Effect of Functionalized Carbon Microspheres Combined with Ammonium Polyphosphate on Fire Safety Performance of Thermoplastic Polyurethane

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ABSTRACT: In this article, carbon microspheres (CMSs) synthesized by the hydrothermal method and CMSs-Fe (with Fe\(^{3+}\) adsorbed on the surface of CMSs) were combined with ammonium polyphosphate (APP) to achieve the fire safety improvement of thermoplastic polyurethane (TPU). The fire safety performance of TPU composites was investigated by the cone calorimeter test, microscale combustion calorimeter test, thermogravimetric analysis/infrared spectrometry, Raman spectrometry, X-ray photoelectron spectroscopy, and scanning electron microscopy. The results showed that CMSs and CMSs-Fe can improve the fire safety performance of TPU/APP composites and the effect of CMSs-Fe was better than that of CMSs. The peak heat release rate of the sample containing 0.25 wt % CMSs and 7.75 wt % APP was 16.7% lower than that of the sample containing 8.00 wt % APP, and the content of toxic gases was also reduced in the fire smoke. Also, total heat release and total smoke release of the sample containing CMSs-Fe were 54.7% and 11.6%, respectively, lower than those of the sample containing 0.25% CMSs. It confirmed the contribution of CMSs to the flame retardant system, and the performance of CMSs is improved by adsorbing Fe\(^{3+}\).

1. INTRODUCTION

Thermoplastic polyurethane (TPU) has been widely used in many fields as a new multifunctional engineering plastic with outstanding performance.\(^1,2\) However, the wide spread use of TPU poses a risk arising from its shortcomings of easy combustion and smoke generation.\(^3–6\) To overcome this shortcoming, there have been many flame retardants used for the fire safety improvement of TPU. Also, it has been proved that the use of additive flame retardants is an effective method.

In recent years, a wide range of flame retardants for TPU have been discovered, and intumescent flame retardants (IFRs) have become one of the hottest research areas because of their environmentally friendly, low toxicity, and non-corrosive properties.\(^7,8\) The IFR system relies mainly on three components: acid source, carbon source, and gas source.\(^9\) APP is often used as an acid source and as a gas source, and can be used both as an acid source and as a gas source.\(^4,10\) However, there are also some problems in the practical use of APP, such as its low flame retardant efficiency, large addition amount, and easy to cause smoke generation during combustion. The deficiencies of APP are generally compensated by adding it to TPU together with the synergistic flame retardant. Liu et al. found that the pHRR of polyisocyanurate-polyurethane foams reduced from 159.8 to 76.8 kW/m\(^2\) with the addition of 5.0% aluminum hydroxide and 15.0% APP.\(^11\) Liu et al. changed the molten viscosity by adding carbon black and APP to the TPU, which greatly reduced the TSR of the TPU composites.\(^12\) Also, in the research of Nie et al., with addition of 23.0% APP and 2.0% ferric pyrophosphate (Fe-PP) for PP, the value of pHRR decreased from 179.0 to 95.0 kW/m\(^2\).\(^2,13\)

Carbon materials have found some applications in flame retardancy now. For example, carbon black, carbon nanotubes, and graphene have been combined with APP to reduce the flammability of the polymer. However, they all have more or fewer disadvantages such as high price and complicated synthesis process.\(^12,14,15\) Carbon microspheres (CMSs) are new carbon nanomaterials that have received wide attention due to their high specific surface area, thermal stability, low density, unique electronic properties, and specific structure.\(^16\) Moreover, the synthesis process of CMSs is simple and convenient to apply. They have been used in lithium battery materials, supercapacitor electrode materials, adsorption and...
catalyst carriers, and other fields.\textsuperscript{17-20} Research on the use of CMSs to improve the flame retardancy of materials has made some progress. Mei et al. grafted CMSs onto the surface of wool fiber, finding that the LOI value raised to 29.5\% when the grafting ratio of CMSs on the surface of wool fiber was 6\%.\textsuperscript{21} Yang et al. prepared CMSs coated with Mg(OH)\textsubscript{2} and proved that it can reduce the flammability of polyethylene terephthalate in subsequent tests.\textsuperscript{22} There is no related report on the use of CMSs to improve the fire safety performance of TPU.

