

Study on Surface Modification and Flame Retardants Properties of Ammonium Polyphosphate for Polypropylene

Zhouqiao Lei, Youming Cao, Fei Xie, Hui Ren

Faculty of Polymer Materials and Engineering, Guangdong University of Technology, Guangzhou Higher Education Mega Center, Guangzhou City 510006, People's Republic of China

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ABSTRACT: Microencapsulation ammonium polyphosphate used as flame-retardant in polypropylene was prepared with hydroxyl silicone oil (HSO) and melamine-formaldehyde (MF) resin in this article. Fourier transform infrared and energy dispersive spectrometer were used to identify the structure of HSO-MFAPP. For the HSO-MFAPP/polypropylene (PP) composites, the flame retardant effect was evaluated by the limiting oxygen index and UL-94 testing, the compatibility was observed with scanning electron microscope, and the thermal stability was studied by thermogravimetric analysis. The results showed that the

microencapsulation of ammonium polyphosphate (APP) with HSO-MF was prepared by *in situ* polymerization, and the flame retardant properties and water resistance of the PP/HSO-MFAPP/pentaerythritol (PER) composites were much better than the ones of the PP/APP/PER composites. Moreover, the compatibility of HSO-MFAPP with PP was better than that of unmodified APP. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 781–788, 2012

Key words: microencapsulation; ammonium polyphosphate; intumescent flame retardation; HOS; PP

INTRODUCTION

Polypropylene (PP) occupies large part in the polymer consumption owing to superior mechanical properties.¹ It is used in many industrial applications such as: automobile, electronic piece, electric shell, insulation, architectural material, and so on.² However, PP has many drawbacks: the most fatal shortcoming is easy flammability. Meanwhile, smoke and poisonous gas are emitted while it is burning.³ These defects limit the range of application of PP. So, many researchers focus on the flame retardancy of PP to expand the scope of its applying fields.

Compared with halogen-containing flame retardants giving rise to toxic gas and acidic fumes on burning process; halogen-free flame retardants (HFFR) possess environmental-friendly property.⁴ As a HFFR, intumescent flame retardant (IFR) systems were proverbially applied in polymer. A typical IFR system is a system of ammonium polyphosphate (APP), pentaerythritol (PER), and melamine (MEL).⁵ Many researchers have performed extensive

studies on the APP/PER/MEL intumescent flame retardation of polyolefins.^{6,7} Except the advantages, APP/PER/MER compositions also have shortcomings of water-solubility and poor compatibility with polymeric matrices, which can cause them easy to migrate to surface of polymeric matrices, when they are exposed to water or a moisture environment.^{8,9}

To overcome the above disadvantages, the technique of microencapsulation with water-insoluble polymers is a perfect choice. Wu and coworkers have done many researches on the microencapsulation of APP. The works have been reported on the preparation and characterization of microencapsulated APP with melamine-formaldehyde (MF) resin,¹⁰ urea-melamine-formaldehyde¹¹ (UMF), and poly(vinyl alcohol) (PVA)-melamine-formaldehyde resin shell.¹² Microencapsulation ammonium polyphosphate (MCAPP)/PER can more effectively improve the water resistance and the limiting oxygen index (LOI) of PP composites when it is used in PP.^{9–14} It had been found that hydroxyl silicone oil (HSO) can be used for synergism with APP/PER/MEL systems.¹⁵

It had never been reported on the microencapsulation of APP with HSO-MF by means of *in situ* polymerization. Therefore, the aim of this work was to prepare the microencapsulation of APP with HSO-MF and the microencapsulated APP was used for the flame retardant of PP. The main study focus on the surface modification of APP, the structure

Correspondence to: Z. Lei (leizq8677@yahoo.cn).

