

The investigation of intumescent flame-retarded polypropylene using poly(hexamethylene terephthalamide) as carbonization agent

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Abstract A novel intumescent flame retardant, containing ammonium polyphosphate (APP), and poly(hexamethylene terephthalamide) (PA6T), was prepared for flame retarding polypropylene (PP). The flame retardation of the PP composites was characterized by limiting oxygen index (LOI). The thermal degradation of the composites was investigated by means of thermogravimetric analysis (TG) and TG coupled with Fourier transform infrared spectroscopy (TG-FTIR). The morphology of the char obtained after combustion of the composites was studied by scanning electron microscopy. It has been found the intumescent flame retardant showed good flame retardancy, with the LOI value of the PA6T/APP/PP (5/25/70) system increasing from 17.5 to 32. Meanwhile, the TG and TG-FTIR work indicated that PA6T could be effective as a carbonization agent and there was a synergistic reaction between PA6T and APP, which effectively promoted the char formation of the PP composites. Moreover, it was revealed that uniform and compact intumescent char layer was formed after combustion of the intumescent flame retarded PP composites.

Keywords Polypropylene · Intumescent flame retardant · TG · TG-FTIR

Introduction

Polypropylene (PP), as one of the three general plastics, is widely used in many fields, such as, housing, wire, cables,

automobiles, electronic and electric industry, because of its low density, low toxicity, excellent electrical resistance, and ease of processing and molding [1, 2]. However, the easy flammability restricts its many applications. Traditionally, Bromine-containing flame retardants are the most effective and show a good ratio of property to price in flame retardancy of PP. But some of them are limited in use because of the evolution of toxic gases and corrosive smoke during combustion [3]. Therefore, lots of attention has been focused on halogen-free flame retardant. The halogen-free flame retardants commonly used include aluminum hydroxide and magnesium hydroxide, phosphorus-containing compounds, and phosphorus-nitrogen-containing compounds [4]. However, high loadings of them are needed in order to obtain a good flame retardant level, which destroy physical and mechanical properties of the polymer composites obviously [5–7].

In recent years, intumescent flame retardant (IFR) additives have received great attention. It involves the formation on heating of a swollen multicellular thermally stable char insulating the underlying material from the flame action [8]. A typical intumescent system comprises an acid source—a dehydration catalyst for char formation, a carbon source—a carbonization agent (carbon-rich compounds) and a gas source—a blowing agent. Among of those IFR ingredients, Ammonium polyphosphate (APP) is widely used as a blowing agent and an acid source in the typical IFR system. It can react with the carbonization agents, such as pentaerythritol (PER), mannitol or sorbitol, to generate the char [9, 10]. But the hydrophilic property of these hydroxyl-containing carbonization agents makes this IFR system moisture sensitive, which will decrease the flame retardancy because of the exudation of the additive [11]. Thus, lots of attention has been paid on the application of different carbonization agents. Recently, it was

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found that polyamide could also act as carbonization agent, such as PA6, PA66, PA11 [12–15]. Levchik et al. [12] have demonstrated that PA6 could be used as carbonization agent, and PA6/APP mixture led to flame retardancy properties of interest, by developing an intumescent charred shield. It was also found a chemical interaction taking place between APP and PA6 on heating, resulting in destabilization of PA-6 and modification of its degradation to form some crosslinking chemical structure to strengthen the char layer. In addition, Liu et al. [15] adopted PA11 as charring agent to flame-retard PP, in combination with PER and APP. It was found PA11 showed not only good charring ability, but also good compatibility with polymeric matrix.

In this study, a novel intumescent flame retardant, containing poly(hexamethylene terephthalamide) (PA6T) as carbonization agent and APP, was prepared to intumescent flame-retarded PP. Flammability and thermal stability of the novel IFR/PP system have been investigated.

Experimental

Materials

Polypropylene (PP) (F401) used in this work was produced by Panjin Ethylene Industrial Company. Ammonium polyphosphate (APP) was obtained from Zhejiang Longyou GD Chemical Industry Company. Poly(hexamethylene terephthalamide) (PA6T) used in our research was synthesized according to the literature [16], its structure is shown in Fig. 1.

