



Investigating the Effect of Aluminum Diethylphosphinate on Thermal Stability, Flame Retardancy, and Mechanical Properties of Poly(butylene succinate)

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Poly(butylene succinate) is one of the most promising biodegradable polymers, but its applications are limited by poor flame retardancy. In this work, poly(butylene succinate)/diethylphosphinate (PBS/AIPi) composites were fabricated to investigate the effect of AIPi on their thermal stability, flame retardancy, and mechanical properties. It was found that the high content of AIPi decreased the thermal stability of PBS, and the decrease became stronger under the air atmosphere. When the content of AIPi reached 25wt%, the flame retardancy was improved with limited oxygen index (LOI) of 29.5%, V0 rating in UL-94 vertical burning test, and 49.3% reduction on the peak of heat release rate (PHRR) in cone calorimeter test. Meanwhile, the addition of AIPi could improve the mechanical properties of PBS with high tensile strength and Young's modulus, which was ascribed to the compatible effect of maleic anhydride-grafted poly(butylene succinate) (PBS-g-MA) with good filler dispersion and strong matrix-particles interaction. Thus, the AIPi was an effective flame retardant to PBS, so that PBS/AIPi composites displayed excellent flame retardancy without seriously sacrificing other comprehensive performances.

Keywords: poly(butylene succinate), diethylphosphinate, flame retardancy, polymer composites, comprehensive performances

INTRODUCTION

In the last decade, biodegradable polymers have drawn particular attention due to their advantages of biodegradability, good mechanical properties, easy processing, and chemical resistance (Chen et al., 2017; Chen Y. et al., 2019; Delamarche et al., 2020; He W. et al., 2020; Li et al., 2018; Xiong et al., 2019; Xu et al., 2019; Yang et al., 2020; Zhang et al., 2021; Zhang et al., 2020). As a typical representative, poly(butylene succinate) (PBS) has wide applications in the fields of biomedical materials, transport, construction, electrical industry, and packing materials (Bahrami et al., 2021; Hu et al., 2019; Li et al., 2020; Xue et al., 2019; Zhao et al., 2020). Unfortunately, PBS is flammable as common thermoplastics (Liu et al., 2016; Chen H. et al., 2019; Gu et al., 2019; Hu et al., 2019; He L. et al., 2020), which greatly

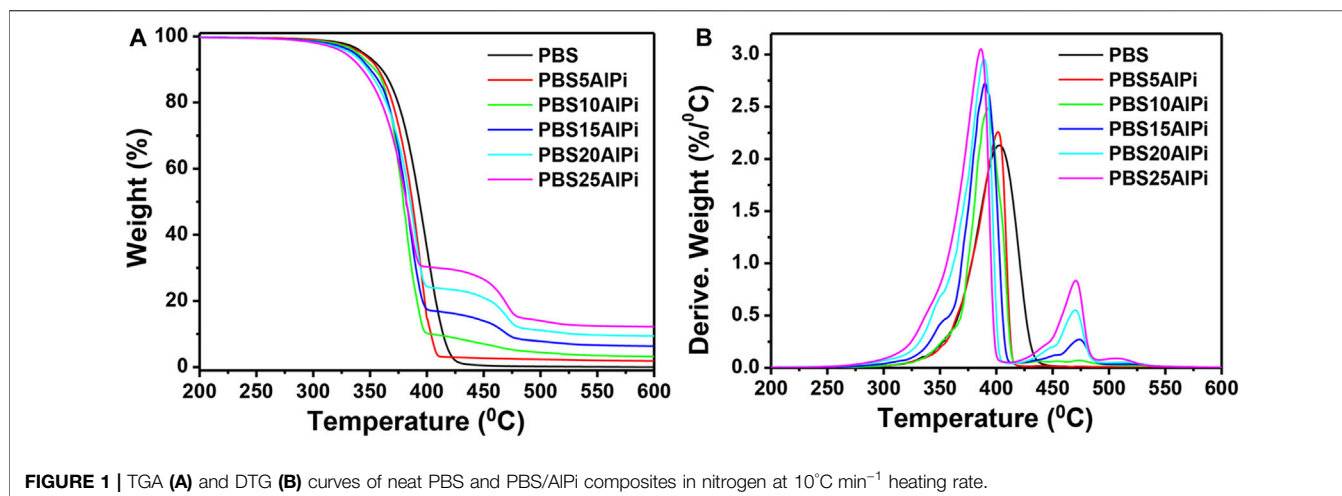


TABLE 1 | Thermal decomposition properties of neat PBS and PBS/AIPi composites in nitrogen.

Samples	$T_{5wt\%}$ (C)	$T_{10wt\%}$ (C)	T_{max1} (C)	T_{max2} (C)
PBS	343.5	358.1	403.2	–
PBS5AIPi	342.8	357.2	401.1	472.4
PBS10AIPi	338.8	354.1	392.6	472.2
PBS15AIPi	336.2	350.6	389.1	472.5
PBS20AIPi	333.1	347.9	388.5	472.4
PBS25AIPi	327.7	343.2	386.1	472.4

limits its application in some special fields with high flame retardancy requirements. Therefore, it is an urgent task to improve the flame retardancy of PBS to meet various applications.

To improve the flame retardancy of PBS, an easy and convenient way is to directly add flame retardants for preparing PBS composites (Wang et al., 2019; Yue et al., 2021) because it could meet the current machining technology for continuous production on a large scale. As typical flame retardants, ammonium polyphosphate (APP) and Mg(OH)₂ have been used in the PBS system. Hu et al. (Hu et al., 2020) have reported that when 30 wt% APP was added to PBS, the peak of heat release rate (PHRR) and total heat release (THR) decreased by 19 and 25%, respectively. Our previous work (Chen et al., 2016) has also confirmed that the least amount of Mg(OH)₂ was 40wt% in the PBS system to reach the V0 rating in the UL-94 vertical burning test. These results indicated that both of them are not high-efficiency flame retardants for PBS. Meanwhile, the processability and mechanical properties of the PBS matrix were seriously deteriorated due to the high addition amount of flame retardants. Consequently, it is still a challenge to improve the flame retardancy of PBS without seriously sacrificing other comprehensive performances.