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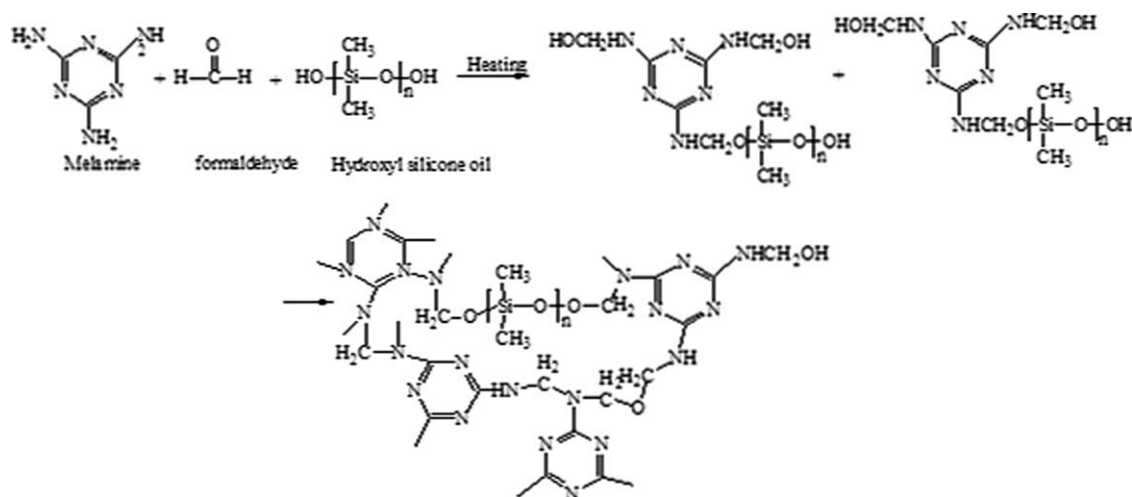


Figure 1 The reaction scheme of the formation of HSO-MF prepolymer and HSO-MF resin.

identification of HSO-MFAPP, and water solubility, heat properties and flame retardence properties of PP composites.

EXPERIMENTAL

Materials

PP (T30S) with a melt flow index of 3.0 g/10 min⁻¹ (230°C/2.16 kg) was provided by Da Qing Petroleum Chemical Company, P. R. China. APP with average degree of polymerization $n > 1000$ was kindly supplied by Hangzhou JLS Flame Retardants Chemical Corporation, P. R. China. Melamine and 37% formaldehyde solution were chemical reagents, respectively, purchased from Shanghai Lingfeng Chemical Reagent Corporation and Tianjin Baishi Chemical Corporation, P. R. China. PER was provided by Tianjin Kermel Chemical Reagents Development Centre, P. R. China. HSO was provided by Guangzhou Juchengzhaoye Youjiguiyuanliao Co., P. R. China.

Preparation of microencapsulated APP

Preparation of the prepolymer solution: the mixture of melamine (3 g), HSO (3 g), and 50 mL acetone were put into a three-neck bottle with a stirrer. The PH of the mixture was adjusted to 4–5 with acetic acid, heated to about 80°C and incubated at that temperature for 1.5 h with stirring. Then 3 g melamine and 10 mL formaldehyde solution were added into the system, the temperature was kept at 80°C for 1 h. The prepolymer solution was prepared, and it was ready for the next step.

Preparation of microencapsulated APP : APP (30 g) was dispersed in 40 mL ethanol with a stirrer. The pre-polymer solution obtained from the above step was added to the mixture, and the PH of the

mixture was adjusted to 4–5 with sulfuric acid. The resulting mixture was heated to 80°C and incubated at that temperature for 3 h with stirring. The mixture was filtered, washed with distilled water, and vacuum drying at 105°C, and the pure HSO-MFAPP powder was finally obtained. Figure 1 shows the condensation reaction scheme of HSO-MF resins; Figure 2 shows the reaction of APP and HSO-MF prepolymer.

Preparation of flame retarded PP composites

Samples were mixed at 50 revolutions per minute screw speed at 180°C for 10 min. At first, PP was melted at 180°C in the torque rheometer for 2 min, and then APP/PER or HSO-MFAPP/PER was added into the molten PP.

Mixed materials were hot-pressed at 180°C under 10 MPa for 10 min into sheets after mixing; the samples were hot-pressed at 180°C under 10 MPa for 10 min into the sheets with dimensions of 160 × 160 × 0.3 cm. The formulation were given in Table I.

MEASUREMENTS

Fourier transforms infrared spectra

Powders were mixed with KBr powders, and the mixture was pressed into a tablet. The Fourier transform infrared (FTIR) spectra of samples were recorded using a Nicolet MAGNA-IR 750 spectrophotometer.

Thermogravimetry

Thermogravimetric analysis was performed using TA Instruments STD 2960. The samples were heated from room temperature to 700°C at heating rate 10°C min⁻¹ under nitrogen with a flowing rate of 10 mL min⁻¹.