CMSs are used as templates for preparation of metal oxides hollow microspheres due to their excellent adsorption properties.\textsuperscript{23} According to this characteristic, iron ions can be adsorbed to the surface of CMSs by a simple method. This study aims to improve the fire safety performance of TPU by using CMSs and CMSs-Fe with APP as a flame retardant. CMSs are synthesized by the hydrothermal method. The sample was prepared by the melt blending method and characterized by CCT, SEM, XPS, MCC, TG-IR, EDS, Raman spectra, etc.

2. RESULTS AND DISCUSSION

2.1. Characterization of CMSs and CMSs-Fe. 2.1.1. SEM of CMSs and CMSs-Fe. SEM photographs of CMSs and

![Figure 1. SEM image of CMSs: (A) magnification 10,000 times and (B) magnification 50,000 times; SEM image of CMSs-Fe: (C) magnification 10,000 times and (D) magnification 50,000 times; (E) EDS of CMSs-Fe.](image-url)
CMSs-Fe are shown in Figure 1A−D. It was seen that the particle size distribution of the CMSs synthesized by the hydrothermal method is relatively uniform with a diameter between 100 and 500 nm. Furthermore, the TPU/CMSs and TPU/CMSs-Fe composite masterbatch were prepared to solve the problem of uneven dispersion due to adhesion between single CMS. The iron ions adsorbed on the surface of CMSs cannot be found by SEM photographs, but through the EDS test curve of Figure 1E, it can be confirmed that iron was adsorbed on the surface of CMSs.

2.1.2. XPS of CMSs and CMSs-Fe. The surface element composition and chemical state of CMSs and CMSs-Fe were detected by XPS, and the results of XPS are shown in Figure 2.

Figure 2. XPS spectra of CMSs: (A1) survey spectra, (A2) C1s spectrum, and (A3) O1s spectrum and CMSs-Fe: (B1) survey spectra, (B2) C1s spectrum, (B3) O1s spectrum, and (B4) Fe2p spectrum.

Figure 3. (A) SPR and (B) TSR curves of TPU composites from CCT.
and correspond to their satellite peaks at 715.6 and 736 eV. As shown in Figure 2A, the Fe element (0.48 atomic %) appears on the surface of CMSs-Fe. As shown in Figure 2B, the element (80.63 atomic %) and O element (19.37 atomic %) are seen that the surface of CMSs is mainly composed of C containing group such as carbonyl group. XPS survey spectra divided into these two peaks in Figure 2B3. It indicated that the surface of CMSs contains more active oxygen-containing group such as carbonyl group. XPS survey spectra of CMSs and CMSs-Fe are shown in Figure 2A, B. It was shown that the Fe element is successfully attached to the surface of the CMSs.

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Figure 2. (A) XPS survey spectra of CMSs and CMSs-Fe are shown in Figure 2A1, B1. It was seen that the surface of CMSs is mainly composed of C element (80.63 atomic %) and O element (19.37 atomic %) and Fe element (0.48 atomic%) appears on the surface of CMSs-Fe as shown in Figure 2A2. As shown in Figure 2B4, the Fe2p spectrum separates two broad peaks at 710.9 and 726.1 eV, which are attributed to Fe2p3/2 and Fe2p1/2 respectively, and correspond to their satellite peaks at 715.6 and 736 eV. It showed that the Fe element is successfully attached to the surface of the CMSs.

2.2. Fire Safety Performance of TPU Composites. 2.2.1. Characteristics of Smoke Generation. Smoke is one of the main factors that threaten human life in the fire, so smoke suppression is an important part of improving the safety performance of materials. The smoke production rate (SPR) and total smoke release (TSR) represent the smoke generation during combustion of the material. Figure 3A shows the SPR curve of TPU composites (the related data are listed in Table 1). From the development trend of the SPR curve of TPU, the SPR has a fast rising phase after ignition, and the phase ends at 95 s. Then the SPR remains within a certain range until the 190 s starts to rise sharply, reaching the peak SPR at 225 s. However, when the APP and CMSs are added to TPU, the rapid rise phase of SPR ends at 75–85 s and then rapidly drops and remains at a low level until the end of combustion. This was because the TPU composite carbonized after initial combustion to form a char residue layer, which causes heat transfer and material exchange (oxygen, combustible gas, smoke precursors, etc.) between the upper and lower sides to be hindered, and further spread of flame begins to be inhibited. The carbon layer formed by the pure TPU material is porous and fragile, so its combustion continues to become more intense. Also, for samples with APP and CMSs, the char residue structure becomes dense, so the severity of the combustion rapidly decreases and remains at a lower level.

