

Thermal Degradation, Flame Retardance and Mechanical Properties of Thermoplastic Polyurethane Composites Based on Aluminum Hypophosphite*

Shou-song Xiao, Ming-jun Chen, Liang-ping Dong, Cong Deng^{**}, Li Chen and Yu-zhong Wang^{a**}
Center for Degradable and Flame-Retardant Polymeric Materials, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), College of Chemistry, Analytical and Testing Center, Sichuan University, Chengdu 610064, China

Abstract Aluminum hypophosphite (AP) was used to prepare flame-retarded thermoplastic polyurethane (FR-TPU) composites, and their flame retardancy, thermal degradation and mechanical properties were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis (TGA), cone calorimeter (CC) test, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and tensile test. TPU containing 30 wt% of AP could reach a V-0 rating in the UL-94 test, and its LOI value was 30.2. TGA tests revealed that AP enhanced the formation of residual chars at high temperatures, and slightly affected the thermal stability of TPU at high temperatures. The combustion tests indicated that AP affected the burning behavior of TPU. The peak of heat release rate (PHRR), total heat release (THR) and mass loss rate (MLR) greatly reduced due to the incorporation of AP. The tensile test results showed that both the tensile strength and the elongation at break slightly decreased with the addition of AP. The digital photos and SEM micrographs testified that AP facilitated the formation of more compact intumescent char layer. Based on these results mentioned above, the flame-retarding mechanism of AP was discussed. Both the self-charring during the decomposing process of AP and its facilitation to the charring of TPU led to the great improvement in the flame retardancy of TPU.

Keywords: Thermoplastic polyurethane; Aluminium hypophosphite; Flame retardance; Thermal degradation; Mechanical property.

INTRODUCTION

Thermoplastic polyurethane (TPU) is widely applied in the plastic field for its outstanding properties, such as high tensility, excellent low temperature flexibility, outstanding wear, abrasion resistance, *et al.*^[1–3] However, its applications in many fields are greatly limited due to its flammability and melt-dripping during combustion^[4–5]. Therefore, it is necessary to endow TPU with good flame retardancy to extend its applications.

Chen *et al.*^[6] have summarized that various flame retardants can be used to promote the thermal stability and flame retardance of TPU, mainly including halogen-containing and halogen-free flame retardants. Generally, the halogen-containing flame retardants are highly efficient to improve the flame retardancy of polymers. Levchik *et al.*^[7] detailedly introduced their applications in modifying the flame retardancy of TPU. However, the halogen-containing flame retardants are being phased out for their proven or suspected adverse effects on the environment^[8–10]. Now most attentions have focused on exploring plentiful halogen-free flame retardants to

* This work was financially supported by the National Natural Science Foundation of China (Nos. 50933005 and 51121001) and the Program for Changjiang Scholars and Innovative Research Teams in Universities of China (IRT 1026).

** Corresponding authors: Yu-zhong Wang (王玉忠), E-mail: yzwang@scu.edu.cn

Cong Deng (邓聪), E-mail: dengcong@scu.edu.cn

Received May 13, 2013; Revised June 24, 2013; Accepted June 27, 2013

doi: 10.1007/s10118-014-1378-0

enhance the flame retardancy of polymers, such as mineral flame retardants, phosphorus-based flame retardants and nitrogen-based flame retardants, *etc.* The use of mineral flame retardants has been reported to improve the flame retardancy of TPU. Pinto *et al.*^[11] found that TPU composites with 70 phr of aluminium hydroxide (ATH) had good flame retardancy, and its rating reached a V-0 in UL-94 test. However, the loading of this category of flame retardancy should be very high for achieving the excellent flame retardancy of polymers. Generally its loading is beyond 50 wt%, which is prone to lead the severe deterioration of the mechanical properties of polymer matrix^[12, 13]. Nitrogen-containing and phosphorus-containing flame retardants also presented great effects on the flame retardancy and mechanical properties of polymers^[14–18]. Chen *et al.*^[19] reported that the microencapsulation of APP led to the increase in flame retardance for TPU. Bourbigot *et al.*^[20] found that polyhedral oligomeric silsesquioxanes greatly improved the fire retardance of TPU. Lin *et al.*^[14] reported that the IFR (CFA/APP) led to the tensile strength of TPU deteriorated greatly, which decreased from 38.7 MPa for neat TPU to 9.2 for FR-TPU. Until now, much progress have been made to promote the flame retardancy of TPU using nitrogen-containing or phosphorus-containing flame retardants^[6, 21, 22].

