

Microencapsulation of APP-I and Influence of Microencapsulated APP-I on Microstructure and Flame Retardancy of PP/APP-I/PER Composites

Jian Zhou, Lin Yang, Xinlong Wang, Quanjun Fu, Qiaolu Sun, Zhiye Zhang

School of Chemical Engineering of Sichuan University, Chengdu, Sichuan 610065, China

Correspondence to: Z. Zhang (E-mail: nic1201@163.com)

ABSTRACT: In this article, the microencapsulated ammonium polyphosphate crystalline with form I (APP-I) coated with melamine-formaldehyde (MF) was prepared by *in situ* polymerization. Results of Fourier transform infrared spectra (FTIR), thermogravimetry (TG) energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) demonstrate that APP-I is successfully microencapsulated with MF. Compared with APP-I, the microencapsulated APP-I with MF (MFAPP-I) is of much smaller spheroidal particle size and lower solubility in water. In this study, the polypropylene (PP)/APP-I/pentaerythritol (PER) and PP/MFAPP-I/PER composites are prepared, and flame retardancy, thermal stability, and microstructure of corresponding composites are carefully investigated by limiting oxygen index (LOI), UL-94 testing, TG, EDS, and SEM. Experimental results show that PP/MFAPP-I/PER composites have advantages over PP/APP-I/PER composites in terms of flame retardant properties and water resistance. Results of TG, SEM, and EDS show that the microencapsulated APP-I with MF resin is conducive to increase the amount of residual yield and improve thermal stability of PP/MFAPP-I/PER composites and the compatibility and dispersion of MFAPP-I. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 36–46, 2013

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INTRODUCTION

Owing to the superior mechanical properties and physiochemical properties, PP is used in a wide variety of applications such as auto industry electricity, engineering, housing materials and transportation, etc.^{1–4} However, due to its chemical constitution, PP is highly flammable. This defect limits the range of its application. Therefore, the flame retardancy becomes an essential and imperative requirement for PP.

Among the flame retardants for PP, the intumescent flame retardants (IFR) have aroused a great attention in recent years. They are not only more environmentally friendly⁵ than the traditional halogen-containing flame retardants, but also more efficient as flame retardants. For instance, with antidripping property, they are inclined to emit lower smoke and lower toxic gases in combustion, which conform to the developing tendency of flame retardants. Unfortunately, due to their special chemical structure, most of IFR systems have some defects⁶ such as moisture-prone and poor compatibility within polymer matrix. A typical IFR system consists of three components: an acid agent (e.g., APP), a carbonization agent (e.g., PER), and a blowing agent (e.g., melamine). A lot of efforts have been exerted to overcome these disadvantages. For example, some pioneers^{7–9}

had found that improvement of polymerization degree of APP and surface modification of APP particles with surfactants can enhance its water resistance. However, it fails to find a better way to improve flame retardant efficiency and meanwhile not to destroy the mechanical properties of polymeric materials.

Wu^{10–12} et al. have done many researches on the microencapsulated APP (MUFAPP) can more effectively enhance water resistance. As reported by Wu et al., the LOI value of PP/MUFAPP/dipentaerythritol composites achieve peak at 33.5, and the composites can pass the V-0 rating. Lei¹³ reported on the microencapsulated APP coated with hydroxyl silicone oil and melamine-formaldehyde (HSO-MF). The LOI value can reach to 32 when APP content is 30%. Wang¹⁴ incorporated the microencapsulated APP into ethylene vinyl acetate (EVA) copolymer. With 22.5% of APP content, the LOI value can reach to 31, which enables it to pass the V-0 rating. In the aforementioned researches, only ammonium polyphosphate with crystalline form II (APP-II) was used as the acid agent of IFR. Little research has been touch upon ammonium polyphosphate with crystalline form I (APP-I). Both APP-II and APP-I are of orthorhombic systems. The surface of former is smooth, while the latter is rough. APP-II is slightly soluble in water, and the polymerization degree of it is much higher than that of APP-I.

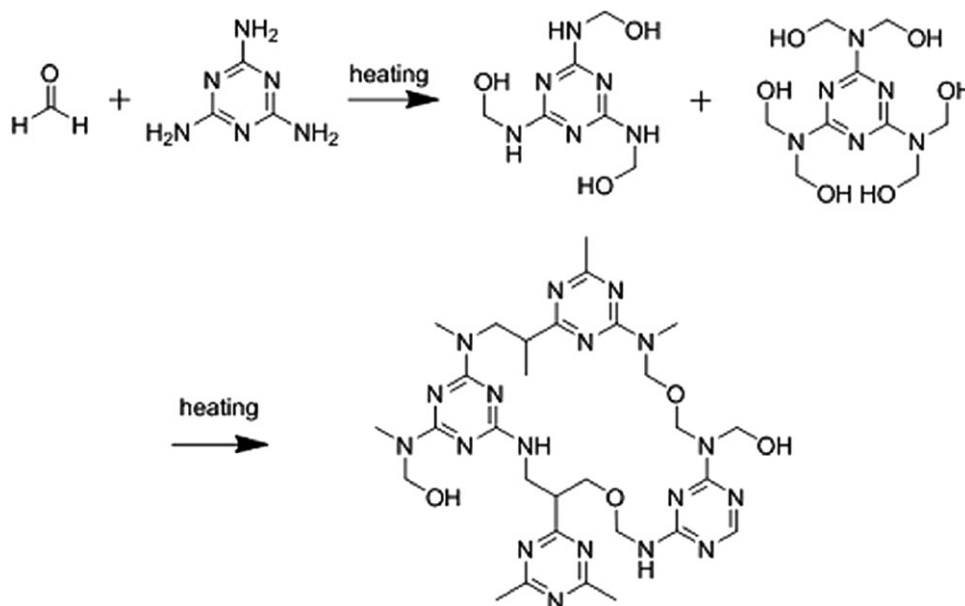


Figure 1. The reaction mechanism between formaldehyde and melamine.

Highly soluble in water, APP-I is mainly used in coating and fertilizer industry.¹⁵ Therefore, it is not an effective intumescent flame retardant for plastic materials. Individually used as flame retardant agent, APP-I, highly soluble in water, can migrate to the surface of PP, when the plastic materials have long been exposed to damp environment, resulting in the decrease of flame retardant effect. Little has been reported about the microencapsulated APP-I with melamine-formaldehyde (MF) by means of *in situ* polymerization.

The aim of this study is to prepare the microencapsulated APP-I with MF, so as to add it to PP/MFAPP-I/PER composites. The microencapsulated APP-I may improve the flame retardant efficiency and compatibility of PP/MFAPP-I/PER composites. Microencapsulated APP-I with MF is prepared by *in situ* polymerization and characterized by Fourier transform infrared (FTIR), thermogravimetry (TG) and scanning electron microscopy (SEM). The influence of MFAPP-I on the microstructure and the flame retardancy of PP/MFAPP-I/PER composites is carefully evaluated by limiting oxygen index (LOI), UL-94, TG, SEM, and EDS.