Compared with the peak SPR value of TPU (0.101 m²/s), that of TPU-APP (0.040 m²/s) is reduced by 60.4%. It could be explained by the early decomposition of APP to produce phosphoric acid, polyphosphoric acid, metaphosphoric acid, and other products to help form a carbon layer with a threedimensional mechanism, which can better block heat and hold gas-phase products, so that the subsequent combustion intensity greatly weakened and the peak SPR is reduced. Then, with the further addition of CMSs, the peak SPR values are lower. The CMSs0.50 sample with 0.5% CMSs and 7.5% APP showed the lowest peak SPR value (0.029 m²/s), which is 71.3% lower than that of TPU and 27.5% lower than that of TPU-APP. The peak SPR values of samples containing CMSs-Fe are slightly higher than those of samples containing CMSs, but both of them have a tendency to decrease with increasing addition. This shows that CMSs effectively reduce the peak SPR value of TPU and play a role in suppressing smoke.

The TSR curve of TPU composites is shown in Figure 3B. The TSR value of TPU (1005.3 m²/m²) is the highest and that of TPU-APP (452.4 m²/m²) is the lowest in all samples at the same begins to be inhibited. These results indicate that the addition of CMSs and CMSs-Fe are slightly higher than those of samples containing CMSs, TPU-APP. The peak SPR values of samples containing CMSs-Fe are slightly higher than those of samples containing CMSs, but both of them have a tendency to decrease with increasing addition. This shows that CMSs effectively reduce the peak SPR value of TPU and play a role in suppressing smoke.

Figure 3. (A) HRR and (B) THR curves of TPU composites from CCT.

Table 1. Datasheets of CCT

| sample code | TTI (s) | pHRR (kW/m²) | pSPR (m²/s) | THR (MJ/m²) | TSR (m²/m²) | CO (%) | CO2 (%) | mass (%) |
|-------------|--------|--------------|-------------|-------------|-------------|-------|---------|---------|
| TPU         | 72 ± 2 | 0.010 ± 0.0008 | 0.101 ± 0.0008 | 88.2 ± 2.2 | 1005.3 ± 28.3 | 0.034 ± 0.0007 | 0.711 ± 0.006 | 12.3 ± 0.4 |
| TPU-APP     | 65 ± 1 | 0.040 ± 0.0003 | 37.2 ± 0.6 | 542.1 ± 14.7 | 0.023 ± 0.0002 | 0.212 ± 0.004 | 53.7 ± 1.8 |
| CMSs0.125   | 64 ± 1 | 0.044 ± 0.0004 | 53.2 ± 1.1 | 538.4 ± 12.0 | 0.018 ± 0.0001 | 0.121 ± 0.002 | 28.0 ± 0.3 |
| CMSs0.25    | 70 ± 3 | 0.037 ± 0.0001 | 92.9 ± 1.9 | 619.9 ± 12.9 | 0.019 ± 0.0001 | 0.120 ± 0.001 | 23.2 ± 0.5 |
| CMSs0.50    | 60 ± 2 | 0.029 ± 0.0001 | 70.0 ± 1.5 | 470.0 ± 10.4 | 0.016 ± 0.0002 | 0.126 ± 0.002 | 27.5 ± 0.2 |
| CMSs-Fe0.125| 58 ± 1 | 0.047 ± 0.0005 | 75.5 ± 1.3 | 583.8 ± 9.8 | 0.019 ± 0.0003 | 0.143 ± 0.003 | 24.9 ± 0.1 |
| CMSs-Fe0.25 | 64 ± 2 | 0.044 ± 0.0003 | 42.1 ± 0.8 | 547.4 ± 7.6 | 0.017 ± 0.0002 | 0.120 ± 0.001 | 44.2 ± 0.4 |
| CMSs-Fe0.50 | 54 ± 1 | 0.043 ± 0.0002 | 60.6 ± 1.0 | 628.5 ± 11.8 | 0.017 ± 0.0004 | 0.187 ± 0.002 | 28.1 ± 0.1 |
end of the experiment. The low TSR of TPU-APP benefits from its short burning time, and the TSR values of CMSs0.25 (366.6 m²/m²) and CMSs-Fe0.125 (353.0 m²/m²) are lower when the burning of TPU-APP ends at 755 s. It is explained as that the participation of CMSs improves the carbonization performance of APP. CMS in TPU can increase the viscosity of the melt during pyrolysis, promoting the fixation of the smoke precursor in the condensed phase. However, the thermal insulation effect of the carbon layer containing CMSs is weakened. Under the continuous high heat radiation, the combustion process cannot be completely ended, thus making the burning time greatly extended, resulting in a high TSR. Also, from the trend of pSPR and TSR of samples containing CMSs-Fe, the participation of a small amount of CMSs-Fe makes the sample have a high pSPR and a low TSR, which also confirms the above conjecture and also indicates the strengthening effect of iron on the carbon layer.