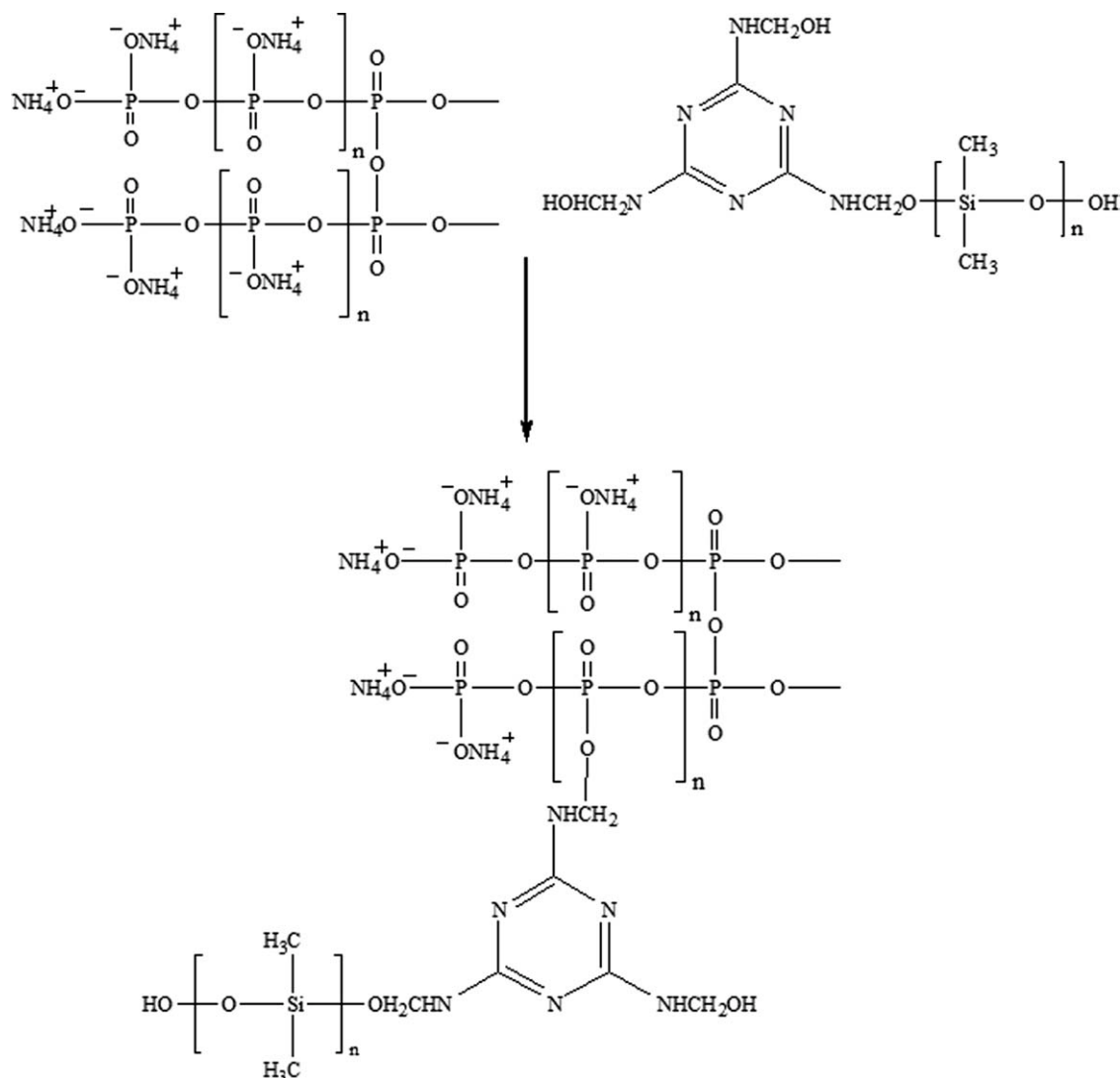


Figure 2 The reaction of APP and HSO-MF prepolymer.

Limiting oxygen index

LOI was measured according to ASTM D 2863. The apparatus was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, P. R. China). The specimens used for the test were of dimensions $100 \times 6.5 \times 3 \text{ mm}^3$.

UL-94 testing

UL-94 vertical burning tests were carried out on an AG5100A instrument (AnGui Analysis Instrument Company, P. R. China). The specimens used for the test were of dimensions $130 \times 13 \times 3 \text{ mm}^3$ according to UL-94 test standard.

Scanning electron microscopy (SEM)

The SEM micrographs of the particles and the PP composites after being gold-sputtered were obtained by a Hitachi X-650 (Hitachi, Guangzhou, Guangdong,

P.R. China) scanning electron microscope (SEM). Surface elemental composition analysis of APP and HSO-MFAPP particles were performed when we test the SEM micrographs of the particles and the PP composites.

Measurement of water solubility

Ten grams accurate weight (0.002 g) APP or HSO-MFAPP was put into a conical flask, added 100 mL distilled water at different temperature, stirred at that temperature for 1 h using magnetic stirrer. The suspension was then filtered, and 50 mL of filtrate was taken out and dried to constant weight at 105°C . Solubility of samples in water can be calculated.

