$.

4. Conclusions

In this work, the novel 3D hollow LDH/MoS$_2$ hybrid materials were synthesized by hydrothermal method and their composition and structure were characterized by XRD, FTIR, SEM, TEM and TGA. Afterward, the MoS$_2$, LDH and LDH/MoS$_2$ filled TPU composites were prepared by the melt blending method. The CCT results indicated that the flame retardancy and smoke suppression performance of TPU composites were greatly enhanced by the addition of LDH/MoS$_2$ hybrid materials, and the PHRR and PSPR values were significantly reduced. The TGA results showed that the incorporation of LDH/MoS$_2$ hybrid materials enhances the thermal stability of TPU composites. In addition, the existence of LDH/MoS$_2$ hybrid materials inhibited the release of combustible volatiles (hydrocarbons) and the precipitation of toxic volatiles (CO and HCN) in TPU, indicating that LDH/MoS$_2$ hybrid materials can dramatically enhance the fire safety of TPU. SEM and XRD results indicated that the metal oxides generated during the combustion of TPU composites contribute to compact carbon layers, and the protective carbon layers can act as barriers between the combustion zone and the matrix to protect the unburned matrix. To sum up, the improvement of flame retardancy and smoke suppression performance, thermal stability and fire safety of TPU/LDH/MoS$_2$ can be ascribed to the catalytic carbonization of LDH as well as the physical barrier effect of MoS$_2$.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/polym14081506/s1, Figure S1: Plan scan images and EDS spectrum of NiFeCe-LDH/MoS$_2$ (a,b) and NiFeTb-LDH/MoS$_2$ (c,d); Figure S2: N$_2$ adsorption-desorption isotherms of NiFeCe-LDH (a) and NiFeTb-LDH (b); Figure S3: XPS spectra of NiFeCe-LDH/MoS$_2$ (a) and NiFeTb-LDH/MoS$_2$ (b); Figure S4: Digital photos of carbon residues of TPU (a), TPU/MoS$_2$ (b), TPU/NiFeCe-LDH (c), TPU/NiFeTb-LDH (d), TPU/NiFeCe-LDH/MoS$_2$ (e) and TPU/NiFeTb-LDH/MoS$_2$ (f); Figure S5: TG-FTIR spectra of thermal decomposition products of TPU (a) and TPU/NiFeTb-LDH/MoS$_2$ (b).

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