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Synthesis of novel phosphorus-based flame retardants containing 9,9-bis (4-hydroxyphenyl) fluorine and their reinforcements on the fire safety of polypropylene

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Abstract Fabricating an effective synergism to improve the flame-retardant (FR) efficiency is recently considered to be a very promising way to prepare high-efficient FRs system. A novel FRs containing phosphorus and (4-hydroxyphenyl) fluorene have been synthesized and characterized by FTIR, ^{1}H NMR and MS. The FRs were then incorporated into polypropylene (PP) in different ratios, and then, ammonium polyphosphate (APP) was added to the FRs/PP system, with subsequent investigation into the synergistic effects between FRs and APP. Limited oxygen index (LOI), UL-94 test and cone calorimeter test were adopted to investigate the FR properties of the flame-retardant PP composites. The LOI value is as high as 31.0%, when FRs/APP is 2/3. Moreover, due to the synergistic FR effects between FRs and APP, the pHRR of PP7 decreases from 783 kW m^{-2} (PP0) to 110 kW m^{-2} (PP7), which is 85% lower than those of PP. Meanwhile, thermogravimetric analysis (TG) was used to study the thermal degradation characteristics of the PP composites. The char residues increased from 0.02 mass% to 15.85 mass% at 650 °C when FRs/APP is 3:2, indicating that there are synergistic flame-retarding effects between FRs and APP. Generally, the stable char layers of FR/APP/PP composites are responsible for the improved FRs properties, and the char layers could not only effectively prevent the release of combustion gases from releasing but also hinder the propagation of oxygen and heat into the interior substrate.

Keywords Polypropylene · Flame retardants · Phosphorus · Fire safety

Introduction

As one of the significant general commodities of polymers, polypropylene (PP) has broad applications in nonwoven fabrics, coverings, containers, automobiles, construction, electronic and electric industry due to its outstanding mechanical properties, low density and good chemical resistance [1–4]. However, its limiting oxygen index (LOI) value is only 17.8% and the characteristic of easy combustibility of pure PP limits its further application in some aspects at which required high flame retardancy [5, 6]. As a result, the improvement in flame-retardant properties of PP materials has become an urgent and attractive topic all over the world. Among the various many ways of flame retardation of PP, halogenated fire retardants is considered to be the most efficient, but those halogen flame retardants also bring a number of problems, taking raising the volume of smoke and toxic gas for example.

Among the various halogen-free flame retardants, phosphorus-based flame retardants have been a hot spot and are considered as green environmental friendly flame retardants [7–9]. Flame-retarded materials by phosphorus-based flame retardants are essentially a special case of the condensed phase flame-retardant mechanism. The phosphorus-based flame retardants exhibit flame retardation by forming condensed char layer on the surface of polymer.

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The stable char layers could protect the underlying polymer matrix from further degradation. Therefore, the flame-retardant efficiency of phosphorus-based flame retardants mainly depends on the physical barrier effect of the char layer [10, 11]. However, the flame-retardant efficiency and the thermal stability of phosphorus-based flame retardants are not high. To overcome this disadvantage, many researchers have made great effect to develop novel phosphorus-based flame retardants with high thermal stability and high flame-retardant efficiency.

Among the various phosphorus-based flame retardants, phosphate ester-based flame retardants have attracted much attention due to its special structural design [12, 13]. Compared with the aliphatic phosphate ester, the cyclic phosphate ester has high thermal stability and excellent charring properties, which is an important object of the organic phosphorous flame-retardants research [11, 14]. Moreover, aromatic phosphate ester-based flame retardants belong to polyaromatic ring compounds, and the own rigid groups could impart the flame retardants with good chemical stability and thermal stability. As far as we concern, bisphenol fluorene has been widely used to improve the performance of polymers such as thermal stability and mechanical properties, but flame retardants based on bisphenol fluorine are rarely reported [15, 16]. Thus, a new idea has arisen that whether the cyclic phosphate ester and the bisphenol fluorene can be combined in one molecule as a novel thermal stable flame retardants.

Therefore, by considering all those aspects at present work, we prepared a novel kind of phosphorus-based flame retardants with cyclic phosphate ester and bisphenol fluorene. Then, the novel synthetic flame retardant was used to flame retard PP together with APP at the loading of 30 mass%, and the flame-retardant properties, thermal degradation behavior and combustion behavior of the composites were characterized and discussed.

Experimental

Materials

Polypropylene (PP) was supplied by Shanghai Secco Petrochemical Co., Ltd. Phosphorus oxychloride ($POCl_3$) was distilled at 104–106 °C before use. (4-Hydroxyphenyl) fluorine was supplied by Suqian City Wing Sing Pharmaceutical Co., Ltd. Neopentyl glycol was purchased from Datianfengtuo Chemical Reagent Co., Ltd. (Beijing, China). Anhydrous potassium carbonate was supplied by Beifangtianyi Chemical Industry Co., Ltd. (Tianjin, China). Other reagents were used as received without further purification.

Synthesis of the flame retardants (FRs)

In a 250-mL three-necked flask with a flux condenser, thermometer, a mechanical stirrer and dropping funnel, neopentyl glycol (20.8 g, 0.2 mol) and chloroform (100 mL) were mixed. After the solids were dissolved completely in ice-water bath, 39.8 g (0.26 mol) of phosphorus oxychloride was then slowly dropped into the above reaction vessel within 2 h, and then, the temperature of the mixtures was increased to refluxing temperature for 4 h. After that, the solvent was removed by a rotary evaporator; then, the white powders were obtained (intermediate II) [17]. The schematic processes for the reactions are presented in Scheme 1(a).

The intermediate II 73.8 g (0.4 mol) and acetonitrile (300 mL) were added into a three-necked flask with an ice bath equipped with a mechanical stirrer, flux condenser, dropping funnel and drying tube with calcium chloride. Then, 35.0 g of 9,9-bis (4-hydroxyphenyl) fluorene (0.1 mol) was added to the mixtures and the mixtures were kept stirring in the ice-water bath. Triethylamine (1.5 mL) was then slowly dropped into the above reactants, and the temperatures of the mixtures were increased to 60 °C for another 10 h. After that, the acetonitrile was removed by rotary evaporator and the white products were obtained. The white products were washed by distilled water and further recrystallized from distilled water and ethyl alcohol for two times. Then, the white products were obtained (49.46 g, 76.6%). The schematic processes of the reaction are presented in Scheme 1(b).

^1H NMR: 7.742–6.662 ppm, $–C_6H_2–$ in the benzene ring; 4.252–3.957 ppm, OCH_2; 1.325, 0.918, 1.325 and 0.918 ppm $–CH_3$.