2.2.2. Characteristics of Heat Generation. Another main threat in the fire field is the high temperatures caused by the combustion of materials, so the thermal parameters are an essential indicator when evaluating the fire safety performance of materials.

The HRR curve of TPU composites is shown in Figure 4A. After ignition, the HRR value of the TPU composite rises rapidly and reaches a peak in a period of time. The HRR value of the TPU is 678.9 kW/m² at 230 s. When APP is added, the pHRR value is reduced to 233.5 kW/m² at 95 s, which is only 34.4% of TPU. All other samples had lower pHRR values around 95 s, which are 210.2, 194.6, 197.4, 209.0, 210.0, and 199.6 kW/m². The above results show that the combination of CMSs and APP can effectively lower the pHRR value of TPU composites. The existence of CMSs provides the carbon source for the flame retardant system containing APP, which contributes to the formation of the carbon layer during combustion. However, after 120 s, the HRR values of TPU composites containing CMSs and APP start to be higher than those of TPU composites containing APP alone, which is due to the reduced thermal insulation properties of the carbon layer formed by the synergistic effect between CMSs and APP, resulting in the continuous decomposition of the matrix material into combustible gases participating in the combustion process under the high heat radiation of CCT.

Figure 4B clearly shows that CMSs-Fe performs better than CMSs in reducing THR. The THR of TPU-APP is greatly reduced compared to that of TPU, but the addition of CMSs increases the THR of the samples. However, the THR value of CMSs-Fe0.25 is lower than that of TPU-APP until the flame is out, and its final THR value is only 13% higher than the latter. The results of THR are consistent with the results of TSR. CMSs help accelerate the formation of the carbon layer but are not conducive to the thermal insulation and strength of the carbon layer, which makes the sample perform poorly in the later stage of testing. The CMSs-Fe has improved this situation to some extent, which is due to the strengthening effect of iron in the formation of the carbon layer.

2.2.3. Release Curve of CO and CO₂. In addition to high temperature and smoke, the toxic gases produced by the decomposition of materials are harmful to people in the fire. CO is such a gas that it can both poison people and be a flammable gas, which is highly harmful. Figure 5A shows the release curve of CO (the specific values are listed in Table 1). The concentration is reduced with the addition of APP and CMSs. The peak of CO concentration of TPU-APP is 0.023%, reducing by 32.4% compared with that of TPU (0.034%). It is worth noting that the samples, which are further added with CMSs and CMSs-Fe, show a stronger effect of CO suppression than TPU-APP. The peaks of CO concentration of CMSs0.125, CMSs0.25, and CMSs0.5 are 0.018, 0.019, and 0.016%, reducing by 21.7, 17.4, and 30.4% compared with that of TPU-APP, respectively. Also, the peaks of CO concentration of CMSs-Fe0.125, CMSs-Fe0.25, and CMSs-Fe0.5 are 0.019, 0.017, and 0.017%, reducing by 17.4, 26.1, and 26.1% compared with that of TPU-APP, respectively. It proves that the presence of APP can suppress the production of CO, reducing the fire risk of TPU materials. Moreover, the peaks of CO concentration, which contain APP, CMSs, or CMSs-Fe, appear in advance, and its reason is the addition of APP to TPU, which also corresponded to the curves of SPR and HRR.

CO₂ is a kind of gas produced in large quantities in the combustion of materials. Excessive concentration of carbon dioxide in the air may cause difficulty in breathing or even suffocation. Figure 5B shows the release curves of CO₂ (the specific values are listed in Table 1). The peak of CO₂ concentration of TPU-APP is 0.21%, reducing by 70.4% compared with that of TPU (0.71%). Especially noteworthy is the fact that the CO₂ concentration curve samples containing both APP and CMSs (CMSs-Fe) lost their sharp peak and their maximum CO₂ concentration is decreased by 25%
compared with the peaks of CO₂ concentration of TPU-APP. The test results of CO and CO₂ concentration show that the CMSs and CMSs-Fe have reduced harmful gases generated by TPU combustion and improved its fire safety performance.

