

Flame-Retardant Polycarbonate/Acrylonitrile-Butadiene-Styrene Based on Red Phosphorus Encapsulated by Polysiloxane: Flame Retardance, Thermal Stability, and Water Resistance

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Received 15 December 2010; accepted 3 May 2011

DOI 10.1002/app.34845

Published online 1 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Red phosphorus encapsulated by polysiloxane (MRP) was prepared, and the chemical structure and morphology of MRP were characterized by FTIR and TEM, respectively. A series of flame retardant polycarbonate/acrylonitrile-butadiene-styrene containing MRP (PC/ABS/MRP) were prepared via melt-blending. The flame retardance of PC/ABS/MRP was investigated by limiting oxygen index (LOI) and UL-94 test. It was shown that the LOI value was increased to 27.7 and UL-94 achieved a V-0 rating at a 15 wt % loading of MRP. Cone calorimetric results showed that the peak of heat release rate (PHRR) of PC/ABS/15% MRP decreased from 452.7 to 198.0 kW/m²,

and the total heat release decreased from 92.9 to 60.7 MJ/m² compared with virgin PC/ABS. Thermal stability analysis showed that the char yield of the PC/ABS/15% MRP increased from 0 to 16.1 wt % under air atmosphere, and from 15.2 to 27.4 wt % under nitrogen atmosphere compared to virgin PC/ABS, respectively. The sample PC/ABS/15% MRP also showed excellent water resistance of flame retardance in 70°C water for 168 h. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2867–2874, 2012

Key words: PC/ABS; encapsulation; flame retardance; thermal stability; water-resistant

INTRODUCTION

Polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) alloys are widely used in electrical, automotive, and high technology fields due to its high performance, including toughness, heat resistance, and ease of processing at a lower cost.¹ PC has a relatively high tendency to charring with a V-2 rating in the UL-94 test itself;² however, ABS is easily combustible, and it will decrease the UL-94 rate of PC corresponding to the content of ABS (see: the content of ABS reaches 30 wt %, UL-94 rate of the blend generally decreases to NR), and then more effective flame retardance will be required in PC/ABS.^{1,3,4} Flame retardants in commercial use for PC are mostly halogen-containing, phosphorus-containing products and siloxanes, while flame retardants in commercial use for ABS are mostly halogen-containing and silicon containing compounds.

Because of the environmental consideration, halogen-free flame-retardants now are developed to meet the constantly changing demand of new regulations, standards, and test methods.⁵ Red phosphorus (RP) is an effective flame retardant for many resins.^{6,7} In ABS, for example, the introduction of RP could provide a V-0 rating.^{8,9} However, RP can easily absorb moisture and be oxidized. Moreover, throughout the melting process, it can release highly toxic phosphine (PH₃), and its fine dust is easy to explode, which becomes a real threat for wider application. It is necessary to modify RP to resolve the above-mentioned problems. Microencapsulation for RP is the most effective method.^{10–12} This microencapsulated RP is coated with appropriate substances so as to be screened from moisture, decrease the formation of PH₃ and also improve its effectiveness as flame retardant. It is reported that only 5 wt % of MRP additive can greatly decrease the peak of heat release rate, effective heat of combustion and increase the limiting oxygen index, time to ignition, and pyrolysis temperature of polyolefin materials.¹³

Recently, silicon-containing compounds used as flame retardant have received more and more attentions owing to the environmentally friendly consideration.^{14–19} Wenjun Zhou reports a silicone-based

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Contract grant sponsor: National Science Foundation of China; contract grant number: 50933005; Contract grant sponsor: NSFC.

flame retardant for PC materials.²⁰ The silicone is effective in retarding the combustion of PC. Branched methylphenyl siloxanes have been examined and studied.² Normally 5 wt % of the branched siloxane in combination with PTFE provides a significant increase of LOI from 26 to 33–40^{21,22} and only 2 wt % is required for a V-0 rating in the UL-94 test.^{23–25} Because RP is very effective to flame retard ABS and silicone-containing compounds are very effective flame retardants for PC, the microencapsulated RP will have very effective flame retardance to PC/ABS and improve the water-resistance of RP as well as. As a result, it will be meaningful to make coated RP with silicon-containing compounds.²⁶

In this work, the RP coated with polysiloxane is prepared, and it is a halogen-free flame retardant. Its structure is characterized by FTIR spectrum and transmission electron microscopy (TEM). Flame retardant properties are investigated by limit oxygen index (LOI), vertical burning test (UL-94), and cone calorimetric analysis. The residual morphology after LOI test is investigated by scanning electron microscopy (SEM). Thermal stability behavior is researched by thermogravimetric analysis (TGA), and water resistance properties of PC/ABS/MRP are investigated.

