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ORIGINAL PAPER

Effect of a novel intumescent retardant for ABS with synergist $Al(H_2PO_2)_3$

Yi Liu · JiangSong Yi · XuFu Cai

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Abstract A novel intumescent flame retardant (IFR), containing ammonium polyphosphate (APP) and poly(hexamethylene terephthalamide) (PA6T), was prepared for acrylonitrile–butadiene–styrene (ABS). Limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis (TGA) were used to investigate the flammability property and thermal stability of the IFR/ABS systems. It was found that the flame retardancy of the IFR/ABS systems was improved significantly. When the components of the IFR were 25% APP and 5% PA6T, the LOI value of IFR/ABS system reached to the maximum of 29, but only UL-94V-1 rating was passed. Thus, $Al(H_2PO_2)_3$ was incorporated into ABS/APP/PA6T system as a synergistic agent, it was found 2% addition of $Al(H_2PO_2)_3$ caused PA6T/APP/PA6T/$Al(H_2PO_2)_3$ (70/23.3/4.7/2) to pass V-0 rating of UL-94 test. Meanwhile, the TGA curves indicated that PA6T could be effective as a charring agent and there was a synergistic reaction between PA6T and APP, which effectively promoted the char formation of IFR/ABS composites. Moreover, the residual char obtained after the LOI test of the IFR/ABS was characterized by Fourier transform infrared spectra (FTIR). Results indicated that P–O–C chemical bond was formed in the residual char, which could indicate the cross-linking reaction between PA6T and APP could occur. Furthermore, scanning electron microscopy (SEM) was used to investigate the morphology of the residual char formed in the LOI tests. It was revealed that both ABS/APP/PA6T (70/25/5) and PA6T/APP/PA6T/$Al(H_2PO_2)_3$ (70/23.3/4.7/2) formed uniform and compact intumescent charred layers.

Keywords Flame retardant · Ammonium polyphosphate Acrylonitrile–butadiene–styrene · Poly(hexamethylene terephthalamide) · Thermogravimetric analysis

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Y. Liu · J. Yi · X. Cai (✉)
Department of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China
e-mail: Caixf2004@sina.com

Introduction

Acrylonitrile–butadiene–styrene (ABS) is a kind of widely used thermoplastic copolymer due to its attractive properties such as good processability, chemical resistance, and low cost [1–5]. However, its application is restricted because of its easy flammability. So it is necessary to construct a flame-retarded composition for ABS resin [6, 7]. Traditionally, Bromine-containing compounds such as decabromodiphenyl oxide (DBDPO), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPOE) and tetrabromobisphenol (TBBPA), etc. were regarded as very good flame retardants for ABS resin [8]. However, regarding the environmental protection, the application of these halogen-containing flame retardants has been limited because they will generate great quantities of toxic and corrosive fumes during combustion. Consequently, to develop a non-halogenated flame-retardant system becomes an attractive and emergent subject. Among non-halogenated flame retardants, intumescent flame retardants (IFR) with particular char-yielding properties are known to be good candidates for replacing the halogen type ones, which have been widely used in various polymeric materials [9–14].

A typical IFR system is the mixture of three ingredients, namely, a carbon source—a carbonization agent, an acid source—a carbonization catalyst, and a gas source—a blowing agent. On heating, IFR material can form a foamed cellular charred layer on its surface, which can act as a barrier between fire and polymer, and then result in the extinguishment of combustion to protect the underlying materials [15]. Among of those IFR ingredients, the commonly used carbonization catalyst is ammonium polyphosphate (APP). It can react with the carbonization agents, such as pentaerythritol (PER), mannitol or sorbitol, to generate the char [16, 17]. But these polyol kind carbonization agents are confronted with the problems of exudation and water solubility. Besides, they are not compatible with the polymeric matrix, which weaken the mechanical properties of the material. Thus, a lot of attention has been focused on the application of different carbonization agents. Recently, it was found that polyamide could also act as carbonization agent in IFR, such as PA6, PA66, PA11 [18–21]. Levchik et al. [18] have demonstrated that PA6 could be used as carbonization agent, and PA6/APP additives mixture leaded to flame retardancy properties of interest, by developing an intumescent charred shield. It was found that a chemical interaction took place between APP and PA6 on heating, resulting in destabilization of PA-6 and modification of its degradation behavior to form some crosslinking chemical structure to strengthen the char layer. In addition, Liu et al. [21] adopted another polyamide, PA11, as charring agent to flame-retard PP, in combination with PER and APP. PA11 showed not only good charring ability but also good compatibility with polymeric matrix.