2.2.4. Mass Change Curve. The mass change curve of the TPU composite is shown in Figure 6 (the specific values are listed in Table 1). It is clear that the mass loss of TPU composites containing APP and CMSs (CMSs-Fe) is much less than that of pure TPU. However, corresponding to the results of TSR and THR, the mass loss of TPU-APP is lower than that of other samples with CMSs or CMSs-Fe. It is explained as that the thermal insulation performance and stability of the carbon layer generated by the CMSs synergistic APP are weakened compared with the APP alone, so that the heat is more transmitted to the lower layer, causing the material to continuously decompose. The gas generated by the decomposition and the high heat radiation from the cone calorimeter further cause the carbon layer to be destroyed, and finally, the burning time of the material is greatly prolonged, resulting in a decrease in residual mass. Another point that can be found is that CMSs-Fe0.25 has the lowest mass loss in all samples at the same burn time, further validating the positive effects of CMSs-Fe on the flame retardant process.

2.2.5. Thermal Decomposition Characteristics. The HRR obtained by the MCC test is expressed as the amount of heat released per unit time of the material per unit mass at a specific heating rate, as shown in Figure 7A and Table 2. The peak value of HRR means the maximum decomposition rate of the TPU composite. The decomposition process of TPU is advanced after the addition of APP, with its maximum decomposition rate dropping from 536.9 to 499.5 W/g, and the corresponding temperature decreased by 53 °C. However, with the further addition of CMSs, the temperature corresponding to the maximum decomposition rate is still close to that of TPU-APP. This indicates that the APP contained in the TPU composite leads to its early decomposition. The maximum decomposition rates of CMSs0.125 and CMSs0.25 are higher than that of TPU-APP, but that of CMSs0.50 is lower. The samples containing CMSs-Fe are similar, but the maximum decomposition rate of CMSs-Fe0.50 is the lowest. It is not consistent with the results of the CCT test, which is due to the different test conditions and the heating way for the samples. In the CCT test, the single surface of a large sample (about 50 g) is heated by constant radiance, and the construction of the surface carbon layer is very important for the reduction of the combustion intensity under such conditions; the samples with small mass (about 5 mg) are heated on all sides, and the test temperature is continuously increased, so that the barrier effect of the carbon layer could not be reflected.

Thermogravimetric analysis is an important means of analyzing the thermal degradation behavior of materials at different temperatures and is widely used to assess the fire safety performance of materials. The temperature at which the sample mass loss is 5% is usually considered to be the initial decomposition temperature. Figure 7B,C show the TG and DTG curves of TPU, TPU-APP, CMSs0.25, and CMSs-Fe0.25. The initial decomposition temperature of TPU is 334 °C, and those of TPU-APP, CMSs0.25, and CMSs-Fe0.25 are 307, 310, and 309 °C, earlier than TPU. The early arrival of their peak DTG temperature can also be seen. It is attributed to the reaction between TPU and APP and is consistent with

| Sample Code  | Peak HRR (W/g) | Temperature (°C) | Total HR (KJ/g) | HR Capacity (J/g·K) |
|--------------|---------------|-----------------|----------------|-------------------|
| TPU          | 536.9         | 417.3           | 38.1           | 598               |
| TPU-APP      | 499.5         | 364.6           | 27.7           | 559               |
| CMSs0.125    | 525           | 364.6           | 26.5           | 584               |
| CMSs0.25     | 521.3         | 361.8           | 25.5           | 583               |
| CMSs0.50     | 447.8         | 357.8           | 26.7           | 501               |
| CMSs-Fe0.125 | 629.5         | 357.5           | 27.1           | 704               |
| CMSs-Fe0.25  | 533.7         | 358.1           | 27.8           | 594               |
| CMSs-Fe0.50  | 410.1         | 350.8           | 26.5           | 459               |

Figure 6. Mass change curve of TPU composites from CCT.

Figure 7. (A) HRR curve of TPU composites from MCC, (B) TG curve, and (C) DTG curves of TPU, TPU-APP, CMSs0.25, and CMSs-Fe0.25.
the fact that the ignition time is advanced in the CCT test. At the end of the test, the remaining mass of TPU is about 0.80%, while the remaining masses of the TPU-APP, CMSs0.25, and CMSs-Fe0.25 are much higher than it, which are 27.04, 25.70, and 27.8%. In addition, the DTG peaks of CMSs0.25 and CMSs-Fe0.25 are also lower than that of TPU but higher than that of TPU-APP, which is inconsistent with SPR and HRR but consistent with MCC results. It is due to the similarity of the TG and MCC test conditions. Although the presence of APP and CMSs (CMSs-Fe) promotes the advance formation of the surface carbon layer during thermal degradation of TPU, thereby protecting the internal composite from further thermal degradation, the protection of the carbon layer is weakened under the conditions tested.