MS: $[M + K]^+ = 687.4$; thus, the molecular weight of the FRs is 648.4.

Sample preparation

PP, APP and FRs were dried in vacuum at 80 °C overnight before use. According to Table 1, PP and FRs were put into the universal mill to mix evenly. The temperature of preheating open-type double-roller rubber mixing machine was increased to 170 °C, and then, PP and flame retardants were added to the preheating open-type double-roller rubber mixing machine for mixing. The PP composites were then hot-pressed at 170 °C into sheets of suitable thickness, and the flame-retardant PP composites were cut into pieces of the required specifications.

Scheme 1 Synthesis routes of FRs

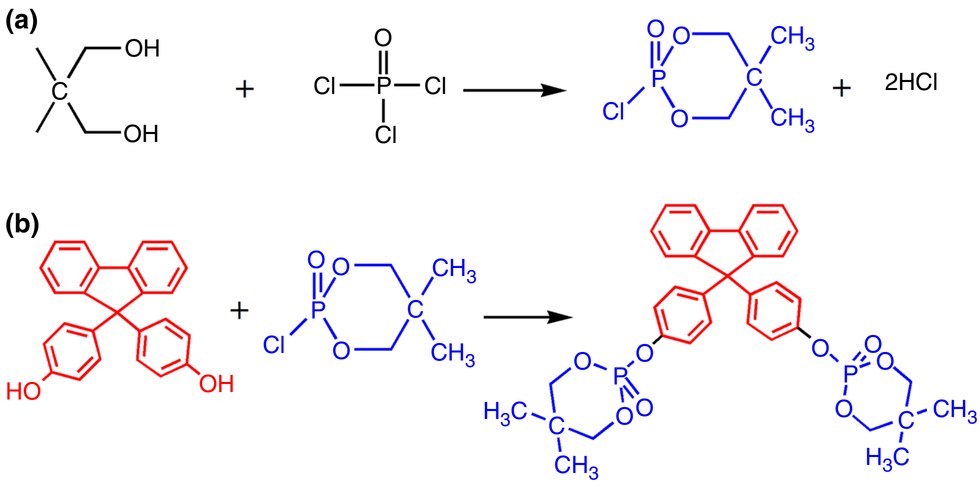

Table 1 The composition of FR/PP and FR/APP/PP composites

Samples	PP/g	FRs/g	APP/g
PP1	90	10	0
PP2	85	15	0
PP3	80	20	0
PP4	70	30	0
PP5	70	20	10
PP6	70	15	15
PP7	70	12	18
PP8	70	10	20

Measurements

The FTIR spectroscopy (wavelength range 4000–500 cm^{-1}) was recorded with Nicolet 6700 FTIR spectrophotometer using the thin KBr disk.

^{1}H NMR measurements were performed on AVANCE 400 Bruker spectrometer at room temperature.

The limiting oxygen index (LOI) values were measured on an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). According to ASTMD2863, the specimens used for LOI were of dimensions 100 mm × 6.5 mm × 3 mm.

The thermogravimetric analysis (TG) was carried out on TGA Q5000 IR thermal gravimetric analyzer (TA Instruments) at heating rates of 10 °C min^{-1}. About 4–10 mg of materials was heated from room temperature to 650 °C under air or nitrogen purges. The specimens used for vertical burning test are 100 mm × 13 mm × 3 mm, and test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China).

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The limiting oxygen index (LOI) values were measured on an HC-2 oxygen index meter (Shangyuan Analysis Instrument Co., China). The specimens used for the test were of dimensions 100 × 6.5 × 3 mm^3.

The flammability of the samples was also characterized by cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. In order to investigate the ignition times, all the samples were irradiated horizontally at a heat flux of 35 kW m^{-1} rather than 50 kW m^{-1}. Each specimen, with the dimensions of 100 mm × 100 mm × 3 mm, was mounted on aluminum foil and placed on a holder filled with the mineral fiber blanket, so that only the upper face was exposed to the radiant heater.

Scanning electron microscopy (SEM) was used to examine the surface morphology of the char residues after the cone calorimeter tests. The surfaces of char were sputter-coated with a conductive gold layer and the samples were tested.

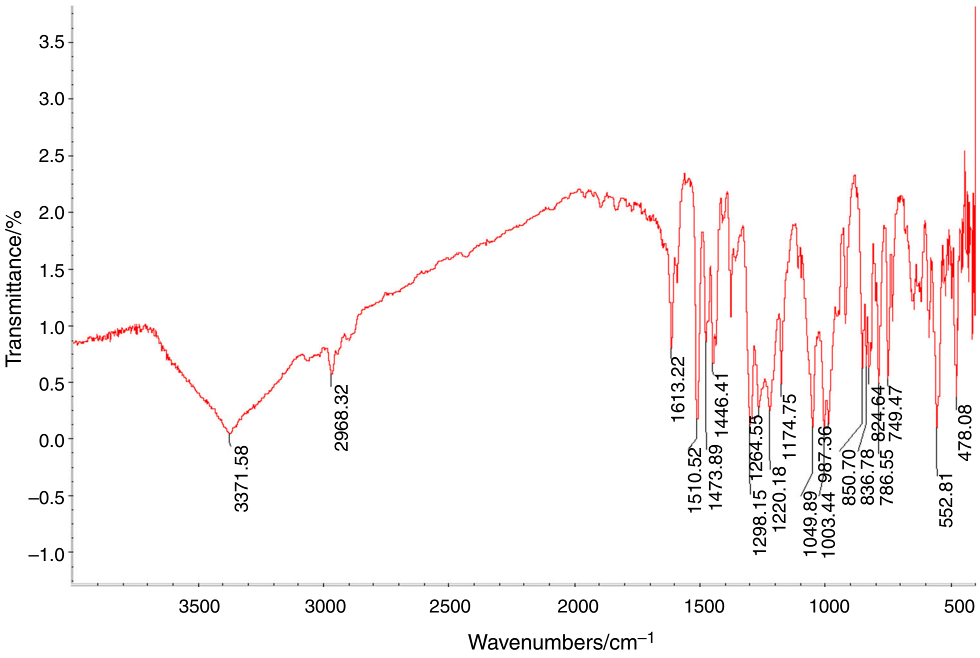
The measurements of tensile strength and elongation at break were carried out according to the Chinese standard of GB 13022-91 with a WD-20D electronic universal testing instrument (Changchun Intelligent Instrument Co. Ltd., Changchun, China) at a crosshead speed of 20 mm/min, and each sample is tested three times.