In this paper, another polyamide, poly(hexamethylene terephthalamide) (PA6T), was used as carbonization agent. It was combined with APP to form a novel IFR for ABS. $Al(H_2PO_2)_3$ also was used as a synergistic agent. Flame retardancy, thermal degradation and charring behavior, chemical structure and morphology of the residual char of the novel IFR/ABS system have been investigated.

Experimental

Materials

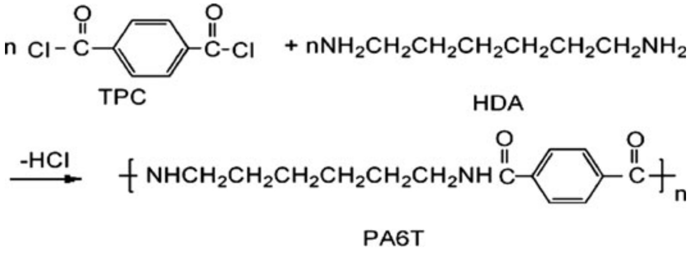
Acrylonitrile–butadiene–styrene (ABS) copolymer (0215-A) was supplied by Jilin Petrochemical Co. (Jilin, China). Ammonium polyphosphate (APP) was obtained from Zhejiang Longyou GD Chemical Industry Corp. (Longyou, China). Poly(hexamethylene terephthalamide) (PA6T) was synthesized according to the literature [22]. Its preparation is described in “Synthesis of PA6T” section. All materials used in synthesizing PA6T including terephthaloyl chloride (TPC), 1,6-diaminohexane (HDA), triethylamine (TEA), calcium chloride ($CaCl_2$), and *n*-methyl-pyrrolidone (NMP) were purchased from Kelong Chemical Reagent Corp. (Chengdu, China). $Al(H_2PO_2)_3$ was supplied by Qingzhou Yichao Co. (Qingzhou, China).

Synthesis of PA6T

A 150 mL three-necked round bottom flask equipped with a stirrer was charged with 3 g $CaCl_2$, 9.1 g TEA (as acid adsorbent), 5.23 g HDA (0.45 mol/L), and 100 mL NMP. The mixture was stirred. When the mixture dissolved completely, the flask was cooled to 0–5 °C. After that, 9.14 g TPC (0.45 mol/l) was added slowly to the flask within about 0.5 h, during which the reaction temperature was still kept at 0–5 °C. Then the flask was heated up to 40 °C and the reaction would be completed after 2 h. After that, the reaction mixture was cooled to room temperature, then the mixture was poured into distilled water and filtered. The obtained white solid was washed with hot water to about 80 °C and dried in a vacuum at 100 °C to constant weight. (Product yield: 78%). The synthesis route was illustrated in Scheme 1.

Preparation of flame-retardant ABS samples

ABS, APP, PA6T were dried in vacuum at 100 °C for 24 h before use. ABS resins with different APP, PA6T, and $Al(H_2PO_2)_3$ content were prepared via a twin screw extruder (*D* = 25 mm, *L*/*D* = 33, TSSJ–25, Chengguang, China) with screw rotating rate of 100 r/min, and the barrel setting temperatures were 200, 215, 220, 220, 230, and 230 °C. Then the extruded composites, dried at 100 °C for 12 h, were



Scheme 1 The synthesis of PA6T

injected into standard testing bars at 220–230 °C for the tests of combustibility, using an injection-molding machine (PS40E5ASE, Nissei Plastic Industrial Co.).

Measurements

Structural characterization of PA6T

IR spectroscopy was applied with a Nicolet IS10 FTIR spectrometer using KBr pellets. ^{1}H NMR (400 Hz) spectra were recorded on a FT-80A NMR by using CF_3COOD as a solvent.

Limiting oxygen index (LOI) and UL-94 tests

Limiting oxygen index (LOI) data of all samples were obtained at room temperature on an oxygen index instrument (XYC-75) produced by Chende Jinjian Analysis Instrument Factory, according to ASTM D2863-97 standard. The dimensions of all samples were $130 \times 6.5 \times 3$ mm^3. Vertical burning rates (UL-94) of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, with sample dimensions of $130 \times 13 \times 3$ mm^3, according to ASTM D3801.

