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Flame-retardant Wrapped Ramie Fibers towards Suppressing "Candlewick Effect" of Polypropylene/Ramie Fiber Composites*

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Abstract In this work, a flame-retardant polypropylene (PP)/ramie fiber (RF) composite was prepared. The ramie fibers were wrapped chemically by a phosphorus- and nitrogen-containing flame retardant (FR) produced *via in situ* condensation reaction so as to suppress their candlewick effect. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) demonstrated that the ramie fibers wrapped chemically by FR (FR-RF) were obtained successfully. Thermogravimatric test showed that the PP/FR-RF composite had more residue and better thermal stability at high temperatures than the PP/RF composite. Cone calorimeter (CC) results indicated that the peak of heat release rate (PHRR) and total heat release (THR) correspondingly decreased by 23.4% and 12.5% compared with the values of neat PP/RF. The PP/FR-RF composite created a continuous and compact char layer after the combustion. Combining FTIR analysis of char residue after CC test with heat conduction coefficient results, it could be concluded that the charring of FR on RF greatly weakened the candlewick effect of RF, and more char residue in the RF domain facilitated the formation of more continuous and compact char layer in the whole combustion zone, consequently protected PP composites during combustion, resulting in the better flame retardancy of PP/FR-RF composite than that of PP/RF composite.

Keywords: Ramie fiber; Polypropylene; Composite; Flame retardance; Candlewick effect.

INTRODUCTION

Compared to synthetic fibers, environmental friendly natural fibers have some advantages, such as their availability, renewability, low density, mechanical properties and so on[1–4]. For example, tensile strength of ramie fibers (RF) can reach 850–900 N/mm^2, and higher than those of flax and jute, and be almost equal to that of glass fiber[5, 6]. So, natural fibers have become alternative reinforcing fillers in various areas of polymer composites. So far, numerous studies for RF composites have been reported[7, 8], including polypropylene/ramie fiber (PP/RF) composites. Similar with the other fibers reinforced polymeric composites, the ramie fiber reinforced polymeric composites are facing a major challenge of flammability for their commercial applications.

At present, many free-halogenated flame retardants have been used to improve the flame retardancy of polymers[9–12]. For PP/RFs composites, the applied flame retardants mainly contain free-halogenated intumescent flame retardant, aluminum hydroxide, magnesium hydroxide and metal borates[10–12]. Generally, these researches focus on the bulk treatment to improve the combustion performance and the results are not so satisfied. Actually, as organic composites, both polypropylene and ramie fiber are sensitive to flame, and furthermore the

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"candlewick effect" caused by ramie fibers can further support the combustion of PP/RF composites[13–15]. As a result, it is very important to reduce the "candlewick effect" in flame retarding PP/RF composites. However, the combustion-supporting role of ramie fibers in polymer matrix is almost ignored by many researchers, especially for short ramie fibers.

Recently, a few researchers realized the importance of interfacial flame retardation in polymer composites[13, 16–18], and they found that the candlewick effect could be weakened by the interfacial flame-resistant method in polymer/fiber composites. It must still be difficult to eliminate the negative influence of ramie fibers in composites completely, because thermal conductivity of PP/RF composites is probably higher than virgin PP and the combustion heat coming from the ramie fibers cannot be ignored when the composite is burnt. It is critical to flame retard PP/RF composites by reducing wick effect and protecting ramie fibers in the combustion process. Unlike the glass fibers in the composites, the ramie fibers in the biocomposites are flammable, so both the "wick effect" and the flammability of ramie fibers will be primary factors that reduce the flame-retardant effects of PP/RF biocomposites. Generally, for the flame-retardant modification of ramie fibers, there are two basic ways in past work, which are impregnation and surface coatings, respectively[19]. These methods usually need a bearing structure created by fibers such as fabric or nonwovens[20–22]. However, short ramie fibers are almost of powders, so the above-mentioned two methods are not effective for the flame retardation of ramie fibers.

In this work, we *in situ* synthesized the phosphorus- and nitrogen-containing flame retardant (FR) on the surfaces of ramie fibers *via* the reaction of hydroxyl groups of the cellulose macromolecules in ramie fibers with phosphorus oxychloride and further 4,4′-diaminodiphenylmethane (DDM), forming the FR-chemically-wrapped ramie fibers (FR-RF). The resulting flame-retardant-modified ramie fibers were used to prepare short ramie fiber reinforced polypropylene composites. Choosing a typical formulation system, we investigated the thermal decomposition and burning behaviors of PP/FR-RF composites without additional flame retardants, and discussed the interfacial flame retardation and the mechanism for suppressing the candlewick effect in PP/FR-RF composites.