Preparation of flame-retarded samples

APP, PA6T were dried in vacuum at 100 °C for 24 h before use. PP with different APP, PA6T content were prepared via a twin screw extruder (TSSJ-25, Chengguang, China) at a temperature range of 200–220 °C. Then the extruded composites were injected into standard testing bars using an injection-molding machine (PS40E5ASE, Nissei Plastic Industrial Co.).

Measurements

Limiting oxygen index (LOI) of all samples was obtained at room temperature on an oxygen index instrument (XYC-

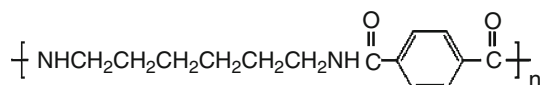


Fig. 1 The structure of PA6T

75) produced by Chende Jinjian Analysis Instrument Factory, according to ASTM D2863-97 standard. The dimensions of all samples were 130 × 6.5 × 3 mm³.

Thermogravimetric analysis (TG) was performed on a TGA/DSC 1 (Mettler/Toledo) at a heating rate of 10 °C min⁻¹. 5–10 mg of the sample was examined under pure nitrogen at a flowing rate of 50 mL min⁻¹ from 50 to 700 °C.

TG coupled with Fourier transform infrared spectroscopy (TG-FTIR) consisted of a TGA/DSC 1 (Mettler/Toledo) coupled with a IS10 FTIR spectrometer (Nicolet), at a heating rate of 10 °C min⁻¹. 5–10 mg of the sample was examined under pure nitrogen at a flowing rate of 50 mL min⁻¹ from 50 to 700 °C.

FTIR characterization of the residual char was carried out with a Nicolet IS10 FTIR spectrometer, using KBr pellet.

The surface morphology of the char obtained after combustion was observed by a HITACHI X-650 scanning electron microscope (SEM).

Results and discussion

Flammability

In our research, PA6T was mixed with APP to produce a novel intumescent flame retardant (IFR). And a series of IFR with different mass ratio of PA6T to APP were compounded with PP to obtain the IFR-PP systems. Table 1 gives the LOI values of the IFR-PP systems at 30% additive level. As shown in Table 1, PP is an easily flammable polymeric material with its LOI value only 17.5. When the addition of APP was 30%, without PA6T, LOI value of the PP-APP system only increased to 20, which indicated that addition of APP only could not enhance the flame retardancy of the PP composites. However, when APP was mixed with PA6T, then incorporated into PP, LOI values of

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

Sample	Components/%			LOI/%
	PP	APP	PA6T	
1	100	0	0	17.5
2	70	30	0	20
3	70	15	15	26.5
4	70	20	10	29
5	70	22.5	7.5	29.5
6	70	24	6	30
7	70	25	5	32
8	70	25.7	4.3	27
9	70	26.3	3.7	26



Fig. 2 Digital picture of samples after combustion (left to right PP, APP-PP, IFR-PP)

the IFR-PP systems were immediately increased. It was also observed that LOI values of IFR-PP systems increased obviously with the increasing addition of PA6T. When the mass ratio of PA6T to APP increased to 1:5, that is, PA6T was 5% and APP was 25%, the IFR-PP system showed the best flame retardancy with its LOI value reaching the maximum of 32. However, when the ratio of PA6T to APP continued to increase, LOI values of the IFR-PP systems decreased. When the mass ratio of PA6T to APP was 1:1, the LOI value decreased back to 26.5. Figure 2 shows the digital picture of the samples after combustion, it was observed both of PP and PP/APP(70/30) samples had almost no residual char obtained. However, a great quantity of residual char was produced of the PA6T/APP/PP(5/25/70) sample.

Table 2 gives LOI values of the IFR-PP systems with different addition of IFR, setting the ratio of PA6T to APP as 1:5. It was found, LOI values of the IFR-PP systems increased with the increase of IFR loading. LOI value of IFR/PP system was 26 with the addition of the 25% IFR. However, when the addition of the IFR increased to 40%, the LOI value reached to 36. This experimental result above demonstrated that this new IFR is effective in flame retarded PP.