Thermogravimetric analysis (TGA) test

Thermogravimetric analysis (TGA) was performed on a WRT-2R thermal analyzer by Shanghai Precision and Scientific Instrument at a heating rate of 10 °C/min. 5–10 mg of the sample was examined under pure nitrogen at a flowing rate of 50 mL/min at temperature ranging from 50 to 750 °C.

Fourier transform infrared (FTIR) characterization of the residual char layer

Fourier transform infrared spectrum (FTIR) was obtained with a Nicolet IS10 FTIR spectrometer using KBr pellet.

Scanning electron microscopy (SEM) analysis

The surface morphology of the char obtained after the LOI test was observed by using a HITACHI X-650 scanning electron microscope (SEM). The specimens were previously coated with a conductive gold layer.

Results and discussion

Characterization of PA6T

Figure 1 presents the FTIR spectrum of the synthesized PA6T. The absorption bands at 3075 cm^{-1}, 1541 cm^{-1}, 1496 cm^{-1} correspond to vibrations of the

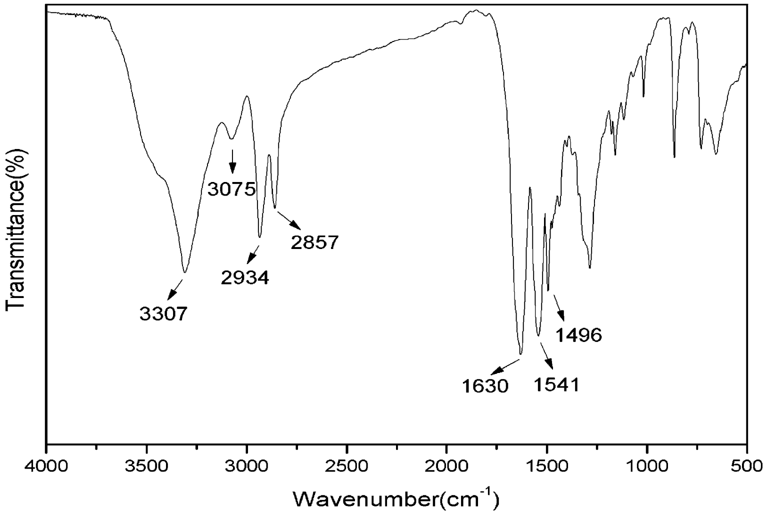


Fig. 1 The FTIR spectra of PA6T

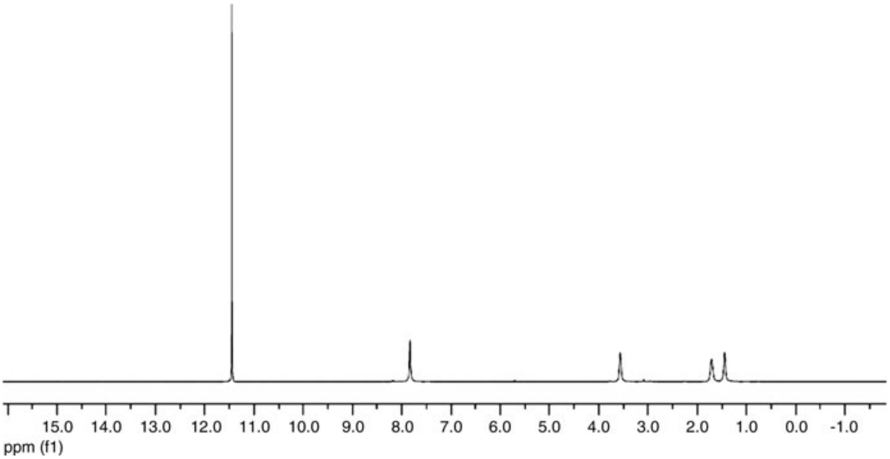


Fig. 2 The 1H NMR spectra of PA6T

benzene ring, and the peaks at 2934 cm^{-1},2857 cm^{-1} are assigned to –CH_2– stretching band. The absorptions at 1630 cm^{-1} and 3307 cm^{-1} are associated with the stretching mode of C=O and N–H from the amide group. The ^1H NMR spectra of PA6T is shown in Fig. 2. As can be seen, the peak at 7.832 ppm is assigned to the proton of benzene ring. The peaks at 1.711 ppm and 1.446 ppm correspond to two types of –CH_2– protons, namely –N–CH_2–C–, –C–CH_2–C–, the former is attributed to the –CH_2– protons adjacent to the amide group. All the information above confirms that the target product is synthesized successfully.