In past researches, the reports concerning the effect of flame retardant on the mechanical properties of TPU showed that its mechanical properties were greatly damaged by the incorporation of flame retardants. Chattopadhyay *et al.*^[8] explained that the leading reason for the decreases was that the compositions were too complicated in polyurethane, including the urethane group, isocyanates, polyol, urea, ester, ether, aromatic, *etc.* The formed large number of hydrogen bonds among these compositions were sensitive to the added flame retardants^[23, 24], finally resulting in the deterioration of mechanical properties of TPU. Therefore, it is urgent to develop novel flame retardants which do not greatly damage mechanical properties of the polymer matrix. Meanwhile, their high flame-retarded efficiencies can also militate in polymer matrix. At present, almost all the traditional flame retardants cannot fulfill the two requirements mentioned above. In this study aluminum hypophosphite (AP)^[13, 25] was used to prepare the FR-TPU. The results showed that AP endowed TPU with good flame-retarded performances, and exhibited only a little negative influences on the mechanical properties and thermal stability of TPU.

EXPERIMENTAL

Materials

Thermoplastic polyurethane (TPU 585) was purchased from BASF (Germany). AP was provided by Weili Flame Retardant Chemicals Industrial Co. Ltd., Chengdu, China.

Sample Preparation

Both TPU and AP were dried in an oven at 80 °C for 10 h, and then TPU blended with different ratios of AP were extruded by a twin-screw extruder (CET 20, Kebeilong Keya, China) at the following temperature profile: 165, 175, 185, 170, 160 and 145 °C from the feed zone to the die. The obtained extrudates were cut into pellets, and then the samples for combustion and mechanical tests were molded by compression molding at 200 °C. Here, it should be noted that the following TPU/AP25, TPU/AP30 and TPU/AP35 represents that the contents of AP are 25, 30 and 35 wt% in the composites, respectively.

Measurements

The flame retardancy and flammability were determined by LOI tests (JF-3 oxygen index meter, Jiangning, China; using specimen dimensions of 130 mm × 6.5 mm × 3 mm according to ASTM D2863-97), UL-94 measurements (CZF-2-type, Jiangning, China; using specimen dimensions of 130 mm × 13 mm × 3 mm according to ASTM D3801) and cone calorimeter tests (FTT cone calorimeter; square specimens with dimensions of 100 mm × 100 mm × 3 mm were irradiated at a heat flux of 35 kW/m² according to ISO 5660 standard procedures without the use of the “frame and grid”).

Tensile test results were obtained by universal experimental machine (CMT2000, SANS Inc., China) in accordance with the procedures described in GB/T 1040-1992 under an extension speed of 10 mm/min at room temperature. The tensile specimens were dumbbells with the sizes of 160 mm × 10 mm (the breadth of cabined

section) $\times$ 4 mm, and the lengths of these cabined sections were 100 mm. Some residues collected from the cone tests were further analyzed by SEM. The SEM observations were performed by a scanning electron microscope (XL-3, Philips, Netherlands) at an accelerating voltage of 20 kV. All specimens were coated with a conductive layer before being examined.

Thermogravimetric analysis (TGA) was used to investigate the decomposing behaviors of various TPU samples using a TG thermogravimetric analyzer instrument (209 F1, NETZSCH, Germany) at a heating rate of 10 K/min under N₂ flow of 50 mL/min. The specimens (about 4–6 mg) were heated from 40 °C to 700 °C.

Fourier transform infrared (FTIR) spectra were recorded using a spectrometer (MAGNA-IR 750, Nicolet Instrument Co., USA). The sample powders of residual chars were obtained from TG tests.