Results and discussion

Characterization of FRs

The chemical structures of FRs were characterized by FTIR, ^{1}H NMR and MS. The FTIR spectrum of FRs is shown in Fig. 1. The peak at 2968.32 cm^{-1} corresponds to the vibration absorption peak of methylene, and the peaks

Fig. 1 FTIR spectra of FRs



at 1613.22–1510.52 cm^{-1} belong to the stretching vibrations of benzene rings. Moreover, the strong absorptions band at 1174.75 cm^{-1} indicate the existence of P=O bonds and the characteristic peak for P–O bond exists at around 967.36 cm^{-1} [18]. Combining with the ^{1}H NMR and MS results (Figs. 2, 3), it is obvious that the FR has been successfully synthesized.

The TG results usually reflect quantitative information about the thermal stability and thermal degradation behaviors of the flame retardants. The thermal decomposition properties of FRs were investigated by TG in air atmosphere at the heating rates of 10 °C min^{-1}, as shown in Fig. 4. It can be seen that there are two degradation steps, and the first step is at the temperature range of 150–260 °C (mass loss 25%), while the second step is at the temperature ranges of 260–370 °C (mass loss 55%). The first step, which begins at around 150 °C, consists essentially of degradation of phosphate ester and the formation of phosphor materials due to the weak bond energy of P–O–C bonds. The second step begins at around 250 °C and has a maximum mass loss at around 300 °C. During the second step, the 9,9-bis (4-hydroxyphenyl) fluorine may degrade, which may be due to the catalyzing effect of phosphorus. Moreover, it is found that the char residues at 500 °C are as high as 41 mass%, and the high char residues indicate that the FRs may have the potential to be a high efficiency flame retardants. In order to investigate the thermal changes of FRs during the degradation process, the surface morphologies of FRs at different temperatures are investigated by SEM, as shown in Fig. 5. It can be found that the FR changes from massive particles to continuous carbon layers with the increase in temperature. The formation of continuous carbon layers is very important during flame-retardant process, because the carbon layers could protect the underlying polymer matrix from further degradation. Generally, the continuous carbon layers of FRs at high temperature may contribute greatly to the formation of condensed char layers during the thermal degradation process of flame-retardant PP.

Flame-retardant properties of FR/PP and FR/APP/PP composites

LOI and UL-94 tests are used to evaluate the flame retardancy of polypropylene. LOI is the minimum oxygen concentration by volume for maintaining the burning of polymeric materials; thus, it is an important parameter for evaluating the flame-retardant properties of polymeric materials. The UL94, which is vertical burning test method, contains three ratings: V-0, V-1 and V-2. The LOI and UL94 values of the samples are shown in Table 2. As for PP, the LOI value is only 17.8%. However, when 30 mass% of FRs was incorporated into the PP matrix, the LOI value increased to 24.8%, which is only 40% higher than those values of PP. Those indicate that FRs can improve the flame retardancy of PP. However, when APP was added into the FRs/PP system, the LOI values increased with the increased loading of APP. For example, the LOI values of PP4 are only 24.8%, but when APP replaces parts of FRs in the FRs/PP system, the LOI values increased to 31.0% (PP7), which is a great improvement. However, when the APP content is further increased, the

Fig. 2 ^{1}H NMR of FRS

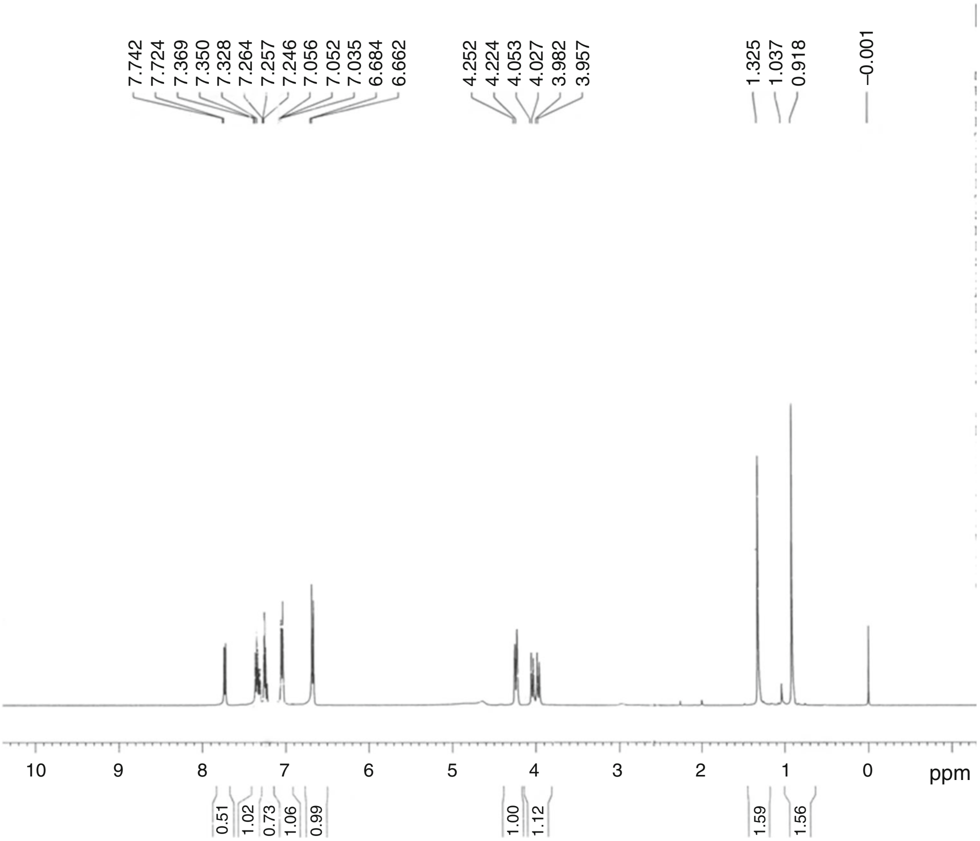
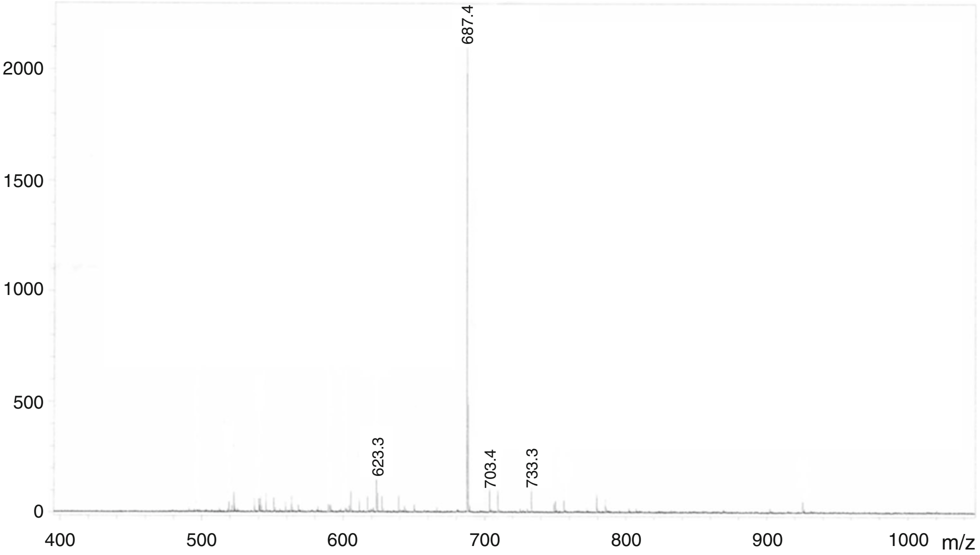


