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Intumescent Flame-retardant Modification of Polypropylene/Carbon Fiber Composites

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Abstract: To improve the flame resistance of polypropylene (PP)/carbon fiber (CF) composite materials, triazine char-forming agent (TCA) was compounded with ammonium polyphosphate (APP) or modified APP (CS-APP) in a 2:1 ratio to prepare intumescent flame retardant (IFR) and the modified intumescent flame retardant (CS-IFR) in this paper. Flame retardancy and thermal degradation behaviors of the composites modified by IFR and CS-IFR were characterized by Fourier Transform Infrared (FTIR), contact angle measurement, oxygen index (OI), vertical burning tests (UL-94), thermogravimetric analyer (TGA), and thermogravimetric analyzer coupled with Fourier transform infrared (TG-FTIR). It was found that 25.0 phr of IFR and 24.0 phr of CS-IFR could improve the LOI value of PP/CF composites to 28.3% and 28.9%, respectively. At the same time, a UL-94 V-0 rating was achieved. The experimental results show that the IFR and CS-IFR prepared could effectively improve the flame retardancy and thermostability of PP/CF composites, and they would greatly expand the application range of PP/CF composite materials.

Key words: carbon fiber; polypropylene; intumescent flame retardant; flame retardant modification; composite materials

1 Introduction

Polypropylene (PP) is a translucent polyolefin resin, which becomes one of the most widely used thermoplastics in the world due to its low density, good mechanical properties, excellent acid and alkali resistance, and good machinability[1-4]. However, with a limiting oxygen index (LOI) of only about 17%-18%, PP is easily ignited and burns out directly in the air. The PP burning is fast and accompanied by severe droplets[5-7]. Besides, its heat release rate is high. Therefore, to use PP without flame-retardant modification will be a great fire hazard and directly threaten the safety of our personal lives and property.

Carbon fiber (CF) is an excellent inorganic filler with high elastic modulus, high strength, low density and corrosion resistance. The CF reinforced PP composite materials not only possess greatly improved mechanical properties but also have a light weight. At present, PP/CF composites are extensively applied in transportation, aerospace, medical and new energy fields. CF itself is a high temperature resistant and non-flammable inorganic fiber, but it will continuously transport the molten resin to the flame end in the PP/CF composite system, just like the "wick" of a candle[8]. CF accelerates the combustion and the dripping of the material. Therefore, it is necessary to study the modification of flame retardant properties of PP/CF composites.

There has been a small amount of research on flame-retardant modification of PP/CF composites so far. These works mainly focus on two aspects. On the one hand, some researchers have made attempts to modify the CF surface and weaken the thermal conductivity of the CF by such means as grafting CF with a flame-retardant functional group and coating the CF surface with an endothermic heat-insulating layer[9-13]. On the other hand, some investigators try to modify the flame retardance of the matrix material, and adding a suitable flame retardant is proven the most convenient and effective[1,14,15].

IFR, which has broad development prospects due to its strong designability and adaptability, is a hot research topic in the field of flame retardants. Yun Liu *et al*[16] reported the flame retardant effect of intumescent flame retardant OMMT/APP/Ca on long glass fiber reinforced polypropylene (LGFPP). The results show that OMMT/APP/Ca / LGFPP composites have good flame retardancy. When the content of OMMT/APP/CA is 20%, the LOI values of the material are improved to 31.3%. It has passed UL-94 V-0 flame retardant test, and the mechanical properties of the material are less deteriorated than before. Lai Xuejun *et*

al[17] replaced the dehydrating agent and foaming agent with melamine pyrophosphate (MPP). They studied the flame retardant mechanism of MPP / PER / PP composite flame retardant system. The results show that MPP / PER system is suitable for flame retardant modification of PP. The LOI of PP increases to 29.0% when the content of MPP / per is 25% at a mass ratio of 3:1.

There is no effective flame retardant for PP/CF composites nowadays. We studied the combustion behaviors and flame retardant mechanism of PP/CF composites modified by different flame retardants, and obtained the formula of flame retardant PP/CF Composite with better comprehensive properties. In additon, part of the experimental data and stage conclusions can also be used as reference examples of the same type of research.