EXPERIMENTAL

Materials

Ramie fibers with an approximate length of 2 mm were purchased from Sichuan JB & Ramie Co. Ltd (China). 4,4′-Diaminodiphenylmethane (DDM) was bought from Sinopharm Chemical Reagent Co. Ltd (China). PP (MFR = 3.0 g/10 min) was purchased from Petro China Lanzhou Petrochemical Co. Ltd. Maleic anhydride-grafted polypropylene (PP-*g*-MAH) was obtained from Ningbo Nengzhiguang New Meterials Technology Co. Ltd. (China). Phosphorus oxychloride ($POCl_3$), sodium hydroxide (NaOH) and triethylamine (TEA) were bought from Kelong Chemical Reagent Co., Ltd. (China), and all of them were analytical grade and used without further purification.

Surface Flame-retardant Modification of Ramie Fibers

The ramie fibers were wrapped chemically by a phosphorus- and nitrogen-containing flame retardant (FR) produced *via in situ* condensation reaction, which can be completed by the following three steps[23]: The first step was alkaline treatment on ramie fibers，in which the fibers were immersed in 5 wt% NaOH solution for 24 h to activate the hydroxyl group, then washed with water until the pH of water was equal to 7, followed by drying in an oven at 80 °C for 12 h. In the second step, 10 g treated ramie fibers, 500 mL chloroform and 16 mL TEA as catalyst were placed in a 1000 mL three-necked flask, and allowed to react for 1 h at 65 °C, accompanied by stirring. Subsequently, the chloroform solution of $POCl_3$ was added, and then the reaction continued for 8 h; DDM chloroform solution was dripped into the flask, and the reaction lasted for another 16 h. Finally the mixture was washed with acetone and deionized water three times, respectively. The resultant product was dried at 80 °C for 12 h in a vacuum oven and sifted to remove impurities. The yellow ramie fibers wrapped chemically by phosphorus- and nitrogen-containing flame retardants (FR-RF) were obtained. The content of shell (flame retardant) as a percentage of the total functionalized RFs is about 15%.

Synthesis of FR

The synthetic procedure of FR is almost the same as the second step for the preparation of FR-RF, but without RF in this process[23].

Preparation of PP Composites

The short ramie fibers (RF or FR-RF) and PP pellets with PP-*g*-MAH were blended using a torque rheometer (XSS-300, Shanghai Kechuang Rubber Plastics Machinery Set Ltd., China) with the rotation speed of 50 r/min at 180 °C for 10 min according to the formulations given in Table 1. The composites obtained were then hot-pressed into sheets at 200 °C to characterize the structures and properties. Here, PP-*g*-MAH is used as compatibilizer to increase the compatibility between the polar hydrophilic ramie fiber and the nonpolar hydrophobic polypropylene[24]. The compatibilizer has negligible impact on the flame retardant performance of composites[23, 25]. In order to achieve the objective of this study, we only choose a typical formulation of composites (See Table 1) for various relevant studies.

Table 1. Formulations of the composites

Samples	PP (phr)	PP-*g*-MAH (phr)	RF (phr)	FR-RF (phr)
PP	100	–	–	–
PP/RF	100	5	40	–
PP/FR-RF	100	5	–	40

Characterization

FTIR spectra were recorded by a Nicolet FTIR 170SX spectrometer (Nicolet, America) using the KBr disk, and the wave number range was set from 500–4000 cm^{-1}.

The surface morphologies of samples were observed by using a JEOL JSM 5900LV SEM (JEOL，Japan) at the accelerating voltage of 5 kV. This instrument is equipped with an energy dispersive X-ray spectrometer (EDX).

The limiting oxygen index (LOI) value was measured using an HC-2C oxygen index instrument (Jiangning, China) according to ASTM D2863-97 with a sheet dimension of 130 mm × 6.5 mm × 3.2 mm.

The flammability of the sample was measured by a cone calorimeter (CC) device (Fire Testing Technology, UK). The samples with the dimension of 100 mm × 100 mm × 3 mm were exposed to a radiant cone at a heat flux of 50 kW/m^2.

Thermogravimetric analysis (TGA) was carried out by a TG 209F1 (NETZSCH, Germany) thermogravimetric analyzer at a heating rate of 10 K/min under the nitrogen flow of 50 mL/min with the temperature range from 40 °C to 700 °C.

XPS spectra were recorded by an XSAM80 (Kratos Co, UK), using Al Kα excitation radiation ($h\nu$-1486.6 eV).

Thermal conductivity was tested by a Hot Disk 2500-OT (Hot Disk, Sweden) thermal constant analyzer. This method is based on the use of a small temperature modulation in a parallelepiped-shape sample (16 mm × 16 mm × 8 mm) and allows obtaining all of these thermophysical parameters in only one measurement with their corresponding statistical confidence bounds.

RESULTS AND DISCUSSION

Characterization of FR-RF

The FTIR spectra of pristine RF and FR-RF are shown in Fig. 1. Compared with pristine RF, new absorption bands corresponding FR appeared at 3300–3500 cm^{-1} (N—H), 1512 cm^{-1} and 811 cm^{-1} (phenyl), 1203 cm^{-1} (P=O), 1025 cm^{-1} (P—O), and 900 cm^{-1} (P—N), indicating that RF was functionalized by FR. Meanwhile, the relative intensity of C—H vibration at 2900 cm^{-1} and characteristic absorption peaks of RF's at 1000–1200 cm^{-1} decreased. The disappearance of the peak at 550 cm^{-1} (P—Cl) indicated the completion of reaction. All these results demonstrated that RF might be wrapped chemically by FR[26].

