Effects of Interfacial Modification on the Thermal, Mechanical, and Fire Properties of High-Impact Polystyrene/Microencapsulated Red Phosphorous

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ABSTRACT: In this study, polystyrene (PS)-encapsulated magnesium hydroxide-microencapsulated red phosphorus (MHRP) was prepared by *in situ* polymerization of styrene on the surface of MHRP in a high speed mixer. The encapsulated MHRP flame retardant was successfully applied in the fire resistance to HIPS by melt blending in a corotating twin-screw extruder. The effects of PS-encapsulated MHRP on the properties of HIPS composites were studied by mechanical, thermal, and combustion tests (HBR, LOI, UL-94, and cone calorimetry). The experimental results showed that compared to the composites containing untreated MHRP, the thermal, mechanical, and flame-retardant properties of those containing PS-encapsulated MHRP were found to be prominently improved. This improvement was mostly attributed to an effective dispersion of the encapsulated filler and a good interfacial compatibility between the filler and the matrix. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2139–2144, 2008

Key words: high-impact polystyrene; microencapsulated red phosphorus; thermal properties; mechanical properties; flammability

INTRODUCTION

The reduction and substitution of flame retardants containing halogen are progressing in terms of toxicological and environmental aspects. Red phosphorus (RP) is one of the ecologically and physically most harmless alternative fire retardants, because encapsulation and the use of master batches have been established successfully to eliminate problems of handling safety and stability.[1] Therefore, the largest handicap for its widespread application as an alternative flame retardant is the reddish-brown color of polymeric materials containing RP.

However, RP is a very effective flame retardant, which can be used to reduce the flammability of hydrocarbons and polymers with heteroatoms and which has been commercialized successfully in some systems such as glass fiber-reinforced polyamide 66.[2–7] The flame retardancy of RP in polymers can act in both the condensed phase and the gas phase.[3,8–11] Condensed phase mechanisms of RP increase char formation, which decreases the com-

bustible volatiles and therefore the total fuel support of the flame. Furthermore, the char can act as a barrier, decreasing the mass loss rate. Gas phase mechanisms of RP reduce the effective heat of combustion by flame inhibition. The mode of action of RP depends on the chemical structure of the polymer. Polymers with heteroatoms such as oxygen are polar and adsorb water. The presence of water in a polymer is one of the most important prerequisites for condensed phase mechanisms of RP as it was proposed for glass fiber-reinforced polyamide 66. In nonpolar polyolefin, phosphorus can barely be fixed by oxidation in the condensed phase. In this case, phosphorus sublimates that result in a gas phase mechanism. Magnesium hydroxide (MH) is well established as an acid-free, halogen-free, and smoke suppressing flame retardant.[12–14] It decomposes endothermically and releases water at about 327–427°C, so that the flame-retardant effect is based on cooling and dilution. High filler loadings of MH are necessary to achieve sufficient flame retardancy, which often causes a drawback in mechanical and processing properties. Based on these results, the combination of RP with a moderate loading of MH in a nonpolar polymer, such as high-impact polystyrene (HIPS), is promising. MH may act as a water-releasing source, inducing the oxidation of phosphorus in the condensed phase to increase residue.

Braun et al.[15] studied flame-retardant mechanisms of RP and MH in HIPS. A recent work reported by Lu et al.[16] showed that MH sulfate hydrate whisker-flame and MH microencapsulated red phosphorus (MHRP) have been found to have synergistic effects. However, there is little information in the literature about the effects of interfacial modification on the thermal, mechanical, and fire properties of HIPS/MHRP by *in situ* polymerization of styrene on the surface of MHRP in a high speed mixer.

In our laboratory, a new approach for surface modification of flame retardants has been explored.[17,18] The previous investigation showed that for HIPS/MH composites, compared to the composites containing untreated MH, flame-retardant properties of those containing polystyrene (PS)-encapsulated MH were found to be significantly improved. This improvement is mostly attributed to a better dispersion of the encapsulated filler and a strong adhesion between the filler and the matrix.[18]

In this work, PS-modified MHRP was prepared by *in situ* polymerization of styrene on the surface of MHRP in a high speed mixer. The untreated or PS-modified MHRP flame retardants were applied in HIPS by melt blending in a corotating twin-screw extruder. It was expected that the PS covered on the surface of MHRP can improve the physical properties of the resulting HIPS composites.