2 Experimental

2.1 Materials

Ammonium polyphosphate (APP, industrial) was purchased from Hongtai Industrial Co. Ltd (Shenzhen, China). Triazine char-forming agent (TCA, industrial) was purchased from Dao-ran New Material Co. Ltd (Jinan, China). PP was purchased from Sinopec Hainan Refining and Chemical Co. Ltd. Titanate coupling agent (CS-201) was purchased from Chuang Shi Chemical Additive Co. Ltd (Nanjing, China). Ethanol (analysis) was purchased from Chemical Reagent Co. Ltd. Oxidized carbon fiber (NCF_2) was prepared by using the nitric acid liquid phase to oxidize the CF surface[18].

2.2 Modification of APP

The dried APP powder was dispersed in a single-necked flask containing absolute ethanol at a mass ratio of 1:3. After thorough stirring, a solution of CS-201(the solvent was ethanol) with a concentration of 10% was added (the amount of CS-201 was the 1% of APP). The mixture liquid in the flask was then stirred for 1 h at 50 ℃. Afterwards, the modified product was filtered and vacuum-dried for 8h at 90 ℃ to afford CS-APP.

2.3 Preparation of samples

Based on previous research in the laboratory, the NCF_2 was added to the PP matrix as the reinforcement prior to the addition of the flame retardant. The formula is presented in Table 1.

After the fully dried PP, NCF_2 and flame retardant were separately prepared according to the formulation, they were sequentially extruded through an extruder, granulated by a pelletizer, dried in an oven, and formed by an injection machine and a hot press to yield the corresponding flame-retardant PP/CF composite spline. Specifically, the temperature of the extruder was set at 165 ℃(1#-5#), 185 ℃(6#-9#), or 195 ℃(10#-11#),

and the main engine speed and the barrel rotation speed were 80 r/min and 90 r/min, respectively. The temperature of the injection machine was 200 ℃, the injection pressure was 7 MPa, the injection time was 12 s, the clamping time was 9 s, and the cooling time was 6s. The injection mold should be preheated in the oven at 80 ℃ for 1 hour before use. The temperature of the hot press was 185 ℃ and its pressure was 10 MPa.

Table 1 Composition of flame-retardant PP/CF composites (phr)

Samples	PP	NCF_2	IFR[a]	CS-IFR[b]
1#	85	15	—	—
2#	85	15	20	—
3#	85	15	22	—
4#	85	15	24	—
5#	85	15	25	—
6#	85	15	—	20
7#	85	15	—	22
8#	85	15	—	24
9#	85	15	—	25
10#	100	—	22	—
11#	100	—	—	22

a APP: TCA = 2:1; b CS-APP: TCA = 2:1; phr: parts per hundreds of resin

2.4 Characterization

We analyzed the chemical differences between APP and CS-APP in KBr pellets through FTIR spectra. Spectra in the optical range of 500-4 000 cm^{-1} were obtained by an average of 32 scans at a resolution of 4 cm^{-1}.

The water contact angles of APP and CS-APP were compared to study the variations in the surface hydrophilicity.

OI tests were carried out as per GB/T2406.2-2009 to quantify how easy a material will combust. Each set of tests involved 5-10 splines with a size of 80 mm×10 mm×4 mm. The LOI can be calculated by Eq.(1)：

$$LOI = \frac{[O_2]}{[O_2]+[N_2]}\times100\% \qquad (1)$$

In the formula, $[O_2]$ represents the oxygen concentration in the environment, and $[N_2]$ represents the concentration of nitrogen in the environment. The sum of the two values is 1.

According to GB/T2408-2008, UL-94 tests were conducted to measure the flame-retardant properties of materials, simulate the combustion process and detect the flame rating of materials. Five splines with a size of 130 mm×13 mm×3 mm were experimented in each set of tests.