Fig. 3 Mass spectrometry of FRS



LOI value decreases to 28.0%. The LOI results indicate that synergistic flame-retarding effects exist between FRs and APP, and the FR/APP/PP systems exhibit improved LOI values. As for the UL94 results, the experimental results of the vertical burning rate indicate that the PP systems gave no rating. When 30% FRs were introduced into the PP matrix, the FRs/PP system can only reach the V-1 rating. Those indicate that FR has flame-retardant effect on the flame retardancy of PP. As for the APP/FRs/PP system, the materials can reach the V-0 rating. Those indicate that synergistic flame-retarding effects exist between FRs and APP in the PP matrix, which is in accordance with the LOI results. Generally, the LOI and UL94 results indicate that FR has effects on the flame

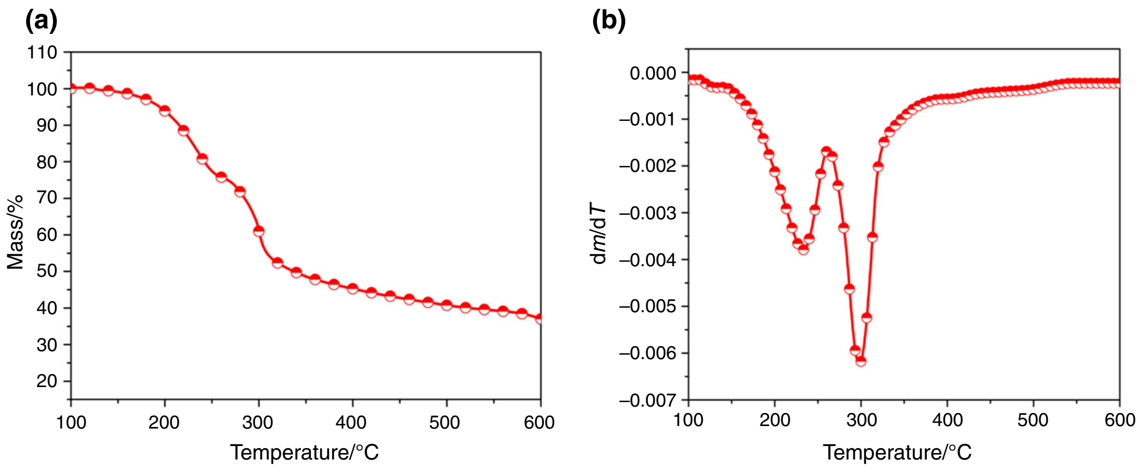
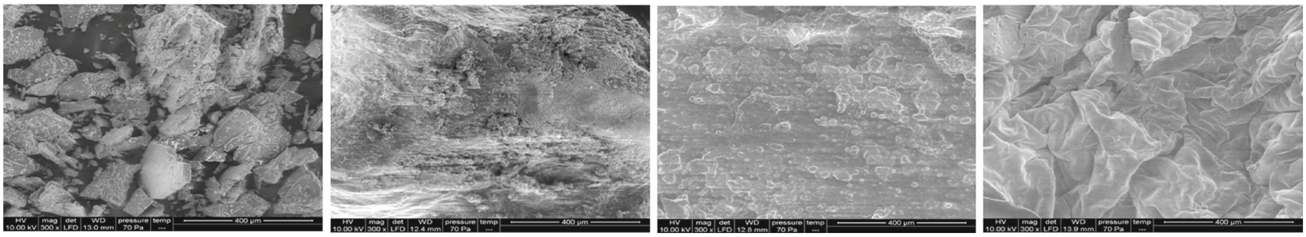


Fig. 4 TG and DTG curves of FRs in air atmosphere



25 °C 300× 200 °C 300× 300 °C 300× 500 °C 300×

Fig. 5 The SEM of the char residues at different temperatures

Table 2 LOI and UL 94 values of PP, FR/PP and FR/APP/PP composites

Samples	LOI/%	UL94
PP0	17.8	NR
PP1	19.6	V-2
PP2	21.4	V-2
PP3	22.5	V-2
PP4	24.8	V-1
PP5	29.0	V-0
PP6	29.0	V-0
PP7	31.0	V-0
PP8	28.0	V-0

retardancy of PP, but the effect is not significant. When the FRs and APP were incorporated into PP system, the flame-retardant effect is improved greatly due to the synergistic flame-retarding effects existed between FRs and APP.