Content of the HSO-MF resin measurement

APP (M_1) was microencapsulated by HSO-MF resin, then, MCAPP was filtered, washed with distilled

TABLE I
Formulation of Flame Retarded PP Composites

Sample code	PP (wt %)	APP (wt %)	HOS-MFAPP (wt %)	PER (wt %)	MF-APP (wt %)	HOS-APP (wt %)
Pure PP	100	0	0	0	0	0
PP-1	70	30	0	0	0	0
PP-2	70	22.5	0	7.5	0	0
PP-3	70	15	0	15	0	0
PP-4	70	7.5	0	22.5	0	0
PP-5	70	0	0	30	0	0
PP-6	70	0	30	0	0	0
PP-7	70	0	22.5	7.5	0	0
PP-8	70	0	15	15	0	0
PP-9	70	0	7.5	22.5	0	0
PP-10	70	0	0	7.5	22.5	0
PP-11	70	0	0	7.5	0	22.5
PP-12	70	0	0	0	30	0
PP-13	70	0	0	0	0	30

water, and vacuumed drying at 105°C to constant weight (M_2), the content of the HSO-MF resin was calculated by:

$$\begin{aligned} &\text{content of the HSO - MF resin} \\ &= (M_2 - M_1)/M_1 \times 100\% \end{aligned}$$

RESULTS AND DISCUSSION

The characterization identify of HSO-MFAPP

The FTIR spectra of pure APP and HSO-MFAPP were showed in Figure 3. Figure 3 indicated that the typical absorption peaks of pure APP and HSO-MFAPP emerged at 3212 cm^{-1} (N-H), 1252 cm^{-1} (P=O), 1070 cm^{-1} (P-O symmetric stretching vibration), 884 cm^{-1} (P-O asymmetric stretching vibration), 1020 cm^{-1} (PO_2 , PO_3). It need to be noted that besides the IR spectrum of HSO-MFAPP have simi-

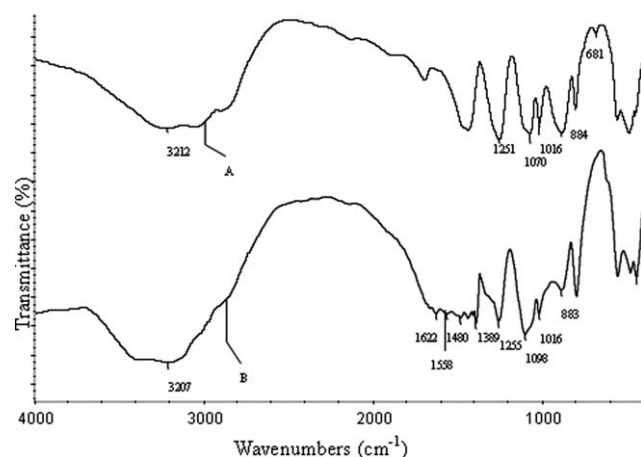


Figure 3 FTIR spectra of (A) pure APP and (B) HSO-MFAPP.

TABLE II
Surface Elemental Compositions of APP and HOS-MFAPP

Sample	C (wt %)	O (wt %)	N (wt %)	P (wt %)	Si (wt %)
APP	29.86	46.65	11.34	12.49	–
HOS-MFAPP	32.51	28.44	27.60	10.51	0.94

lar absorption peaks at above nearby of wave number, it also exhibited other absorption peaks at 1558 cm^{-1} , 1480 cm^{-1} , 1389 cm^{-1} , the peaks are due to the ring vibration of melamine from MF resin, stretching vibration of C–O, the peak of 1098 cm^{-1} may be attributed to the stretching vibration of Si–O–Si. Therefore, the difference of absorption peaks had proven that the HSO-MF was grafted on the surface of APP.

Furthermore, the surface elemental composition analysis of APP and HSO-MFAPP particles have been performed, and the results are listed in Table II. It can be seen that the nitrogen and carbon percentage of APP is 11.34% and 29.86%, respectively. In the case of HSO-MFAPP, the nitrogen percentage and carbon percentage is increased to 27.60% and 32.51%, respectively. The content of phosphorus element and oxygen element of APP are 12.49% and 46.65 %, respectively. For HSO-MFAPP, the percentage of phosphorus and oxygen decreased to 10.51% and 28.44%, respectively. Simultaneously, there is 0.94% silicon element on the surface of HSO-MFAPP. From the results, we can obtain the conclusion that the surface of APP particles was well covered by the HSO-MF.