EXPERIMENTAL

Materials

PP (white powder, isotactic index = 96%, melt flow index = 3.5 g/10 min, apparent density = 0.43 g mL⁻¹) was provided by Kaikai Petroleum chemical company. Nearly 37% formaldehyde, pentaerythritol (PER) and melamine were provided by the Kelong Chemical Reagent Factory (Chengdu, China). APP-I (average degree of polymerization was about 50) was kindly donated by Shanghai Xushen Nonhalogen Smoke Suppressing Fire Retardants.

Preparation of Microencapsulated APP-I

About 63 g melamine, 110 mL 37% formaldehyde solution, and 250 mL distilled water were put into a three-neck flask

equipped with a condenser and a stir. Then after adjusting to pH 8–9 by adding 25% ammonia water, the mixture is heated to 85°C and this temperature is kept for about 15 min. Then the solution is transferred to another three-neck flask in which 100 g APP-I and 100 mL distilled water are contained. The temperature of this system is kept at 85°C for 2.5 h. After that the mixture is filtered, washed with distilled water, and dried at 100°C. Eventually, the MFAPP-I powder is obtained. The content of Phosphorus (P₂O₅) of MFAPP-I and APP-I is tested by weight method.¹⁶ The phosphorus content of APP-I is 64.96%, and that of MFAPP-I is 31.00%.

The result demonstrates the content of APP-I is about 47.8% in MFAPP-I. The reaction mechanism¹¹ is shown below in Figure 1.

Preparation of the Flame Retarded PP Composites

All flame retarded PP composites are prepared in a twin screw extruder at about 190°C. The mixed samples are hot-pressed at about 180°C under 10 MPa for 10 min into sheets of suitable thickness and then cooled to ambient temperature at the cooling rate of 30°C min⁻¹ in the mold at 10 MPa.^{17,18} The blend compositions with their sample codes were listed in Table I.

Measurements

FTIR. All the specimens measured with FTIR are prepared by the following steps: powder samples are mixed with KBr powders, and the mixture is pressed into a tablet. FTIR analysis is conducted with a Nicolet 6700 spectrophotometer (Nicolet, USA).

Thermogravimetry. Thermogravimetric analysis was performed employing TA Instruments NETZSCH TG 209 F1 Iris (Germany). The samples are heated from room temperature to 800°C at the heating rate of 10°C min⁻¹ under nitrogen atmosphere with a flowing rate of 10 mL min⁻¹.

Table I. Composition of Samples and the Flame Retardancy of Composites

Sample code	PP (wt %)	APP-I (wt %)	MFAPP-I (wt %)	PER (wt %)	P ₂ O ₅ (wt %)	LOI (%)	UL-94
Pure pp	100	0	0	0	0	19	NR ^a
PP/APP-I/PER-1	86.7	5	0	8.3	3.248	24	NR
PP/APP-I/PER-2	81.7	10	0	8.3	6.496	26.8	NR
PP/APP-I/PER-3	76.7	15	0	8.3	9.744	30.9	V-1
PP/APP-I/PER-4	71.7	20	0	8.3	12.99	38.2	V-0
PP/APP-I/PER-5	66.7	25	0	8.3	16.24	39	V-0
PP/APP-I/PER-6	61.7	30	0	8.3	19.48	39.6	V-0
PP/MFAPP-I/PER-1	86.7	0	5	8.3	1.55	25.2	NR
PP/MFAPP-I/PER-2	81.7	0	10	8.3	3.10	29.4	V-1
PP/MFAPP-I/PER-3	76.7	0	15	8.3	4.65	31.8	V-0
PP/MFAPP-I/PER-4	71.7	0	20	8.3	6.20	32.6	V-0
PP/MFAPP-I/PER-5	66.7	0	25	8.3	7.75	33.2	V-0
PP/MFAPP-I/PER-6	61.7	0	30	8.3	9.30	35.7	V-0

^aNR means no rating.

Limiting Oxygen Index. LOI is measured as per GB 2406.2-2009 (China) with an XZT-100A oxygen index meter (Kecheng, China).

UL-94 Testing. UL-94 vertical burning tests are carried out with a CZF-3 instrument (Jiangning Analysis Instrument Company, China). As per UL-94 test standard,¹³ dimension of specimens in the test shall be 127 × 12.7 × 3 mm³.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy. The SEM and EDS of particles and PP composites are obtained by adopting a Hitachi S-4800 (Hitachi, Japan) scanning electron microscope (SEM) and Oxford IE250 (Oxford, England) energy dispersive spectroscopy (EDS). Surface elemental composition analysis is performed with EDS. The operating voltage of SEM is 20 kV.

Measurement of Water Solubility

Nearly 10.0000 ± 0.0001 g of APP-I or MFAPP-I are weighted and then mixed with 100 mL water in a beaker. The mixture is stirred in the water bath at 25°C ± 0.1°C for 30 min, separated in a centrifuge at a speed of 3000 r min⁻¹ for 15 min and filtered. Later 20 mL of the upper clear liquid is transferred in another beaker. Then the mixture in beaker is dried at 115°C ± 5°C until it reached its constant weight. The solubility (g/100 mL) is calculated by the following equation:

$$S = (m_1 - m_2) / 20 \times 100$$

where S is solubility, m_1 is the total weight of the beaker with dried sample, and m_2 is weight of the beaker.

Determination of Water Resistance of Flame Retarded PP Composites

The specimens are immersed in the distilled water at 50°C and kept at this temperature for 24 h. Then these treated specimens are taken out, and dried to their constant weight at 110°C.

RESULTS AND DISCUSSION

Characterization of MFAPP-I and APP-I

FTIR of MFAPP-I and APP-I. The FTIR spectra of MF, APP-I and MFAPP-I are shown respectively in Figure 2. Apparently, the main absorption peaks of APP-I appear approximately at 3225 cm⁻¹ (N—H stretching vibration), 1448 cm⁻¹ (N—H bending vibration), 1254 cm⁻¹ (P=O), 1070 cm⁻¹ (the symmetric stretching vibration of P—O), 1018 cm⁻¹ (PO₂, PO₃), and 799 cm⁻¹ (P—O bending vibration).¹⁹ And the main absorption peaks of MF appear around 3396 cm⁻¹ (N—H stretching vibration), 1555 cm⁻¹ (C=N stretching vibration) and 1336 cm⁻¹ (C—N stretching vibration). The typical absorption peaks of MFAPP-I occur at 3217, 1562, 1340, 1256, 1070, and 959 cm⁻¹. The absorption peaks of 1562 and 1340 cm⁻¹ are ascribed to the ring vibration of melamine in the MF