The thermal properties of FR/PP and FR/APP/PP composites

TG profiles for PP and the flame-retardant PP composites at the heating rate of 10 °C min^{-1} in air atmosphere are shown in Fig. 6, and the data are shown in Table 3. Pure PP has a small amount of volatiles when the temperature increases to 265 °C. With the further increase in the temperature, the mass loss increases remarkably and the resulting char residue at 650 °C is only 0.02 mass%. As shown in Fig. 7, the thermal decomposition of PP in air is characterized by one decomposition steps, and FR/PP composites exhibit improved thermal stability than that of pure PP. Compared with pure PP, the incorporation of FRs and APP can improve the thermal stability of PP. For example, the $T_{5\%}$ of PP is only 291.83 °C, but as those for PP4 and PP7, the $T_{5\%}$ increased to 314.50 and 311.83 °C respectively. That is because the FRs could form a complete connector (Fig. 5), the complete connector could delay the inner PP matrix from degradation, so the $T_{5\%}$ of the flame-retardant PP increases significantly. Moreover, it is interesting to observe that the char residues of flame-retardant PP increase with the increased loading of FRs. For example, PP0 has only 0.02 mass% char residues at 650 °C, while the char residue of PP4 at 650 °C is as high as 4.72 mass%. As compared to FRs, FRs/APP system performs much better on improving the char residues at 650 °C. PP7 has the highest char residues at 650 °C (15.85 mass%), which indicates that there are synergistic effect between FRs and APP on catalyzing the char formation. Those results are in accordance with the LOI

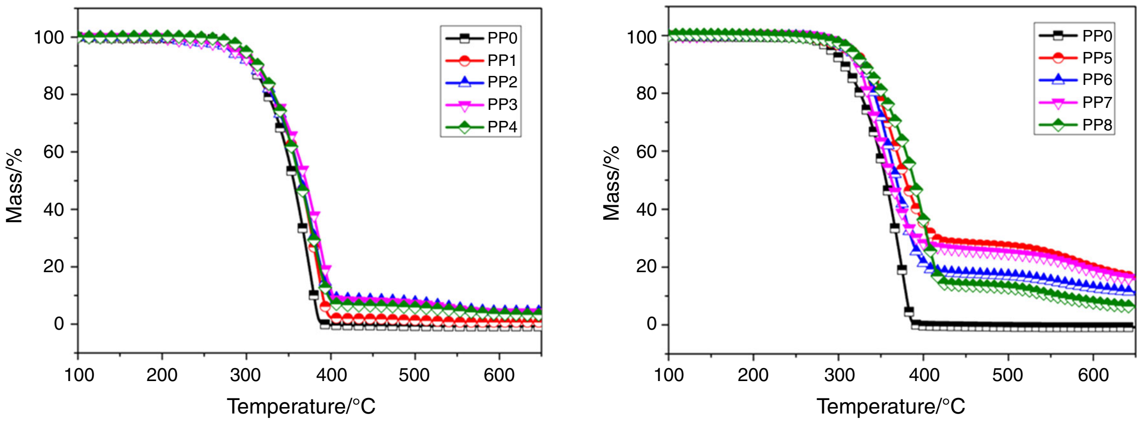


Fig. 6 TG curves of PP, FR/PP and FR/APP/PP composites in air atmosphere

Table 3 Thermogravimetric data of the PP composites in air

Samples	$T_{1\%}$/°C	$T_{5\%}$/°C	Char 650 °C
FRs	133.33	175.33	39.04
PP0	265.50	291.83	0.02
PP4	270.13	314.50	4.72
PP7	286.00	311.83	15.85

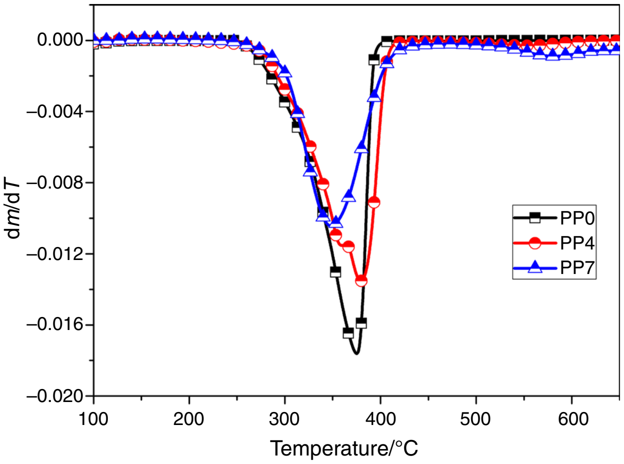


Fig. 7 DTG curves of PP0, PP4 and PP7 in air atmosphere

results. Generally, the char layers, which can protect the underlying materials from heat and oxygen, are an important factor in the flame retardancy of polymeric materials [19, 20]. Due to the synergistic flame-retardant effect, the FRs/APP system has a higher efficiency on catalyzing the formation of char layers during the thermal degradation process, and the higher char residues at high temperature will result in the improved flame-retardant effects such as LOI and UL-94 results.

The combustion properties of FR/PP and FR/APP/PP composites

Cone calorimetry is one of the most effective bench scale methods to study the flammability of polymeric materials. Heat release rate (HRR), in particular peak HRR (pHRR), is considered to be the most important parameter to evaluate the fire safety of polymer materials. The heat release rate (HRR) and total heat release (THR) curves of PP, FR/PP and FR/APP/PP composites are shown in Figs. 8 and 9, respectively. As shown in Fig. 8, when FR was introduced into PP matrix, the pHRR of FR/PP composites decreased from 783 kW m^{-2} (PP0) to 545 kW m^{-2} (PP4), which is 30% decrease. As shown in Fig. 9, the THR of FR/PP composites decreased from 198 MJ m^{-2} (PP0) to 139 MJ m^{-2} (PP4), which is 29% decrease compared with PP. Therefore, it can be assumed that the FR exhibits good flame retardancy on PP at the loading of 30 mass%. As shown in Fig. 8, the ignition times (ITT) are slightly decreased when the FRs and APP were incorporated into the PP matrix. Such a decrease is attributed to the low thermal stability and catalysis charring effect of FRs, which speeded up the thermal degradation of PP. As compared to FRs, FRs/APP system performs much better on improving the flame-retardant properties of PP. When APP was introduced into the FRs/PP system, both the pHRR and THR were decreased. The pHRR of PP7 is only 110 kW m^{-2}, which is 85% lower than those of PP. With the further increase in APP content, the pHRR of FR/APP/PP composites increases slightly. That is because the suitable proportions of carbon sources in FRs and acid sources exhibit synergistic flame-retarding effect, and the synergistic flame-retarding effect is in accordance with the LOI and TG results. Moreover, THR of PP decreased with the increased loading of APP. For example, the THR of PP is 197.2 MJ m^{-2}, while THR of PP8 is only 37.9 MJ m^{-2}. The reduced pHRR and THR are attributed to the