EXPERIMENTAL

Materials

All the materials and solvents were commercially available and were used without further purification. PC (K-1300) was obtained from Teijin, Japan. ABS (MAGNUM, 3404-7) resin was obtained from DOW. PC/ABS blends were prepared by melt blending in twin-screw extruder with 3 : 1 mass ratio. Triethoxyvinylsilane (VTES) were provided from Kelong Chemical Reagent Factory (Chengdu, China). RP was purchased from Qing Long flame (Jiangsu, China). Tetramethyl ammonium hydroxide (TMAH) and sodium dodecyl sulfate (SDS) were used without purification.

Preparation of MRP

Two gram of SDS and 200 mL water were added into a 500-mL three-necked flask equipped with a reflux condenser and an addition funnel. The mixture was heated to 85°C with stirring to make SDS be dissolved. TMAH (0.2 g) used as catalyst was added into the solution. Until TMAH dissolved completely, 40 mL of VTES was added dropwise for about 3 h. Another 4 h later, the emulsion was transferred to 1000-mL three-necked flask with magnetic stirrer and addition funnel maintained at room temperature. RP (18.7 g) was added and dispersed

in solution with ultrasonic bath agitation. A 400 mL 1 wt % calcium chloride solution as an electrolyte to break the emulsion was added dropwise for 5 h, and the solution was stirred continuously for several hours. Stand for all night, and the mixture was filtered to get the precipitate. The precipitate was washed with water and ethanol, and dried to give a gray solid (MRP), yield, 56%; encapsulating amount, 38.9%; conversion rate of VTES, 73.6%). Target MRP was pulverized into gray powders and dried at 80°C under vacuum for 10 hours to meet the further application.

Preparation of flame-retardant samples

PC/ABS and MRP were fed into a twin-screw extruder operating at about 240°C, and then the extrudates were comminuted into pellets. PC/ABS/5% MRP, PC/ABS/10% MRP, and PC/ABS/15% MRP were prepared with different mass ratios of MRP. These samples were respectively made to the definite dimension according to the standard of UL-94, LOI, and cone calorimeter.

Characterization

The structure of MRP was determined by FTIR, which was performed on a Nicolet FTIR 170SX infrared spectrometer with KBr pellets. TEM observed on a JEM 100CX II that was used to investigate the surface of the MRP. The sample was dispersed in ethanol under ultrasonic bath agitation, and then deposited on a copper grid for observation.

TGA was performed on a NETZSCH 209F1 thermogravimetric analyzer at a heating rate of 20°C/min from 40 to 700°C under nitrogen and air atmosphere at a flow rate of 60 mL/min. Flame-retardance of the target samples were evaluated through LOI, UL-94 vertical burning test, and cone calorimetric analysis. LOI values and UL-94 vertical burning ratings of virgin and added PC/ABS with different mass ratios of MRP were tested on an HC-2C oxygen index meter (Jiangning, China) according to ASTM D2863-97 and a CZF-2 instrument (Jiangning, China) according to ASTM D3801, respectively. Testing bars of the samples with the three-dimensional size of 130 × 6.5 × 3.2 mm³ (LOI) and 130 × 13 × 3.2 mm³ (UL-94) were compression-molded under 10 MPa and at 240°C. The cone calorimeter test was conducted to research the fire performance on a FTT cone calorimeter at an external heat flux of 35 kW/m² according to ISO 5660-1. Testing samples with a three-dimensional size of 100 × 100 × 3 mm³ were injection-molded using a K-TEC 40-155 injection-molding machine (Ferromatic Milacron, Europe). SEM observation using a FEI INSPECT F was used to investigate the morphology of char after LOI test.

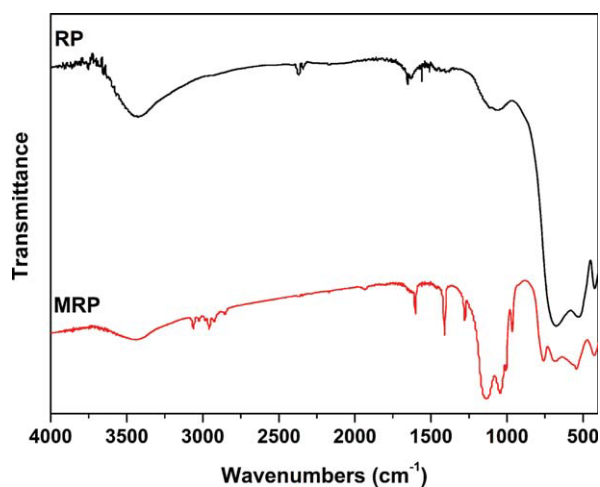


Figure 1 Infrared spectra of RP and MRP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The water-resistance test was conducted in water at 70°C for a period of 24 h according to GB-11547-89. Testing samples with a three-dimensional size of $130 \times 6.5 \times 3.2 \text{ mm}^3$ (LOI) and $130 \times 13 \times 3.2 \text{ mm}^3$ (UL-94) were injection-molded using a K-TEC 40-155 injection-molding machine (Ferromatic Milacron, Europe).

RESULTS AND DISCUSSION

Preparation and characterization of MRP

Polycondensation of the monomer VTES is carried under TMAH catalyst through emulsion polymerization. Initial hydrolysis of the monomer results in silanol functional oligomer and the Si—OH functions condense to form polysiloxane.¹⁴ The emulsion is broken under vigorous agitation through salting out, and then RP is encompassed by polysiloxane to prepare MRP.