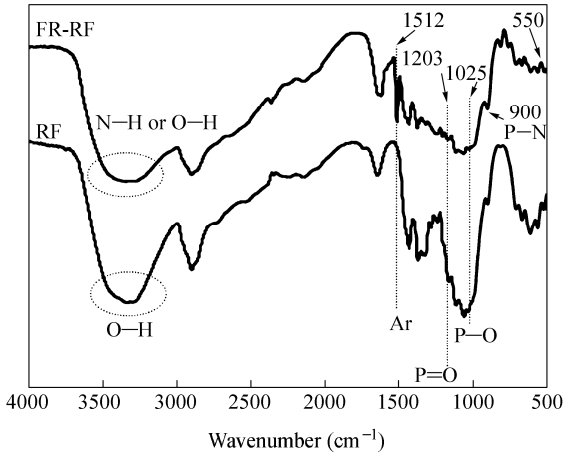


Fig. 1 FTIR spectra of pristine RF and FR-RF

To further confirm the occurrence of the chemically wrapping reaction, XPS analysis was performed. The XPS spectra of RF and FR-RF are shown in Fig. 2. For RF, there is a strong O1s peak at the binding energy of around 532.7 eV and a weaker peak assigned to C1s at around 284.6 eV. For FR-RF, a great drop was observed for the relative intensity of O1s peak at 532.6 eV, indicating that the content of hydroxyl group on the surface of RF might decrease; Meanwhile, new peaks appeared at 133.7 eV (P2p) and 400.0 eV (N1s). These results obtained from XPS analysis are consistent with the IR results, and demonstrated that RF wrapped by FR should be successful[22].

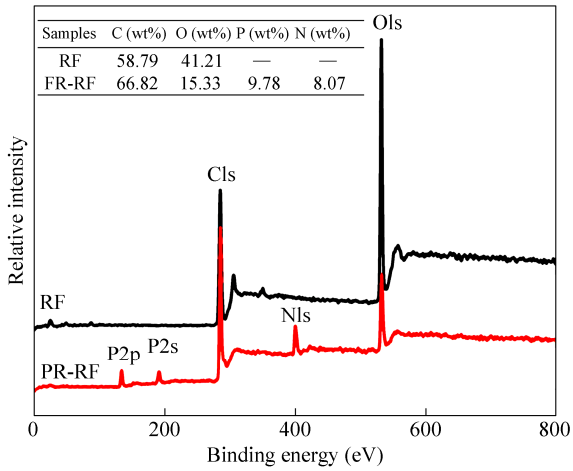
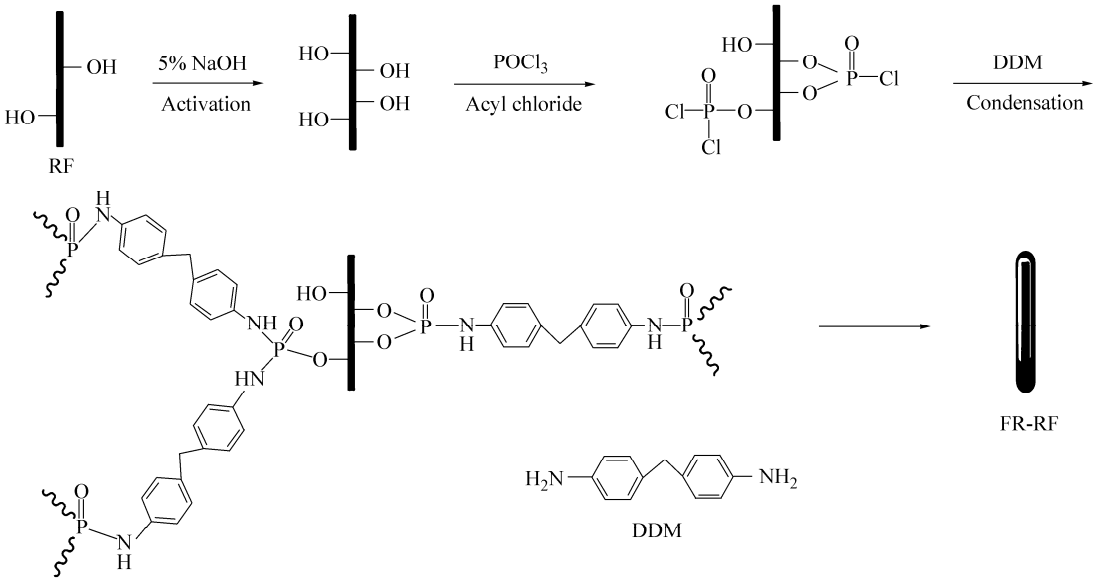


Fig. 2 Surface XPS spectra of pure RF and FR-RF

According all the above information, a possible synthetic scheme was proposed, as shown in Scheme 1. RF was activated by alkali treatment, and more hydroxyl groups (—OH) were exposed to the surfaces of RF and reacted with P—Cl. After adequate reactions, RF's were wrapped by FR produced *via* condensation of the remaining P—Cl with DDM. The surface morphologies of RF and FR-RF were observed through SEM. Figure 3(a) shows that the surface of RF is smooth, while after being coated by FR, the surfaces of FR-RF are quite rough, as shown in Fig. 3(b). In addition, the diameter of FR-RF is about 30 μm, and much larger than that of pristine RF. All these results illustrated that FR was grafted on the surface of RF.