Dialkylphosphinate salt belongs to a new class of additive-type phosphorus-containing flame retardants (Hou et al., 2021; Liu et al., 2014; Wang et al., 2015). The most important advantage of these salts is their high phosphorus content. Furthermore, they

are environmentally friendly flame retardants because no harmful and toxic substances are released during combustion. Especially, aluminum diethylphosphinate (AIPi) is one of the most commonly used dialkylphosphinate salts, which has been widely added to improve the flame retardancy of polyethylene (PE), polyamide 6 (PA6), polyurethane (PU), polybutylene terephthalate (PBT), and epoxy resin (EP) (Ma et al., 2019; Oliwa et al., 2020; Pan et al., 2020; Hu et al., 2021; Liu et al., 2021). It is acceptant that AIPi can not only play a flame retardant role in the condensed phase to promote the formation of polymer carbon but also remove high energy active free radicals in the combustion zone (Liu et al., 2021). However, to the best of our knowledge, the application of AIPi on biodegradable polymer systems was rarely reported.

In this study, AIPi was employed to modify biodegradable PBS, and maleic anhydride-grafted poly(butylene succinate) (PBS-g-MA) was used as their compatibilizer (Chen et al., 2015). The current research aimed to investigate the effect of AIPi on thermal stability, flame retardancy and mechanical properties of PBS composites. The thermal stability was investigated by thermogravimetric analysis (TGA) in nitrogen and air atmospheres, respectively. Furthermore, flame retardancy was evaluated by LOI, UL-94, and cone calorimeter tests. Meanwhile, the flame retardant mechanism was discussed by analyzing the action of AIPi on the gas phase and condensed phase. Finally, their mechanical properties were studied by tensile and impact tests.

EXPERIMENTAL SECTION

Materials

PBS (trade name GS PLA, Japan) was bought from Mitsubishi Chemical Corp. (Toyota, Japan). The melt flow index was 4.5 g/10 min at 190°C under 2.16 kg of weight. Aluminum diethylphosphinate (AIPi) was provided by Qingdao Fuslin Chemical Technology Co., Ltd. Maleic anhydride-grafted poly(butylene succinate) (PBS-g-MA) was synthesized via reactive melt-grafting process according to previous literature

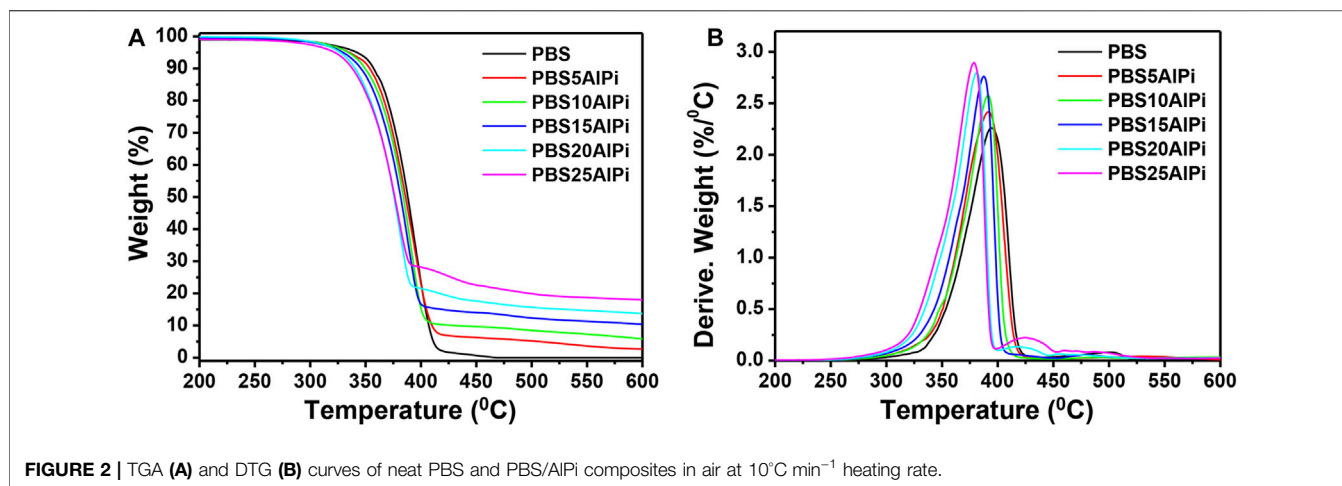


FIGURE 2 | TGA (A) and DTG (B) curves of neat PBS and PBS/AIPi composites in air at $10^{\circ}\text{C min}^{-1}$ heating rate.

TABLE 2 | Thermal decomposition properties of neat PBS and PBS/AIPi composites in air.

Samples	$T_{5\text{wt}\%}$ (C)	$T_{10\text{wt}\%}$ (C)	$T_{\text{max}1}$ (C)	$T_{\text{max}2}$ (C)
PBS	340.9	356.6	394.6	–
PBS5AIPi	334.8	353.7	392.1	427.0
PBS10AIPi	333.5	349.4	391.6	427.2
PBS15AIPi	329.6	345.8	387.3	427.2
PBS20AIPi	326.8	341.1	382.2	427.2
PBS25AIPi	322.3	337.9	379.4	427.3

(Phua et al., 2013b). The ratio of PBS, maleic anhydride, and dicumyl peroxide (DCP) was 100/10/1.5 by weight, and the grafting degree of MA onto PBS (G_d) was 4.2 wt%.