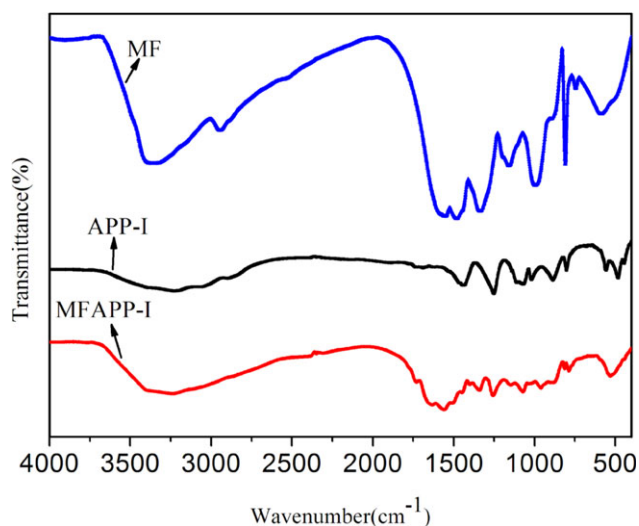


Figure 2. FTIR spectra of MFAPP-I and APP-I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

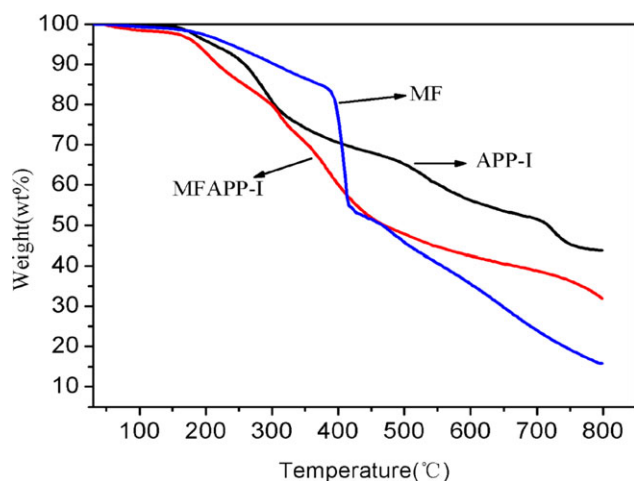


Figure 3. TG curves of MF, MFAPP-I and APP-I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resin.¹³ Comparisons of FTIR spectra of MF, APP-I, and MFAPP-I duly show that no new absorption peaks appeared in FTIR spectra of MFAPP-I, which verifies no chemical bond was established. The MFAPP-I is merely the results of physical modification of APP-I when added MF resin.

TG Analysis of MFAPP-I and APP-I. Figure 3 shows TG curves of MF, MFAPP-I and APP-I. The thermal degradation of APP-I consists of three main steps in nitrogen atmosphere: at 200–440°C, 440–540°C, and 540–750°C. It begins to decompose at about 200°C, and the weight loss is contributed to the thermally unstable structural groups in APP as stated by Camino.²⁰ Camino pointed out that the elimination of NH_3 and H_2O in thermal degradation process of APP can be divided into two

steps within the range of 165–550°C. With the elimination of NH_3 and H_2O , the crosslinked $-\text{P}-\text{O}-\text{P}-$ structure is formed. The temperature range of the second degradation step is around 440 and 540°C, and the weight loss rate is about 9%. The main reason may lie in the dehydration in the formation of polyphosphoric acid. The third step occurs within the range of 540–750°C, and the residue yield of APP-I at 800°C is about 43.73%. With regard to MFAPP-I, its initial decomposition temperature, lower than that of APP-I, is 190°C, due to the lower thermal stability of MF resin. It can be seen that two main steps are involved in the thermal degradation of MFAPP-I. The temperature of maximum mass loss rate of the two steps is 322 and 483°C, respectively. Moreover, char yields of MFAPP-I at 800°C is about 30.09%, lower than that of APP-I.

SEM of APP-I and Microencapsulated APP-I. SEM micrographs of MFAPP-I and APP-I are shown in Figure 4. It can be clearly seen that with rough surface, APP-I is of blocky structure. However, MFAPP-I, with smooth surface, is of spheroidal structure. The spheroidal particle size becomes homogenous distributed, with particle diameter of 250 nm. Because APP-I is easily soluble in water, the microencapsulation of APP-I can be considered as homogeneous reaction, which is conducive to decrease the particle size and improve the dispersion of APP-I. Figure 5 shows SEM and EDS of MFAPP-I. The spheroidal particles are analyzed with EDS. The elemental compositions of spheroidal particles are listed in Table II. Carbon content of spheroidal particles is ~24%, and phosphorus content is about 7.73%. The results demonstrate that MF resin and APP-I are included in MFAPP-I. The aforementioned results proved that the microencapsulated APP-I with MF resin by means of the *in situ* polymerization has been well performed in this study.

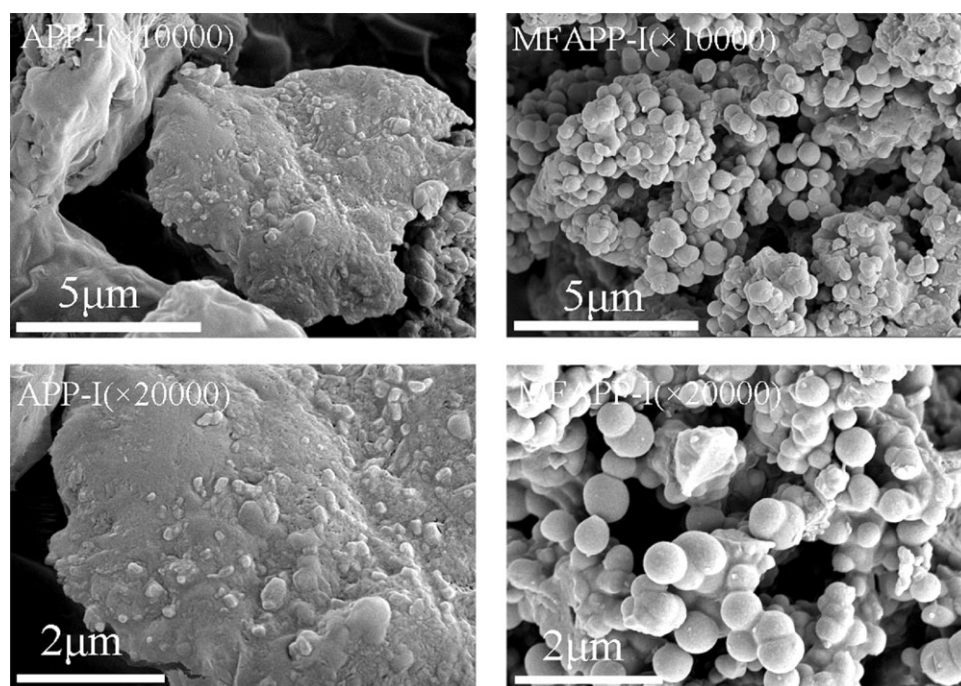


Figure 4. Surface morphologies of APP-I and MFAPP-I.