The purpose of TGA tests was to measure the thermal stability of materials. It is based on the principle that the mass of a polymer decreases gradually due

to pyrolysis as the temperature increases at a constant rate. By analyzing the linear relationship between the polymer weight loss rate and temperature, the effect of the addition of flame retardants on the initial decomposition temperature of the material, the maximum decomposition rate temperature, and the amount of residual carbon can possibly be clarified. During the tests, samples (10 mg) were heated from 40 ℃ to 800 ℃ at a rate of 10 ℃/min in a nitrogen atmosphere.

TG-FTIR tests aim to further explore the mechanism of action of the flame retardant. The tests combine the thermal weight loss with the infrared spectra to measure the gas composition of the polymer at different temperatures by real-time monitoring. TG-FTIR is a powerful tool for studying the flame-retardant mechanism. Specifically, samples were heated from room temperature to 800 ℃ at a rate of 10 ℃/min in an air atmosphere, and the scanning period of the infrared spectrometer was set to 1 min.

Field emission scanning electron microscopy was used to analyze the morphology of the carbon layer formed during the combustion of the polymer. The carbon layer at the front of the sample after the LOI tests was observed under cold field emission scanning electron microscopy.

Melt flow rate (MFR) test was conducted to investigate the effect of flame retardant addition on material processing properties.

Mechanical properties measurement includes tensile property, bending property and notched impact property tests. It mainly explores the influence of the addition of the flame retardant on material mechanical properties.

3　Results and discussion

3.1　Characterization of CS-APP

Fig.1 shows FT-IR spectra of APP, CS-201, and CS-APP. In the spectrum of APP, the asymmetric vibration absorption peak at 3 218 cm^{-1} corresponds to the N-H bond in NH_4^+ and the symmetric stretching vibration absorption peak at 1 257 cm^{-1} indicates the presence of the P=O bond. Besides, vibration absorption peaks at 1 056 cm^{-1}, 1 024 cm^{-1}, 881 cm^{-1} and 797 cm^{-1} represent the P-O bond in HPO_4^{2-}, PO_3^{3-}, P-O, and P-O-P, respectively. In CS-201 spectrum, P-O absorption peak also appears at 881 cm^{-1} and 797 cm^{-1}, and an absorption peak symbolizing the presence of O-Ti-P appears at 1 032 cm^{-1}, indicating that the two drugs are indeed APP and CS-201. The comparison of the infrared spectra of APP and CS-APP reveals that their absorption peaks almost fully overlap, which suggests that CS-201 does not react chemically with APP. In other words, CS-APP is a mixture combined with physical adsorption.

Fig.2 presents the water contact angles of APP and CS-APP. It can be seen from the figure that after modification, the water droplets on CS-APP notably elevates in height, and the surface water contact angle increases from 18.1° to 43.8°. The APP is highly hydrophilic because there is a large amount of -OH and NH^{4+} on its surface. However, after modification by CS-201, a layer of hydrophobic fatty chain molecules is attached to the surface of CS-APP, which, therefore, shows the hydrophobic characteristics. The above experiments confirm that our modification achieves the intended purpose.
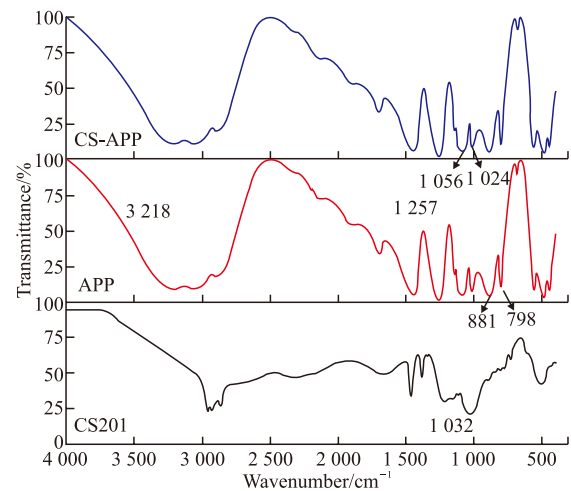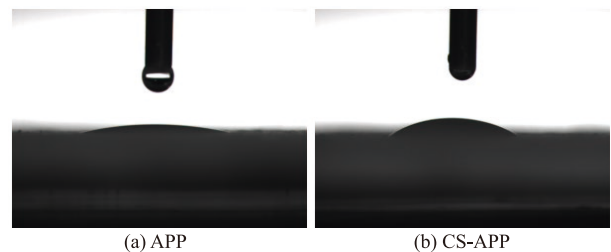