Table 2 Effect of IFR addition on flame retardancy of IFR-PP systems

Sample	Components/%		LOI/%
	PP	IFR	
10	75	25	26
11	70	30	32
12	65	35	34
13	60	40	36

Thermal stability

The thermal degradation behaviors of the IFR-PP systems were investigated by TG in pure nitrogen. Figures 3 and 4 show the TG and DTG curves of the IFR-PP system and its components, main data collected from these curves was shown in Table 3. As shown from Fig. 3 and Table 3, PA6T showed very high thermal stability with its initial temperature 421 °C, based upon 5% mass loss. It was also found that the thermal degradation process of PA6T only had one step with the main peak of mass loss at 472 °C (Fig. 4), with char residue of only 6.54% at 700 °C, which demonstrated PA6T itself showed poor charring ability. The same happened to PP, the char residue of which at 700 °C was only 1.2%. However, when PA6T was mixed with APP, then incorporated into PP, the char residue at 700 °C of the flame-retarded PP composites was greatly improved to 12.7%. As known, the char residue always played a very important role in intumescent flame retarded system, so this

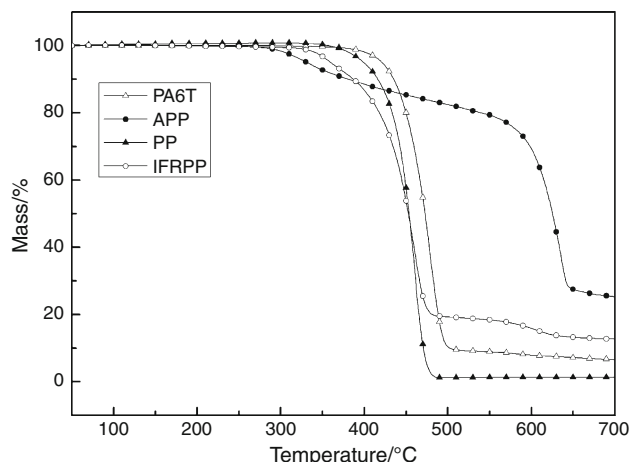


Fig. 3 TG curves of IFR-PP systems

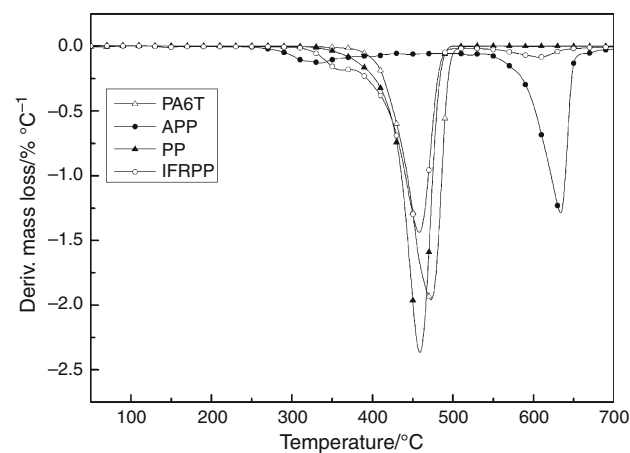


Fig. 4 DTG curves of IFR-PP systems

Table 3 Thermal degradation data under pure nitrogen by TG

Sample	T_{initial} /°C	$R_{1\text{peak}}$ %/°C	$T_{1\text{peak}}$ /°C	$R_{2\text{peak}}$ %/°C	$T_{2\text{peak}}$ /°C	$R_{3\text{peak}}$ %/°C	$T_{3\text{peak}}$ /°C	Char residue at 700 °C /%
PA6T	421	2.0	472					6.54
APP	331	0.13	334	1.3	633			25.3
PP	399	2.4	459					1.2
PP/APP/PA6T(70/25/5)	359	0.18	360	1.44	458	1.29	633	12.7

T_{initial} the initial decomposition temperature (based on 5% mass loss)