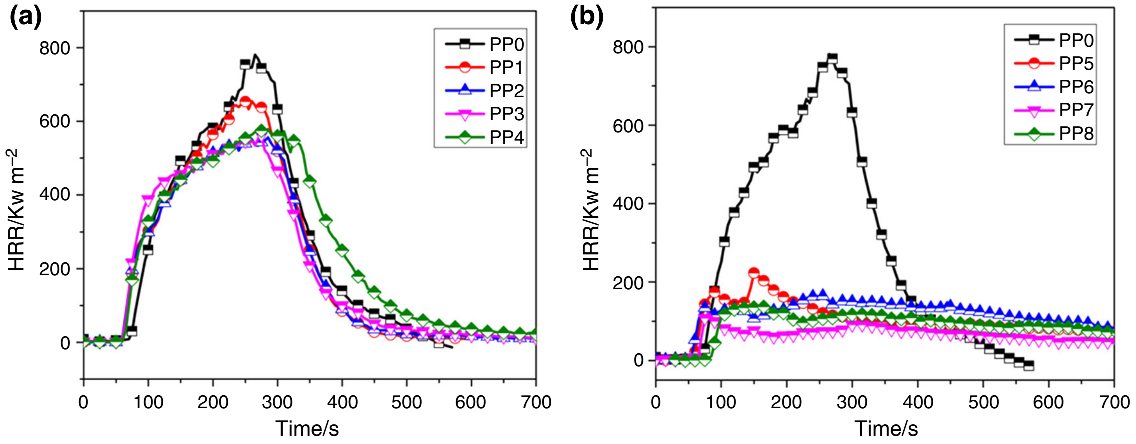


Fig. 8 The HRR curves of PP, FR/PP and FR/APP/PP composites during the cone test

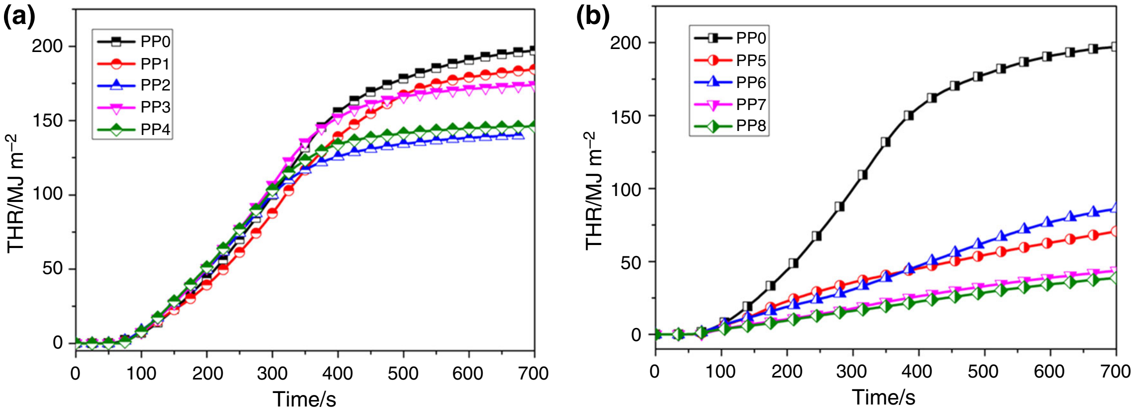


Fig. 9 The THR curves of PP, FR/PP and FR/APP/PP composites during the cone test

catalyzing charring effects of APP and FRs. Moreover, the decreased pHRR and THR imply great improvement on the fame retardancy of PP, which is in accordance with the LOI and TG results.

The char residues of PP, FR/PP and FR/APP/PP composites during and after the cone tests are shown in Fig. 10, which directly reflects the morphology of the char layers. As for the char residues of pure PP, it can be found that the PP was ignited easily and the flame highness of PP is higher than those of PP4 and PP7. Moreover, there are almost no char residues for PP after the cone test. When FR was incorporated into PP, the char layers of FR/PP composites expanded distinctly, indicating that condensed char layers were formed during combustion. The catalytic charring effect of FRs plays an important role in the char formation, but the char layers of FRs/PP are lower than those of FR/APP/PP composites. This phenomenon is due to the introduction of APP in the PP matrix, and APP has better catalyzing charring effect during the thermal degradation process of PP. The stable char layer could not only effectively prevent the release of combustion gases but also hinder the propagation of oxygen and heat into the interior substrate. As a result, the flame of FR/PP and FR/APP/PP composites during the cone test is weaker than those of PP. Generally, it can be found that the results of cone and char morphology for the composites are in accordance with the results of LOI and TG results. Thus, it is believed that this condensed chars are responsible for the improved thermal stability, enhanced flame retardancy and higher char residues.

The changes of the chemical structures in the condensed phase during the thermal oxidative degradation of PP composites were measured by the FTIR after heated at different temperatures, as shown in Fig. 11. As for PP4 at 300 °C, the peaks at 2968.98 and 2917.78 cm^{-1} are due to the stretching vibration of methyl and methylene, respectively. The characteristic peak at 1634.45 cm^{-1} is due to the stretching vibration of benzene ring, and the peaks at 1463.34 and 1376.74 cm^{-1} are due to the bending vibration of C=C bonds and C–H bonds. Moreover, the peak at 1112.64 cm^{-1} is due to the O–P–O bonds. When the temperature was further increased to 400 °C, the intensity

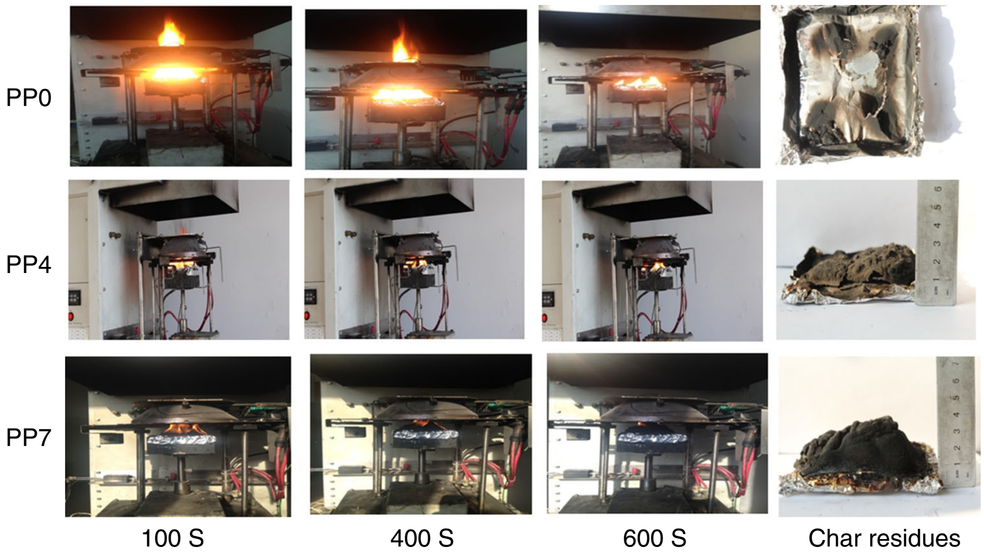


Fig. 10 The char residues of PP, FR/PP and FR/APP/PP composites during and after the cone tests