X-ray photoelectron spectroscopy (XPS) spectra were recorded by an XSAM80 (Kratos Co, UK), using Al K α excitation radiation (hv-1486.6 eV).

RESULTS AND DISCUSSION

Flame Retardance

The LOI and UL-94 results of neat TPU and FR-TPU are presents in Table 1. It can be seen that neat TPU has no rating in UL-94 tests and a low LOI value of 23.5. In addition, serious melt-dripping was observed after being ignited in vertical burning test. The LOI value increases with increasing the AP content, and then it reaches a maximum LOI of 30.2 at 30 wt% of AP. Meanwhile, the corresponding UL-94 rating is V-0. Figure 1 shows the digital photos of the samples obtained from the LOI tests. Obviously, neat TPU has no char left after the combustion. However, all the TPU samples containing AP have residual chars, and the residue increases with the addition of more AP. According to these results, it can be concluded that the flame retardancy of TPU can be improved by the incorporation of AP.

Table 1. The results of the LOI test and UL-94 tests

TPU (wt%)	AP (wt%)	LOI (%)	UL-94
100	0	23.5	N.R.
75	25	28.2	V-2
70	30	30.2	V-0
65	35	29.6	V-0



Fig. 1 Digital photos of the residual chars for neat TPU and TPU/AP systems after the LOI tests

Cone Calorimetric Analysis

At present, CC measurement is widely used to assess the fire behavior of materials in real accident^[26]. In this study, it was employed to evaluate the flame retardancy of neat TPU and TPU/AP systems. All the curves of heat release rate (HRR), total heat release (THR), mass loss (ML) and the peak of HRR are presented in Fig. 2, and their corresponding quantitative data and the time to ignition (TTI) are listed in Table 2.

It can be seen that the THR, PHRR, TTI and ML rate (MLR) of TPU obviously decrease with the incorporation of AP, while the residual char significantly increases. For neat TPU, the values of the THR, PHRR, TTI and MLR are 70.6 MJ/m², 508.1 kW/m², 47 s and 0.09 g/s, respectively. With increasing the AP content up to 25 wt%, these values are 63.4 MJ/m², 349.3 kW/m², 35 s and 0.05 g/s, correspondingly. When the concentration of AP further increases to 30 wt%, these values further go down. Compared with neat TPU, the

THR, PHRR, TTI and MLR at the loading of 30 wt% of AP are reduced by 13%, 39%, 67% and 56%, respectively. For char residue, it greatly increases to 37.0 wt% at the loading of 30 wt% of AP from 9.3 wt% for neat TPU. Generally, the increase of residual chars is regarded as an important factor to improve the flame retardancy. A well-known flame-retarded protection mechanism has been interpreted by Vandersal *et al.*^[27] In which the most important point is that during the combustion process the formation of a thermal barrier (charring) at the surface of the condensed phase can block the release of gaseous fuel, and can also prevent the transfer of heat back to the burning polymer. In terms of TPU systems, the more chars resulting from the incorporation of AP as a physical barrier could reduce the transfer of matter such as combustible volatile gases and oxygen. As a result, the amount of decomposition gases produced significantly decreased. Moreover, the fuel gases could be physically separated from the oxygen, which prevented the combustion process being sustained, finally leading the improvement of the flame retardance of TPU.