Flame retardancy

In our research, PA6T was mixed with APP to produce a novel IFR. And a series of flame retardants with different weight ratio of APP to PA6T were compounded with ABS to obtain the IFR/ABS systems. Table 1 gives the LOI values and vertical burning rates of the IFR/ABS systems with a total loading of the APP and PA6T additives of 30%. As shown in Table 1, ABS is an easily flammable polymeric material with its LOI value only 18.5. When the addition of APP was 30%, without PA6T, LOI of the ABS/APP system increased to 25. But it failed in vertical burning test. However, when APP was mixed with PA6T, then incorporated into ABS, LOI values of the IFR/ABS systems are greatly increased. It was observed in Table 1 that LOI values of IFR/ABS systems increased with the increasing addition of PA6T. When the weight ratio of PA6T to APP increased to 1:5, that is, PA6T was 5% and APP was 25%, the IFR/ABS system showed the best flame retardancy with its LOI value reaching the maximum of 29. However, when the ratio of PA6T to APP continued to increase, LOI values of IFR/ABS systems decreased. When the weight ratio of PA6T to APP was 1:1, the LOI value decreased to 26.5. In addition, when the weight ratio of PA6T to APP was between 1:8 and 1:4, all the IFR/ABS systems reached V-1 rating during the UL-94 test.

Table 2 gives LOI and UL-94 data of IFR/ABS systems with different addition of IFR (the ratio of APP to PA6T was 5:1). It was found, with increase in the IFR loading, LOI values and UL-94 ratings of IFR/ABS systems increased. When the addition of the IFR was 25%, LOI value of IFR/ABS system was 27, and it failed in the UL-94 test. However, when the addition of the IFR was 40%, the LOI value reached 33 and UL-94V-0 rating was passed.

To get better flame retardancy, $Al(H_2PO_2)_3$ was added into the IFR/ABS systems as a synergistic agent. Table 3 gives LOI and UL-94 data of IFR/ABS systems with different addition of $Al(H_2PO_2)_3$. As can be seen, the addition of $Al(H_2PO_2)_3$ did not make a change with the LOI values, even caused a little bit decrease to 28.5.

Table 1 Effect of IFR on flame retardancy of IFR-ABS systems

Sample	Components (%)			Flame retardancy	
	ABS	APP	PA6T	LOI (%)	UL-94
1	100	0	0	18.5	Burning
2	70	30	0	25	Burning
3	70	15	15	26.5	Burning
4	70	20	10	27	Burning
5	70	22.5	7.5	27.5	Burning
6	70	24	6	28	V-1
7	70	25	5	29	V-1
8	70	25.7	4.3	28.5	V-1
9	70	26.3	3.7	28	V-1
10	70	26.7	3.3	27.5	V-1

Table 2 Effect of IFR addition on flame retardancy of IFR/ABS systems (APP:PA6T = 5:1)

Sample	Components (%)		Flame retardancy	
	ABS	IFR	LOI (%)	UL-94
11	75	25	27	Burning
12	70	30	29	V-1
13	65	35	31	V-1
14	60	40	33	V-0

Table 3 Effect of $Al(H_2PO_2)_3$ on flame retardancy of IFR/ABS systems(PA6T/APP:1/5)

Sample	Components (%)			Flame retardancy	
	ABS	IFR	$Al(H_2PO_2)_3$	LOI (%)	UL-94
15	70	30	0	29	V-1
16	70	29	1	28.5	V-1
17	70	28	2	28.5	V-0
18	70	27	3	29	V-0
19	70	26	4	29	V-1

However, when the addition of $Al(H_2PO_2)_3$ was 2% or 3%, V-0 rating of the UL-94 test was reached. That was probably because $Al(H_2PO_2)_3$ had played a good synergistic role to catalyze the reaction between PA6T and APP to make char formation stronger to have a better flame retardant performance for ABS.