Scheme 1 Schematic synthetic routes of FR-RF

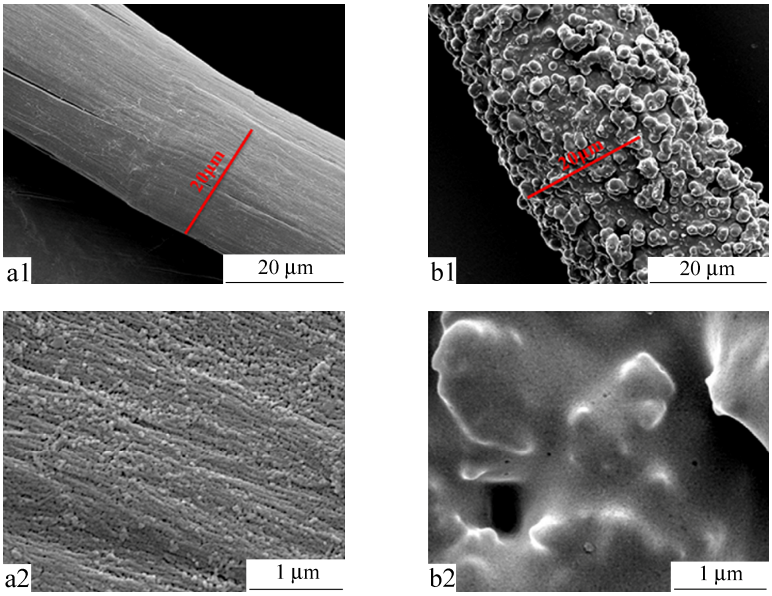


Fig. 3 SEM images of pure RF (a1 and a2) and FR-RF (b1 and b2)

Thermal Decomposition Behaviors

Figure 4 presents TGA and derivative thermogravimetry (DTG) curves of pristine (RF) and treated ramie fibers (FR-RF) under N_2 atmosphere and the detailed data for these samples are listed in Table 2. Pristine RF had a drastic decomposition stage caused by the rupture of glycosidic bonds at about 290–380 °C[27], and only 7.9 wt% residue was left at about 700 °C. Model compound FR started to decompose at 199 °C, and its T_{max1} was about 241 °C, finally 26.5 wt% residue char was left at 700 °C, indicating that FR had good char-forming capacity, but had lower temperature of initial weight loss ($T_{5\%}$). Obviously, the wrapping of FR on RF changed the decomposition behavior of RF. The initial thermal degradation process of FR-RF occurred at around 260 °C, in which the release of water, decomposition and cross-linking reactions might take place[23], and its temperature at the maximum degradation rate (T_{max1}) was about 314 °C. For FR-RF, its char residue is 41.9 wt% at 700 °C,

which is much higher than those of RF and FR. The significant increase of char residue should be due to the protection of better char layer formed during the thermal degradation of FR-RF.

Table 2. TGA data of neat PP and PP composites under N_2

Samples	$T_{5\%}$ (°C)	T_{max1} (°C)	The rate of T_{max1} (%/min)	T_{max2} (°C)	The rate of T_{max2} (%/min)	Residue (wt%)		
						500 °C	600 °C	700 °C
RF	321	369	24.4	–	–	11.7	9.7	7.9
FR	199	241	10.2	323	3.6	27.9	27.2	26.5
FR-RF	265	314	11.5	–	–	47.3	43.8	41.9
PP	394	453	24.2	–	–	0	0	0
PP/RF	344	367	5.9	461	20.8	0	0	0
PP/FR-RF	281	291	3.8	472	18.1	14.0	13.1	12.6