Fig.1　FTIR spectra of CS-APP

(a) APP　　　　　　　(b) CS-APP

Fig.2　Water contact angles of APP and CS-APP

3.2　Thermal properties of samples

Table 2 represents the combustion performance of PP/CF composite materials modified by IFR and CS-IFR flame retardants. When more than 20 phr of IFR or CS-IFR was added in the material, all the samples, except the 2# sample, had a LOI value higher than 26%, which reached the standard of the nonflammable material. Additionally, all the samples passed the UL-94 tests and reached the standard of flame retardant materials, except for the 2# and 3# samples. The results indicate that IFR and CS-IFR are applicable to flame retardant modification of PP/CF and have good flame-retardant effects.

Further comparison of the flame-retardant effect between IFR and CS-IFR suggests that the LOI and UL-94 test results of CS-IFR are better than those of

IFR when the addition amount of the two flame retardants was the same, whether the test material was pure PP resin or PP/CF composite materials. It suggests that CS-IFR has a better flame retardant effect than IFR, and there are two reasons accounting for it. On the one hand, CS-201 contains flame-retardant pyrophosphate, so it works in coordination with the IFR system to enhance the flame-resistance performance of the flame retardant. On the other hand, the weakened agglomeration tendency of CS-APP after modification promotes its dispersion and even distribution in the PP matrix, thereby increasing the flame-retardant effect of CS-APP. What's more, according to table, the optimum addition amount of IFR and CS-IFR is 24-25 phr and 20-24 phr, respectively.

Table 2 Combustion properties of flame-retardant PP/CF composites

Samples	PP /phr	NCF₂ /phr	IFR /phr	CS-IFR /phr	LOI /%	UL-94
0#	100	—	—	—	18.5	Failed
1#	85	15	—	—	21.3	Failed
2#	85	15	20	—	25.3	Failed
3#	85	15	22	—	26.2	Failed
4#	85	15	24	—	27.3	V-1
5#	85	15	25	—	28.3	V-0
6#	85	15	—	20	27.0	V-1
7#	85	15	—	22	27.8	V-1
8#	85	15	—	24	28.9	V-0
9#	85	15	—	25	29.2	V-0
10#	100	—	22	—	27.4	Failed
11#	100	—	—	22	28.7	V-1

(a) 4#   (b) 6#   (c) 8#   (d) 11#
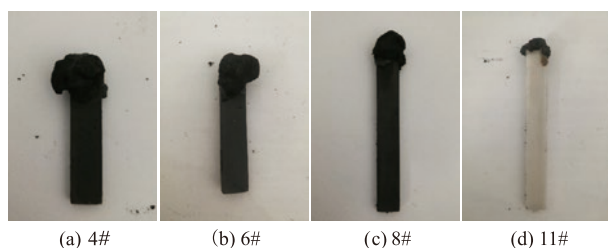
Fig.3 Residual spline of the flame-retardant PP/CF composites after LOI tests

Fig.3 compares the morphologies of the combusted PP/CF composites after LOI tests. It can be seen that the foamed porous carbon layer was formed at the burned place of all the samples, and the portion below the carbon layer remained intact. A small amount of fluid still dripped from the PP sample, but there were no molten droplets falling from the PP/CF sample. The results indicate that the intumescent flame retardant well isolates the material from heat and oxygen, inhibits the material combustion, and suppresses the formation of droplets.

Through comparing Fig.3(c) and Fig.3(d), it was found that when the same amount of the flame retardant was added, there were more carbon and less molten droplets formed in the burned PP/CF sample. The reason is that the presence of fibrous CF in PP/CF contributes to the formation of a more loose carbon layer.