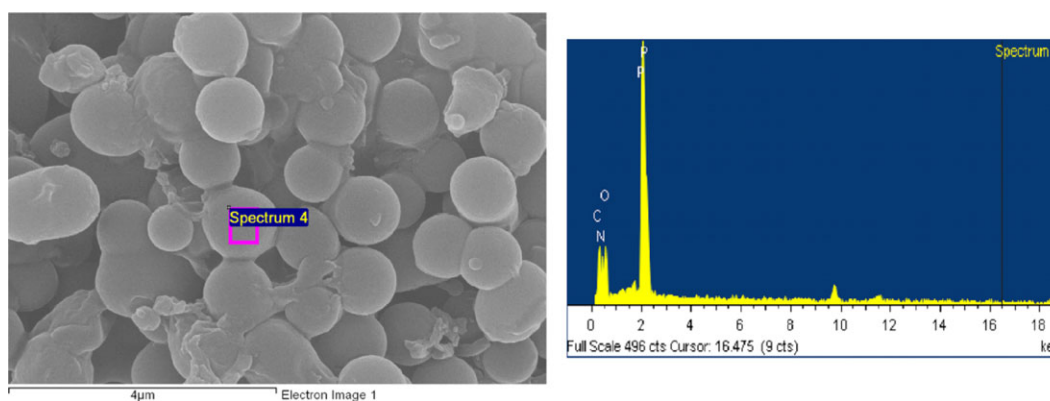


Figure 5. EDS of MFAPP-I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Solubility of MFAPP-I. Table III shows the solubility of APP-I and MFAPP-I at 25°C. It can be seen that the solubility of APP-I is 9.38 g/100 mL H₂O at 25°C. The main reason lies in the fact that APP-I, with low degree of polymerization, can be easily attacked by water. When APP-I particles are microencapsulated by MF resin, the solubility of MFAPP-I decreases to 1.36 g/100 mL H₂O at 25°C. The solubility of MFAPP-I may depend on the solubility of MF resin. Despite the fact that APP-I is high water solubility, the MFAPP-I is suitable to be used as the flame retardant for polymer materials.

Characterization of PP/MFAPP-I/PER and PP/APP-I/PER Composites

Flame Retardancy of the Composites. To evaluate the flame retardant property of PP composites, LOI and UL-94 tests are conducted and the testing results are given in Table I. The LOI value of pure PP, which is a kind of highly flammable polymeric material, is merely 19. The introduction of APP-I or MFAPP-I can remarkably improve LOI value of PP composites. The LOI value of PP/APP-I/PER composites increases with the increasing APP-I content. When the APP-I content reaches 20%, LOI value of PP/APP-I/PER-4 increases to 38.2, and then the increase of LOI slowed down with the further increase of APP-I content. Moreover, The LOI value of PP/MFAPP-I/PER composites increases with increasing load of MFAPP-I. When the load of MFAPP-I accounts for 30% of the composite, LOI value of PP/MFAPP-I/PER-6 increases to 35.7. When the content of APP-I or MFAPP-I does not exceed 15%, LOI value of PP/MFAPP-I/PER composites is higher than that of PP/APP-I/PER composites. The main reason of this phenomenon may due to the fact that the microencapsulated APP-I improve the dispersion of APP-I and the compatibility between APP-I and PP in PP/

MFAPP-I/PER composites. When the content of APP-I or MFAPP-I exceeds 15%, LOI value of PP/MFAPP-I/PER composites is lower than that of PP/APP-I/PER composites. The most likely reason is that APP-I content of PP/APP-I/PER composites is much higher than that of PP/MFAPP-I/PER composites, due to the fact that the APP-I content only reaches 47.8% in MFAPP-I.

Based on data of UL-94 column in Table I, a conclusion can be drawn that, when the APP-I content is lower than 20%, PP/APP-I/PER composites show severe flammable dripping, and merely UL-94 V-1 rating can be achieved even when LOI value of PP/APP-I/PER-3 could reach 30.9. Only when the APP-I content reaches 20%, PP/APP-I/PER-4 can pass the V-0 rating. However, when the MFAPP-I content is only 10%, PP/MFAPP-I/PER-2 can pass the V-1 rating even when its LOI value is only 29.4. When the load of MFAPP-I accounts for 15% of the composite, PP/MFAPP-I/PER-3 can pass the V-0 rating. In the study, LOI value of PP/APP-I/PER-2 and PP/APP-I/PER-3 reach 26.8 and 30.9 respectively, but the two samples can not pass the V-0 rating. Although the LOI value of PP/MFAPP-I/PER-3 is only 31.8, much lower than that of PP/APP-I/PER-4, PP/MFAPP-I/PER-3 can pass the V-0 rating too.

Therefore, the microencapsulated APP-I is proved to be beneficial to improve the flame retardancy of PP composites and enables the flame retardant PP composites pass the V-0 rating more easily. The microencapsulated APP-I can also reduce APP-I content in flame retardant PP composites, and make the composites pass the V-0 rating. And this may reduce the effect on the mechanical properties of flame retardant PP composites.

Figure 6 shows photographs of PP/APP-I/PER and PP/MFAPP-I/PER composites after LOI test. The sequential numbers of composites in Figure 6 correspond to the sample code of Table I respectively. It can be seen that in molten state, residues of

Table II. Surface Elemental Composition of MFAPP-I

Element	Weight %	Atomic %
C (K)	24.33	29.56
N (K)	37.45	39.01
O (K)	30.48	27.79
P (K)	7.73	3.64
Totals	100	

Table III. Solubility of APP-I and MFAPP-I

Sample	Solubility (g/100 mL H ₂ O)
APP-I	9.38
MFAPP-I	1.36

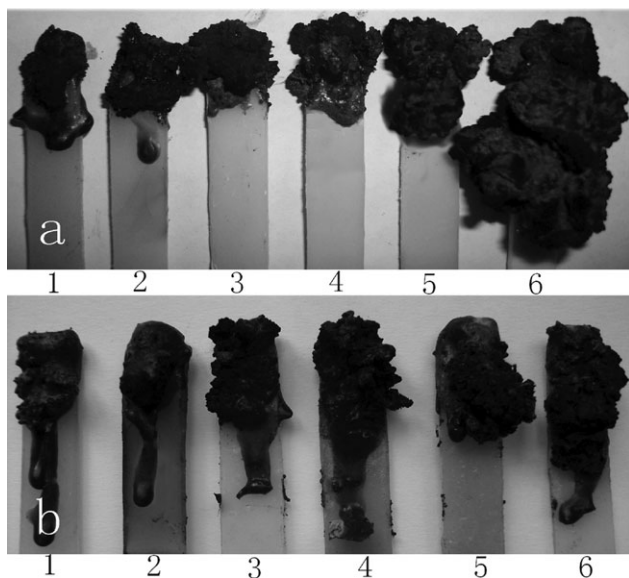


Figure 6. Photographs of specimens after LOI test (a) PP/MFAPP-I/PER (b) PP/APP-I/PER.