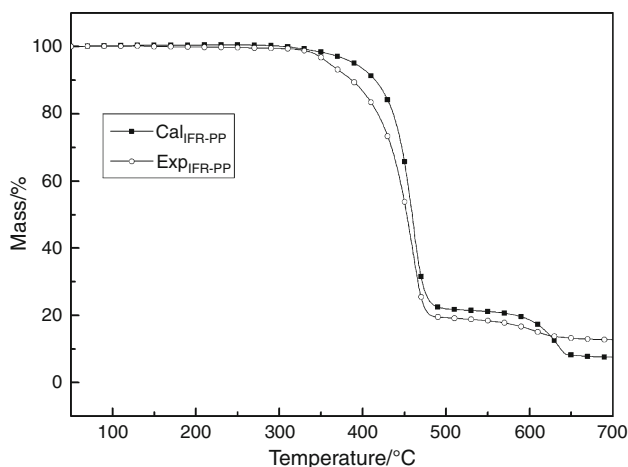
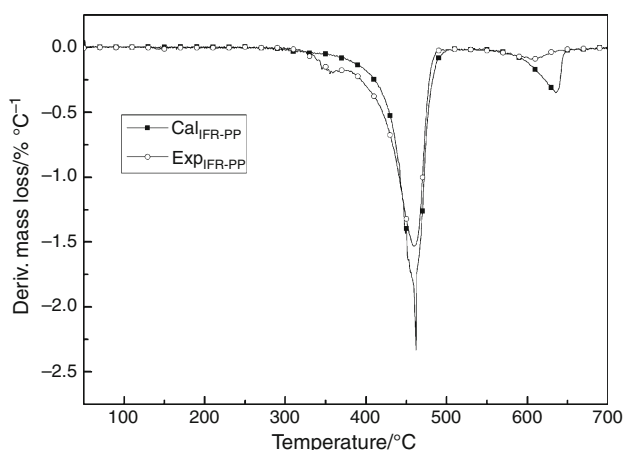
$R_{1\text{peak}}$ the decomposition speed at the first decomposition peak

$T_{1\text{peak}}$ the temperature of the first decomposition peak

$R_{2\text{peak}}$ the decomposition speed at the second decomposition peak

$T_{2\text{peak}}$ the temperature of the second decomposition peak

is related to its good performance on the LOI test before. Figures 5 and 6 show the experimental and theoretical TG and DTG curves of PP/APP/PA6T (75/25/5) system. The theoretical curves were calculated based upon the mass percentage of the ingredients in the IFR-PP system.

**Fig. 5** Experimental and theoretical TG curves of IFR-PP system**Fig. 6** Experimental and theoretical DTG curves of IFR-PP system

As could be seen, obvious difference between the experimental and theoretical curves was observed. It was found, the addition of IFR promoted decomposition of the IFR-PP system, with more mass loss at 350–600 °C (Fig. 5), compared with the theoretical curve. However, the experimental residual char became more than the theoretical one after 640 °C, which could be related to that, the thermal degradation peak found around 650 °C in the theoretical DTG curve did not exist in the experimental DTG curve in Fig. 6. It could be deduced some high-temperature stable material was produced in the char after the former decomposition step. All above indicated that the addition of IFR had modified the thermal degradation behavior of the IFR-PP system.

To further investigate the thermal degradation behavior of the IFR-PP system. TG-FTIR work was carried out on PA6T and PA6T/APP(1/5) mixture in pure nitrogen. Figures 7 and 8 give the experimental and theoretical TG and DTG curves of PA6T/APP(1/5) mixture, respectively. As shown in Fig. 7, remarkable difference was observed between the experimental and the theoretical TG curves of PA6T/APP system, that is, the experimental residual mass was much lower than the theoretical residual mass at 310–500 °C. This could indicate some kind of reaction between APP and PA6T happened, accelerating thermal degradation of the mixture obviously at first and leading to a very fast mass loss. However, an interesting phenomenon happened. The experimental residual mass became higher than the theoretical one after 600 °C. Some obvious difference was also found between the experimental and theoretical DTG curves in Fig. 8. First, the peak of mass loss appearing at 470 °C in the calculated curve was greatly advanced to 358 °C in the experimental one, and then, the mass loss rate around 640 °C in the experimental curve was less than the calculated DTG curve. So according to the analysis above, it was deduced some high temperature stable char residue was formed after the synergistic reaction between PA6T and APP to prevent the mass loss with temperature increasing.