Figure 1 shows the FTIR spectra of RP and MRP. The absorbing peaks at 1134.9 and 1045.8 cm^{-1} correspond to the vibration of Si—O—Si. The peaks at 543.2 cm^{-1} are attributed to RP. They could be also observed on the spectrum of MRP; however, relative intensities of the characteristic peaks are decreased. The above information confirms the polymerization of VTES and implies that RP is coated with polytriethoxyvinylsilane (PVTES).

The TEM micrograph of MRP is observed on a JEM 100CX II transmission electron microscope. Figure 2(a,b) present the TEM images of RP and MRP, including (a) magnified to 100,000 times and (b) to 140,000 times. It is found that PVTES disperse around the RP particle. It is clear that the surface of RP particle is coated by PVTES.

Figure 3(a,b) shows that compared with the unmodified RP, the char yield of MRP is improved from 61.3 to 74.3 wt % in nitrogen, and the maximum mass loss rate is reduced greatly from 14.0 to 6.4 wt %/min, as shown in Table I. It could be ascribed to the following factors: firstly the encapsulating polysiloxane could decompose in the relative lower temperature range (see 200–300°C), which could be confirmed by the shift of $T_{2\%}$ of MRP mainly caused by PVTES. Decomposed products of the polysiloxane are generally silicon dioxide, which is very stable at high temperature.²⁷ Thermostable coating would help to relieve the decomposition of RP and increase the char residues, which could be clearly seen in Figure 3(a,c). It is shown that there is one weight-increasing stage of RP in air, while two weight-increasing stages of MRP. Because RP could undergo oxidation reaction in air, and due to polysiloxane with a C=C double bond, it could undergo oxidation reaction at lower temperature as well as. All the above information indicates that the encapsulation structure of MRP is effective.

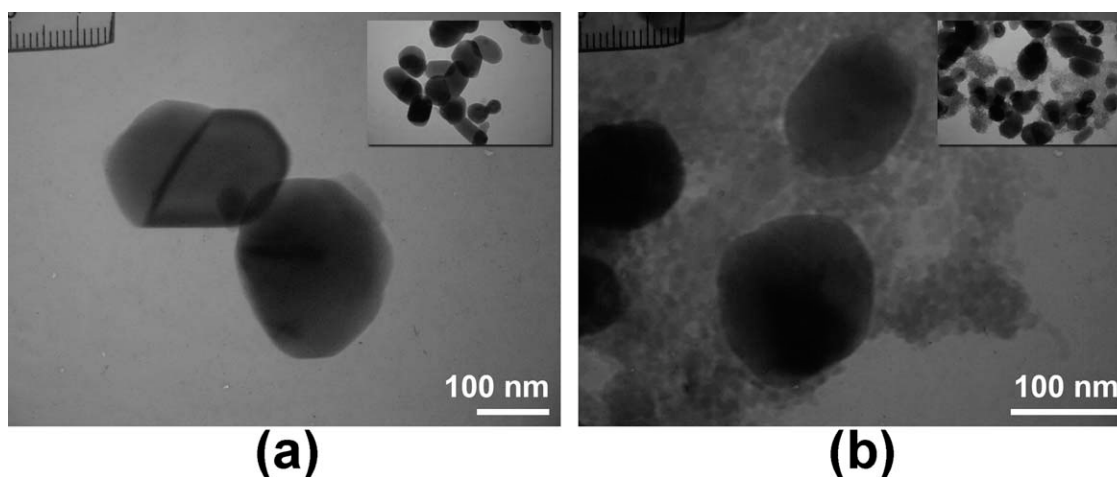


Figure 2 TEM images of RP (a) and MRP (b).