PP/APP-I/PER composites did not form the intumescent char. Figure 6(a) shows that residues of PP/MFAPP-I/PER composites formed the intumescent char. This clearly demonstrates that the microencapsulated APP-I contribute to form the intumescent char and enhance antidripping effects of PP/MFAPP-I/PER composites in LOI test. The main reason behind this phenomenon may be that MFAPP-I and PER strengthen the char formation capability, and accelerate char formation process in PP/MFAPP-I/PER composites. When the PP/MFAPP-I/PER composites are in combustion, the MFAPP-I is degraded at first and then formed the intumescent char, protecting the interior of PP.

TG Analysis. Figures 7 and 9 show the TG curves of PP, PP/APP-I/PER, and PP/MFAPP-I/PER composites. It can be seen that pure PP begin to degrade at about 263°C and the temperature of maximum mass loss rate (T_{max}) is 451°C. PP/APP-I/PER

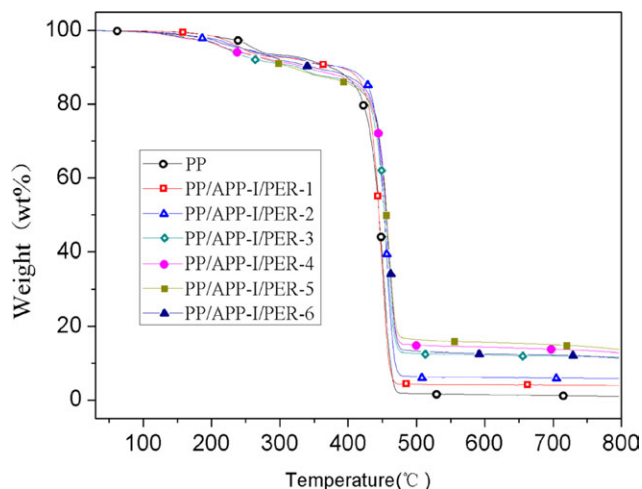


Figure 7. TG curves of PP/APP-I/PER composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

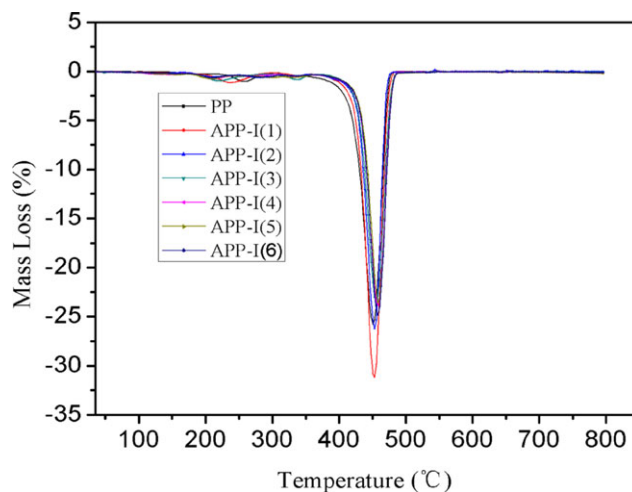


Figure 8. DTG curves of PP/APP-I/PER composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

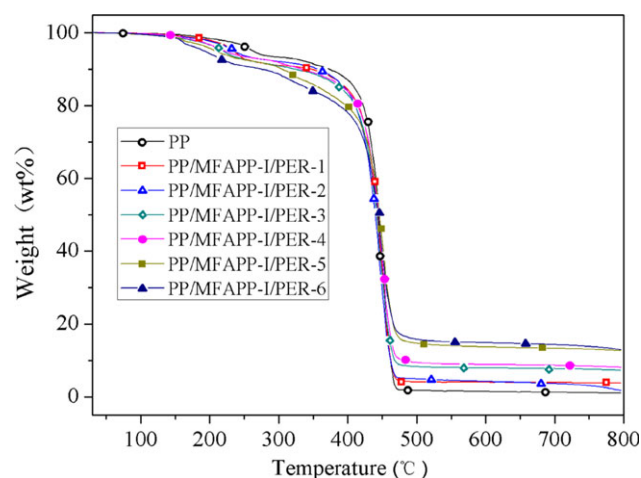


Figure 9. TG curves of PP/MFAPP-I/PER. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

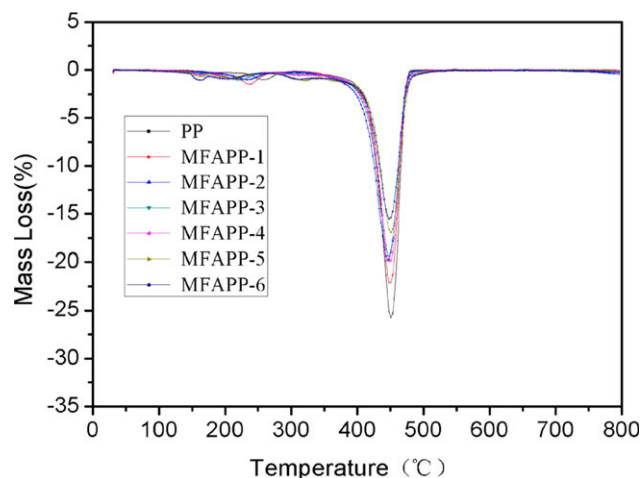


Figure 10. DTG curves of PP/MFAPP-I/PER composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

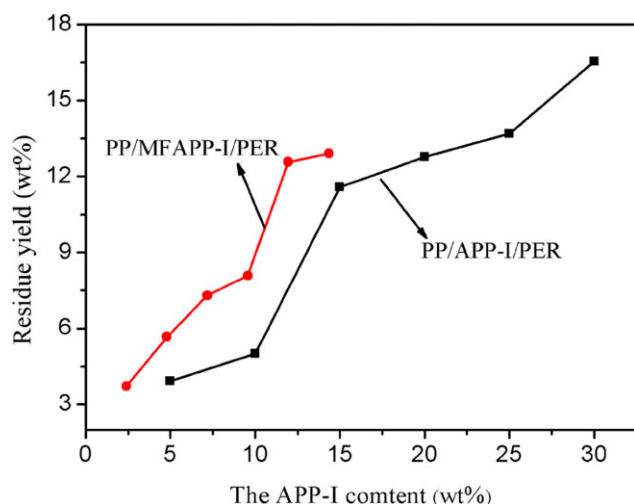


Figure 11. Residue yield of PP/APP-I/PER and PP/MFAPP-I/PER composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites and PP/MFAPP-I/PER composites begin to degrade at about 220°C, a temperature lower than that of pure PP. The result may be explained by the following reasons. As can be seen from Figures 8 and 10, all the composites have an endothermic peak at about 240°C, which are attributed to the transformation of crystal structure and to melting of pentaerythritol. APP-I begins to decompose at about 200°C, forming phosphoric acid, liberating ammonia and H₂O. Compared with T_{\max} of pure PP, the addition of flame retardant bears no influence on the T_{\max} of the composites. It can be seen from Figure 7, pure PP is almost completely decomposed at about 466°C in nitrogen atmosphere and PP/APP-I/PER composites at about 470°C. In Figure 9, PP/MFAPP-I/PER composites have almost completely decomposed at about 465°C, which is slightly lower than that of PP/APP-I/PER composites. But the residue yields of the former are higher than the latter.