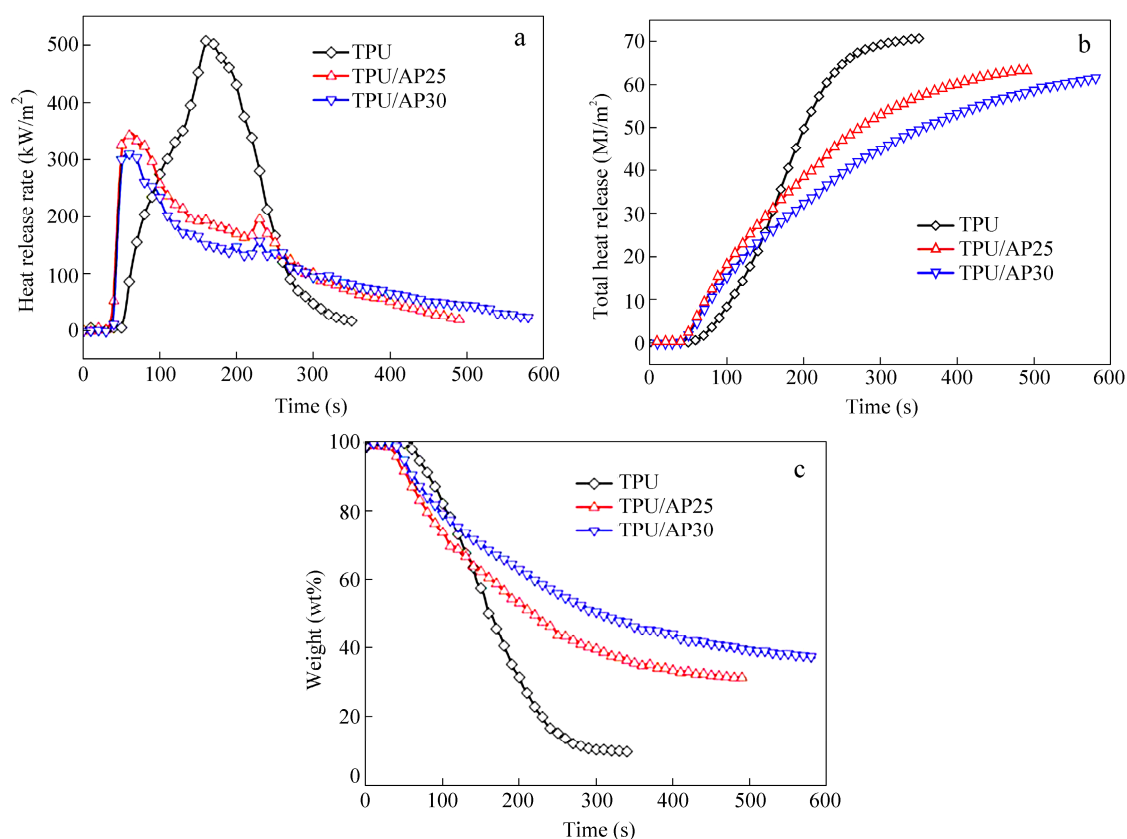


Fig. 2 The HRR(a), THR(b) and ML(c) curves of TPU and TPU/AP systems in cone calorimeter tests

Table 2. CC test results of TPU and TPU/AP systems

	Sample		
	TPU	TPU/AP25	TPU/AP30
THR (MJ/m ²)	70.6	63.4	61.64
PHRR (kW/m ²)	508.1	349.3	311.06
TTI (s)	47	35	33
MLR (g/s)	0.09	0.05	0.04
Residual char (wt%)	9.3	31.2	36.9

The digital photographs of TPU and TPU/AP residues obtained from CC tests are shown in Fig. 3. It is clear that there are a small amount of residues left for neat TPU, and the formed char layer is very loose; while the residues of FR-TPU are more compact than those of neat TPU. The SEM micrographs of the formed chars in CC tests are presented in Fig. 4. Figure 4(a) shows that the formed chars at the outer surface are very loose for neat