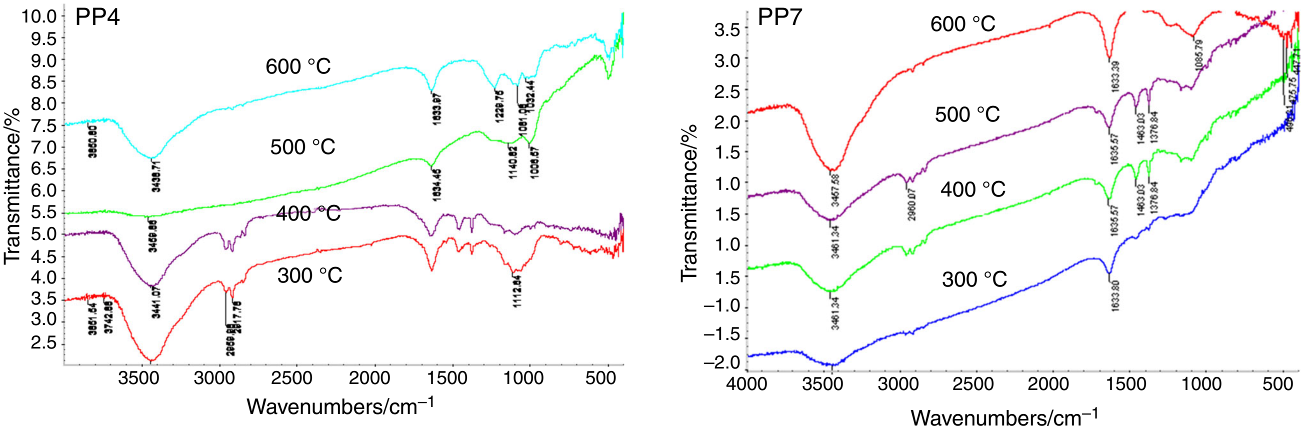
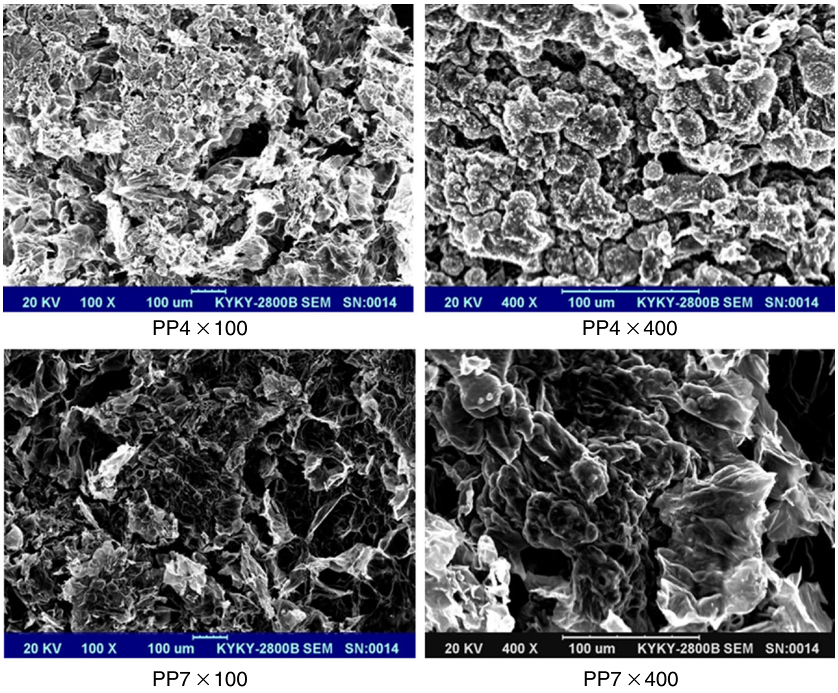


Fig. 11 The FTIR of PP4 and PP7 at different temperatures

of the absorption peaks of O–P–O bond decreased, resulting in weaker broad peaks. As for the composites at 500 °C, the characteristic absorption peaks of methyl and methylene disappeared, indicating that molecular chains of PP had broken completely. When the temperature increased to 600 °C, the band for P=O at 1229.25 cm^{-1} still existed, indicating that phosphorus-based elements existed at high temperature and the phosphorus-based elements could reinforce the char layers greatly. As for PP7 at 400 °C, the intensities of peaks at 1463.03 cm^{-1} for C=C bonds and 1376.84 cm^{-1} for C–H bonds increased, and the peaks at around 1200–1000 cm^{-1} for the O–P–O and P=O bonds were enhanced, indicating that FRs and APP decomposed and formed phosphoric acid or metaphosphoric acid. When the temperature of PP7 increased to 500 °C, the characteristic peaks of methylene bond disappeared, but the peaks for the O–P–O and P=O at around 1200–1000 cm^{-1} still existed, indicating phosphorus-based char layers formed at this temperature.

In order to further investigate the relationships between the morphology of the formed char layers and flame-retardant properties of APP/FR/PP composites, scanning electron microscopy (SEM) was used to investigate the microstructure of char layers after the cone test, as shown in Fig. 12. The char layer of PP4 is uneven and could not form an integral carbon layers. Thus, the barrier effect of the char layers is very limited during the combustion of PP4. That is because the catalytic charring effect of FRs is limited, when the amount of gas under the carbon layer reaches a certain value, the gas breaks through the carbon layer overflow, making the integrity of carbon layer damaged [21, 22]. As those for PP7, the surface of the char layers is more continuous and has inflated holes, which is mainly attributed to the APP in the FRs/PP system. The results indicate that the addition of APP can enhance the



PP4 × 100 PP4 × 400
PP7 × 100 PP7 × 400

Fig. 12 The SEM of the char residues after the cone test

quality of the char layers. The condensed char layers could effectively reduce the escape of flammable volatile components, protect the under lying materials form oxygen, suppress the further degradation and combustion of PP matrix and then lead to outstanding flame retardancy for APP/FR/PP composites. Generally, APP has a good synergistic effect with the flame-retardant FRs, and the flame-retardant PP exhibited reduced pHRR and THR.