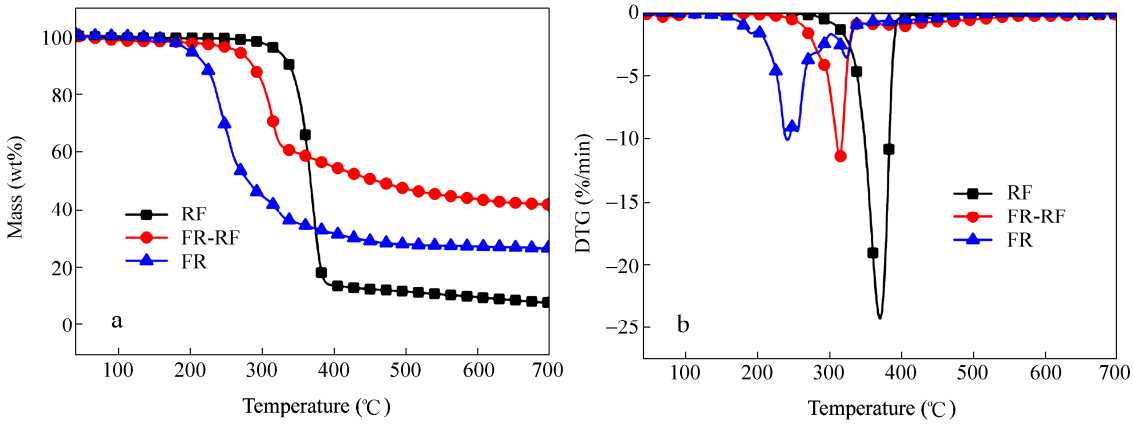


Fig. 4 TGA (a) and DTG (b) curves for FR, pristine RF and FR-RF under N_2 atmosphere

TGA and DTG curves of PP and its composites are shown in Fig. 5. There are two main decomposition stages for PP/FR-RF composites. The first mass loss (ML) should be due to the pyrolysis of FR and the decomposition of ramie fibers caused by acid released from FR degradation[13]. In this stage, $T_{5\%}$ decreased to 281 °C because of low $T_{5\%}$ of FR-RF compared with PP/RF composites. During the second ML, T_{max2} increased to 472 °C. Compared with neat PP and PP/RF composites, the thermal degradation process of PP/FR-RF composites was delayed. Besides, the char residue of PP/FR-RF composites was 12.6 wt%, but nothing for PP and PP/RF composites. Obviously, at high temperature PP/FR-RF composites had better thermal stability than

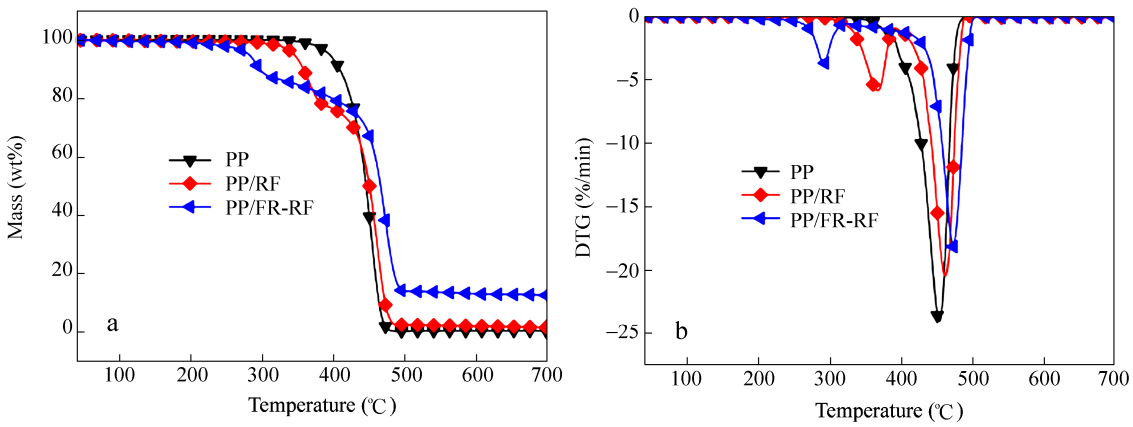


Fig. 5 TGA (a) and DTG (b) curves for PP and its composites under N_2 atmosphere

PP and PP/RF composites. The possible reason should be that FR wrapped on RF decomposed first, then formed char residue at low temperatures, then the char residue formed limited the transfer of heat and fuel transfer from the polymer towards the flame as well as the diffusion of oxygen into the material, which consequently led to the better thermal stability of PP/FR-RF composites.

Burning Behaviors

In LOI test, it was observed that the LOI value increased to 20% for PP/FR-RF composites from 18% for PP or PP/RF composites. In addition, it was found that the burning rate became very slow for PP/FR-RF composites compared with the other two systems. These results indicated that the functionlization of RF improved the flame retardancy of PP/RF composite to some extent.

The flammability of composites has been widely estimated by CC testing because the combustion behaviors in CC test are similar with that occurred in real accident[28, 29]. The results of combustion tests are presented in Table 3, including heat release rate (HRR), total hear release (THR), ML, *etc*.