TG-IR was used to analyze the gas-phase product of thermal degradation of TPU composites. Figure 8 provides infrared spectra of gas-phase products of TPU, TPU-APP, CMSs0.25, and CMSs-Fe0.25 at 180−720 °C. The specific infrared absorption peaks in the infrared spectrum represent certain products, which can be used to determine the composition of the gas-phase product. The gas-phase products thermally degraded by the sample mainly include H2O (3400−4000 cm−1), CO2 (2300−2400 cm−1), carboxylic acid (1700−1850 cm−1), and aliphatic hydrocarbons (2800−3150, 1250−1500, and 950−1150 cm−1). TPU will decompose violently to generate a large amount of H2O and CO2 when heated, and according to this, the progress of TPU decomposition can be judged. The infrared absorption peak of CO2 (2350 cm−1) appears at 220 °C (Figure 8), indicating that TPU starts a small amount of decomposition at this temperature, and this continues until 360 °C. After 360 °C, the intensity of the infrared absorption peak of CO2 increases rapidly, representing the accelerated decomposition of TPU. The infrared absorption peak of CO2 begins to decrease after reaching a maximum at 460 °C and enters a stable CO2 release stage at 560−700 °C. The same trend as the infrared absorption peak of CO2 is that of H2O (3400−4000 cm−1) and aliphatic hydrocarbons (2800−3150, 1250−1500, and 950−1150 cm−1), all of which are derived from multiple depolymerizations of TPU. The infrared absorption peak of the carboxylic acid (1700−1850 cm−1) appears at 460 °C, and the carboxylic acid comes from the soft segment of the TPU, which is released when the decomposition is most severe. The CO2 infrared absorption peaks of TPU-APP, CMSs0.25, and CMSs-Fe0.25 begin to increase at 300 °C, reaching the highest at 360 °C, and then enter the steady state after 600, 520, and 580 °C, respectively. On the one hand, the early decomposition of TPU-APP, CMSs0.25, and CMSs-Fe0.25 contributes to the construction of the carbon layer; on the other hand, the maximum values of the CO2 infrared absorption peak of them are much smaller than that of TPU. This is evidence that APP and CMSs (CMSs-Fe) reduce the severity of TPU cleavage. In addition, a decrease in the infrared absorption peak at 3000 cm−1, which represents an unsaturated C−H structure in an aromatic compound, generally considered to be a source of the smoke. The smoke suppression effect of APP and CMSs (CMSs-Fe) was also confirmed.

2.3. Characterization of Char Residue. Figure 9 shows photographs of the carbon residue and its SEM images. The carbon residue is from the CCT test, and its complete surface is selected for SEM testing. The surface of the carbon residue after TPU combustion exhibits a light and fragile characteristic, and its SEM image also shows a structure whose surface is not compact and small holes that can be released by the
combustible gas. This obviously does not effectively shield heat transfer and upper and lower material exchange during combustion. From the SEM images, the surface layers of the carbon residue of TPU-APP, CMSs0.25, and CMSs-Fe0.25 are smoother and more compact than that of the TPU, which greatly improve the heat transfer resistance and the effect of combustible products. From the photograph of the carbon residue, the carbon layer generated by TPU combustion is relatively low, and the samples containing APP have a relatively high carbon layer after combustion. Even if the carbon layer of the TPU-APP is broken when it is taken out after the test because of the high expansion of the burning test device, its remaining height is still 3.5 cm, which is the same as that of the CMSs. The thinner carbon layer has a weaker ability to block heat and decomposition products, which is the reason why the burning time of samples containing CMSs is prolonged. This situation arises because the increase in viscosity of the TPU matrix by CMSs weakens the degree of expansion of the carbon layer. In addition, CMSs-Fe0.25 has a carbon layer height of only 3.1 cm, but its thermal parameters and smoke parameters are lower than those of CMSs0.25. This shows that CMSs-Fe not only has the effect of CMSs accelerating the formation of carbon layers but also makes the carbon layer more compact and strong, and its mechanism is shown in Scheme 1.