The smoke release and mechanical properties of FR/PP and FR/APP/PP composites

In order to further estimate the fire risks of the PP, FR/PP and FR/APP/PP composites, the smoke data obtained from the cone test were analyzed. Figure 13 shows the specific extinction area (SEA) and carbon monoxide release rate (COY) of PP, PP4 and PP7. It can be found that the introduction of FRs and APP can influence the smoke release of PP significantly. Compared with PP0, the SEA and CO release increased with the addition of flame retardants. As for PP, the av-SEA was 226.20 m^2 kg^{-1} and the av-COY was 0.02 kg kg^{-1}. However, when FRs are introduced into PP matrix, the av-SEA of PP4 increased to 589.17 m^2 kg^{-1} and the av-COY increased to 0.05 kg kg^{-1}. Those indicate that the addition of FRs could increase the smoke release, resulting in the increased smoke toxicity of PP. That may be due to the fact that the FRs could inhibit the complete combustion of PP. However, compared with PP4, the introduction of APP into FRs/PP system can reduce the av-SEA and the av-COY slightly. The av-SEA of PP7 decreased to 457.00 m^2 kg^{-1}, and av-COY of PP7 decreased to 0.04 kg kg^{-1}. From the char residues of PP7 after the cone test, it can be found that the addition of APP can benefit to the formation of condensed carbon layers, and the condense carbon layers could reduce the release of smoke toxicity to a certain extent. Generally, FRs could increase the smoke release of PP, but the incorporation of APP into the FRs/PP system could reduce the smoke release to a certain extent, which may due to the condensed flame-retardant mechanism.

The mechanical properties of PP and the flame-retardant PP composites are evaluated by tensile tests, as shown in Fig. 14. According to the tensile strength of PP and the flame-retardant PP composites, it is very interesting to find that FR has the effect of improving the tensile strength of PP: 30 mass% FRs in the PP matrix which leads to a 63% increase in the tensile strength of PP, but the elongation at break of the flame-retardant PP decreases when FRs and APP are incorporated into PP matrix. Generally, FRs can act as plasticizer, and plasticizer can improve the processing performance of PP, resulting in improved tensile strength.

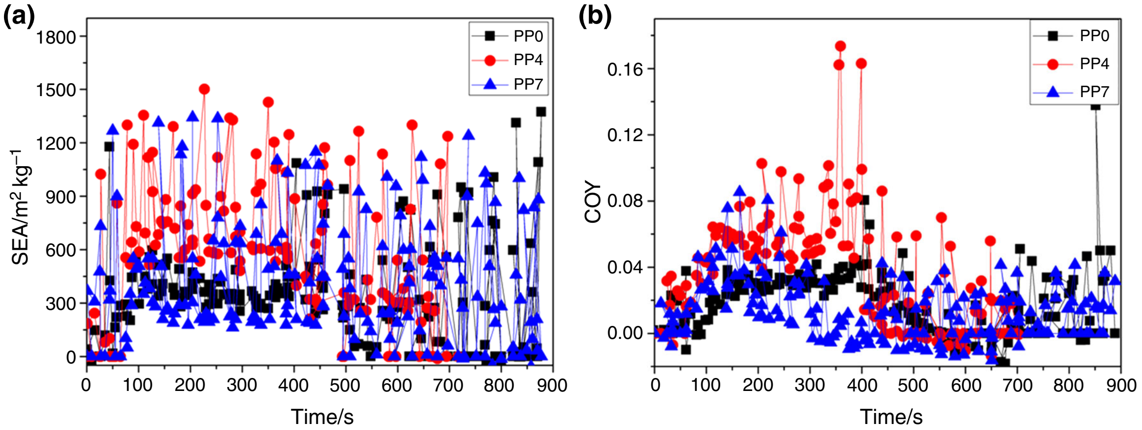


Fig. 13 The SEA and av-COY curves of PP0, PP4 and PP7 during the cone test

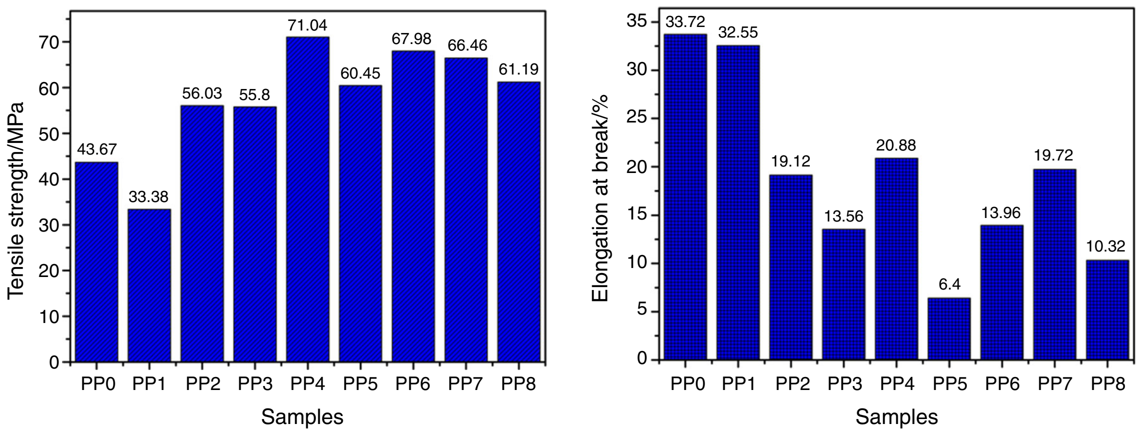


Fig. 14 The mechanical properties of PP, FR/PP and FR/APP/PP composites

Conclusions

A novel flame retardants (FRs) containing phosphorus and (4-hydroxyphenyl) fluorene have been synthesized and characterized. The FR combined with APP was then incorporated into PP at different ratios. The flame-retardant PP exhibited both good flame retardancy and thermal properties when the two components of flame retardants existed at an appropriate proportion. The flame-retardant PP can reach UL-94 V0 rating, and the LOI is as high as 31% when the mass fraction ratio of FRs/APP is 3:2. The improved flame-retardant effect may be attributed to the synergistic flame-retardant effect between FRs and APP. The char residues at 650 °C in an air atmosphere increased from 0.02 to 15.85 mass% notably when FRs/APP is 3:2, indicating an improvement of thermo-oxidation resistance. From the cone test, it is found that both the THR and pHRR of the flame-retardant PP are reduced, and there are synergistic effects between FRs and PP in the flame retardancy of PP. Compared to the FR/PP composites, av-SEA and av-COY results indicate that APP also exhibits good smoke suppression properties due to the stable char layer of FR/APP/PP composites. Generally, the stable char layer of FRs/APP/PP system could not only effectively prevent the release of combustion gases but also hinder the propagation of oxygen and heat into the interior substrate.

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