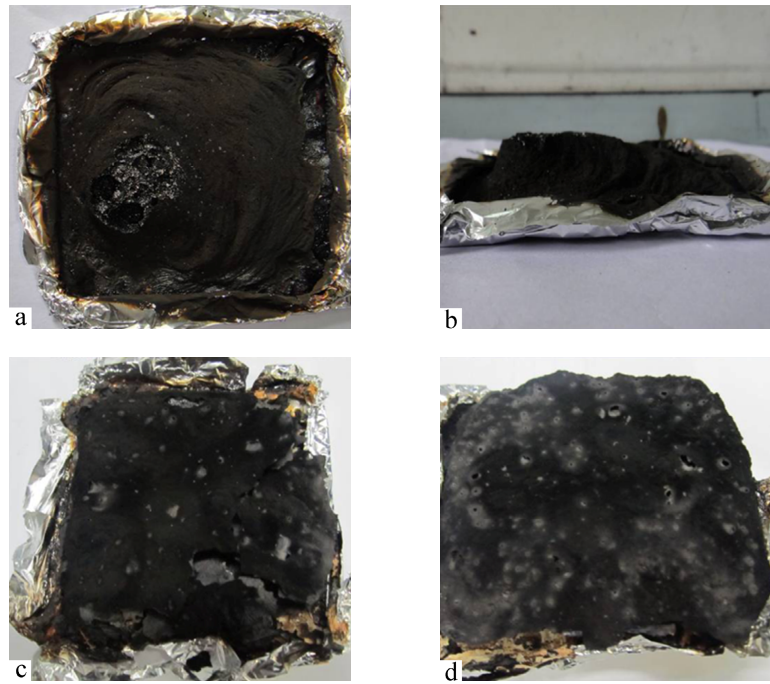


Fig. 3 The digital photographs of residual chars after CC tests: (a) neat TPU (one direction), (b) neat TPU (another direction), (c) TPU/AP25 and (d) TPU/AP30

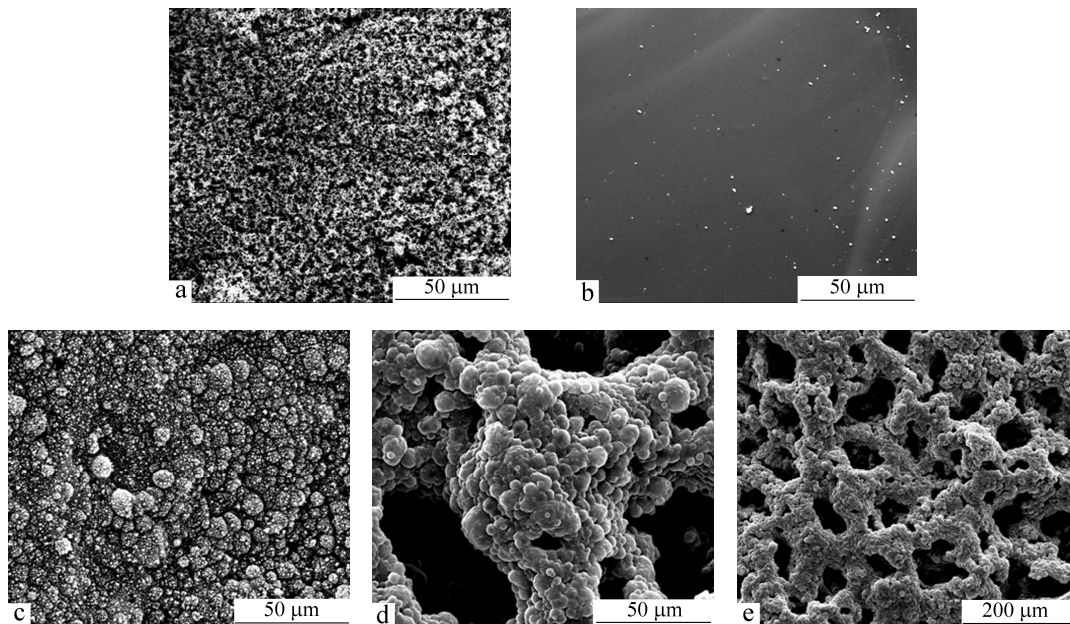


Fig. 4 SEM micrographs of the residual chars obtained from CC tests for neat TPU: (a) outer surface, (b) inner surface and TPU/AP30: (c) outer surface, (d) inner surface, (e) inner surface at lower resolution

TPU, and there are some holes locating in the outer layer in μm scale. For the surface of the inner char layer, it is relatively smooth, and no any special structure can be observed for this sample. For TPU containing 30 wt% of AP, more compact chars formed at the outer surface during the combustion process, as shown in Fig. 4(c). Obviously, there are much less holes in this layer than the outer layer of neat TPU. The more significant difference can be found in the inner layer between neat TPU and TPU/AP30. For neat TPU, the inner surface is quite smooth; while a network structure can be observed in the inner surface for TPU/AP30. According to Liu's report^[28], the char residues with higher mechanical strengths could impart better fire prevention, especially contribute to reduce the HRR and THR of the burning sample. So the formed network char layer with higher mechanical strength must be an important factor to promote the flame retardance of TPU.