EXPERIMENTAL

Materials

HIPS (PH-88HT, $\overline{M}_w$ = 200,000 g/mol, melt flow index = 4.5 g/10 min at 200°C and 5 kg) with a density 1.04 g/cm³ was provided by Zhenjiang Chimei (China). MHRP (shell was MH, core was RP, shell/core = 60/40 w/w) used as filler, was supplied by Shanghai Xusen Nonhalogen Smoke Suppressing Fire Retardants (China). The average volume particle size was 4.5 μm, and the specific surface area, 1.8 m²/g 3-(methacryloxy)propyltrimethoxy silane (MPS), was provided by Hubei Wuhan University Silicone New Material (China). Styrene, azobisisobutyronitrile (AIBN), and hydrochloric acid were purchased from Shanghai Chemical Reagents Company (China) and used without further treatment, except styrene, which was distilled before use.

Preparation of PS-encapsulated MHRP

MHRP powder was dried at 120°C for 6 h and then placed in a high speed mixer heated to 70°C with a rotation speed of 1200 rpm. Then, to a solution of MPS in acetone, water and acetic acid were added with stirring for 20 min. For interested readers, a more detailed discussion and relevant references about the preparation procedure and the proposed chemical structure of the product of the chemical bonding between PS, MPS, and MH are found in Ref. 18. The modified powder was dried at 80°C for 12 h. Finally, the modified powder, monomer (styrene), and additional initiator (AIBN) were placed into the mixer with agitation fixed at 1200 rpm and heated in an oil bath to 80°C for 45 min. The crude product at the end of polymerization was dried. The PS-encapsulated MHRP was designated as MHRP-T in the following discussion.

Characterization of MHRP-T

The thermogravimetric analysis (TGA) data were obtained using a SDT Q600 thermogravimetric analyzer (America). In each case, a 10–20-mg sample was tested under nitrogen atmosphere at a heating rate of 10°C/min. Relative error was not more than 10%.

Material preparation of composites

These raw materials were first mixed in a high speed mixer for about 20 min. Then the mixture was extruded and pelletized in a corotating twin-screw extruder (Nanjing Keya Machinery) with an L/D ratio of 42 and a screw diameter of 35 mm. The temperature profiles of the barrel were 180, 190, 200, 210, 210, and 215°C from the hopper to the die, respectively. The screw speed was set at 400 rpm. A series of samples with different compositions were obtained as shown in Table I. The specimens for combustion and rheological tests were molded with an injection-molding machine (CJ80M2V, Zhende Plastics Machinery), and the injection temperature was 210°C.

Characterization of composites

Flammability of the samples was studied by a horizontal burning test according to ASTM D 635.

UL-94 vertical burning tests were performed with a plastic sample of dimensions 127 × 12.7 × 3 mm³ suspended vertically above a cotton patch. The test was carried out using a CZF-3 type instrument (China) according to ASTM D 635-77.

The flammability of materials was determined using limiting oxygen index (LOI) using a JF-3 type instrument (made in china) on sheets 120 × 6.5 × 3 mm³ according to the standard oxygen index test ASTM D2863-77.

Fire behavior was also characterized by a cone calorimeter according to ASTM E 1354/ISO 5660 (Fire Testing Technology, East Grinstead, UK). All samples (100 mm in diameter and 4 mm in thickness) were measured in a horizontal position. The heat

TABLE I
Composition and Flammability of the Flame-Retarded HIPS and Its Composites

Sample code	Composition (wt %)			HBR	LOI (%)	UL-94 testing
	HIPS	MHRP[a]	MHRP-T[b]			
1	100	0	0	FH-3-36 mm min^{-1}	18.2	Fail
2	90	10	0	FH-2-8 mm	20.3	Fail
3	85	15	0	FH-2-5 mm	21.5	Fail
4	80	20	0	FH-2-2 mm	21.5	Fail
5	75	25	0	FH-1	22.0	V-1
6	90	0	10	FH-2-4 mm	20.5	Fail
7	85	0	15	FH-2-3 mm	21.5	Fail
8	80	0	20	FH-1	22.0	Fail
9	75	0	25	FH-1	22.5	V-0

[a] MHRP represents MH microencapsulated RP.
[b] MHRP-T represents MHRP encapsulated with polystyrene by *in situ* polymerization.

flux was maintained at 35 kW/m^2. The real irradiation sample area was 0.007854 m^2. Exhaust flow was set at 24 L/s, and the spark was continuous until the sample was ignited. We will mainly focus here on the time to ignition (s), the heat release rate (HRR) curves, and the peak of heat release rate (PHRR) (kW/m^2). All samples were run in triplicate, and the average value is reported; results from the cone calorimeter are generally considered to be reproducible to ±10%.