Table 3. Cone calorimeter data of neat PP, PP/RF and PP/FR-RF composites

Samples	PP	PP/RF	PP/FR-RF
TTI (s)	20	20	14
PHRR (kW/m^2)	788.6	714.3	547.5
Time to PHRR (s)	125	160	70
MHRR (kW/m^2·s)	322	271	206
THR (MJ/m^2)	103	96	84
Average MLR (g/s)	0.069	0.069	0.053
Char mass (%)	1.3	1.5	14.2

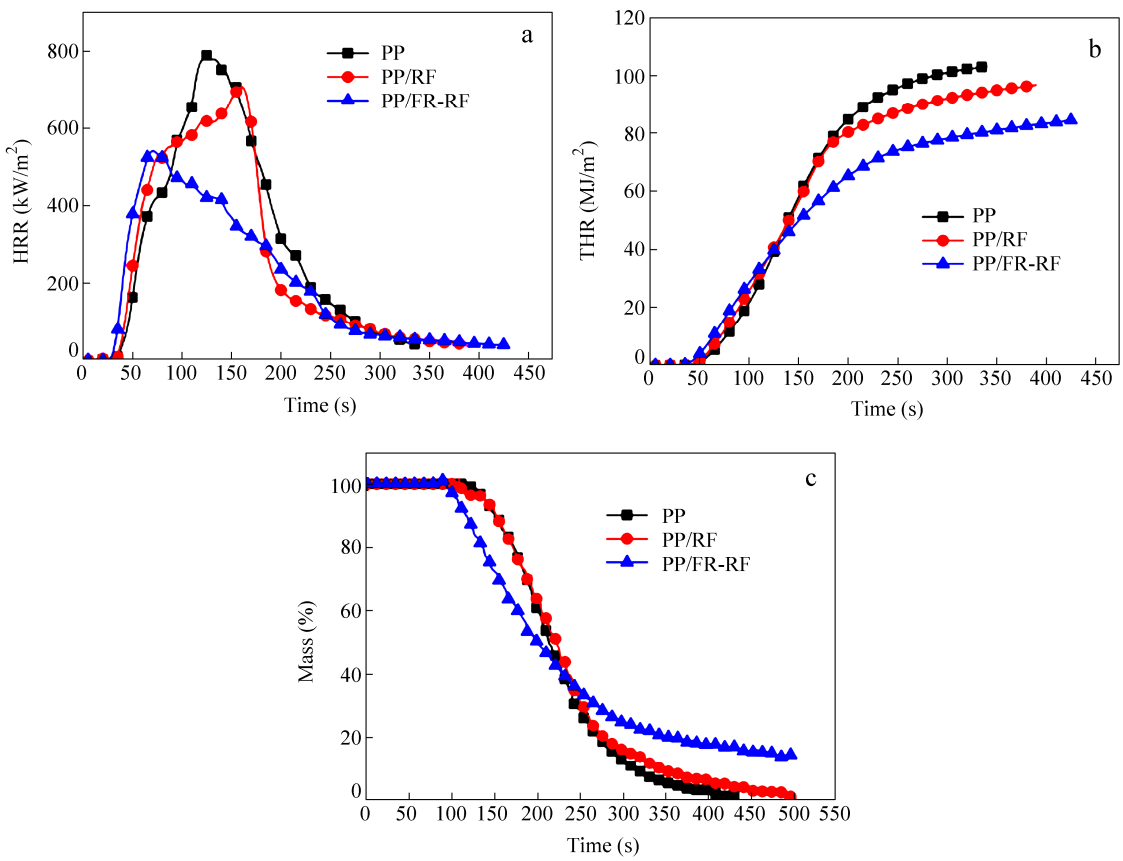


Fig. 6 HRR (a), THR (b) and ML (c) plots of neat PP, PP/RF and PP/FR-RF composites

HRR and THR are very important to evaluate the combustion performance of materials. Figures 6(a) and 6(b) show the HRR and THR curves, respectively. Neat PP had a sharp peak of HRR (PHRR), which was 788.6 kW/m^2. After the addition of RF, the PHRR of PP/RF composites was about 714.3 kW/m^2, which is little lower than that of PP. For THR, neat PP had the release of 103 MJ/m^2, which is a little higher than the value of PP/RF composites. Obviously, the RF is the same combustible as PP. For PP/FR-RF composites, the PHRR and THR were significantly lower than the corresponding values of neat PP and PP/RF composites, which were 547.5 kW/m^2 and 84.5 MJ/m^2, and correspondingly decreased by 23.4% and 12.5% compared with PP/RF composites, respectively. Figure 6(c) presents the ML curves of PP, PP/RF composites and PP/FR-RF composites.

Obviously, the char residue of PP/FR-RF composites is much higher than those of PP and PP/RF composites. Generally, the more char residue can contribute to the flame retardancy of material. In addition, the ignition time of PP/FR-RF composites decreased compared to neat PP and PP/RF composites. It should be caused by the degradation of FR-RF in advance.

The digital photos of the residues of neat PP, PP-RF and PP/FR-RF composites are shown in Fig. 7. There was no residue left for neat PP, while a poor and unexpanded char layer was formed for PP/RF. However, PP/FR-RF composites created a continuous and compact char layer after combustion, which contributes to thermal and oxygen blockage. These results illustrate that the FR wrapped chemically on RF facilitated the formation of an expandable char layer, which should be an important factor for the better combustion performance of PP/FR-RF than neat PP or PP/RF composites.