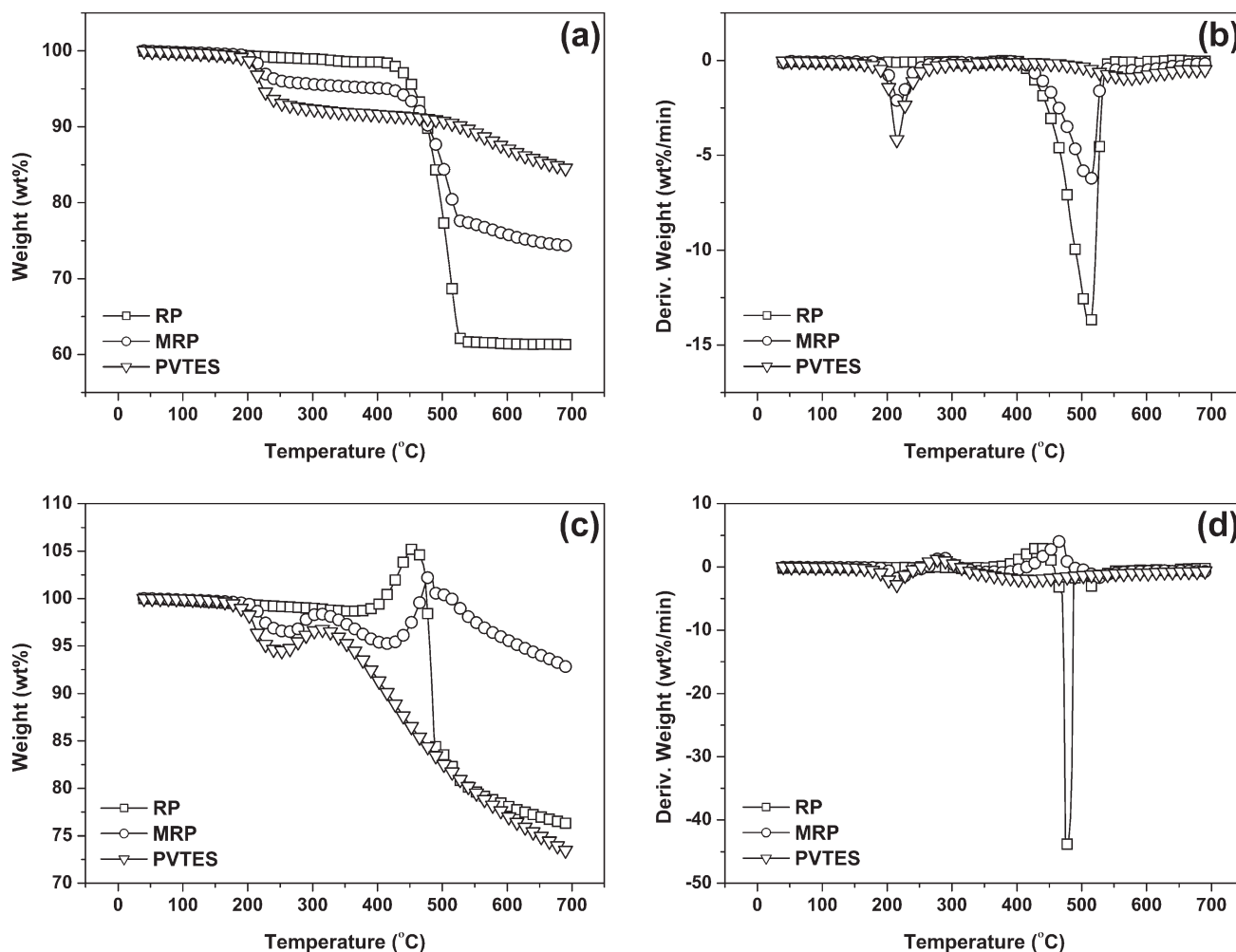


Figure 3 TG and DTG curves of RP, MRP, and PVTES under nitrogen (a and b) and air (c and d) atmosphere.

Thermal properties of virgin PC/ABS and FR-PC/ABS

Thermal properties of three different mass ratios of MRP in PC/ABS are compared with that of the virgin PC/ABS. Figure 4 shows the TG curves of four different mass ratios MRP employed in PC/ABS.

TG curves of the four samples show that the residual weights of samples increase with the increasing

addition of MRP, because the addition of MRP could promote the formation of the stable carbonaceous layer that cover the burning surface of samples and inhibit oxygen from entering the flaming zone.⁷ Also, the formation of carbonaceous layer is very effective to retard the spread of fire. The carbonaceous layer acts as an insulating barrier between material and outside environment, which would

TABLE I
Thermal Decomposition Parameters of RP, MRP, and PVTES from TG and DTG in Nitrogen and in Air

Samples	Nitrogen atmosphere					Air atmosphere			
	$T_{2\%}$ (°C)	$T_{5\%}$ (°C)	T_{\max} (°C)	Mass loss rate at T_{\max} (wt %/min)	Char yield at 700°C (wt %)	$T_{5\%}$ (°C)	T_{\max} (°C)	Mass loss rate at T_{\max} (wt %/min)	Char yield at 700°C (wt %)
RP	427.4	456.4	511.9	14.0	61.3	480.8	474.1	45.6	76.2
MRP	218.0	417.0	511.6	6.4	74.3	620.2	485.7	2.9	92.6
PVTES	209.8	224.0	215.8	4.2	84.3	230.1	210.9	3.06	73.3

$T_{2\%}$: Temperature of 2% mass loss.

$T_{5\%}$: Temperature of 5% mass loss.

T_{\max} : The maximum thermal degradation temperature.