Thermal degradation and charring behavior

The thermal degradation behaviors of the flame retarded ABS systems were investigated by TGA in pure nitrogen. Figures 3, 4, and 5 show the related curves of the IFR/ABS systems, main data collected from the TG curves was shown in Table 4. As shown from Fig. 3 and Table 4, PA6T showed very high thermal stability with its initial temperature 483 °C, based upon 5% weight loss. It was also found that the thermal degradation process of PA6T only had one step with the main peak of thermal degradation at 557 °C. And when temperature was 700 °C, the char residue of PA6T was only 5.9%, which demonstrated PA6T itself showed poor charring ability. However, when IFR was added into ABS, the char residue was greatly improved, that is, the char residue weight of ABS/APP/PA6T (70/25/5) and ABS/APP/PA6T/$Al(H_2PO_2)_3$ (70/23.3/4.7/2) was 17% and 14.5%, respectively. Figure 4 shows the experimental and theoretical TG curves of ABS/APP/PA6T (75/25/5), and the theoretical TG curve was calculated based upon the weight percentage of the ingredients in the IFR/ABS system. As could be seen, obvious difference between the two curves was observed, for example, the T_{initial} and the char residue at 500–670 °C and 700 °C. It was found, the T_{initial} of the experimental curve was lower compared with the theoretical curve, which indicated the addition of IFR could accelerate the initial degradation of the ABS/APP/PA6T system.

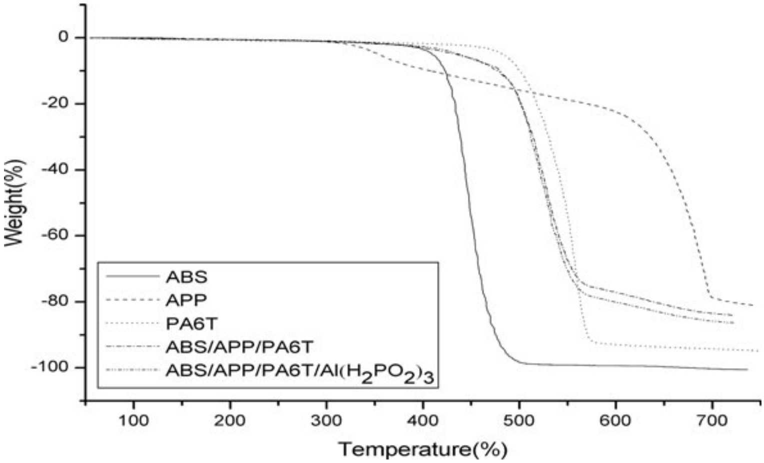


Fig. 3 TG curves of the IFR/ABS system

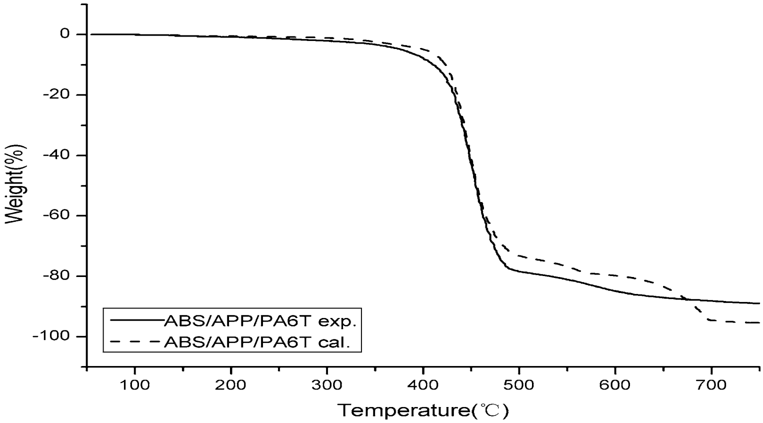


Fig. 4 Experimental and theoretical TG curves of the ABS/APP/PA6T (70/25/5)

Furthermore, the theoretical residual mass of ABS/APP/PA6T was higher than experimental residual mass at 500–670 °C. It was probably because that the addition of IFR promoted the thermal degradation of the IFR/ABS system to a large amount of volatile low molar mass compounds. However, after 700 °C, the experimental TG curve of ABS/APP/PA6T exhibited higher char residue, which was 17%, compared with the theoretical 5.5%. This was probably because ‘‘high temperature’’ stable residual char layer began to form in the IFR/ABS system at about 500 °C. It could act as a barrier between the flame and the polymer to protect the underlying material. As a result, it prevented the weight loss even at higher temperature, which was greatly relative with the good flame retardant performance in the LOI and UL-94 tests. All the information above could demonstrate the novel IFR was effective in the IFR/ABS system.