Preparation of PBS/AIPi Composites

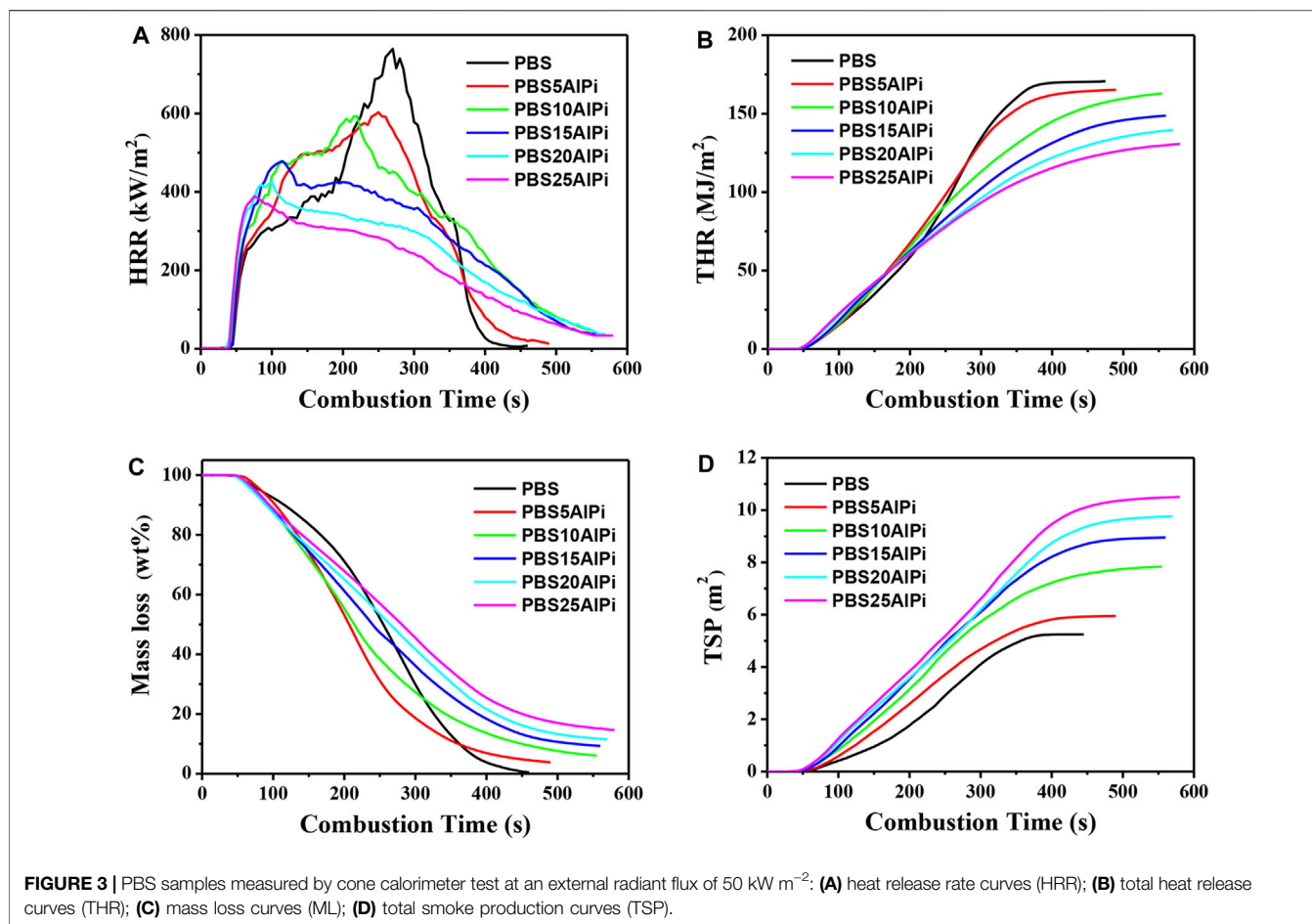
PBS/AIPi composites were prepared by melt compounding in a HAAKE batch intensive mixer (HAAKE Rheomix 600, Karlsruhe, Germany) at 135°C with a rotor speed of 80 rpm; the mixing time was 6 min for each sample. The content of PBS-g-MA (as a compatibilizer) was kept as 15 wt% in all PBS composites, and the content of AIPi was changed from 5 to 25 wt%. For convenience, the obtained samples were designated as PBSx AIPi. Here, x denotes the weight percentage of AIPi in the PBS composites.

Characterization

Thermogravimetric analysis (TGA) was performed on a TA STD Q600 thermal analyzer. The PBS samples with mass 8.0 ± 0.2 mg were heated from room temperature to 600°C at $10^{\circ}\text{C min}^{-1}$ under nitrogen and air atmosphere, respectively. The limited oxygen index (LOI) was tested on a JF-3 oxygen index meter (Jiangning, China) with sheet dimensions of $130 \times 6.5 \times 3.2$ mm³, according to ISO4589-1984. The vertical burning testing was carried out according to the UL-94 (ANSI/ASTMD635-77) with sheet dimensions of $125 \times 12.7 \times 3.2$ mm³. Cone calorimeter testing (icone, FTT, United Kingdom) was conducted according to ISO 5660-1. The sample dimension was $100 \times 100 \times 6$ mm³; it was backed by aluminum foil and irradiated at a heat flux of 50 kW m^{-2} . The photographs of residual chars after cone calorimeter testing were collected by a digital camera. The dispersion of AIPi in PBS matrix was examined with the scanning electron microscope (XL30 FESEM FEG, FEI Co.). The samples were fractured in liquid nitrogen, and the fracture surfaces were coated with gold before SEM observation. Uniaxial tensile tests were performed at room temperature with an Instron 1,121 testing machine (Canton, MA). Specimens were compression-molded into sheets with 1 mm thickness, then cut into a dumbbell shape with gauge dimensions of $20 \text{ mm} \times 4 \text{ mm} \times 1 \text{ mm}$. The measurements were conducted at a crosshead speed of 20 mm min^{-1} . At least five runs for each sample were measured and averaged.