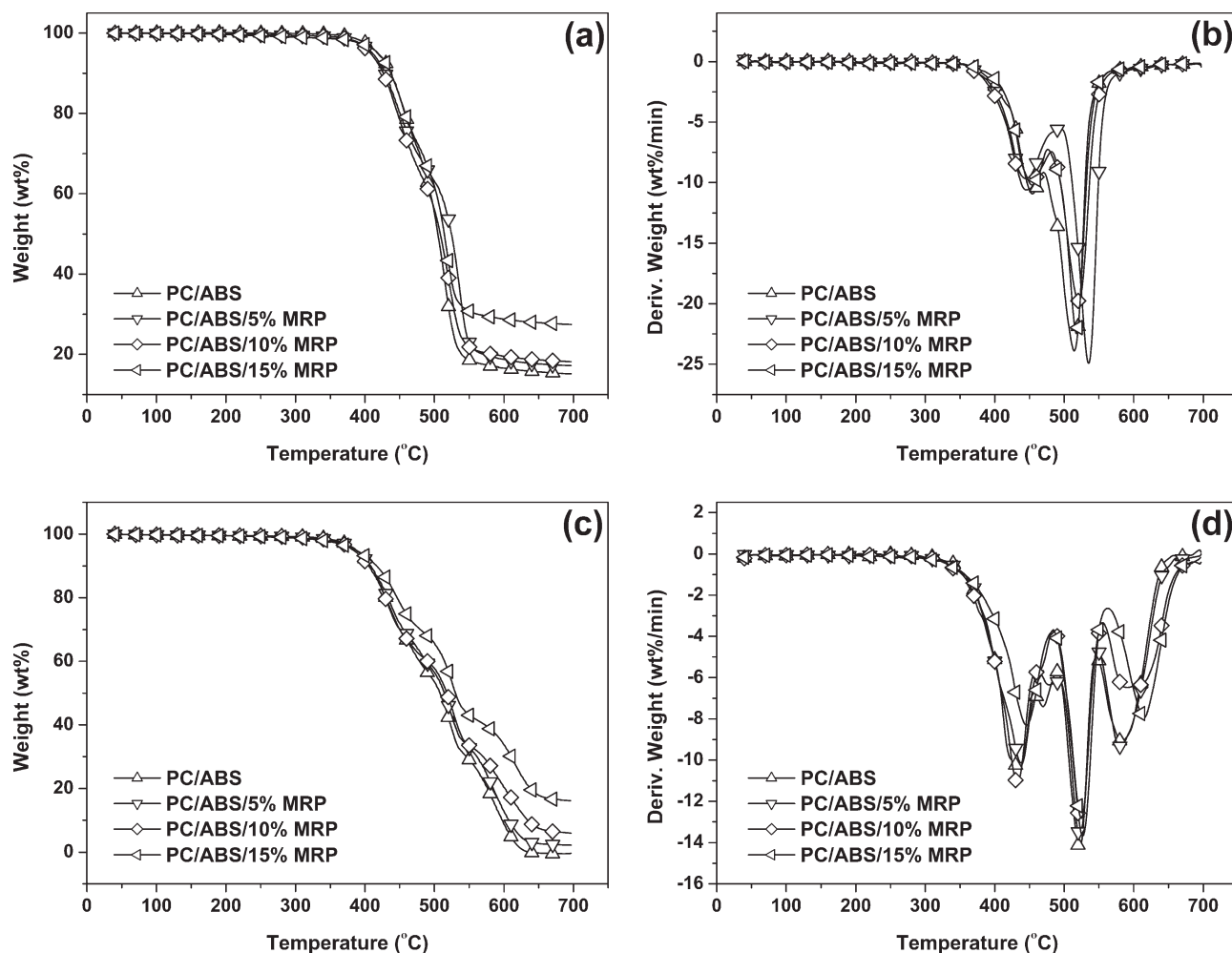


Figure 4 TG and DTG curves of unfilled PC/ABS, PC/ABS/5% MRP, PC/ABS/10% MRP, and PC/ABS/15% MRP under nitrogen (a and b) and air (c and d) atmosphere.

play an important role in increasing the flame retardance of PC/ABS. Among the samples of FR-PC/ABS the addition of 15 wt % MRP into PC/ABS exhibits greater thermal stability, due to its highest char yield. Compared parameters of PC/ABS under both nitrogen and air atmosphere are shown in Table II. Results suggest that there is little difference in the maximum thermal degradation temperature (T_{max}), but the initial thermal degradation tempera-

tures ($T_{5\%}$) are delayed and there is more char residual under N_2 condition as the existence of oxygen in the air can promote the materials to decompose earlier, and it could promote the carbonaceous to decompose further.

Flame retardance of FR-PC/ABS

To investigate the flame retardance of MRP on PC/ABS, we have tested the limiting oxygen index (LOI)

TABLE II
Thermal Decomposition Parameters of PC/ABS with Various MRP Additions (wt %) from TG in Nitrogen and Air at a Heating Rate of 20°C/min

Samples	Nitrogen atmosphere			Air atmosphere		
	$T_{5\%}$ (°C)	T_{max} (°C)	Char yield at 700°C (wt %)	$T_{5\%}$ (°C)	T_{max} (°C)	Char yield at 700°C (wt %)
Virgin PC/ABS	418.3	514.5	15.2	387.6	522.7	0.0
PC/ABS/5% MRP	411.0	535.1	17.2	387.2	522.3	2.2
PC/ABS/10% MRP	408.0	520.5	18.1	383.1	526.7	5.9
PC/ABS/15% MRP	419.0	517.6	27.4	387.2	524.6	16.1