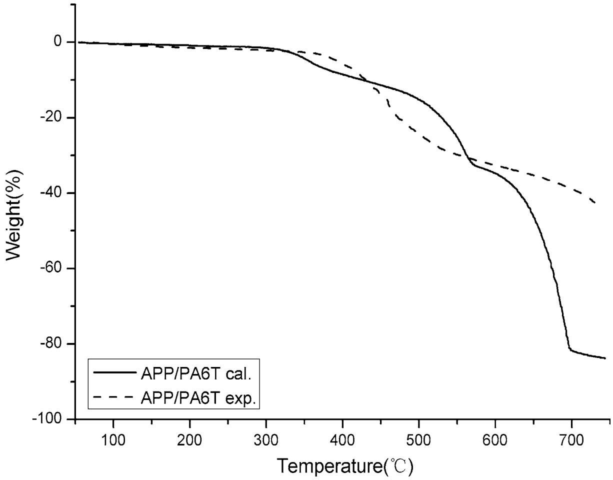


Fig. 5 Experimental and theoretical TG curves of the APP/PA6T (5/1)

Table 4 Thermal degradation data under pure nitrogen by TGA

Sample	T_{initial} (°C)	$R_{1\mathrm{peak}}$ (%min^{-1})	$T_{1\mathrm{peak}}$ (°C)	$R_{2\mathrm{peak}}$ (%min^{-1})	$T_{2\mathrm{peak}}$ (°C)	Char residue (%) at 700 °C	
						Exp.	Cal.
PA6T	483	6.6	557	–	–	5.9	–
APP	354	1.3	355	10.3	680	21.4	–
PA6T/APP(1/5)	402	1.2	430	2.7	460	61.5	18.2
ABS	412	20.6	450	–	–	0	–
ABS/APP/PA6T (70/25/5)	437	6.6	530	–	–	17	5.5
ABS/APP/PA6T/ $Al(H_2PO_2)_3$ (70/23.3/4.7/2)	440	7.5	530	–	–	14.5	–

To further investigate the thermal degradation behavior of the IFR/ABS system the experimental and theoretical TG curves of PA6T/APP (1/5) were obtained, as shown in Fig. 5. As shown, remarkable difference was observed between the experimental curve and the theoretical curve of PA6T/APP system. It was found, the reaction between APP and PA6T slowed down the weight loss of the APP/PA6T system at first. But after that the APP/PA6T system came into a very fast degradation, which caused obvious difference between the experimental curve and the theoretical curve of PA6T/APP system, that is, the theoretical residual weight was much higher than the experimental residual weight at 440–550 °C. However, an interesting phenomenon happened. The experimental residual mass became much higher than the theoretical one after 600 °C, that is, the experimental residual mass was 61.5% compared with the theoretical 18.2%. This is probably because the charring residue formed from the former step prevented the weight loss with temperature increasing. At the end, it was concluded that a novel IFR system containing APP (as acid source and blowing agent) and PA6T (as carbon source) was obtained.

Chemical structural analysis of the residual char

As for the IFR system, it is noted that the intumescent residual char plays a very important role in improving flame retardance of the composites. To better understand the synergistic role of the IFR, the residual char obtained after the LOI test of the IFR/ABS system (sample 7) was investigated by FTIR. As can be seen from Fig. 6, the absorption band at 3394 cm^{-1} is assigned to the stretching mode of –OH from the P–OH group. The absorption band at 1399 cm^{-1} is attributed to the stretching mode of P=O group, and the peaks at 1005 and 879 cm^{-1} correspond to the symmetric and asymmetric vibration of P–O in P–O–P group. Furthermore, the band at 1451 cm^{-1} is assigned to the stretching mode of –NH in NH_4^+ [23, 24]. All the information above could indicate that polyphosphoric acid and NH_3 were produced in residual char at high temperature. Polyphosphoric acid could be contributed to the carbonization of PA6T, NH_3 could dilute the concentration of the oxygen near the surface of material and foam the carbon layer during fire. Moreover, it is also very important to note these peaks, the absorption band at 1205 cm^{-1} attributed to P–O-C structure in P–C complex, 1087 and 1047 cm^{-1} assigned to the symmetric and asymmetric stretching mode of P–O bond in P–O–C structure [25]. These peaks could confirm the existence of P–O–C chemical bonds in the residual char, which could indicate that the cross-linking reaction between PA6T and APP could occur. This cross-linking reaction