Figure 11 shows the amount of residual yield of PP/APP-I/PER and PP/MFAPP-I/PER composites. The residue yield of pure PP is only 0.91%. Compared with pure PP, the residue yield of PP/APP-I/PER composites are much higher. As can be seen from

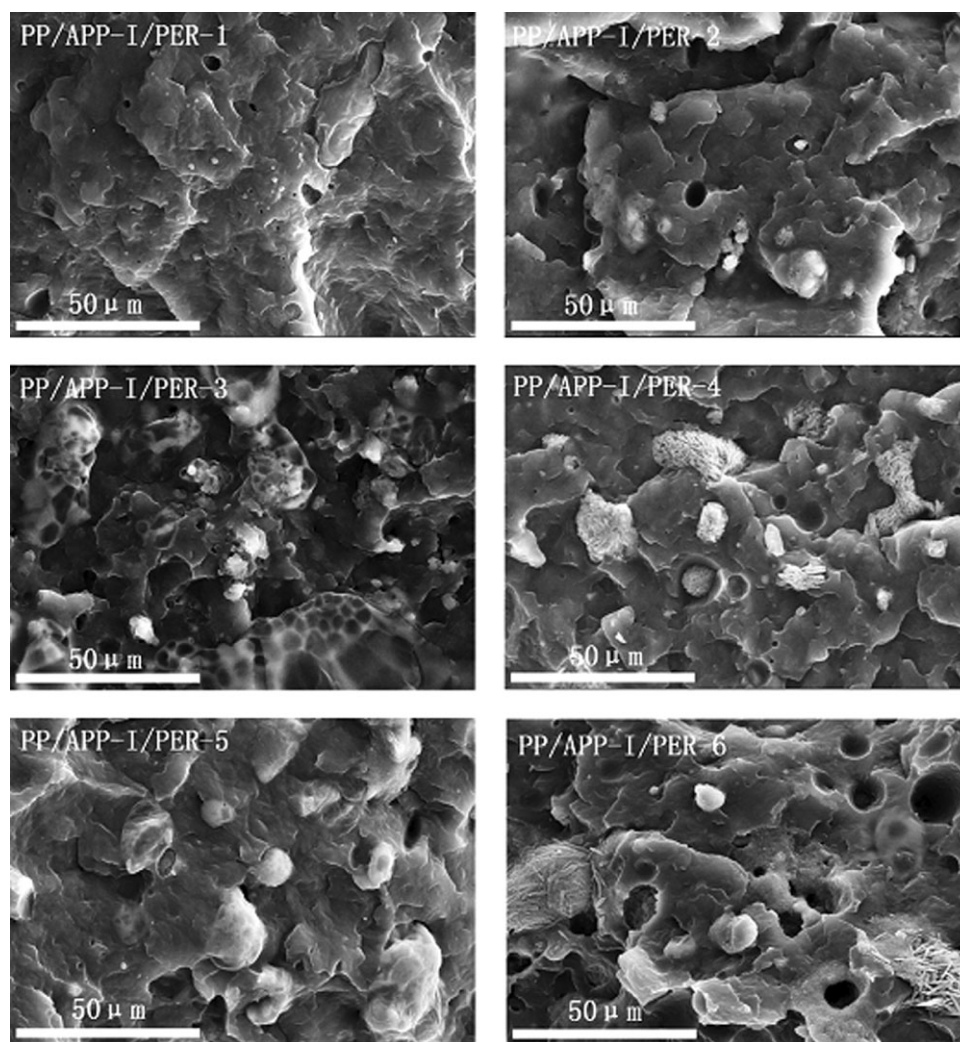


Figure 12. SEM photographs of PP/APP-I/PER composites.

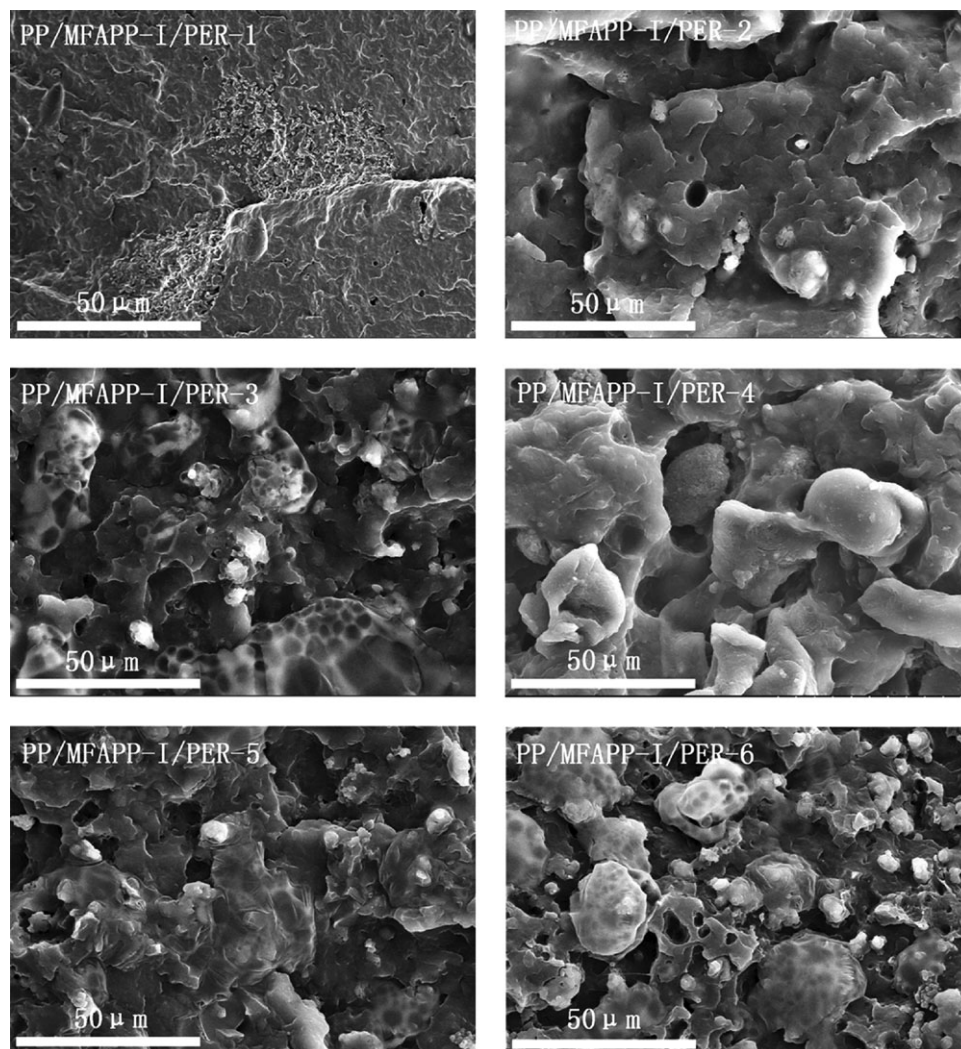


Figure 13. SEM photographs of PP/MFAPP-I/PER composites.