TABLE III
LOI Values and Results of UL-94 Rating Test

Samples	LOI (%)	UL-94 (3.2 mm)
Virgin PC/ABS	20.1	NR
PC/ABS/5% MRP	23.1	NR
PC/ABS/10% MRP	27.0	V-2
PC/ABS/15% MRP	27.7	V-0

values and vertical burning rating (UL-94) of FR-PC/ABS with different mass ratios of MRP. The results are given in Table III. It is found that the LOI value increases with the increasing of MRP concentration and reaches 27.7 at the 15 wt % loading of MRP; Moreover, a strong increase in UL-94 rating could be observed, which is improved from NR to V-0. It is reported that the mechanism of silicon-containing flame-retardants is correlated to the low surface energy of silicon, which moves to the surface of material and acts as protective layer.¹⁷ The other main flame retardant element of MRP is phosphorus. It is believed that RP could depolymerize into white phosphorus (P_4), which can volatilize at high temperature and act in the gaseous phase, or it can diffuse from the bulk of the polymer to the burning surface, where it is oxidized to phosphoric acid derivatives that can eventually come into close contact with the flame and form phosphoric acid.⁷ According to results of Table III, the LOI values of FR-PC/ABS correlate well with UL-94 rating.

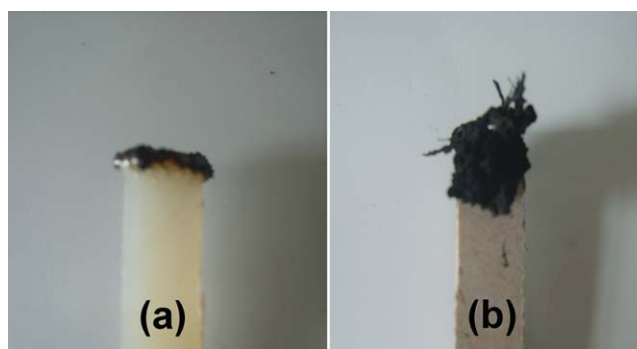


Figure 5 Digital photographs of burning residues after LOI tests: (a) unfilled PC/ABS and (b) PC/ABS/15% MRP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 displays the digital photos for the residues after LOI tests. The SEM micrographs of char after LOI tests are shown in Figure 6. Compared with PC/ABS, the surface of char belonging to PC/ABS/15% MRP is more compact. The compact carbonaceous residue helps to isolate the contact of oxygen with material and retard the material from further combustion. The encapsulation layer of MRP is polysiloxane, which can form a protective layer and promotes the formation of carbonaceous of PC to isolate the material from oxygen for further combustion. The inner layer of MRP is RP, which would act both in the gas and condensed phase to decrease the

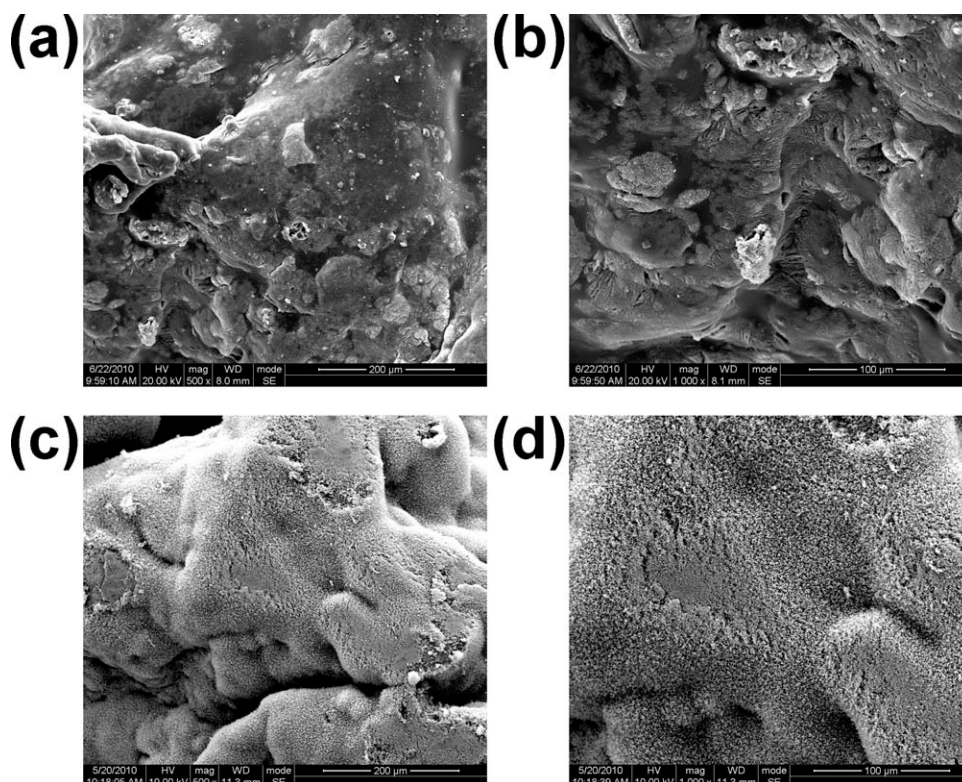


Figure 6 SEM photographs of burning residues after LOI tests: (a and b) unfilled PC/ABS and (c and d) PC/ABS/15% MRP.