The comparison of Fig.3(a), Fig.3(b), and Fig.3(c) shows that almost the same amount of carbon is generated in the three samples, but the carbon layer of the 8# spline is more regular and more uniform than that of the 4# spline. Moreover, the data in Table 3 prove that CS-APP indeed promotes the formation of a better expanded carbon layer to achieve flame resistance of materials.

Table 3 Thermal stability of samples modified with intumescent flame retardants

	0#	1#	3#	7#	10#	11#
$^{a}T_{-5\%}$/℃	388.3	405.9	370.6	368.0	368.7	364.6
$^{b}T_{max}$/℃	457.3	457.5	464.1	466.0	466.2	464.1
$^{c}D_{max}$/(%·min⁻¹)	−22.2	−21.4	−16.3	−13.2	−17.1	−16.3
Char residue/% (800 ℃)	1.7	12.9	22.4	23.0	7.4	9.7

a is the initial decomposition temperature, b is the temperature at the maximum decomposition rate, and c is the maximum decomposition rate

Table 3 and Fig.4 discuss the thermal stability of the flame-retardant PP and PP/CF composites modified by IFR and CS-IFR. Samples 0#, 10#, and 11# are PP materials, and samples 1#, 3#, and 7# are PP/CF composite materials. After the addition of IFR and CS-IFR, the $T_{-5\%}$ and D_{max} of PP materials and PP/CF composite materials are significantly reduced. These two values decline more in PP/CF composites than in PP materials, and more in CS-IFR-modified materials than in IFR-modified materials. The char residue rate of PP materials and PP/CF composites is significantly improved at 800 ℃. Simultaneously, the char residue rate of PP/CF composites is greater than that of PP materials, and CS-IFR-modified materials has a larger char residue rate than IFR-modified materials.