TABLE 3 | Combustion parameters of PBS samples from LOI, UL-94 and cone calorimeter tests.

Samples	LOI (%)	UL-94 (3.2 mm)	Dripping (Yes or No)	t_{ign} (s)	PHRR (kW m^{-2})	THR (MJ m^{-2})	Residual char (wt%)	TSP (m^3)
PBS	21.0 ± 0.3	NR	Yes	48 ± 1	765 ± 11	170 ± 4	0.1 ± 0.1	5.2 ± 0.2
PBS5AIPi	22.8 ± 0.2	NR	No	47 ± 1	606 ± 16	166 ± 3	0.9 ± 0.1	6.0 ± 0.3
PBS10AIPi	23.7 ± 0.3	NR	No	44 ± 2	591 ± 15	163 ± 9	3.0 ± 0.2	7.9 ± 0.3
PBS15AIPi	24.9 ± 0.3	NR	No	42 ± 2	478 ± 16	149 ± 5	4.9 ± 0.1	9.1 ± 0.5
PBS20AIPi	27.1 ± 0.4	V1	No	41 ± 2	423 ± 12	139 ± 3	7.1 ± 0.3	9.8 ± 0.5
PBS25AIPi	29.5 ± 0.4	V0	No	41 ± 2	388 ± 10	131 ± 7	11.7 ± 0.2	10.5 ± 0.6



RESULTS AND DISCUSSION

Thermal Stability of PBS/AlPi Composites

The influence of AlPi on the thermal stability of PBS under nitrogen was investigated by TGA, which reflects the thermal degradation behavior of materials with the increase of temperature (Wang et al., 2020b; Xu D. et al., 2021). As shown in **Figure 1A**, with the increase of AlPi content, the TGA curves slowly shifted to a low-temperature range. The temperatures corresponding to 5 and 10 wt% weight loss ($T_{5\text{wt}\%}$ and $T_{10\text{wt}\%}$) are essential to evaluate the thermal decomposition of polymers on the onset stage. For PBS5AlPi, $T_{5\text{wt}\%}$ and $T_{10\text{wt}\%}$ decreased less than 1°C in comparison with that of neat PBS, indicating that the addition of AlPi with low content has a small impact on the thermal stability of PBS. However, the reduction in thermal stability gradually became larger with high content fillers (**Table 1**). For example, $T_{5\text{wt}\%}$ and $T_{10\text{wt}\%}$ of PBS25AlPi decreased to 15.8 and 14.9°C , respectively. Meanwhile, with the increase of the AlPi loading, **Figure 1B** exhibited a gradual decrease for $T_{\text{max}1}$, corresponding to the maximum weight loss rate of the polymer. Herein, the decrease on $T_{5\text{wt}\%}$, $T_{10\text{wt}\%}$, and $T_{\text{max}1}$ was ascribed to the thermal degradation of PBS during melt

compounding because the increase in viscosity with high content of inorganic fillers could result in the sharp rise of temperature under high shear force, promoting the thermal degradation polymer (Fong et al., 2021). In addition, another characteristic peak was present at approximately 472°C (denoted as $T_{\text{max}2}$ in **Table 1**), which should be assigned to the thermal decomposition of AlPi.

The thermal stability of PBS/AlPi composites under air was also evaluated, which is more important because the melt processing of polymer materials is usually performed in an air atmosphere. As shown in **Figure 2A** and **Table 2**, $T_{5\text{wt}\%}$, $T_{10\text{wt}\%}$, and $T_{\text{max}1}$ exhibited a similar trend to the situation of nitrogen, but the values were relatively smaller owing to the oxidation degradation (Wen et al., 2011). Furthermore, as shown in **Figure 2B**, $T_{\text{max}2}$ appeared at approximately 427°C (45°C lower than that in nitrogen), and the intensity of peaks became much weaker. It is suggested that part of AlPi gradually degraded before $T_{\text{max}2}$, which is accompanied by the degradation of PBS chains. Based on these results, the content of AlPi could influence the thermal stability of PBS/AlPi composites, and the decrease in thermal stability became stronger under air atmosphere at higher AlPi loadings.