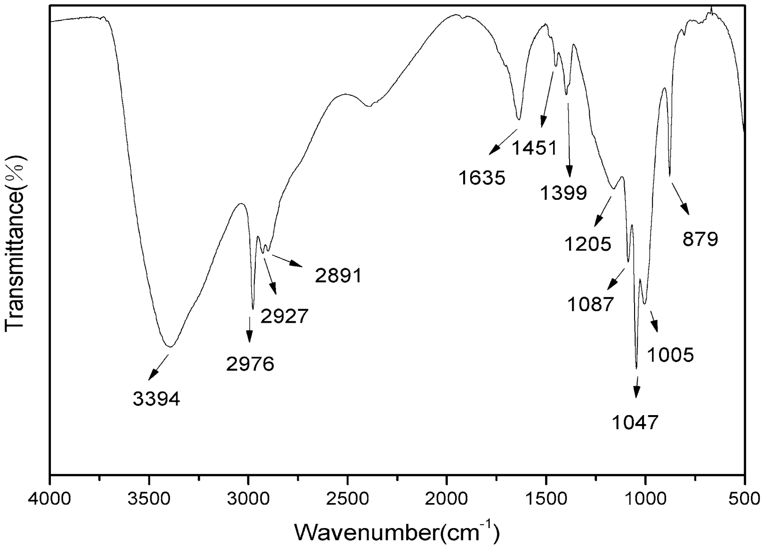


Fig. 6 The FTIR spectra of the residual char

would form some high temperature stable char layer to protect the ABS matrix during combustion. In addition, the peak at 1640 cm^{-1}, ascribed to the C=O absorption, suggests that the oxidization of ABS or the existence of the original composites. The peak at 2976 cm^{-1} (ascribed to asymmetric stretch vibration of CH_3) and the peaks at 2927 and 2891 cm^{-1} (assigned to asymmetric and symmetric deformation vibration of CH_2) could also indicate the composite has not combusted completely.

Morphology of the residual char

Scanning electron microscopy (SEM) was used to investigate the morphology of the residual char formed in the LOI tests, shown in Figs. 7, 8, and 9. Figure 7 shows the morphology of the residual char of the ABS/APP (70/30) system. It was found there were a lot of big holes formed on the surface of the residual char, which was closely related with its bad flame retardant performance. However, when the IFRs were added in ABS, the surface of the residual char became more compact and smooth, which were shown in Figs. 8 and 9, exhibiting the morphology of the residual char of ABS/APP/PA6T (70/25/5) and ABS/APP/PA6T/$Al(H_2PO_2)_3$ (70/23.3/4.7/2), respectively. In Fig. 8, there is still some imperfection observed, such as some small holes, which corresponded with the fact only V-1 rating was reached in UL-94 test. However, when 2% $Al(H_2PO_2)_3$ was added, a cohesive, strong, smooth, and dense morphology structure without clear holes was formed, shown in Fig. 9. It could effectively serve as a barrier between the flame and the polymeric material to protect underlying materials, then UL-94 test V-0 rating was reached.