The surface morphologies of APP and HSO-MFAPP are shown in Figure 4. It clearly be seen that the surface of APP is very smooth, and that of HSO-MFAPP presents a comparably rough. The content of HSO-MF resin microencapsulated on APP was calculated by: Content of the HSO-MF resin = $(M_2 - M_1)/M_1 \times 100\% = (35.1 \text{ g} - 30 \text{ g})/30 \text{ g} \times 100\% = 17\%$. So, we also can obtain the conclusion that the surface of APP particles was covered by the HSO-MF resin from the result of content of HSO-MF resin.

So, the microencapsulation of APP with HSO-MF by means of the *in situ* polymerization method have been performed in this work, and the expected effect has been attained.

Water solubility of HSO-MFAPP

The water solubility of APP and HSO-MFAPP can be seen in Figure 5. From Figure 5, it can be seen that the solubility of APP at 25°C and 80°C is 0.348 g/100 mL H_2O and 3.492 g/100 mL H_2O ,

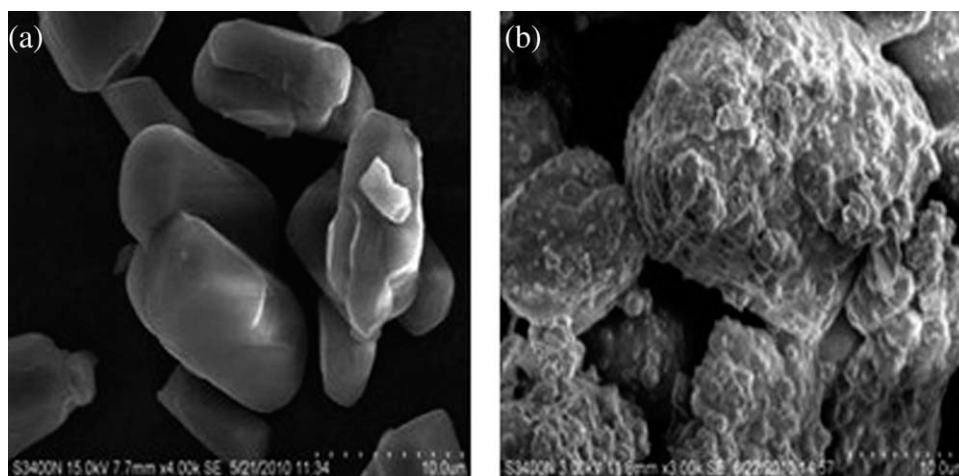


Figure 4 SEM micrographs of surface morphology ($\times 4000$): (a) APP and (b) HSO-MFAPP.

respectively, indicating that APP can be easily attacked by moisture or water, especially at high temperature. After the microencapsulation of APP with HSO-MF resin, the solubility of HSO-MFAPP decreases sharply especially at high temperature. The trend solubility of HSO-MFAPP at 80°C is similar to that of HSO-MFAP at 25°C . The results can be explained that the HSO-MF resin outside APP is hydrophobic, leading to a decrease in the solubility of APP.

Flame retardation of PP composites

The results of the LOI values and UL-94 testing of the PP composites are presented in Table III. To investigate the water solubility of PP composites, we had compared the flame-retardant of PP composites with the flame-retardant of PP composites treated in water at 50°C for 24 h.

In Table III, the mass percentage of PP was fixed at 70% (wt), the total mass percentage of flame retardance agent is 30% (wt).

PP-1~PP-5 were the system of PP/APP/PER composites, It can be seen that LOI values of the pure PP is only 17, and the LOI value of binary composites composed of PP 70% and APP 30% as PP-1 was 19.5, and that of composites composed of PP 70% and PER 30% as PP-5 was 19. The LOI values of PP composites were greatly improved when APP or PER was added into pure PP. It was especially noted that, the ratio of APP/PER was 22.5/7.5 as PP-2, the LOI value of PP/APP/PER reached to the maximum and was 27.5. Meanwhile, the UL-94 rating for PP-2 was raised to V-0.

The reasons of these results can be explained that due to scarcity of carbonization agents for PP/APP binary composites to form an intact multicellular carbon layer to protect the underlying material from the action of the fire, the LOI value of the PP/APP

binary composites hardly had been improvement. When the addition of PER as a carbonization agent added into binary composites was over, the LOI value was decreased because the quality of the inflation carbon layer forming at fire was bad lead to the flame resistance of PP composites was poor.