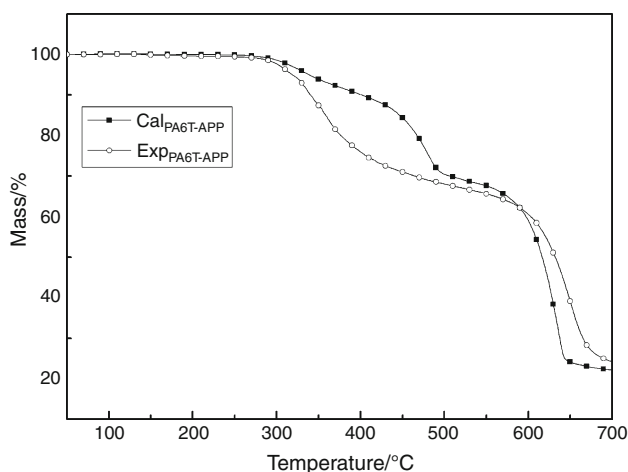


Fig. 7 Experimental and theoretical TG curves of PA6T/APP(1/5) mixture

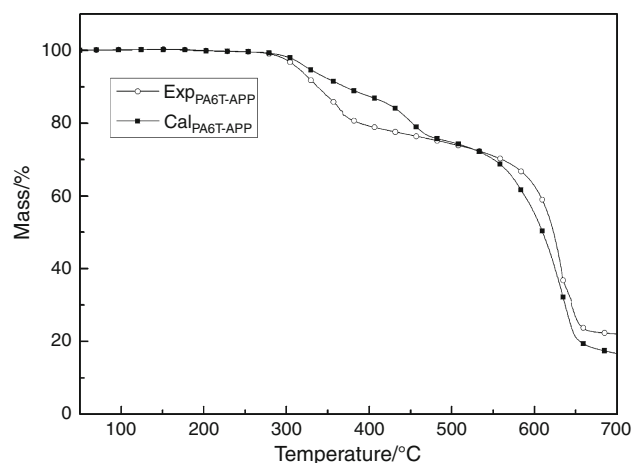


Fig. 9 Experimental and theoretical TG curves of PA6T/APP(1/5) mixture under air

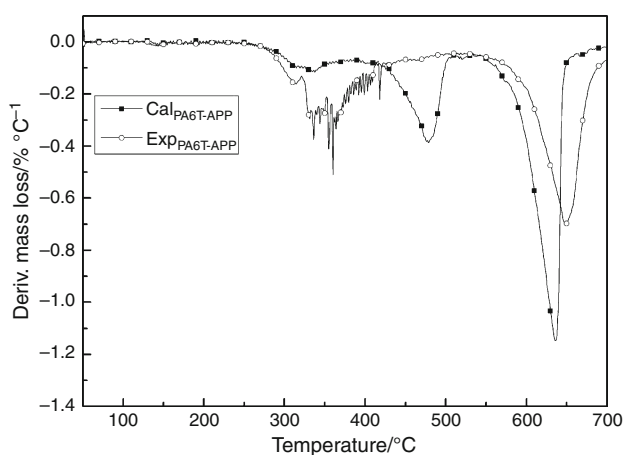


Fig. 8 Experimental and theoretical DTG curves of PA6T/APP(1/5) mixture

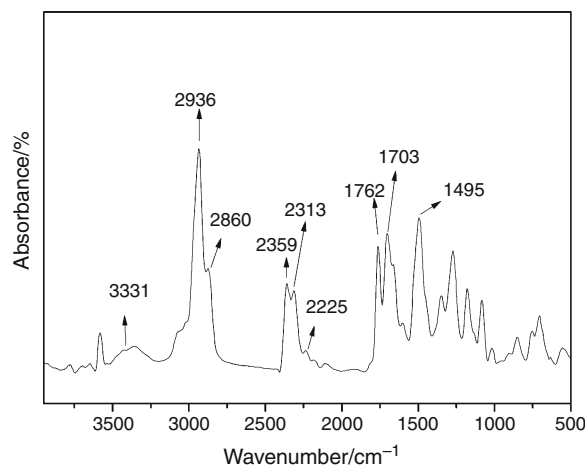


Fig. 10 FTIR spectrum of gaseous products of decomposition of PA6T collected at 472 °C under nitrogen

Because of the presence of oxygen during the LOI tests of the flame-retarded PP system, so the TG work of APP/PA6T (5/1) in air was also carried out to give a better relation between the TG result and flame retardancy improved, shown in Fig. 9. It can be seen that, the TG result in air is quite similar with the one in pure nitrogen shown in Fig. 7. At the beginning, the reaction between APP and PA6T under air accelerated the thermal degradation of the mixture, leading to the experimental residual mass was much lower than the theoretical residual mass at 310–450 °C, however, after 560 °C, the experimental residual mass became higher than the theoretical one.