Thermal Decomposition Behavior

The thermal stabilities of neat TPU and TPU/AP systems were investigated by TGA under a nitrogen atmosphere. Figure 5 shows the ML and derivate thermogravimetric analysis (DTG) as a function of temperature. The detailed data corresponding to Fig. 5 are listed in Table 3. Obviously, AP scarcely affects the $T_{5\%}$ (the temperature at 5 wt% of mass loss) of TPU in the range from 0 to 35 wt%. However, the T_{max} (the temperature at maximum decomposition rate) of TPU decreases with the incorporation of AP. For neat TPU, the $T_{\text{max}1}$ and $T_{\text{max}2}$ are 351.2 °C and 409.9 °C, respectively. With the incorporation of AP, the $T_{\text{max}1}$ decreases to 336.4 °C, 329.1 °C and 322.1 °C at the corresponding loadings of 25, 30 and 35 wt%, and the $T_{\text{max}2}$ reduces to 390.8 °C at the loading of 35 wt%. With changing the content of AP from 25 wt% to 35 wt%, the $T_{\text{max}2}$ almost keeps steady. As for the char residue, it increases to 29.7 wt% for TPU/AP30 from 4.0 wt% for neat TPU. Obviously, the char residue was greatly affected by the incorporation of AP in TG tests. These results demonstrate that the incorporation of AP led the thermal stability of TPU decreasing slightly at high temperatures.

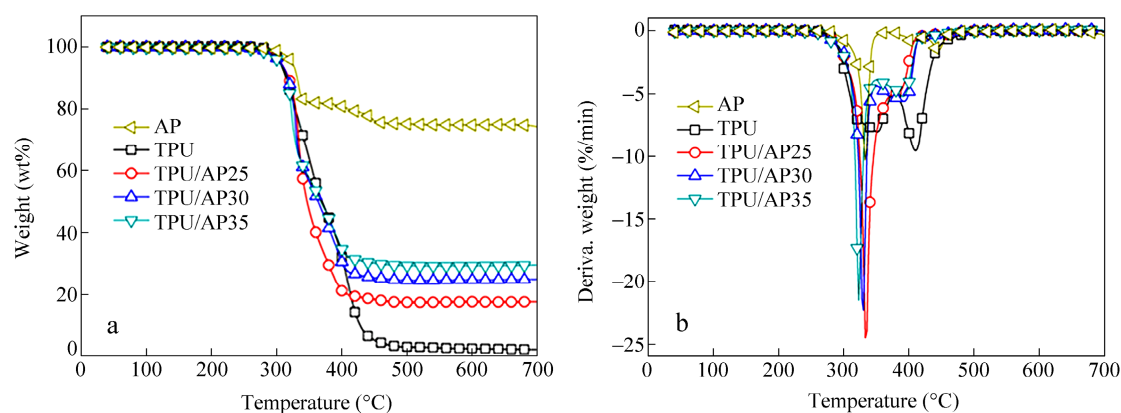


Fig. 5 TGA and DTG curves of neat TPU and TPU/AP

Table 3. TGA data of TPU and TPU/AP

Sample	$T_{5\%}$ (°C)	$T_{\text{max}1}$ (°C)	$T_{\text{max}2}$ (°C)	Char residue at 700 °C (wt%)
TPU	304.7	351.2	409.9	4.01
AP	323.3	333.2	444.6	74.4
TPU/AP25	306.4	333.6	392.6	17.60
TPU/AP30	306.1	329.1	392.0	25.03
TPU/AP35	304.1	322.5	390.8	29.67

Mechanical Test

The mechanical properties of FR-TPU samples with different contents of AP are shown in Table 4. The incorporation of AP affected the tensile strength of TPU. At the content of 25 wt%, the tensile strength is about 26 MPa. Further increasing the AP up to 30 wt%, the tensile strength has no apparent change. The change of the

elongation at break has the same tendency as that of tensile strength. With the addition of AP, the elongation at break slightly decreases to 818% and 779% for TPU/AP25 and TPU/AP30, respectively. A little decrease of the elongation at break means that TPU can preserve the elastomer properties.