In the heating process, IFR and CS-IFR decompose prior to PP because the initial decomposition temperature of the two flame retardants is lower than that of PP. Therefore, the flame retardants protect the main part of the material and absorb heat at beginning. However, with the progress of the heating process, the mass of the flame retardants gradually decreases, which leads to a decline in the $T_{-5\%}$ of the material. The decrease in Dmax and the increase in Tmax indicate that the outer carbon layer inhibits the pyrolysis of the material and mitigates its degradation. It is the flame-resisting mechanism of the flame retardant in condensed phase. Specifically, the phosphoric acid released by the thermal decomposition of the APP in the flame retardant
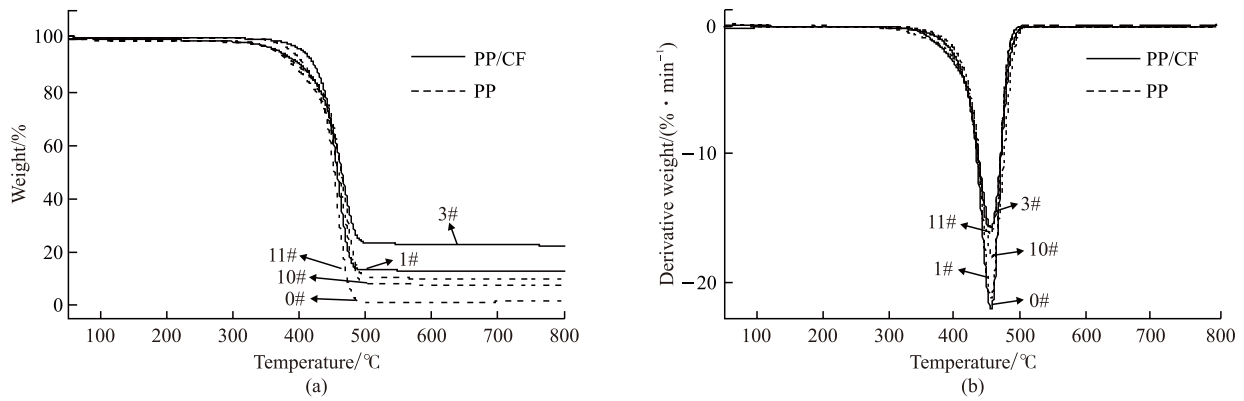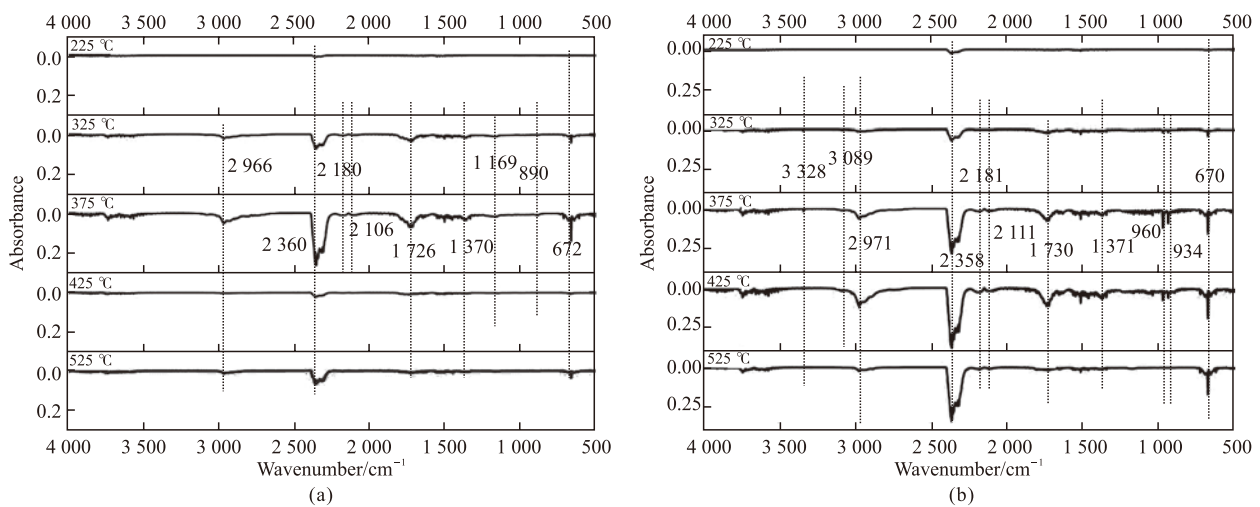
Fig.4 TG and DTA data of samples

Fig.5 TG-IR spectra of PP/CF and CS-IFR/PP/CF composites

hinders the pyrolysis reaction by consuming the free radicals generated by PP decomposition. Meanwhile, the flame retardant coordinates with TCA (the carbon source) to transform the material into char. As a result, more PP resin is left in the solid phase, and the amount of residual carbon is increased.

Based on the above data and analysis, both IFR and CS-IFR can effectively prevent the pyrolysis, promote the char formation and improve the thermal stability and flame retardancy of PP materials and PP/CF composites through the condensed phase. Besides, CS-IFR is obviously superior to IFR in improving the thermal properties of the materials, and the thermal stability of flame-retardant PP/CF composites is better than that of PP materials.

Fig.5 is infrared spectra of the gas products of samples 1# and 7# after pyrolysis at air conditions. As indicated in Fig.5(b), the main gas phase products contain not only CO_2, CO, aliphatic hydrocarbons, aldehydes and ketones formed by the cracking of PP resin, but also NH_3 (new absorption peaks at 3 328 cm^{-1}, 960 cm^{-1}, and 934 cm^{-1}). The NH_3 was generated by thermal decomposition of APP and TCA in the material.

At lower concentrations, NH_3 is a non-combustible gas that promotes the formation of the porous carbon layer and dilutes the combustible gas during the combustion of the material. In addition, no characteristic peak corresponding to the P group is found in the infrared spectra, indicating that the P component in the flame retardant eventually remains in the solid to promote the formation of char. In the meantime, the characteristic peaks representing the presence of olefins and CO can still be observed in the infrared spectrum at 425 ℃ in Fig.5(b), while only the characteristic peak of CO_2 is left at 425 ℃ in Fig.5(a). It verifies the flame retardant effect of CS-IFR in condensed phase.