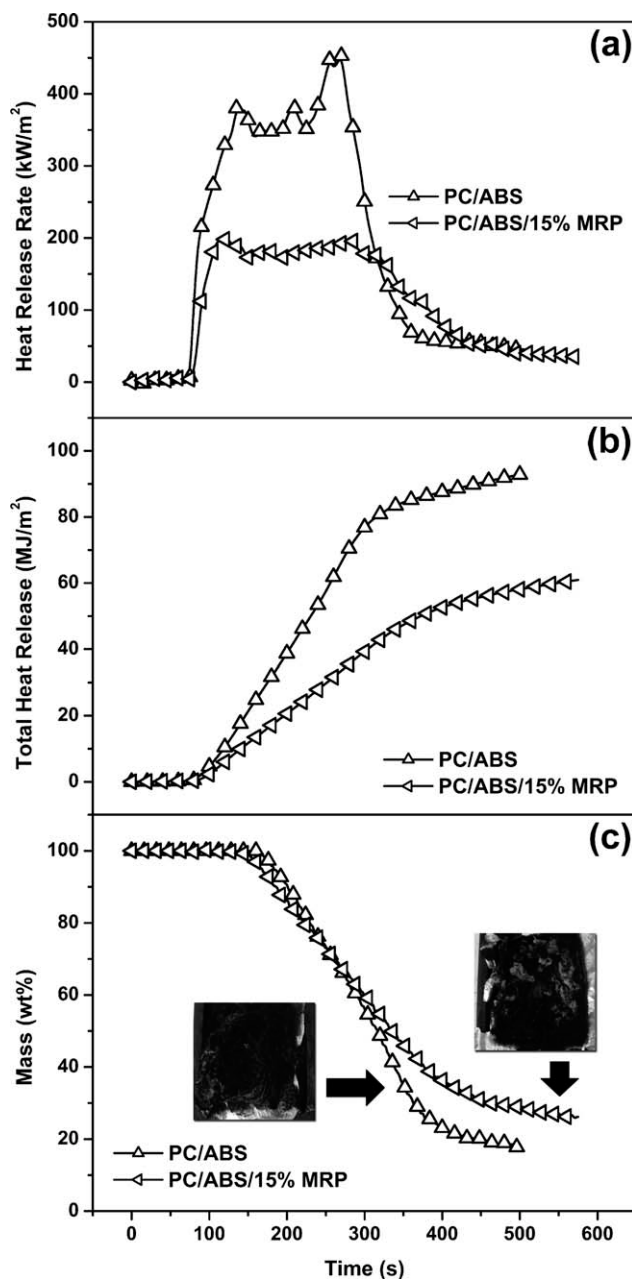


Figure 7 Heat release rate, HRR, (a), total heat release, THR, (b) and residual mass (c) plots of unfilled PC/ABS and PC/ABS/15% MRP as function of burning time. Digital photographs of the burning residues after cone calorimetric analyses are attached in it.

production of fuel and inhibit the transfer of heat and free radicals. It concludes that encapsulation type MRP is an effective flame retardant for PC/ABS.

Cone calorimetric results

The cone calorimeter tests as a tool for assessing the flammability and burning behaviors of PC/ABS containing MRP have been investigated. The results are shown in Figure 7 and Table IV, including time to ignition (TTI), heat release rate (HRR), peak heat release rate (PHRR), time to peak heat release rate (TTPHRR), total heat released (THR), and residual mass.

As shown in Table IV, TTI of virgin PC/ABS is lower than FR-PC/ABS (see at about 6 s), the reason may be due to the fact that initial decomposition temperature of MRP is higher than that of PC/ABS, which could delay the thermal decomposition of PC/ABS.

Figure 7 shows the HRR, THR, and residual mass plots of samples. In the case of PC/ABS/15% MRP, both the PHRR and THR decrease significantly compared to virgin PC/ABS. PC/ABS burns very fast after ignition (see at 72 s) and the HRR value sharply increases to 380 kW/m² within 210 s, then the HRR value uninterruptedly increases to the maximum value of 452.7 kW/m² (PHRR) at 270 s, indicating an easy ignition and propagation behavior. At the end of the test, virgin PC/ABS releases a total heat of 92.9 MJ/m². After 15 wt % MRP has been added into PC/ABS, a greatly decreased PHRR value of 198.0 kW/m² and THR value of 60.7 MJ/m² can be obtained. Moreover, it is worth to note that the TTPHRR value of PC/ABS/15% MRP is much lower than the virgin PC/ABS, which means that the addition of MRP can improve the nonflammability and depress the burning intensity of PC/ABS, indicating that the addition of MRP quickly promotes the formation of char layers at the relatively lower temperature, which act as an insulating barrier to stop the propagation of the heat and oxygen. According to mass plots together with the digital photographs of the burning residues after cone calorimetric analyses in Figure 7, it reveals that the time to flame out of PC/ABS/15% MRP is prolonged compared to virgin PC/ABS, which indicates that a part of PC/ABS/15% MRP has not completely combusted, possibly undergoing a char-forming process. In addition, the burning residue of PC/ABS after cone calorimeter testing is greatly improved from 15.4 to 25.6 wt % when 15 wt % MRP has been added as the flame retardant, which showed an agreement to the results of TG under both nitrogen and air atmosphere. Furthermore, from Figure 7(b,c) it could be mentioned that