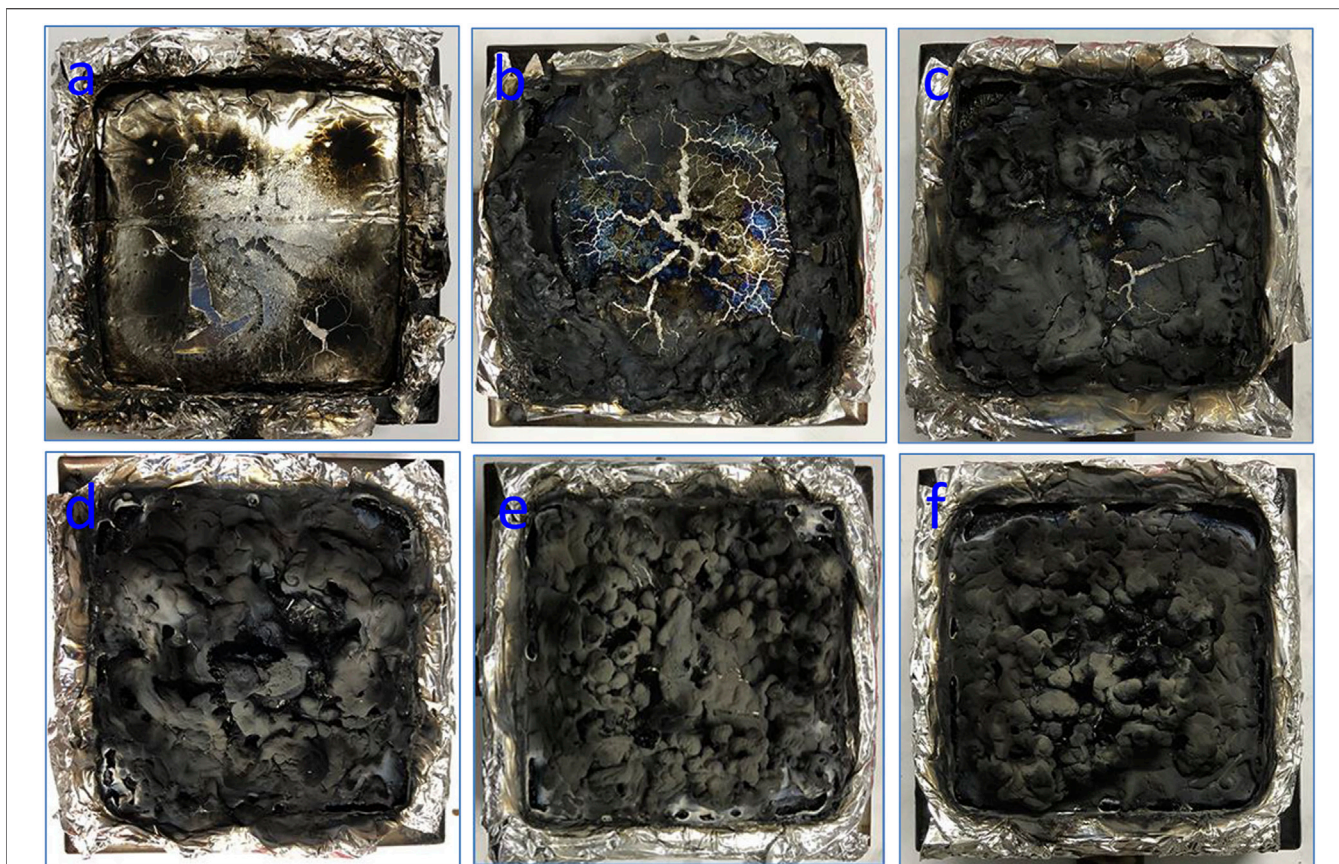


FIGURE 4 | Photographs of the residues after the cone calorimeter test from (A) neat PBS, (B) PBS5AlPi, (C) PBS10AlPi, (D) PBS15AlPi, (E) PBS20AlPi, and (F) PBS25AlPi.