Table 4. The mechanical properties of TPU and TPU/AP

Sample	Tensile strength (MPa)	Elongation at break (%)
TPU	37.8 ± 2.6	825.0 ± 27.1
TPU/AP25	26.2 ± 1.5	818.8 ± 38.3
TPU/AP30	25.4 ± 0.8	779.8 ± 25.5

The Flame-retarded Mechanism of AP

To study the effect of AP on the flame retardancy of TPU, the experimental and theoretical TG and DTG curves of TPU/AP30 were investigated, as shown in Fig. 6. The theoretical curves were based on the hypothesis that there was no any reaction between the two components. As can be seen from this figure, the amount of experimental residual chars is higher than the theoretical one above 550 °C, and the degradation rate of TPU/AP30 is lower than the theoretical rate, implying that some reactions might occur in this stage, and more steady structures might form during the heating process^[29]. FTIR tests of these residual chars were carried out to confirm the occurrence of the reaction mentioned above. Figure 7 shows the FTIR spectra of the residue chars. The peaks at about 1630 cm⁻¹ and 1230 cm⁻¹ indicate the existence of C=C and C—N bonds, respectively. The stretching vibrations of N—H and P—O bonds correspond to the peaks at 1067 cm⁻¹ and 782 cm⁻¹, respectively. The peaks in the range of 980–990 cm⁻¹ are ascribed to the stretching vibration of the C—O bonds in the P—O—C bonds^[30]. A new strong peak assigned to the stretching vibration of the P—O—P bond appears at around 1120 cm⁻¹ for TPU/AP composites, suggesting the formation of Al₄(P₂O₇)₃, which is the most obvious difference between neat TPU and its composites containing AP. In order to further illustrate the formation of Al₄(P₂O₇)₃, XPS for the condensed products of TPU and TPU/AP30 obtained after CC tests was utilized to study the atomic concentration of oxygen (O) and phosphorus (P). The XPS results are shown in Fig. 8. Two peaks at 134 eV and 190.9 eV can be assigned to P2p and P2s, and the relative contents of O/C and P/C for TPU/AP30 are much higher than those of neat TPU. Both the appearance of the peaks corresponding to P and the change of the above relative contents were aroused by the presence of AP. Table 5 illustrates that the contents of O and P increase, which might be due to the formation of the P—O—P and P—O—C structures^[31, 32]. These results illustrate that some reactions occurred indeed during heating, and also demonstrate that the incorporation of AP facilitated the formation of residual chars containing Al₄(P₂O₇)₃.