For the PP/HSO-MFAPP binary composites, the LOI value is higher than that of PP/APP binary composite. For example, the LOI values of PP/HSO-MFAPP binary composite as PP-6 are 25.5, while the LOI value of the PP/APP composites is 19.5. Namely, PP/HSO-MFAPP binary composite have better flame retardance effect. The remarkable increase of the LOI value using HSO-MFAPP may be due to the element Si in the HOSMF resin had synergistic effect in IFR system, meanwhile the HOSMF resin was acted as the blowing agent.

PP-12 is the system of PP/MFAPP composites. Compared with PP/APP composites, the LOI value of PP/MFAPP is 25, which is much higher than the LOI value of PP/APP, the result can be explained

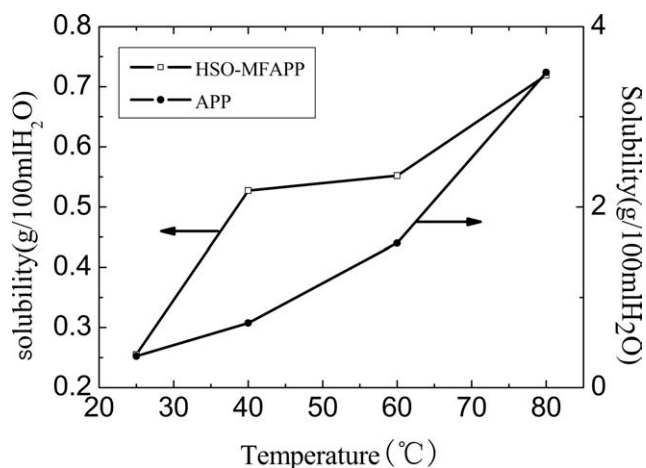


Figure 5 Solubility of APP and HSO-MFAPP at different temperatures.

TABLE III
LOI Value and UL-94 Results of FR PP Composites

Sample code	LOI (%)		UL-94	
	A	B	A	B
Pure PP	17	17	NO rating	NO rating
PP-1	19.5	18	NO rating	NO rating
PP-2	27.5	22	V-0	NO rating
PP-3	26	21	NO rating	NO rating
PP-4	22.4	18.5	NO rating	NO rating
PP-5	19	18	NO rating	NO rating
PP-6	25.5	23.5	NO rating	NO rating
PP-7	32	30	V-0	V-0
PP-8	30.5	28.5	V-0	V-0
PP-9	30	28	V-1	V-1
PP-10	31	29	V-0	V-0
PP-11	31	30	V-0	V-0
PP-12	25	23	NO rating	NO rating
PP-13	25	23	NO rating	NO rating

B column stands for the sample has been immersed in water (50°C) for 24 h.

that MF resin can be acted as the blowing agent. For the PP/HSOMF binary composites, the LOI value is higher than that of PP/APP binary composite. The remarkable increase of LOI value using HSOAPP may be due to the element Si in the HSO had synergistic effect in IFR system.

When the PER was added into the PP/HSO-MF PP binary composites, the LOI had obvious improvement. The LOI values of the PP/HSO-MFAPP/PER composites containing 7.5%, 15%, and 22.5% PER are 32, 30.5, and 30, respectively. The UL-94 rating for PP-7, PP-8, and PP-9 are raised to V-0, V-0, and V-1, respectively. The LOI values of PP/MFAPP/PER and PP/HSOAPP/PER composites containing 7.5% PER are 31 and 31, respectively. The UL-94 rating for PP-10 and PP-11 reached V-0. This can be explained that when PER added into the composites can form an intact inflation carbon layer to protect the underlying material from the action of the fire.

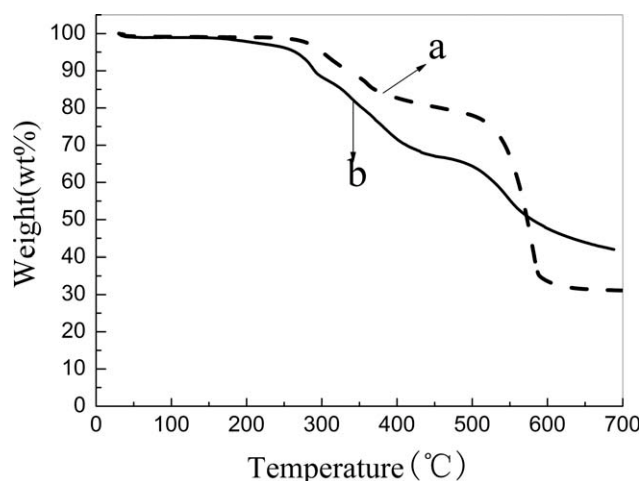


Figure 6 TG curves of pure APP (a) and HSO-MFAPP (b).