To find more details of the reaction between PA6T and APP, FTIR spectra of the gaseous products during the thermal degradation of PA6T and PA6T/APP(1/5) mixture in pure nitrogen were given in Figs. 10 and 11. The FTIR spectrum of PA6T volatiles detected at 472 °C,

corresponding to the largest mass loss of PA6T, was shown in Fig. 10. It was concluded that, water (3500–3800 cm^{-1}), aliphatic hydrocarbons (2936, 2860 cm^{-1}), carbon dioxide (2359, 2313 cm^{-1}), carbonyl compounds (1762, 1703 cm^{-1}), benzenoid hydrocarbons (1495 cm^{-1}) were the major gaseous products during the thermal decomposition of PA6T. In addition, ammonia (3331 cm^{-1}) and nitriles (2225 cm^{-1}) were also found [17, 18].

According to the complicated DTG curve of PA6T/APP system shown in Fig. 8, especially at range of 300–450 °C, the FTIR spectra of volatiles of PA6T/APP mixture in thermal decomposition were detected at 320, 400, 660 °C, respectively, shown in Fig. 11. Compared with the spectrum of PA6T in Fig. 10, obvious difference was found. At 320 °C, corresponding to the beginning of decomposition of the mixture, ammonia (3331, 964, 927 cm^{-1}) was the main product involved, mostly deriving from degradation

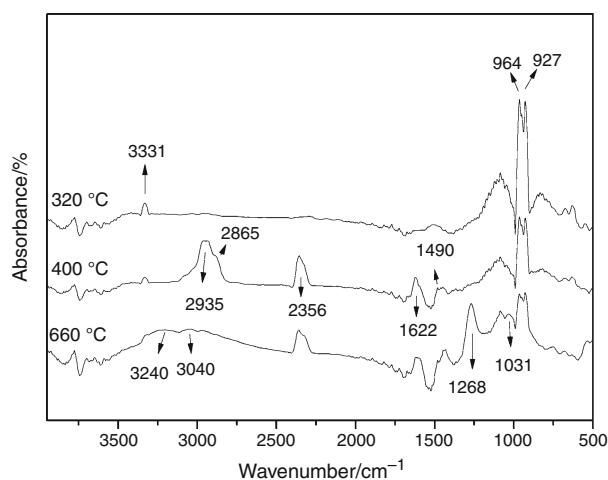


Fig. 11 FTIR spectra of gaseous products of decomposition of PA6T/APP(1/5) under nitrogen collected at different temperature

of APP [18]. When the temperature increased to 400 °C, apart from ammonia, new strong absorptions of aliphatic hydrocarbons (2935, 2865 cm^{-1}), carbon dioxide (2356 cm^{-1}), benzenoid hydrocarbons (1490 cm^{-1}), attributed to the thermal decomposition of PA6T, and nitrogen dioxide (1622 cm^{-1}) were found. However, the carbonyl compounds and nitriles, which were found in the thermal decomposition of pure PA6T (Fig. 10) were not observed. This could indicate the addition of APP modified the composition of the gaseous products of decomposition of PA6T. When the temperature rose to 660 °C, corresponding to the second largest mass loss of the mixture, it could be observed, the absorption peak of aliphatic hydrocarbons became weak, overlapping with absorption peak of ammonia and the probably new wide absorption peaks at 3240 and 3040 cm^{-1} , which were contributed to unsaturated C–H. Furthermore, some new absorption peaks at 1268, 1031 cm^{-1} were also found, attributed to P=O and P–O, respectively [19]. These information above indicated that phosphoric material could be evolved in the gaseous products of decomposition of the mixture.

The TG-FTIR work of the mixture above confirmed the reaction between PA6T and APP. That is, APP destabilized PA6T with modifying the composition of the major volatile products of the mixture: suppression of carbonyl compounds, increase of ammonia, and nitrogen dioxide which could dilute oxygen concentration on combustion. However, this could hardly explain the fire retardant action of PA6T/APP/PP system, because only addition of APP to PP did not show good fire retardant performance (Table 1), in which case, lots of ammonia could be released. So residual char of the PA6T/APP mixture obtained at 700° from the TG-FTIR work was investigated by FTIR to find a better