Table 4 Thermal stability data of samples in the air atmosphere

Samples	$^aT_{-5\%}$/℃	$^bT_{-50\%}$/℃	$^cT_{max}$/℃
1#	288.8	386.6	401.7
7#	304.2	389.7	390.6

a is the initial decomposition temperature, b is the temperature at which the weight loss rate is 50%, and c is the temperature at the maximum decomposition rate

Table 4 shows the thermal stability data of PP/CF and CS-IFR/PP/CF composites in the air atmosphere. Oxygen catalyzes the pyrolysis reaction of the material, so that the $T_{-5\%}$ and T_{max} of the material are lower than those in the nitrogen atmosphere. In addition, compared

with unmodified PP/CF composites, the CS-IFR/PP/ CF composites have higher $T_{-5\%}$ and $T_{-50\%}$ but a lower T_{max}, suggesting that CS-IFR does retard and inhibit the pyrolysis reaction of the material. This result is consistent with the findings achieved by the infrared spectrum analysis of the gas phase products.

Fig.6 signifies the carbon layer morphology of IFR- and CS-IFR-modified flame retardant PP and PP/ CF composite materials after combustion. Comparing sample 7# to sample 11#, it reveals that the carbon layer surface of PP is continuous and relatively flat, with a small number of pores of different sizes distributed on it. This is a feature of the expanded carbon layer, and such a structure can effectively prevent the movement of the resin fluid and block heat and oxygen transmission downward. However, the carbon layer of PP/CF is rough and discontinuous, with mutual perforation holes. The previous LOI sample drawings also prove that the carbon layer of PP/CF is thicker than that of PP, so it can more effectively block the flow of the molten resin and retard the transfer of heat and fuel. Moreover, the carbon layers of samples 3# and 7# have a similar structure and morphology, and they both have an expanded carbon layer with pores due to the presence of CF.

Taking the above analysis results together, it can be concluded that both IFR and CS-IFR can promote the formation of an expanded carbon layer in the PP and PP/CF composites to inhibit the melting and dripping of the material and suppress the combustion. The carbon layer formed by the PP/CF composites has a better effect of inhibiting material melting and dripping than that formed by the PP. Besides, the flame-retardant effect of CS-IFR is also better than that of IFR.

3.3 Mechanical and machining properties of samples

Table 5 represents the mechanical properties of different samples. After the addition of IFR or CS-IFR, all the mechanical properties of the materials show a descending trend, except for the bending properties. The more the flame retardant added is, the more significantly the material mechanical properties decrease. In addition, the mechanical property degradation effect of CS-IFR is greater than that of IFR.

It is common that the flame retardant affects the material mechanical properties[19] since its main function is to improve the flame-retardant property of materials. A large dose of flame retardants usually changes the original structure of a material, and reduces the component bearing the load in the material. The bending strength and flexural modulus reflect the ability of a material to resist bending deformation. The reason for the improvement of the bending property of the material is that the flame retardant, PP and CF rub against