the Figure 8, the more APP-I was added in PP/APP-I/PER composites, the greater the amount of residual char is in PP/APP-I/PER composites. The amount of residual char increased with the increasing MFAPP-I content in PP/MFAPP-I/PER composites. Same content of APP-I is added in PP/MFAPP-I/PER and PP/APP-I/PER composites, but residues of the former are obviously higher than that of the latter. The result may be illustrated by the following reasons. During combustion, on one hand, the microencapsulated APP-I with MF resin decomposes firstly and then the decomposing residues cover the surface of PP, timely protecting the inside material.^{21,22} On the other hand, the incombustible ammonia released from the thermal decomposition of APP-I and MF resin can dilute the air and simultaneously take away part of heat generated in the process. Therefore, the microencapsulated APP-I with MF resin is beneficial to increase the amount of residual char and improve the thermal stability of PP/MFAPP-I/PER composites.

Morphology of PP/APP-I/PER and PP/MFAPP-I/PER Composites. Figures 12 and 13 show SEM photographs of PP/APP-I/PER and PP/MFAPP-I/PER composites, respectively. It

can be seen that there are some holes and tumors in SEM photographs. These tumors are APP-I or MFAPP-I, as verified by the analysis of the EDS in Figure 14. In the preparation phase of SEM samples, APP-I or MFAPP-I is exposed, and some holes can be seen from SEM photographs. Every hole corresponds to an APP-I or MFAPP-I particle. Therefore, both the holes and tumors indicate the presence of APP-I or MFAPP-I. As can be seen from Figure 12, the boundary between APP-I particle and PP is very clear. The number and the size of tumors and holes increase with the increasing APP-I content, and the agglomeration of APP-I is evident. In Figure 13, the boundary between MFAPP-I particle and PP is blurred. Although the number of tumors and holes increases with the increasing MFAPP-I content, the size of tumors and holes is not affected by it, and the distribution of MFAPP-I becomes homogenous. Compared Figure 12 with Figure 13, the microencapsulated APP-I improves compatibility and dispersion of MFAPP-I in PP/MFAPP-I/PER composites.

There are some tumors in the SEM micrographs, which are analyzed with EDS. Elemental compositions of the tumors are listed

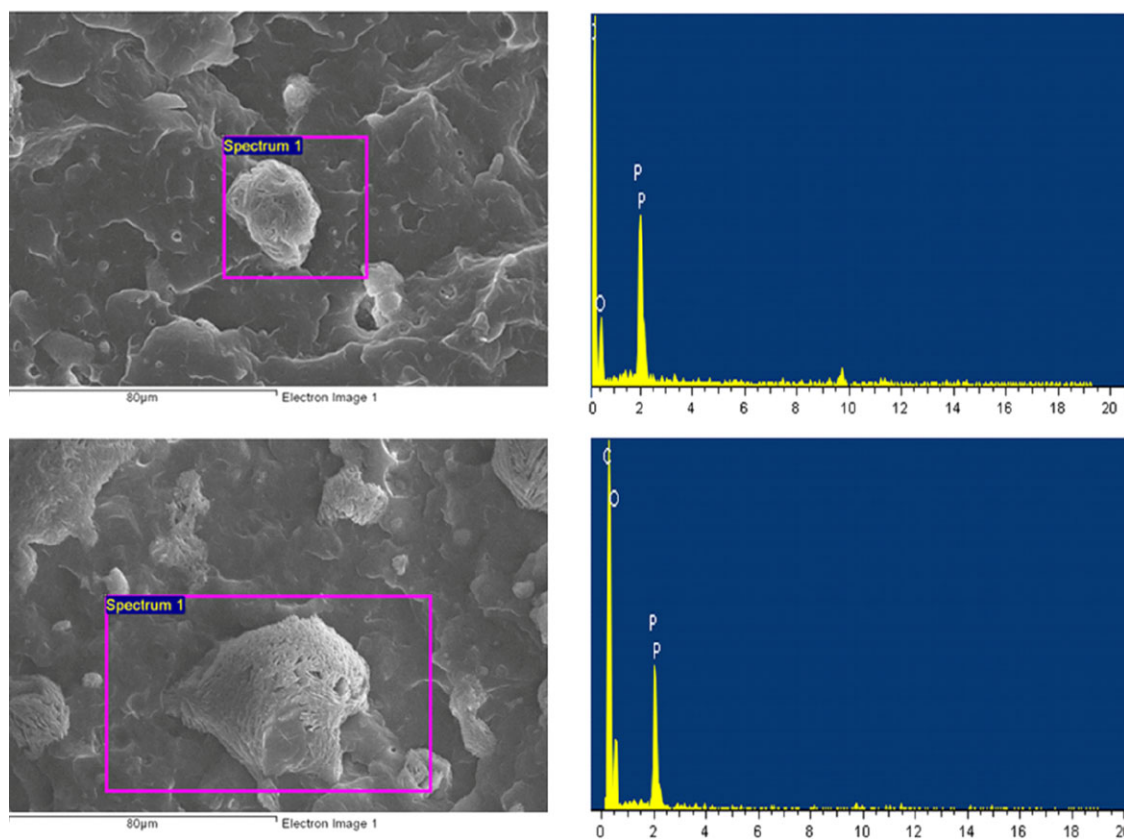


Figure 14. SEM photograph and EDS spectra of (a) PP/APP-I/PER-4 and (b) PP/MFAPP-I/PER-4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in Table IV. The phosphorus content is about 5% in the tumors. In PP/APP-I/PER-4 and PP/MFAPP-I/PER-4, only APP-I and MFAPP-I contain phosphorus. Therefore, the tumors are equivalents of APP-I particles in the SEM micrograph of PP/APP-I/PER-4, and are also the equivalents of MFAPP-I particles in the SEM micrograph of PP/MFAPP-I/PER-4.

Water Resistance of PP/APP-I/PER and PP/MFAPP-I/PER Composites.

The flame retardancy of PP/APP-I/PER-4 and PP/MFAPP-I/PER-4 after the hot water treatment is listed in Table V. For PP/APP-I/PER-4, its LOI value was 38.2 prior to the treatment, and the value decreases to 28.7 after the hot water treatment. Hot water treatment results in decrease not only in LOI value, but also in UL-94 rating. PP/APP-I/PER-4 reduces to no rating after the water treatment. Therefore, the hot water

treatment has a very detrimental effect on the flame retardancy of PP/APP-I/PER composites. The LOI value of PP/MFAPP-I/PER-4 is still as high as 30.4 after the water treatment. Compared with PP/APP-I/PER-4, hot water treatment left no impact on UL-94 test of the PP/MFAPP-I/PER-4. In spite of the little decrease in LOI value of PP/MFAPP-I/PER-4 after water treatment, PP/MFAPP-I/PER-4 still can pass the V-0 rating in the UL-94 test. Therefore, the microencapsulated APP-I with MF resin is in a position to decrease the effect of the hot water treatment and improve the water resistance of PP/MFAPP-I/PER composites.