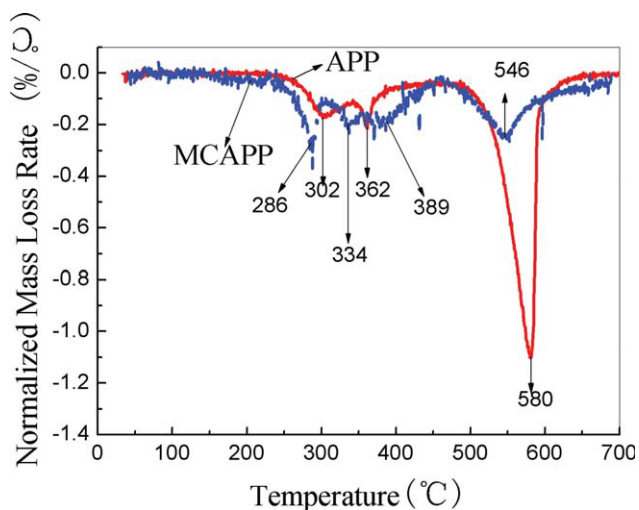


Figure 7 DTG curves of pure APP and HSO-MFAPP. [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.wiley.com].

The flame retardance effect of PP composites was poor when PP composites were soaked in water for 24 h at 50°C, because that APP is easily soluble in water.

The UL-94 rating for PP/HSO-MFAPP/PER, PP/MFAPP/PER, and PP/HSOAPP/PER composites have not changed when composites had been soaked for 24 h in water (50°C). It can be seen that the microencapsulation of APP greatly improved the water resistance property in FR PP composites.

Thermal stability analysis

The thermogravimetry (TG) and differentiable thermogravimetry (DTG) curves of APP and HSO-MFAPP are shown in Figures 6 and 7. The degradation of APP has three main steps in nitrogen atmosphere: 260°C ~ 420°C, 420°C ~ 500°C, and 500°C ~ 680°C, it begin to decompose at about

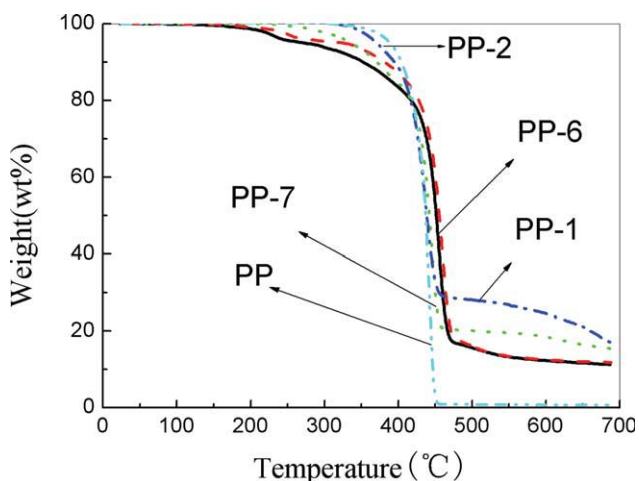


Figure 8 TG curves of pure PP and PP composites. [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.wiley.com].

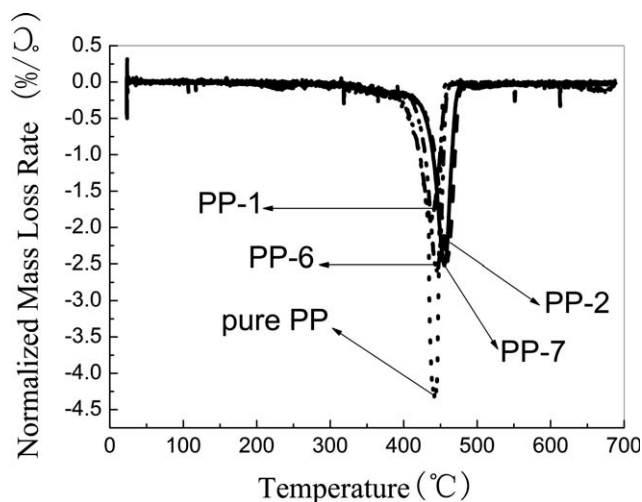


Figure 9 DTG curves of pure PP and PP composites.

260°C, the evolution production of the first step are mainly ammonia and water, meantime, P_2O_5 are formed. Ammonia cannot be completely removed in first stage, which can protect the APP from removing water to form P_2O_5 . The second process (420°C ~ 500°C), about 4% weight loss, is the main remove of water to form polyphosphoric acid. The third step occurs in the range of 500°C ~ 700°C, which is main decomposition process of APP. The temperature of maximum mass loss rate (T_{max}) for three steps are 302°C, 362°C, and 580°C, respectively. The residue of APP at 700°C is about 30%.