Figure 9. Photographs and SEM image (above: magnification 1000 times, below: magnification 5000 times) of the char residue after CCT: (A) TPU, (B) TPU-APP, (C) CMSs0.25, and (D) CMSs-Fe0.25.

Scheme 1. Illustration of the Flame Retardant Mechanism for the Effect of CMSs-Fe on TPU
The degree of graphitization of the carbon residue after CCT testing can be obtained by Raman spectroscopy, which is often used to indicate the density of the carbon layer. Therefore, the higher the degree of graphitization of the carbon layer, the better the performance of blocking flammable gas release and heat transfer. The fitting curve of the Raman spectrum is shown in Figure 10. The degree of graphitization of the carbon layer is represented by the integrated intensity ratio of the D peak (1300 cm\(^{-1}\)) and the G peak (1580 cm\(^{-1}\)) \((I_D/I_G)\), and the higher the value of \(I_D/I_G\) the lower the degree of graphitization. \(^{34}\) From Figure 10A, the \(I_D/I_G\) values of TPU, CMSs 0.25, and CMSs-Fe0.25 are 3.33, 2.89, and 2.69, respectively. This shows that the synergistic use of APP and TPU, CMSs 0.25, and CMSs-Fe0.25 are 3.33, 2.89, and 2.69, respectively. This shows that the synergistic use of APP and CMSs can effectively improve the degree of graphitization of the carbon layer, which is due to the dehydration carbonization effect of APP. Also, the effect of CMSs-Fe is better than that of CMSs, which means that the addition of iron helps to improve the degree of graphitization of carbon residue.

3. CONCLUSIONS

In this paper, the effects of CMSs (CMSs-Fe) and APPs on the fire safety performance of TPU were tested by various measures. The contribution of CMSs (CMSs-Fe) to the flame retardant system was discussed with the sample containing only APP as the control. The further addition of CMSs increases the effect of APP on char formation, but it also weakens the thermal insulation of the carbon layer. Compared with TPU-APP, the pSPR, pHRR, CO, and CO\(_2\) of CMSs0.25 were all reduced, but THR, TSR, and mass loss were all increased. It is worth noting that the samples added to the CMSs-Fe performed better than the samples added to the CMSs. It can be seen from this that CMSs have certain defects, but its value is that the activated surface layer of CMS makes it easy to be modified. On the one hand, it can make up for the defects of CMSs; on the other hand, it acts as a resistance. The carrier of the burning component plays a greater role.

4. EXPERIMENTAL SECTION

4.1. Materials. TPU (Desmopan 9380A) was produced by Covestro, Germany. The basic properties of TPU are as follows: density, 1.11 g/cm\(^3\) (ISO 1183); hardness, 82A (ISO 868); tensile strength, 40 MPa (ISO 527-1, 527-3); elongation at break, 500% (ISO 527-1, 527-3). Analytical pure glucose was produced by Tianjin Beichen Fangzheng Reagent Factory. APP (2500 mesh) was produced by New Thin Metal and Chemical Co. Ltd., Guangzhou, China. Iron nitrate (Fe(NO\(_3\))\(_3\)) was produced by Qidong Mingcheng Chemical Co. Ltd., Jiangsu, China. N,N-Dimethylformamide (DMF) was produced by Aladdin Biochemical Technology Co. Ltd., Shanghai, China.

4.2. Sample Preparation. 4.2.1. Preparation of CMSs and CMSs-Fe. CMSs were produced by the hydrothermal method according to the literature. \(^{36}\) First, an aqueous solution of glucose having a concentration of 0.5 M was prepared, and then 300 mL was transferred to a hydrothermal reaction vessel having a capacity of 500 mL and heated at 180 °C for 12 h in an oven. After cooling, the resulting suspension was filtered, and the solid phase portion was retained. The solid-phase portion was washed with deionized water and absolute ethanol and washed once with DMF to obtain wet slurry CMSs.

Ten grams of freshly prepared CMSs was added into a 200 mL concentration of 0.4 mol/L Fe(NO\(_3\))\(_3\) solution, followed by stirring for 1 h. It was dispersed under ultrasonic waves for 15 min and allowed to stand for 5 h. After standing for 5 h, it was washed, filtered, and dried to obtain CMSs-Fe.