TGA data were obtained using a SDT Q600 thermogravimetric analyzer. In each case, a 10–20-mg sample was tested under nitrogen atmosphere at a heating rate of 10°C/min. Relative error was not more than 10%.

The tensile and flexural behaviors were performed on a Universal Testing Machine (SANS, Shenzhen, China) according to ASTM D638 with a cross-head speed of 5 mm/min. The Izod-notched impact strength was measured with an impact testing machine (XJU-22, Chengdu, China) according to ASTM D256. All experiments were conducted at room temperature and a relative humidity of 50%.

RESULTS AND DISCUSSION

Characterization of MHRP-T

The mass loss data of MHRP-T obtained by TGA was shown in Figure 1. The weight loss between 56 and 120°C was 2.8 wt %, which was due to the desorption of physically adsorbed water and the weight loss from 120 to 255°C was 3.4 wt %, which was due to the decomposition of MPS. Most decomposition occurred at temperatures between 255 and 800°C with the maximum weight change at between 356 and 440°C, the total weight loss was 30.3 wt %. In nitrogen, RP had no weight loss, and so the weight loss was due to the PS grafted on the MH

surface and the loss of the endothermic decomposition release water of hydration from the substrate.

HBR, LOI, and UL-94 testing of composites

The horizontal burning rate (HBR), LOI, and UL-94 tests are widely used to evaluate flame-retardant properties of materials. Table I lists the HBR, LOI, and UL-94 data obtained from all HIPS composites. It is clear that, at the same additive level, the HBR of HIPS/MHRP-T composites were all higher than that of HIPS/MHRP composites. It was expected that the grade of HBR was raised from FH-3 to FH-1 (10 wt %–25 wt %), and UL-94 rating was raised from V-1 to V-0 with the increase in MHRP or MHRP-T content. As for HIPS/MHRP-T composites, UL-94 rating was raised to V-0 at 25 wt % MHRP-T, which showed V-1 in the composites containing MHRP at the same level. Nevertheless, the influence of PS covering on the surface of MHRP on LOI
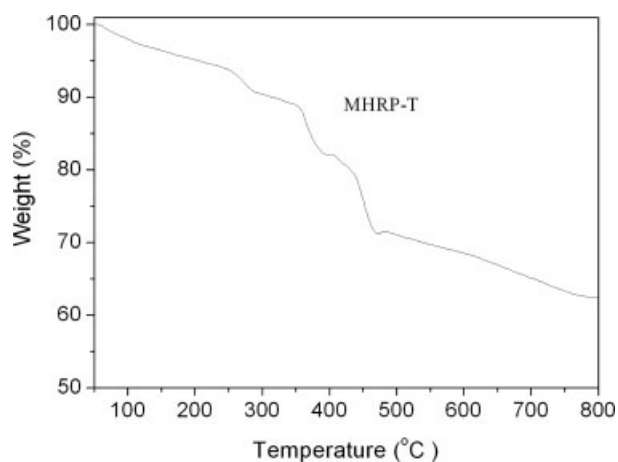

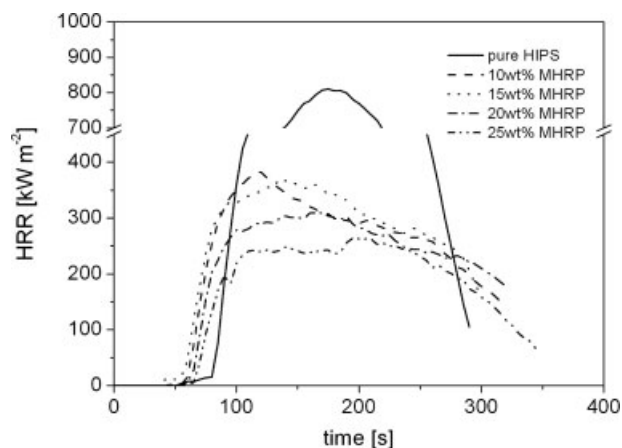**Figure 1** Thermogravimetric analysis curves of MHRP-T.

Figure 2 HRR curves for HIPS composites containing MHRP.

values of HIPS/MHRP-T series was a bit different from that of HIPS/MHRP series.