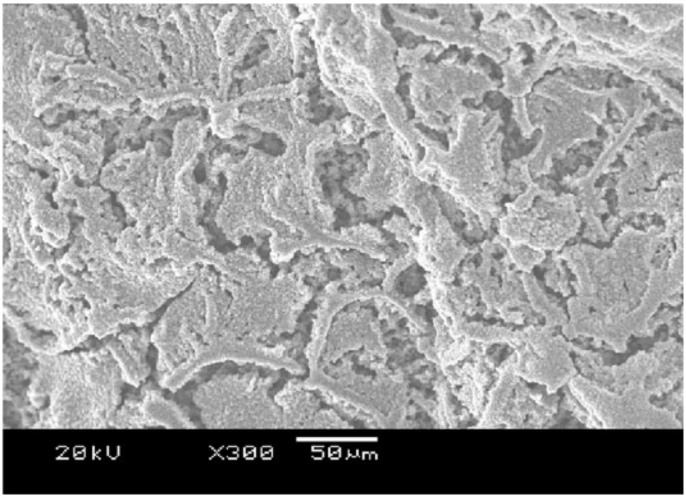


Fig. 7 SEM of the charred surface structure of ABS/APP (70/30) system

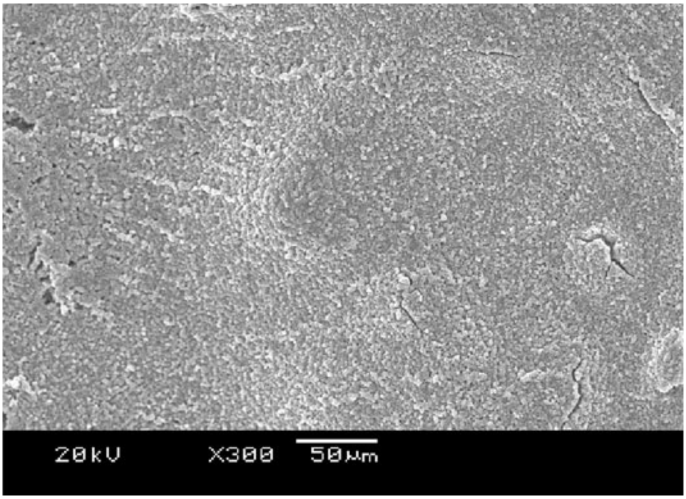


Fig. 8 SEM of the charred surface structure of ABS/APP/PA6T (70/25/5) system

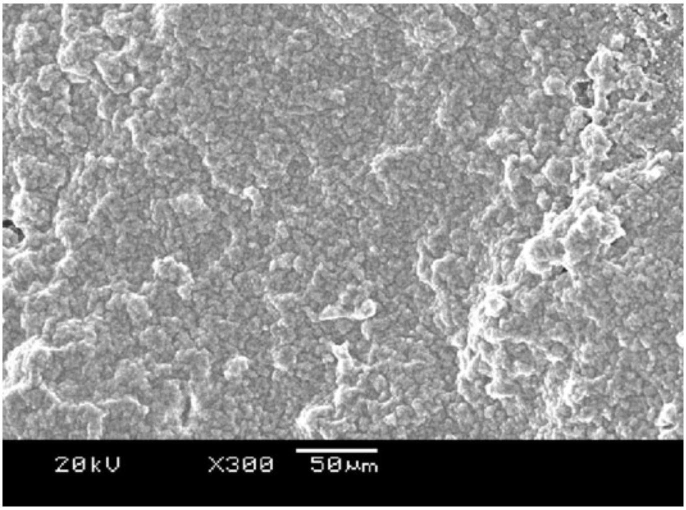


Fig. 9 SEM of the charred surface structure of ABS/APP/PA6T/Al(H_2PO_2)$_3$ (70/23.3/4.7/2)

Conclusions

A novel IFR was prepared for ABS from APP (as carbonization catalyst and blowing agent) and PA6T (as carbonization agent). When the weight ratio of PA6T to APP was 1:5, the total loading of IFR was 30%, LOI value of the IFR/ABS reached 29, and V-1 rating was obtained. When 2% Al(H_2PO_2)$_3$ was added as a synergistic agent to the IFR/ABS system, the UL-94 test V-0 rating was reached. Furthermore, the TGA data and curves showed that the ABS/APP/PA6T had good char formation ability, that is, the experimental residual weight at 700 °C was 17%, much higher than the theoretical one 5.5%. In addition, it could also be concluded that PA6T showed great char formation ability when it was combined with APP. The synergistic reaction between APP and PA6T significantly changed the decomposition course, and greatly enhanced the char formation ability of APP/PA6T(1/5) system, that is, the experimental residual char weight of the system at 700 °C was 61.5%, but the theoretical char residue was only 18.2%. In addition, chemical structural analysis of the residual char obtained after LOI test was carried out by FTIR. Results indicated that P–O–C chemical bond was formed in the residual char, which could indicate the cross-linking reaction between PA6T and APP could occur. Moreover, the morphology of char residues investigated by SEM suggested that the novel IFR/ABS system can form excellent char layer, which hindered the transfer of heat flow and combustible gas and improved the flame retardancy of ABS.

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