Flammability Properties of PBS Composites

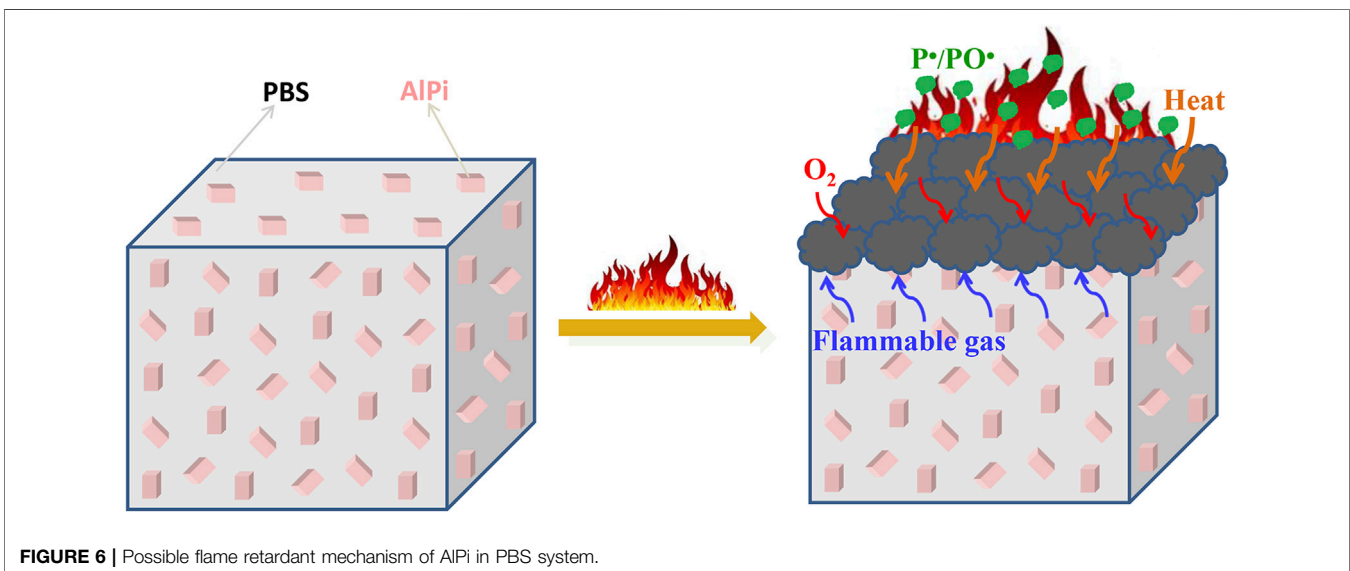
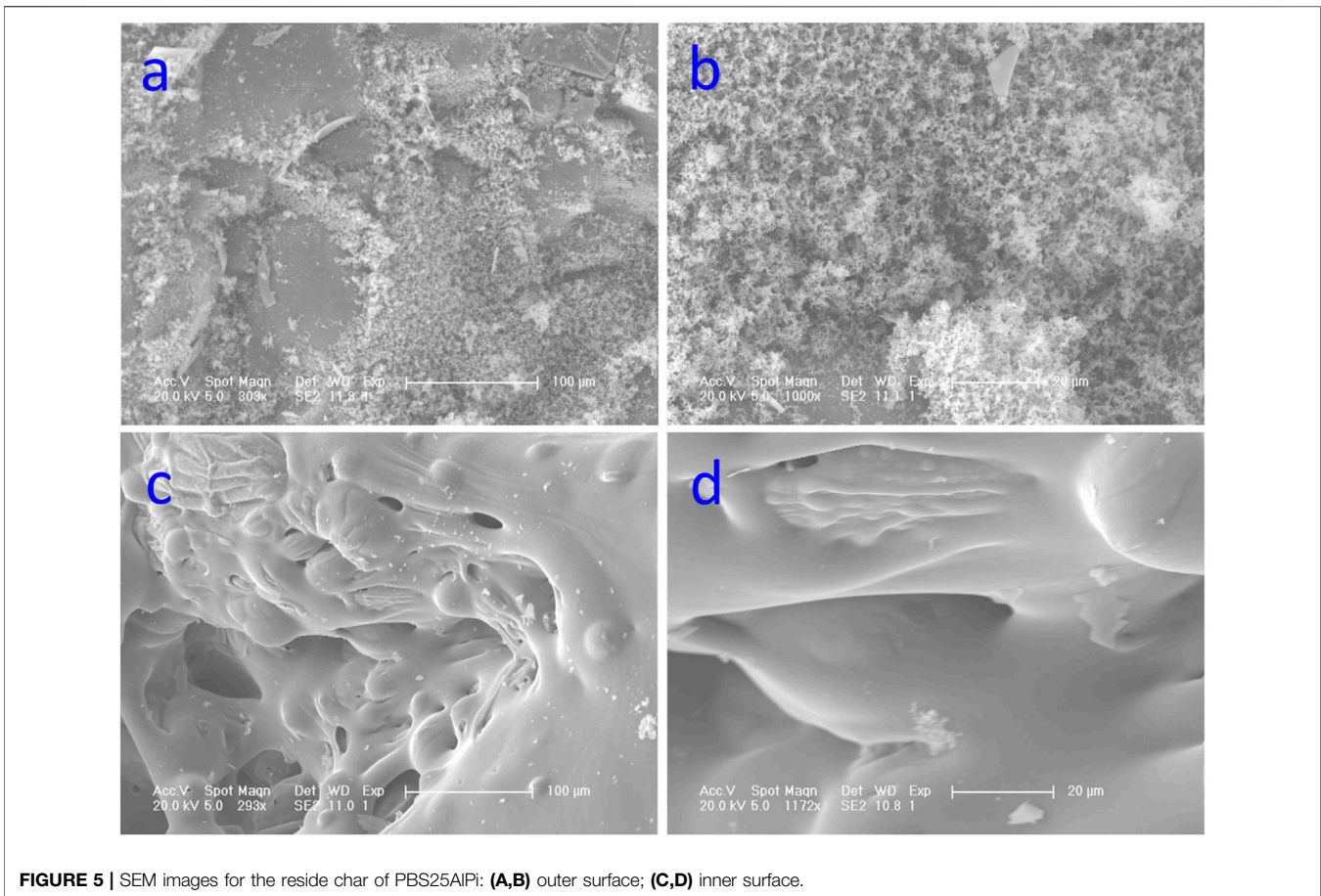
The effect of AlPi on the flame retardancy of PBS matrix was investigated by LOI and UL-94 tests. As listed in **Table 3**, the LOI values gradually increased with the addition of AlPi content, of which the highest value corresponding to PBS25AlPi could achieve 29.5. Moreover, only when the content of AlPi was 20wt%, the UL-94 rating reached V1. With further increasing the AlPi to 25wt%, the UL-94 rating could pass V0. Besides the flame retardant effect, AlPi displayed a positive effect on the inhibition of dripping. For all PBS/AlPi composites, there was no melt dripping, indicating that AlPi was an effective dripping inhibitor for PBS matrix.

Further, the flame retardancy of PBS/AlPi composites was investigated by cone calorimeter testing, which is useful to provide various important information about fire risk during combustion (Zanetti et al., 2002; Wang et al., 2020a; Xue et al., 2020b; Xu et al., 2020), such as time to ignition (TTI), heat and smoke release, and mass loss. First, heat release rates (HRR) and combustion time curves for PBS samples are shown in **Figure 3A**, and detailed parameters are listed in **Table 3**. With the increase of AlPi loading in the PBS system, the ignition time (t_{ign}) became shorter, implying that the PBS/AlPi composites were easier to be ignited than neat PBS. However, a gradual decrease for the peaks of HRR (PHRRs) was present. For instance, the PHRR for

PBS25AlPi was reduced to 388 kW/m^2 , which was reduced by 49.3% compared to that for neat PBS (765 kW m^{-2}). Further, **Figure 3B** shows the curves of total heat release (THR). It is significant that the slope flattened out at the latter half of combustion time, and the final THR value became smaller to a certain extent. These results suggest that AlPi is an effective flame retardant for reducing PHRR and THR.