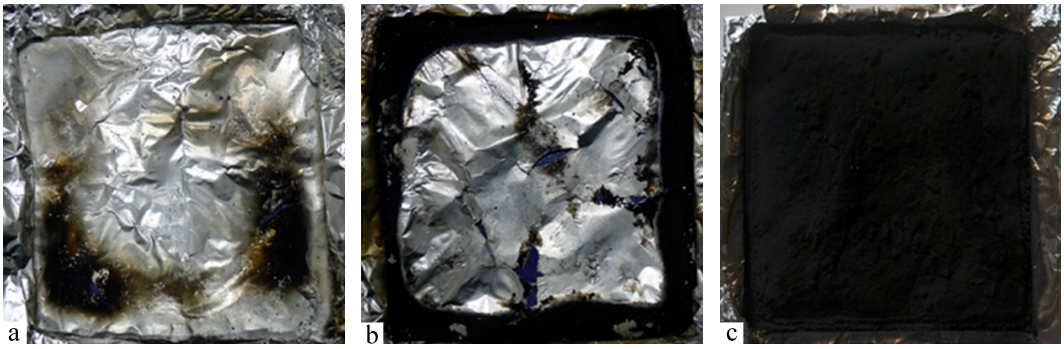


Fig. 7 Digital photographs of residues of neat PP (a), PP/RF composite (b) and PP/FR-RF composite (c) after CC test

Flame-retardant Mechanism

To understand insightfully the flame-retardant mechanism for the wrapped RF, the char residues of PP/RF composites and PP/FR-RF composites were also analyzed by FTIR. As shown in Fig. 8, the band at around 1030–1160 cm^{-1} corresponding to the stretching vibration of C—O—C[30] almost disappeared for PP-RF composites, while the band at around 1630 cm^{-1} ascribed to the stretching vibration of C—C for benzene ring appeared obviously, indicating the break of cellulose backbone and the subsequent carbonization[31]. Figure 7(b) shows that the amount of char residue is very little. For the residue of PP/FR-RF composites, the band corresponding to the stretching vibration of C—O—C still existed at around 1030–1160 cm^{-1}, and some other characteristic absorption peaks of pristine ramie fibers were also seen in the residue of PP/FR-RF composites, suggesting that ramie fibers were engaged in the charring process during the combustion. In addition , the peaks at around 890 and 1250 cm^{-1} assigned to the absorption of P=O and P—O—P, respectively, were observed, suggesting that FR wrapped on the RF was engaged in the charring[20].

SEM micrographs of the residues of PP composites after CC test are shown in Fig. 8. Although the char residue of the PP/RF composite sample is very little after CC test, its char residue was also investigated. For PP/RF composites, RF shrunk after the combustion, and broke successively, consequently left an apparently slender char residue. Furthermore, the surface of the char residue is highly cracked (see Fig. 8a). Comparing the

residue of PP/FR-RF composites with that of PP/RF composites, it can be found that the backbone of the residue is quite different between the two biocomposites. First, the diameter of the fibers for PP/FR-RF composites is wider than that for PP/RF composites, suggesting that the char residue of RF in PP/FR-RF composites was improved compared with that in PP/RF composites. Second, the shape of the former is more regular, but the surface of the char residue for PP/RF composites is cracked, which should be due to the breakage of cellulose backbone and the following release of organic fragments[20]. The possible reason for the regular shape of the residue of PP/FR-RF composites should be due to the contribution of the FR on the interface. The char layer formed during the decomposition of FR could act as a barrier to protect the material underneath, so the candlewick effect could be weakened by the interfacial behaviors, consequently promote the charring of RF. The better char layer formed further suppressed the combustion, and then led to the better combustion performance of PP/FR-RF composites.

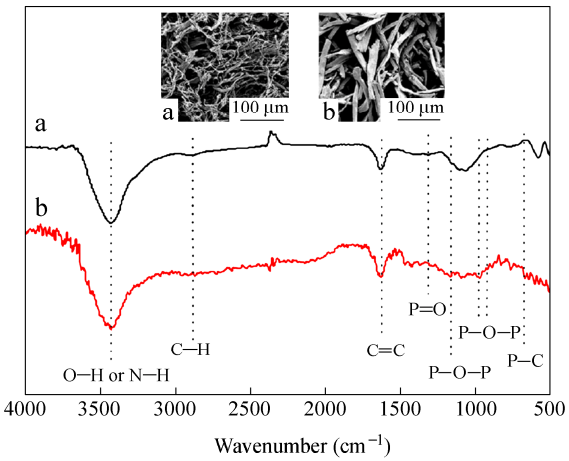


Fig. 8 FTIR and SEM results of PP/RF (a) and PP/FR-RF (b) after CC test

XPS data for the residues of PP/RF composites and PP/FR-RF composites can be used to further interpret the flame-retardant mechanism. The contents of carbon (C), nitrogen (N), oxygen (O), and phosphorus (P) were investigated and summarized in Fig. 9. The high content of C and O in the condensed phase of PP/RF composites should be due to the charring of RF during the combustion, as mentioned in FTIR test. For PP/FR-RF composites, the appearance of P and N indicates that FR must be engaged in the charring process during the combustion. This result is consistent with the FTIR analysis. In addition, C and O could still be observed in the condensed phase, which must be the mixture of the char residue of FR, RF and PP.