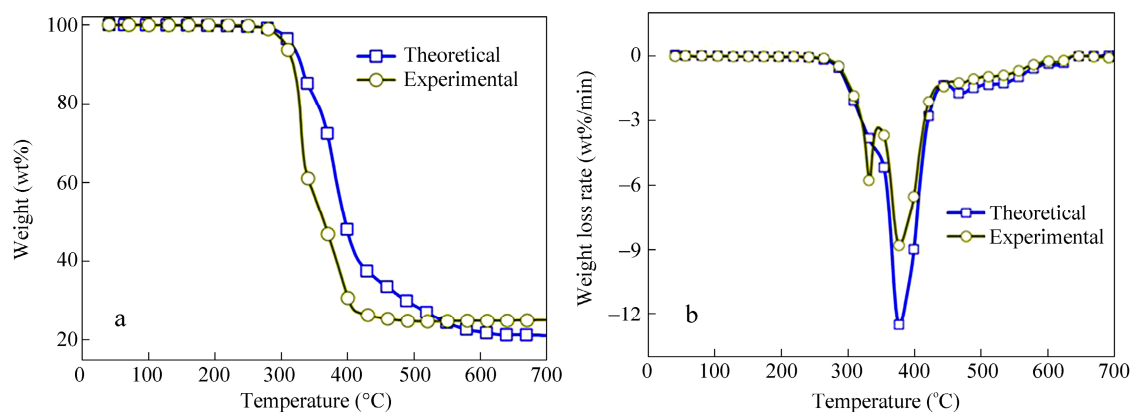
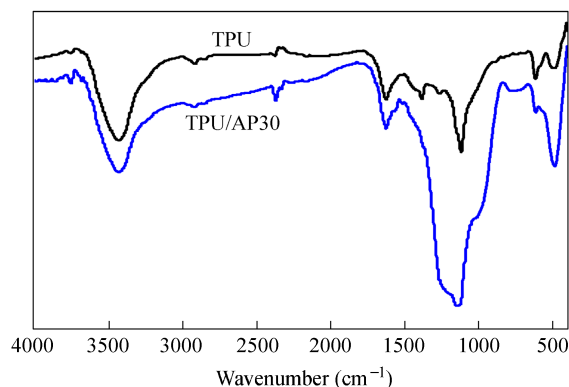
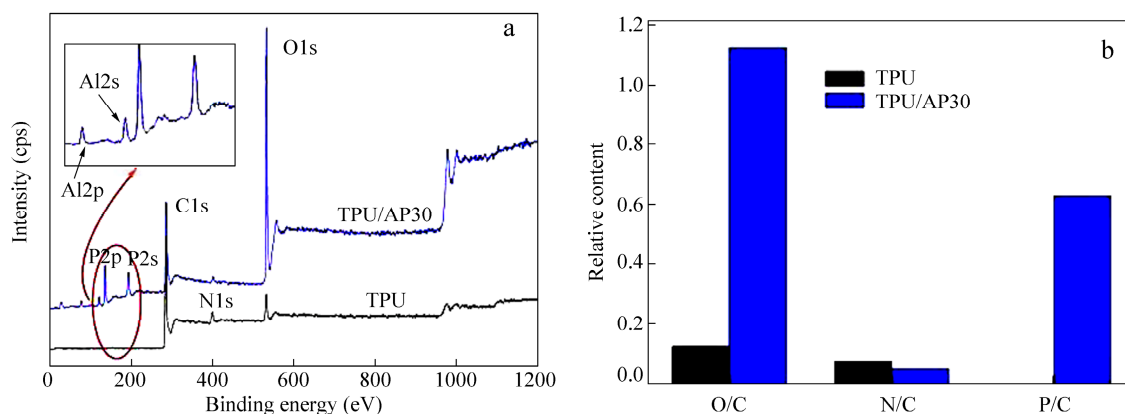


Fig. 6 Experimental and theoretical TG and DTG curves of TPU/AP30 composite

Table 5. The element concentrations of C, N, O and P in the residual chars of neat TPU and TPU/AP30 after CC tests

Samples	Mass content (wt%)			
	C 1s	N 1s	O 1s	P 2p
TPU	81.83	6.01	10.08	0.49
TPU/AP30	32.99	1.64	37.09	20.72

**Fig. 7** FTIR spectra of the residual chars obtained from TG tests for TPU and TPU/AP30**Fig. 8** XPS spectra (a) and the relative contents of N, O and P in the residual chars of TPU and TPU/AP30 (b)

According to the results of TG, FTIR and XPS results, a potential flame-retarding mechanism of AP is interpreted as follows, and the corresponding schematic diagram is shown in Fig. 9. AP decomposes with increasing temperature in TPU/AP system, and then $\text{Al}_4(\text{P}_2\text{O}_7)_3$ forms during the decomposing process of AP. After a further polycondensation, the network pyrophosphate produces, and then deposits in the residual chars. The formed PH_3 molecules during the decomposing process of AP are prone to form the hydrogen bonds with TPU macromolecules, which can facilitate the formation of residual chars. Of course, the final residues also include the chars from the decomposition of TPU. According to the analysis presented above, it can be concluded that both the self-charring during the decomposing process of AP and its facilitation to the charring of TPU enhanced the flame retardance of TPU.

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