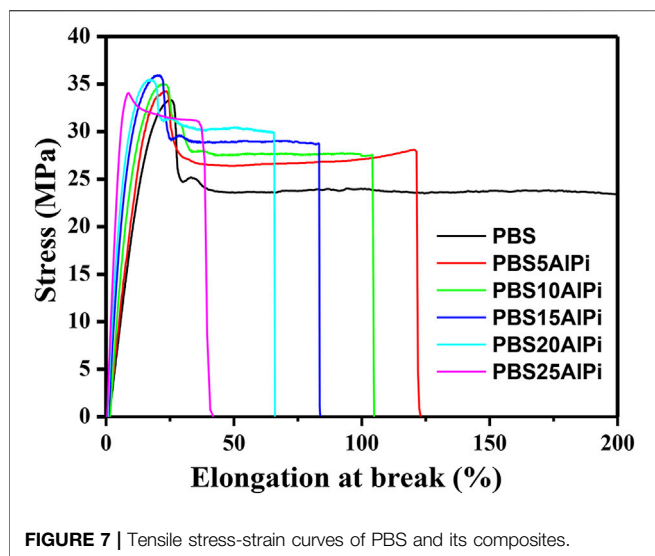
Figure 3C shows the normalized mass loss (ML) curves of PBS samples with combustion time. All PBS/AlPi composites exhibited similar curves, but the slope became smaller with more AlPi fillers, indicating that AlPi as flame retardant could delay the combustion of PBS. Meanwhile, the residual char gradually increased with the increase of AlPi content. Furthermore, the total smoke production (TSP) was evaluated. As shown in **Figure 3D**, the TSP increased with the addition of AlPi (detailed data are listed in **Table 3**). The increase in TSP should be related to the radical trapping effect in the gas phase. The decomposition of AlPi could produce $\text{P}\bullet$ and $\text{PO}\bullet$ radicals (Tang et al., 2020), which could quench $\text{H}\bullet$ and $\text{HO}\bullet$ radicals so that some derived products were generated as smoke particles.

Besides the trapping radicals in the gas phase, AlPi also contributed to the condensed phase through char formation. As shown in **Figure 4A**, neat PBS was typical no-char polymers (burned completely without residual char). With the increase of



AlPi concentration, the char amount increased and the carbon layer became thicker. It is clear that the cracks gradually became smaller until they disappeared (**Figures 4B–F**). To further

evaluate the microstructure, SEM observation was carried out for the char from PBS25AlPi. Interestingly, the char morphologies from the outer surface and inner surface were



different. As shown in **Figures 5A,B**, the outer surface was covered by flocculent porous carbon, which may come from the deposition of P•/PO•-derived solid products. However, the inner surface was compact and cohesive with high supporting strength (**Figures 5C,D**). It was a whole bulk with some cavities, which may result from the release of flammable gases into the gas phase zone.

Based on the above analysis, a possible enhancement mechanism of AlPi in the PBS system was proposed in **Figure 6**. It is reported that AlPi could be thermally decomposed to oligomers of phosphinates, diethylphosphinic acid, and aluminum phosphate (Kaya and Hacaloglu, 2014; Vothi et al., 2020). On the one hand, oligomers of phosphinates and diethylphosphinic acid can further be decomposed to P• and PO• radicals in the gas phase, which could quench H• and HO• radicals in the combustion zone, and some derived solid products were generated as the char of outer layer. On the other hand, aluminum phosphate could construct continuous and compact char as the inner layer. The combined char layer can effectively reduce the heat and mass transfer rate and protect the underlying material from burning (Xu Y.-J. et al., 2021). As a result, the improvements on flame retardancy with LOI of 29.5%, V0 in UL-94, and 49.3% reduction on PHRR were presented. In brief, the enhanced flame retardancy of PBS was attributed to the gas–solid flame retardancy mechanism of AlPi.

Mechanical Properties of PBS Composites

The effect of AlPi on the mechanical properties of PBS was investigated by tensile testing. **Figure 7** shows the stress-strain curves of neat PBS and PBS/AlPi composites. The detailed data for Young's modulus, tensile strength, and elongation at break are listed in **Table 4**. With the increase of AlPi loading, Young's modulus gradually increased due to the reinforcing effect of AlPi as rigid inorganic particles. The tensile strength firstly increased and then decreased with the increase of AlPi content. For PBS15AlPi, it exhibited the highest value of tensile strength of 35.8 MPa. However, the tensile strengths for all PBS composites were higher than that of neat PBS, which should be ascribed to good compatibility between PBS matrix and AlPi particles. In addition, the elongation at break showed a decreased trend with the addition of AlPi loading, indicating a decreased ductility of the PBS matrix. Similarly, the impact strengths of PBS composites also decreased gradually with the increase of AlPi content (**Table 4**).

In polymer/filler composites, the dispersion of fillers and interfacial interaction between two components are the most important factors to determine the final mechanical properties (Sun et al., 2017; Wen et al., 2020b; Xue et al., 2020a; Yang et al., 2019). As shown in **Figures 8A–F**, the fracture surface morphologies of PBS samples were investigated by SEM. It was apparent that AlPi particles were uniformly distributed in the PBS matrix, and no big aggregates were detected. Further, AlPi particles were firmly adhered to the PBS matrix, indicating their strong interfacial interaction (Wen et al., 2020a; Wen et al., 2012). Even for PBS25AlPi with the highest AlPi content, most AlPi particles still exhibited good dispersion without big aggregates, and no debonding cavities were present (blue circles in **Figure 8F**). In our PBS/AlPi system, 15 wt% PBS-*g*-MA was added as a compatibilizer, which was helpful to improve the dispersion of fillers and the matrix-particles interaction (Phua et al., 2013a; Chen et al., 2015). As a result, our PBS/AlPi composites exhibited good mechanical properties with high tensile strength and Young's modulus.

CONCLUSION

PBS/AlPi composites were prepared by melt compounding with PBS-*g*-MA as a compatibilizer, and the effect of AlPi content on thermal stability, flame retardancy, and mechanical properties was investigated. The TGA results indicated high content of AlPi

TABLE 4 | Mechanical properties of PBS samples from tensile and impact tests.