4.2.2. Preparation of TPU/CMSs and TPU/CMSs-Fe Composite Masterbatch. The TPU/CMSs composite masterbatch was prepared by the solution-blending method. TPU was dissolved in DMF (5 mL of DMF/1 g of TPU) at 80 °C for 2 h, then wet slurry CMSs (9 g of TPU/ 1 g of CMSs) were added to TPU solution. After vigorous mechanical stirring and ultrasonic shock at 80 °C for 3 h, the obtained black mixture was dried to a constant weight at 90 °C in a drying oven to obtain a masterbatch with a CMS mass ratio of 10%. \(^{37}\) The preparation method of TPU/CMSs-Fe composite masterbatch was the same as above.

4.2.3. Preparation of Flame Retardant TPU Composites. The TPU composite was prepared by the melt-blending method. Both TPU and APP were dried at 80 °C before use. A specific quality of TPU is first melted in an internal mixer of 180 ± 5 °C, and then a certain quantity of TPU (TPU/CMSs/Fe) composite masterbatch and APP were added. The mass ratio of TPU, TPU/CMSs (TPU/CMSs-Fe) composite masterbatch, and APP was changed to get different materials, and the proportion is shown in Table 3. The material from the mixer is processed through a flat vulcanizer at 180 ± 5 °C (with a size of 100 × 100 × 3 mm\(^3\)).

4.3. Measurements. 4.3.1. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDS). CMSs and char residue from CCT were observed by a JEOL JSM 6700 LV scanning electron microscope (SEM) (JEOL, Japan) and a JMS-700 energy-dispersive X-ray spectroscopy (EDS) (JEOL, Japan) at accelerating voltages of 5 and 8 kV.

4.3.2. X-ray Photoelectron Spectroscopy (XPS). The elemental composition and chemical state of CMSs and

![Figure 10](https://dx.doi.org/10.1021/acsomega.9b04462)
CMSs-Fe were studied by a XPS spectrometer (Thermo ESCALAB 250XI, Thermo Fisher Scientific, USA).

4.3.3. Cone Calorimeter Test (CCT). A cone calorimeter device (Fire Testing Technology, U.K.) was used to study the combustion behaviors of the samples. The CCT test was carried according to the ISO 5660-1 standard. Each sample in size of 100 × 100 × 3 mm³ and wrapped in aluminum foil, and CCT power is set to 35 kW/m². The test ends when the sample being tested is ammable. About 5 mg of sample was placed in a crucible and heated from 40 to 750°C (20 K/min, N₂, 60 mL/min). The pyrolysis gas components from the TG analyzer were then analyzed by an affinity-1 FTIR spectrometer (1705X) (Shimadzu, Japan).

4.3.4. Microscale Combustion Calorimeter (MCC). The flammability of TPU composites was further tested by a microscale combustion calorimeter (MCC-2, Goevmark Ltd., McHenry, Illinois, USA). About 5 mg of TPU composites was put in a crucible and heated from 75 to 750°C at a heating rate of 1 K/s. The total test time is 675 s.

4.3.5. Thermogravimetric Analysis/Infrared Spectrometry (TG-IR). A thermogravimetric analyzer (DT-50) (Setaram Instrumentation Co. Ltd., France) was used to test the thermal stability of TPU composites. About 10 mg of sample was placed in a crucible and heated from 40 to 750°C (20 K/min, N₂, 60 mL/min). The pyrolysis gas components from the TG analyzer were then analyzed by a FTIR spectrometer (6060i, J. A. Word Anal. Calorim.).

4.3.6. Raman Spectrometer. The graphitization degree of char residue after CCT was studied by Raman spectroscopy (Horiba Scientific Lab RAM HR Evolution, France). The laser wavelength is 514 nm during the test, and the wavelength range is 50–4000 cm⁻¹.

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Notes

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**Table 3. Formulations of TPU Composites**

| Sample Code | TPU (wt %) | APP (wt %) | CMSs (wt %) | CMSs-Fe (wt %) |
|-------------|------------|------------|-------------|----------------|
| TPU         | 100.0      | -          | -           | -              |
| TPU/APP     | 92.0       | 8.00       | -           | -              |
| CMSs0.125   | 92.0       | 7.875      | 0.125       | -              |
| CMSs0.25    | 92.0       | 7.750      | 0.250       | -              |
| CMSs0.50    | 92.0       | 7.500      | 0.500       | -              |
| CMSs-Fe0.125| 92.0       | 7.875      | -           | 0.125          |
| CMSs-Fe0.25 | 92.0       | 7.750      | -           | 0.250          |
| CMSs-Fe0.50 | 92.0       | 7.500      | -           | 0.500          |
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