Calorimetry of composites

Figures 2 and 3 show the HRR curves of the HIPS composites with different MHRP and MHRP-T contents obtained from the cone calorimeter test, respectively. As shown in Figure 2, it can be seen that the pure HIPS resin burned very fast after ignition, and a sharp RHR peak appeared with a peak rate of heat release (PHRR) of 907 kW/m². In the case of the HIPS/MHRP composites, their PRHR values were greatly reduced with increasing the MHRP content, as shown in Table II. Moreover, the combustion of the HIPS/MHRP composites was prolonged in comparison with that of HIPS. It was, however, noted that the ignition time of the HIPS/MHRP composites was lower than that of HIPS. The reason may be due to the fact that MHRP decomposes earlier than HIPS itself, and some small volatile molecules were
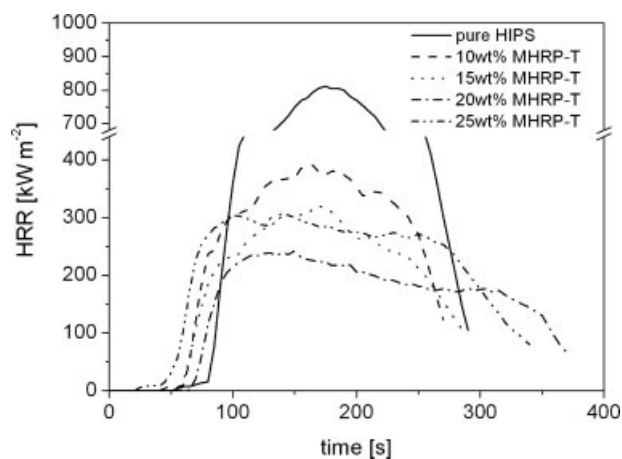
TABLE II
Cone Calorimeter Data of Flame-Retarded HIPS Composites

Sample code	Time to ignition (s)	PHRR (kW/m²)	SEA (m²/kg)
1	65	806	907
2	49	382	1832
3	43	370	1878
4	49	309	1945
5	53	264	1956
6	47	390	1659
7	44	319	1734
8	55	242	1924
9	49	304	1951

produced from the decomposition of MHRP. As for the smoke emission from the burning of the HIPS/MHRP composites, their mean specific extinction area (SEA) values increased as the MHRP content increases. These results illustrated that MHRP was only a HRR reducer, but has no smoke suppression effect.

From Figure 3 and Table II, it can be seen that HIPS/MHRP-T showed a further decrease in PHRR compared with the value of the HIPS/MHRP system at the same additive level (15 or 20 wt %). For the composite with 20 wt % MHRP-T, its PRHR and SEA values were the lowest among HIPS composites. It was also found that flame retardancy of the composite containing 25 wt % MHRP-T declined somewhat, which was needed further study in the future. The result showed that the composites containing MHRP-T give relatively lower PHRR and lower SEA, compared with the values of the composites with MHRP. These results illustrate that the introduction of PS could not only reduce HRR, but also suppress smoke.

It can be seen that the cone calorimeter results corresponded well with the results of horizontal
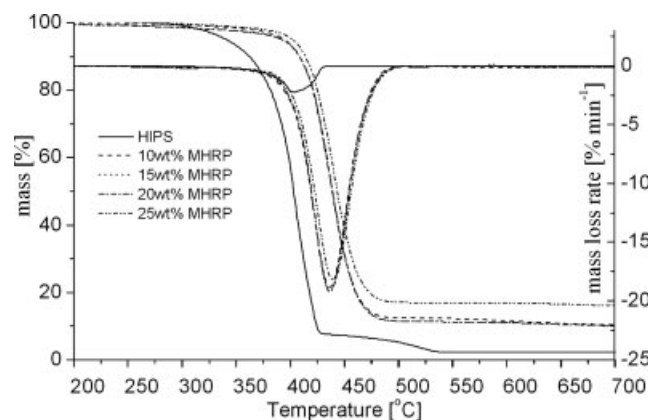

Figure 3 HRR curves for HIPS composites containing MHRP-T.