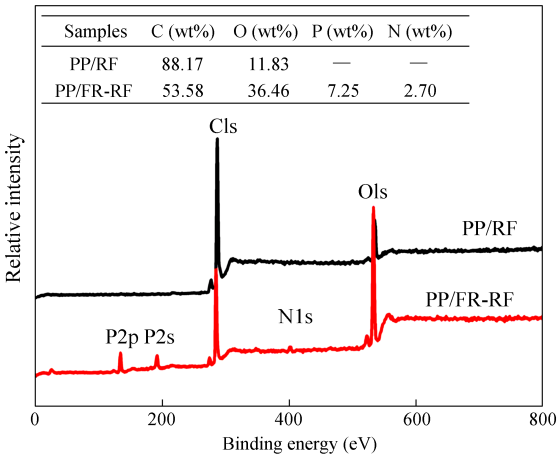


Fig. 9 XPS spectra of PP/RF and PP/FR-RF after CC test

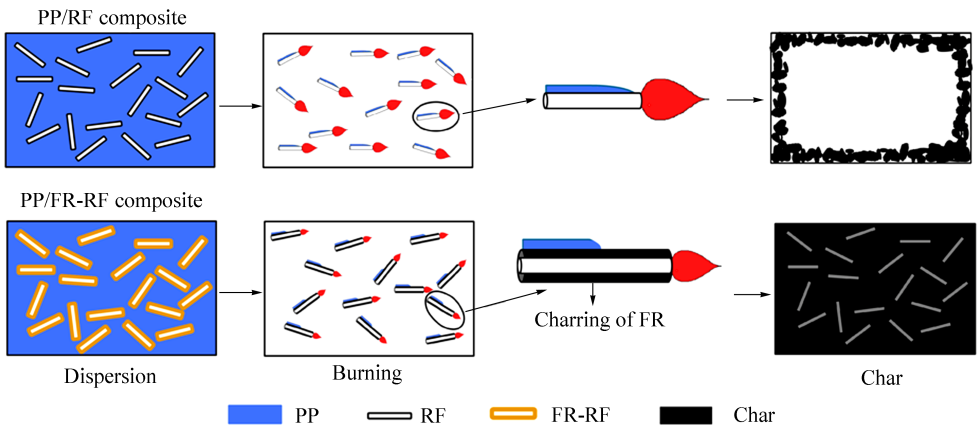
Table 4. The date of heat conduction coefficient of composites

	PP	PP/RF	PP/FR-RF
Thermal conductivity (W/m·K)	0.22	0.41	0.31

Natural fibers have high flammability and heat conduction coefficient. The introduction of ramie fiber into polypropylene may increase the heat conductivity of PP. The data of heat conduction coefficient of neat PP and composites are shown in Table 4. The PP/RF composite had a thermal conductivity coefficient of 0.41 W/m·K, which is significantly higher than that of pure PP, suggesting that the heat could be diffused easily in PP/RF composites, namely, the heat could be transmitted into the unburned area from the burning region. After being wrapped chemically by FR, the thermal conductivity of PP composites was reduced to 0.31 W/m·K, which is lower than that of PP/RF composites.

Obviously, the modification on the surfaces of ramie fibers not only restrained the candlewick effect through the formation of effective char layer in the interface between PP and RF, but also depressed the thermal conductivity in the composite, so the flame retardation of the PP/RF composite was greatly improved due to the wrapped layer of FR.

According to the analysis mentioned above, a flame-retardant mode shown in Scheme 2 can be proposed. When the PP/RF composite is burning, the RF soaked by PP melt as a wick, which leads to the so-called "candlewick effect". With the degradation of FR on the surface of RF, the char layer is formed gradually, and the RF can be protected against the fire attack, so the candlewick effect will be greatly suppressed due to the protection of char residue network. Further, with the formation of char layer, the decomposition of PP will be restrained, and consequently the flame retardancy of PP composites is improved due to the incorporation of FR on the surface of RF.



Scheme 2 Schematic diagram of flame-retardant mode

CONCLUSIONS

The short ramie fibers (RF) were chemically wrapped successfully by a phosphorus- and nitrogen-containing flame retardant (FR) produced *via in situ* condensation reaction. The structure, morphology and thermal decomposition behaviors of the flame-retardant-modified ramie fibers (FR-RF) were characterized by various characterization methods. The chemical incorporation of FR on the surface of RF could increase the residue of the PP/RF composite, and improved its thermal stability at high temperature. At the same loading, the PHRR and THR of PP/FR-RF composites correspondingly decreased by 23.4% and 12.5% in comparison with PP/RF composites. PP/FR-RF composites created a continuous and compact char layer after the combustion, which acted as a barrier for heat transmission to the material below and for fuel transport to the flame. Combined with the results mentioned above, it can be concluded that the incorporation of FR on the surface of RF could greatly

weaken the wick effect and protect the fibers during the combustion, and hence, effectively improve the flame retardancy of the whole composites.

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