In the case of HSO-MFAPP, its initial decomposition temperature is 235°C which is lower than that of APP due to the less thermal stability of MF resin. Above 570°C, HSO-MFAPP is more stable than APP. It can be seen that the HSO-MFAPP has four main steps. The T_{max} for four steps are 286°C, 334°C, 389°C, and 546°C, respectively. Moreover, the residue for HSO-MFAPP at 700°C about 41%, which is obviously higher than that of APP.

The thermal stability of PP and its composites was studied by TG. Figures 8 and 9 show the TG and DTG curves of pure PP resin and PP composites, respectively. It can be clearly seen that the PP begin to degradate at about 330°C and has almost completely decomposed at 460°C in nitrogen atmosphere. The temperature of maximum mass loss rate (T_{max}) is 441°C, as shown in Figure 8.

Figures 8 and 9 show the TG and DTG curves of IFR/PP. Compared with pure PP, the IFR/PP begin to degradate at about 230°C, which was much lower than the pure PP. The low-temperature thermal stability of IFR/PP decreased. Above 420°C, The IFR/PP is more stable than pure PP.

The thermal decomposition between binary and ternary composites has remarkable difference, when PER is added into the PP/APP or PP/HSO-MFAPP binary composites, the initial decomposition temperatures of the ternary composites PP-2 and PP-7 are lower than the ones of the PP/APP (or PP/HSO-MFAPP) due to the weak thermal stability of PER and esterification between acid source and carbonization agent.

The SEM of PP composites

The 1000 times SEM of PP with 30% FR is shown in Figure 10, it can be clearly seen that there is bigger gap between APP particles and PP, and the interface is clear. Meanwhile, the gap between HSO-MFAPP and PP is small, and interface is indistinct. Because the unmodified APP have strong polar groups $-NH_4$ and PP have no any polar groups, the no-match of the polarity make the compatibility between APP and PP be poor, and which results to the emergence of great gap. After the surface modification of APP using HOSMF resin, the strong polar groups $-NH_4$ of APP are enveloped in melamine rings and not emerge polarity out. So, the compatibility between HSO-MFAPP

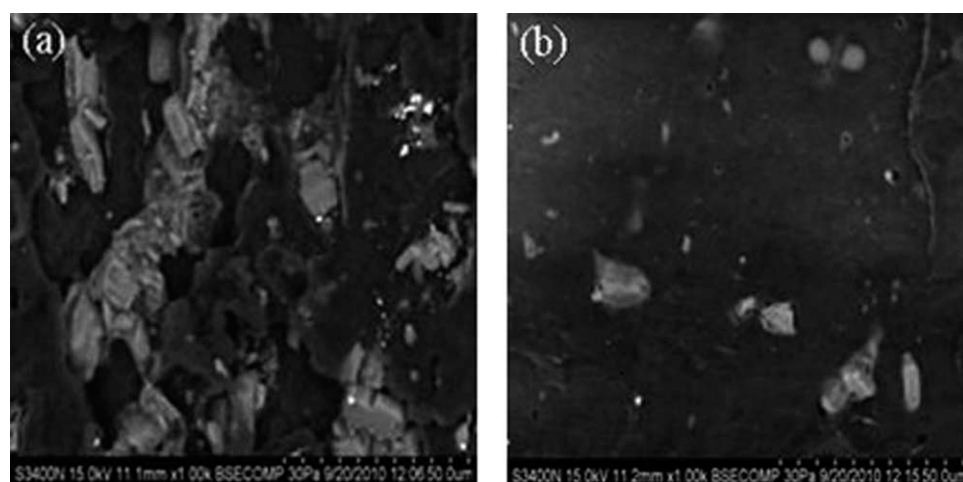


Figure 10 The SEM pictures of PP composites: (a) PP-2, (b) PP-7.

and PP was better, which make the gap of HSO-MFAPP composites reduce.

CONCLUSION

In this work, our conclusion is as follows:

1. Microencapsulated APP with HSOMF shell can be performed by the *in situ* polymerization method. The HSO-MFAPP increases the water resistance in PP matrix and improves the compatibility with PP matrix.
2. For the HSO-MFAPP/PP composites, the LOI values are greatly improved compared with those of the PP/APP composites at the same loading.
3. The flame retardant properties composed of PP, HSO-MFAPP, and PER are best, and the LOI values and UL-94 ratings of the composites are 32 and grade-0. Moreover, after water treatment at 50°C for 24 h, the composites still maintain good flame retardant properties.

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