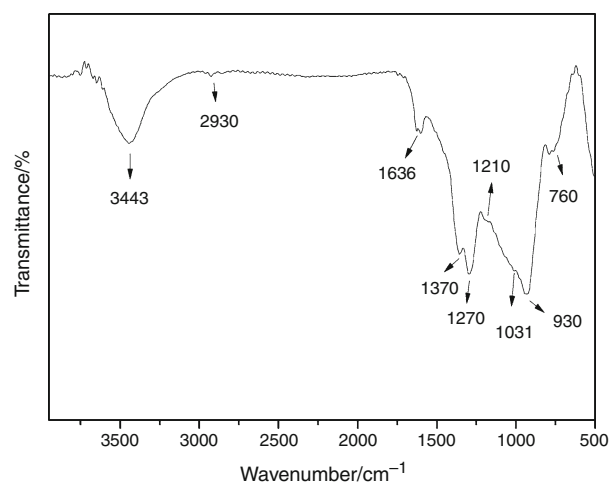


Fig. 12 FTIR spectra of the residual char of PA6T/APP(1/5) at 700 °C

understanding of the flame retardant behavior. As can be seen from Fig. 12, absorption peak of aliphatic hydrocarbon at 2930 cm^{-1} ($-\text{CH}_2$) was very weak, the wild absorption peak around 3443 cm^{-1} , assigned to the stretching mode of $-\text{OH}$ from the P–OH group, and absorption peaks observed at 1636, 1270 cm^{-1} (stretching mode of P=O), 1031 cm^{-1} (P–O) could indicate the presence of polyphosphoric acid [19]. The absorption at 1370 cm^{-1} seems to indicate that phosphorus oxynitrides could be present in this residue. Furthermore, absorptions around 1210, 930, and 760 cm^{-1} could be attributed to a phosphorus-nitrogen crosslinked polymer of the phospham type [20]. However, the exact association of these absorptions to specific bonds is not possible by FTIR because of broad and overlapping peaks. Because of the high temperature stability of these crosslinked materials, the residual char layer containing these materials could perform as a barrier between the flame and the polymeric material during combustion effectively.

Morphology of the residual char

As for the intumescent flame retardant system, it is noted that the intumescent residual char plays a very important role in improving flame retardant behavior of the composites. Morphology of the residual char of PA6T/APP/PP (5/25/70) system obtained after combustion was investigated by SEM. As can be seen from Fig. 13, it was found a cohesive, dense cellular char layer without clear holes formed, which could effectively serve as a barrier between the flame and the polymeric material to protect underlying material, this is related to its great performance in flammability (Table 1).

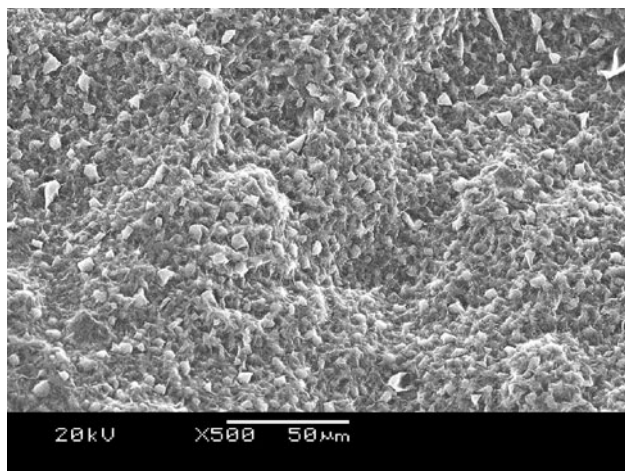


Fig. 13 SEM of the residual char of PA6T/APP/PP (5/25/70) after combustion

Conclusions

A novel intumescent flame retardant was prepared for PP from APP (as acid source and blowing agent) and PA6T (as carbonization agent). When the mass ratio of PA6T to APP was 1:5, the total loading of IFR was 30%, LOI value of the IFR-PP system reached to 32. The TG and TG-FTIR work indicated that, there was some reaction between PA6T and APP, resulting in the modification of the gaseous products of the PA6T/APP (1/5) mixture in thermal degradation and residual char containing some high-temperature stable crosslinked material. Moreover, the morphology of the residual char obtained after combustion of PA6T/APP/PP (5/25/70) investigated by SEM suggested that the novel IFR-PP system can form excellent char layer, which could hinder the transfer of heat flow and combustible gas and improve the flame retardancy of PP.

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