Samples	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ m ⁻²)
PBS	325 ± 26	33.2 ± 0.9	403 ± 22	8.7 ± 0.7
PBS5AlPi	340 ± 34	34.2 ± 0.8	122 ± 12	8.0 ± 0.5
PBS10AlPi	396 ± 45	34.9 ± 0.8	104 ± 10	7.5 ± 0.6
PBS15AlPi	450 ± 68	35.8 ± 1.1	83 ± 10	7.2 ± 0.5
PBS20AlPi	494 ± 58	35.4 ± 1.2	65 ± 9	6.4 ± 0.6
PBS25AlPi	560 ± 84	34.4 ± 1.0	41 ± 6	5.6 ± 0.5

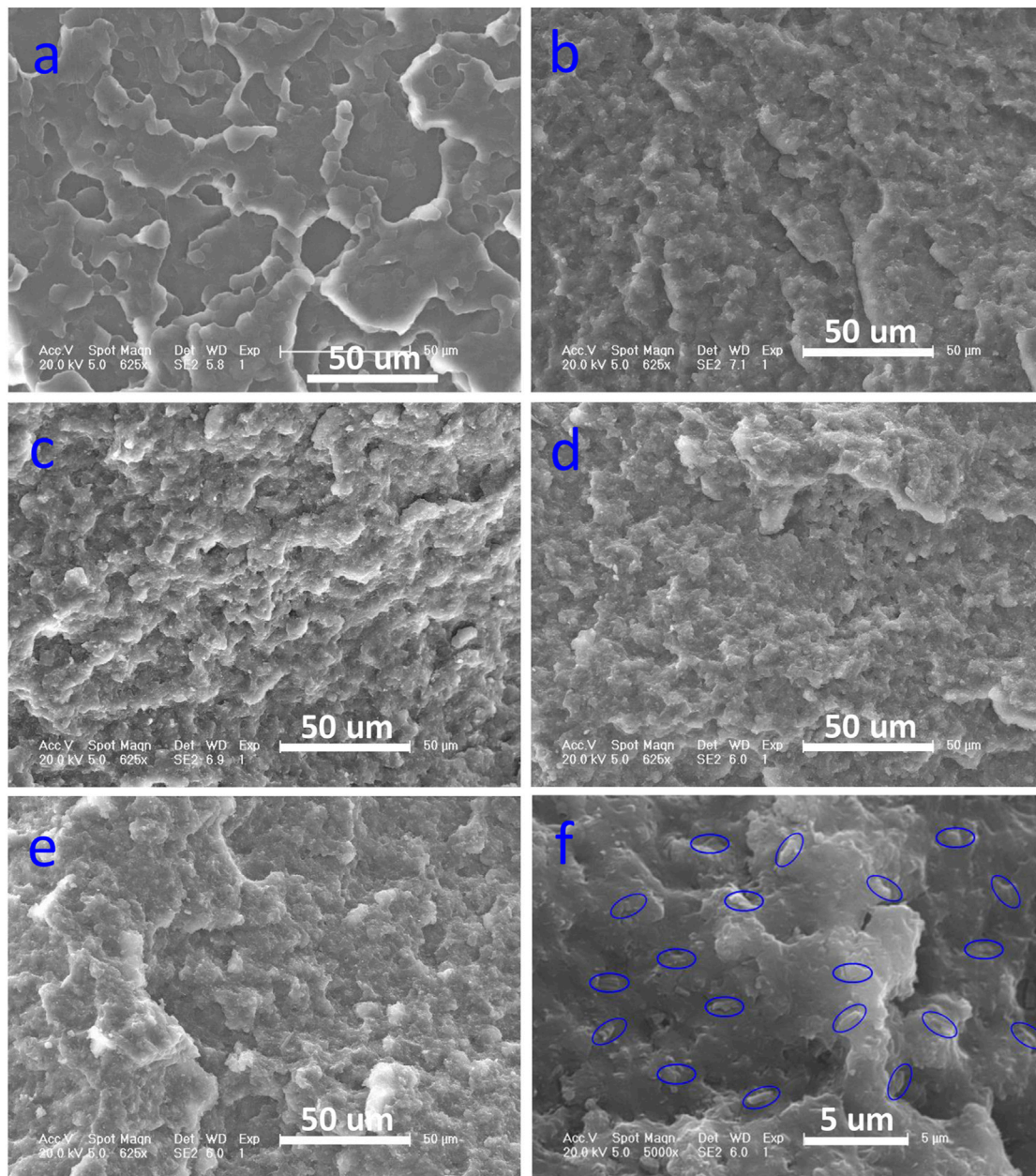


FIGURE 8 | SEM micrographs of the brittle-fractured surface of PBS samples: **(A)** neat PBS, **(B)** PBS5AlPi, **(C)** PBS10AlPi, **(D)** PBS15AlPi, **(E)** PBS20AlPi, and **(F)** PBS25AlPi.

decreased the thermal stability of PBS, and the decrease became stronger under air atmosphere. Further, the flame retardancy of PBS/AlPi composites was also determined by the AlPi content. For PBS25AlPi, the improved flame retardancy with LOI of 29.5%, V0 rating in UL-94 test, and 49.3% reduction on PHRR was presented. The enhancement was attributed to the gas–solid flame retardancy mechanism of AlPi. In addition, the

PBS/AlPi composites displayed good mechanical properties with high tensile strength and Young's modulus, which was contributed to the compatible effect of PBS-g-MA. This work indicates that AlPi was an effective flame retardant to PBS, but more work is still necessary to decrease the amount of AlPi addition and further balance the comprehensive performances of PBS composites.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary files; further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

YW executed the experiment and wrote the manuscript. DJ, XW, and TT conceived and designed the experiment plan. KaS, KS,

KW, and EM revised the manuscript and analyzed the experimental results.

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