Figure 15 is SEM and EDS micrographs of PP/MFAPP-I/PER-4 and PP/APP-I/PER-4 after water treatment. The SEM micrographs of PP/APP-I/PER-4 and PP/MFAPP-I/PER-4 are analyzed with EDS, and the elemental contents are listed in Table VI. For PP/MFAPP-I/PER-4 after water treatment, there are many small

Table IV. Elemental Composition of the Tumor in PP/APP-I/PER-4 and PP/MFAPP-I/PER-4

Element	PP/APP-I/PER-4		PP/MFAPP-I/PER-4	
	Weight %	Atomic %	Weight %	Atomic %
C (K)	70.28	77.68	67.22	74.77
O (K)	23.87	19.81	27.48	22.95
P (K)	5.86	2.51	5.30	2.29
Totals	100.00		100.00	

Table V. Flame Retardancy of PP/APP-I/PER-4 and PP/MFAPP-I/PER-4 Before and After Water Treatment

Sample	Before water treatment		After water treatment	
	LOI	UL-94	LOI	UL-94
PP/APP-I/PER-4	38.2	V-0	28.7	NO rating
PP/MFAPP-I/PER-4	32.6	V-0	30.4	V-0

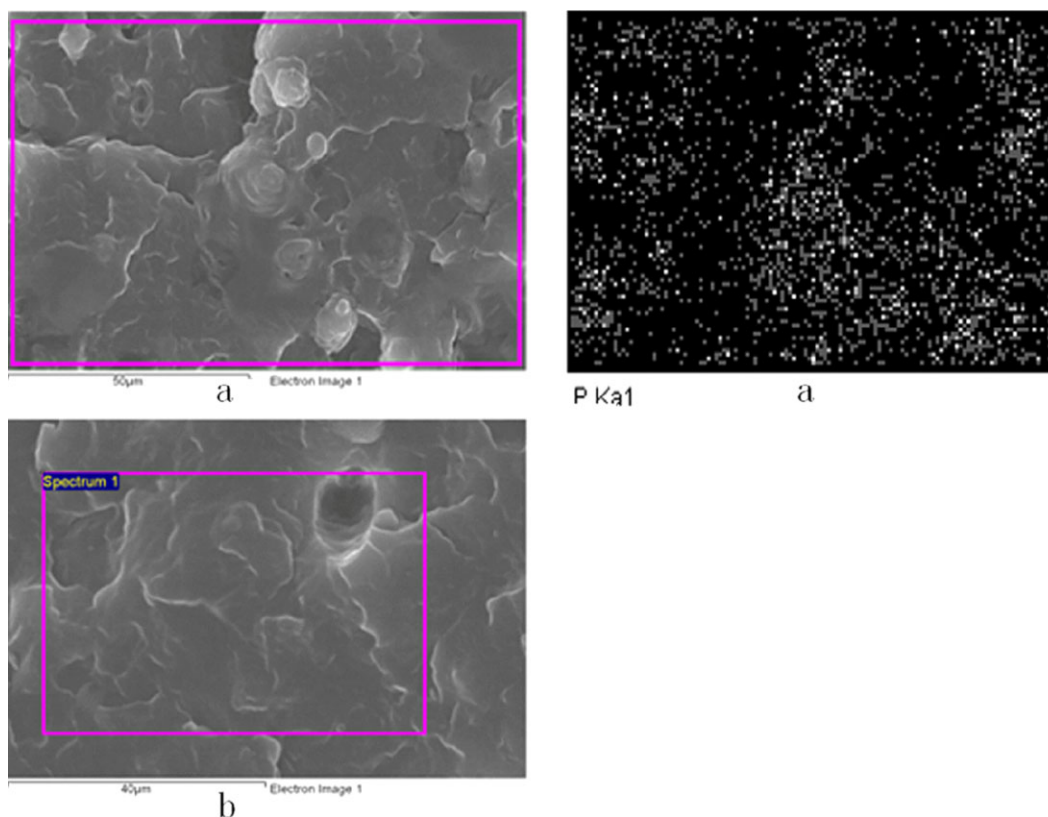


Figure 15. SEM photograph and distribution of P element of (a) PP/MFAPP-I/PER-4 and (b) PP/APP-I/PER-4 after water treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tumors in the fracture surface, as shown in SEM micrograph, and the small ones are MFAPP-I particles. The phosphorous content is about 3.5% in the SEM micrographs of PP/MFAPP-I/PER-4 after water treatment. However, there is almost no tumor and no APP-I particle in SEM micrograph of PP/APP-I/PER-4 after water treatment, and its phosphorus content is zero. It may be because the phosphorus content is so rare that EDS cannot obtain the information. The main reason of this phenomenon may be that, when PP/APP-I/PER-4 is immersed in hot water, the weak compatibility together with high water solubility of APP-I leads to APP-I particles dissolve in the water and remove from the PP matrix. The microencapsulated APP-I with MF resin obviously decreases water solubility of APP-I, and improve the compatibility between APP-I and PP matrix. Therefore, the MFAPP-I particles in PP/MFAPP-I/PER composites are not easily dissolved in water and removed from the PP matrix. Above analysis illustrates why PP/MFAPP-I/PER-4 still has perfect flame retardancy and how the flame retardancy of PP/APP-I/PER-4 is deteriorated after hot water treatment.

CONCLUSIONS

In this article, APP-I is microencapsulated with MF resin by *in situ* polymerization method. The results of FTIR, TG, and SEM proved that APP-I is successfully microencapsulated with MF. MFAPP-I decreases its water solubility and spheroidal particle size.

Added the same load of APP-I, LOI value of the PP/MFAPP-I/PER composites are higher than that of PP/APP-I/PER composites. The microencapsulated APP-I is conducive to improve the flame retardancy of PP composites and make it easier for the flame retardant PP composites to pass the V-0 rating. Compared with APP-I, MFAPP-I improves the water resistance of PP/MFAPP-I/PER composites. The results of TG show that the microencapsulated APP-I with MF resin contributes to the increase of residual char amount and enhance thermal stability of PP/MFAPP-I/PER composites. In addition, the microencapsulated APP-I improves the compatibility and dispersion of MFAPP-I in PP/MFAPP-I/PER composites.

Although APP-I is highly soluble in water, the microencapsulated APP-I with MF resin is an effective intumescent flame retardant for the flame retardant PP composites.

Table VI. Surface Elemental Compositions of PP/APP-I/PER and PP/MFAPP-I/PER After Water Treatment

Element	PP/APP-I/PER-4		PP/MFAPP-I/PER-4	
	Weight %	Atomic %	Weight %	Atomic %
C (K)	84.58	87.96	70.05	78.51
O (K)	15.42	12.04	24.48	20.02
P (K)	0	0	3.48	1.47
Totals	100.00		100.00	

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