Figure 4 TGA and DTG for HIPS composites containing MHRP in nitrogen, heat rate = 10°C/min.
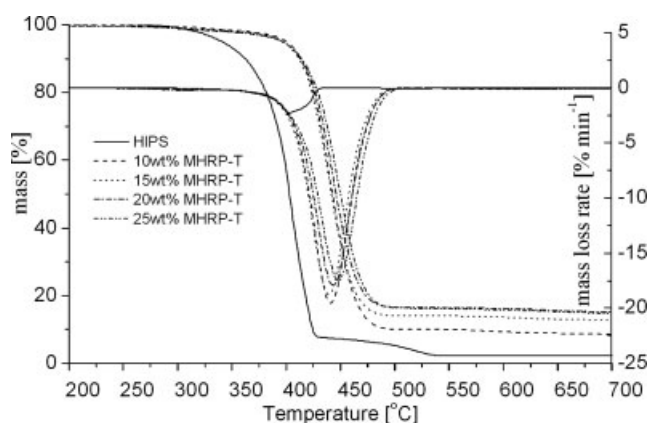
Figure 5 TGA and DTG for HIPS composites containing MHRP-T in nitrogen, heat rate = 10°C/min.

burning tests and UL-94 all of which showed that the fire properties of HIPS/MHRP-T series were found to be significantly improved, compared to those of HIPS/MHRP series. This improvement was mostly attributed to better dispersion of MHRP-T and a better interfacial compatibility between HIPS and MHRP-T. The interaction mechanism between PS-modified MHRP and HIPS is similar as our previous work.[18]

Thermal properties of composites

Figures 4 and 5 show the TGA and DTG curves of HIPS/MHRP and HIPS/MHRP-T series under nitrogen atmosphere, respectively. As shown in Figure 4, it can be seen that the initial decomposition temperature of pure HIPS was 361°C, and the temperature corresponding to the maximum weight change was 403°C. However, for HIPS/MHRP composites, the initial decomposition temperature of HIPS/MHRP series increased from 412 to 417°C with the increase in MHRP content. And the temperature correspond-

ing to the maximum weight change also increased from 437 to 440°C with the increase in MHRP content. The result demonstrated that the thermal stability improved obviously when the MHRP was introduced into HIPS resin.

From Figure 5, it can be seen that, for HIPS/MHRP-T composites, the initial decomposition temperature of HIPS/MHRP-T series increased from 415 to 423°C with the increase in MHRP-T content. And the temperature corresponding to the maximum weight change also increased from 438 to 448°C with the increase in MHRP-T content. The result showed that the DTG signal of HIPS/MHRP-T was reduced slightly, and the maximum of weight change shifted to temperatures about 8°C higher, compared with the values of the composites with MHRP. Hence, the introduction of PS on the surface of MHRP could improve the thermal stability of HIPS composites. This improvement was mostly attributed to better interfacial compatibility between MHRP-T and HIPS, leading to be the better dispersion in the matrix.[18,19]

Mechanical properties of composites

The mechanical properties of composites depend on many factors, including the aspect ratio of the filler, the degree of dispersion of the filler in the matrix, and the adhesion at the filler-matrix interface. Table III lists the mechanical properties of both series of HIPS composites. With the increase in filler loadings, the strength slightly decreased and modulus increased, and the notched impact strength decreased sharply. However, it can be noted that the notched impact strength and unnotched impact strength of HIPS/MHRP-T composites were much higher than that of HIPS/MHRP counterparts. The result demonstrated that, due to the improvement of dispersion and interfacial compatibility, HIPS/MHRP-T composites exhibited excellent mechanical properties, especially relatively high impact properties.

TABLE III
Tensile Strength (σ), Elongation at Break (ε_b), Flexural Modulus, Flexural Strength, and Izod Impact Performance of Specimens of HIPS Composites

Composite code	σ (MPa)	ε_b (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact strength (notched) (J/m)	Izod impact strength (J/m)
1	29.0	36	48	2128	220	860
2	25.6	13	51	2522	74	170
3	26.9	14	51	2562	65	160
4	26.9	11	51	2697	48	130
5	27.1	9	52	2911	38	97
6	26.6	22	52	2463	91	310
7	27.2	23	53	2580	87	280
8	27.4	12	53	2741	65	190
9	27.8	10	53	2867	44	150

CONCLUSIONS

In this study, PS-encapsulated MHRP was prepared by *in situ* polymerization of styrene on the surface of MHRP in a high speed mixer. The untreated and encapsulated MHRP flame retardants were applied in the fire resistance to HIPS by melt blending in a corotating twin-screw extruder. The effects of PS-encapsulated MHRP on the properties of HIPS composites were studied by mechanical and combustion tests (UL-94, LOI, and cone calorimetry). Because the encapsulated layer of MHRP was PS, good interfacial compatibility and effective dispersion of MHRP-T in HIPS were obtained. Therefore, the corresponding flame-retardant composites showed excellent thermal stability, flame retardancy, and mechanical performance.

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