Table 5 Mechanical properties of samples

Samples	Tensile strength /MPa	Elongation at break /%	Bending strength /MPa	Flexural modulus /MPa	Notched impact strength/(kJ·m^{-2})
1#	34.7	11.2	51.8	2663.3	5.5
2#	30.8	10.0	53.3	3145.7	4.1
3#	30.3	8.8	52.8	3196.0	3.9
4#	29.8	8.3	51.9	3115.4	3.7
5#	30.1	9.0	51.8	3305.8	3.9
6#	30.1	8.0	51.6	3166.7	3.8
7#	29.8	9.0	51.9	2924.4	3.8
8#	28.8	8.1	50.9	3108.5	3.7
9#	28.6	7.1	49.7	3237.5	3.7
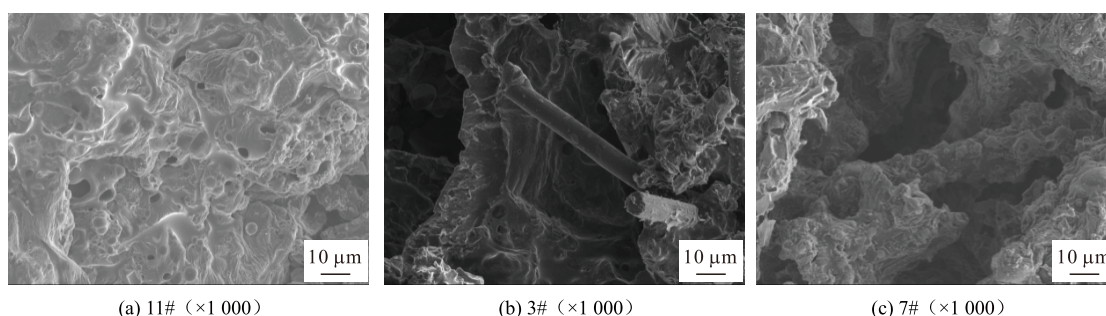
(a) 11# （×1 000）   (b) 3# （×1 000）   (c) 7# （×1 000）

Fig.6 SEM images of the carbon layer of composite materials after combustion: (a) is a CS-IFR/PP sample (11#); (b) is a CS-IFR/PP sample (3#); (c) is a CS-IFR/PP sample (7#)

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each other when they are bent and deformed, making more energy converted into heat.

The melt index of PP/CF composites modified by CS-IFR and IFR was measured at 230 ℃ and under 2.16 kg load, and the data are shown in Fig.7. According to the figure, the addition of the intumescent flame retardants deteriorates of the processing properties of the material. Besides, the effect of flame retardants on material processing properties is dose-dependent. The reason is that flame retardants do not melt at 230 ℃ and prevent the flow of the fluid. The melt index of the CS-IFR-modified materials is generally lower than that of the IFR-modified materials when the addition amount of the two flame retardants is the same. The result implies that the CS-APP has a better compatibility with the resin and produces a stronger friction force with the melt when it flows.
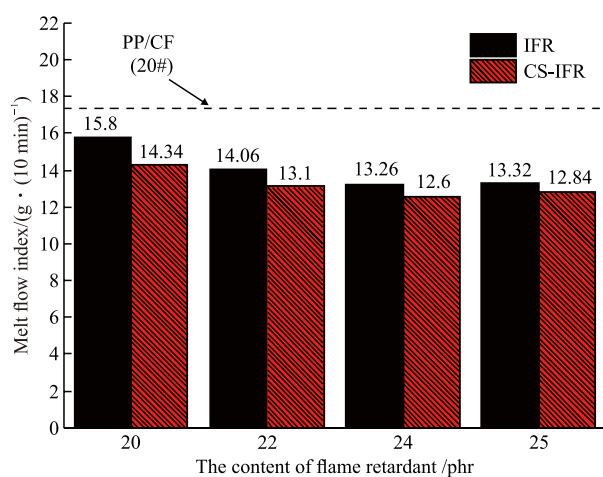

Fig.7 Melt flow index

4 Conclusions

In this paper, the flame-retardant performance of IFR- and CS-IFR-modified PP/CF composites is studied. Both IFR and CS-IFR can effectively improve the flame retardancy of PP/CF composites, and the effect of CS-IFR is better than that of IFR. The mechanism of action of both IFR and CS-IFR is gas phase-supplemented condensed phase flame retardance. When 24 phr of CS-IFR and 25 phr of IFR are added, the LOI values of the material are improved to 28.9% and 28.3%, respectively. Besides, the flame-retardant grade of the material reaches V-0 level. The data prove that CS-IFR and IFR effectively improve the thermal stability of materials. CS-APP is a mixture formed by CS-201 and APP in a physical adsorption manner, and its surface is hydrophobic. The flame retardant CS-IFR prepared from CS-APP greatly enhances the flame resistance of PP/CF composites although it slightly reduced the mechanical strength of the materials. The

carbon layer formed on the carbon fiber inhibits the heat transmission of CF during the combustion process.

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