TABLE IV
Cone Calorimetric Data for Virgin PC/ABS and PC/ABS/15% MRP at 35 kW/m²

Sample	TTI (s)	PHRR (kW/m ²)	TTPHRR (s)	THR (MJ/m ²)	Residual Mass (wt %)
Virgin PC/ABS	66.0	452.7	270.0	92.9	15.4
PC/ABS/15% MRP	72.0	198.0	120.0	60.7	25.6

TABLE V
Results of Water-Resistance Test According to
GB-11547-89 (in 70°C Water)

PC/ABS/15% MRP	LOI (%) ^a	UL-94 (3.2 mm)
0 h	27.1	V-0
24 h	27.1	V-0
72 h	27.0	V-0
120 h	27.0	V-0
168 h	26.9	V-0

^a Samples for water-resistance test were injection-molded.

THR is not proportional to the mass loss precisely, which indicates that there is also a vapor phase action in this system. Thus, it is believed that lower HRR, THR, and more residual mass relate to condensed phase and gas phase mechanism and contribute to better flame retardation of MRP.

Water-resistance test

Generally, PC exhibits great tendency to decomposition, because the ester linkage in the main chain is sensitive to the acid and alkali. Although aromatic phosphorus-containing additives such as triphenyl phosphate (TPP), resorcinol *bis*(diphenyl phosphate) (RDP) and bisphenol A *bis*(diphenyl phosphate) (BDP) are currently accepted for flame retarding PC or PC based blends, somewhat reduced hydrolytic stability caused by the phosphates limits their wider application.² Therefore, an optimal water resistance of the flame-retardant PC/ABS is required. In this article, the corresponding test is done to verify whether PC/ABS/15% MRP is water-resistant according to domestic standard as GB 11547-89.

All samples were impregnated within water at 70°C for a period of 24 h. The test was last for a week. The samples are taken out every second day and used for UL-94 and LOI testing after the samples were dried for 24 hours.

LOI values and UL-94 results of the treated PC/ABS/15% MRP are given in Table V. The flame-retardant PC/ABS containing 15 wt % of MRP showed a little decrease of LOI values, but it still could achieve UL-94 V-0 rating. Because of the low surface energy of the silicone compounds, it would transfer easily to the surface of the sample for hydrophobic polysiloxane. Consequently, the hydrophobicity of the sample surface is clearly enhanced, which has been proved by the LOI and UL-94 testing. This result demonstrates that the composite encapsulation type MRP blending with PC/ABS is not easy to hydrolysis, and retains flame retardance during the test.

CONCLUSIONS

An encapsulation type RP encapsulated with polytriethoxyvinylsilane (MRP) was prepared and char-

acterized. Thermal degradation behavior of PC/ABS and PC/ABS/MRP systems revealed that the addition of MRP enhanced the thermal stability of PC/ABS at high temperature. The residuals from TG test were greatly improved with the addition of MRP. The result showed LOI value was as high as 27.7 and UL-94 V-0 rating was obtained at a loading of 15 wt % MRP into PC/ABS. The MRP could reduce the flammability parameters including HRR and THR, and increase the residual mass clearly. The PHRR and THR were reduced by 56.3 and 34.7% for PC/ABS/15% MRP relative to virgin PC/ABS, respectively. It could be confirmed that MRP was an effective flame retardant to PC/ABS. Research of water-resistant test showed that PC/ABS/15% MRP still maintained the required flame retardance after 168 h in 70°C water.

The authors would also like to thank the Analysis and Testing Center of Sichuan University for the TEM measurement.

References

- Pham, H. T.; Weckle, C. L.; Ceraso, J. M. *Adv Mater* 2000, 12, 1881.
- Levchik, S. V.; Weil, E. D. *Polym Int* 2005, 54, 981.
- Sohn, J. I.; Lim, S. T.; Park, S. H.; Choi, H. J.; Jhon, M. S. *J Mater Sci* 2003, 38, 1485.
- Levchik, S. V.; Weil, E. D. *J Fire Sci* 2006, 24, 137.
- Lu, S. Y.; Hamerton, I. *Prog Polym Sci* 2002, 27, 1661.
- Laoutid, F.; Ferry, L.; Lopez-Cuesta, J. M.; Crespy, A. *Polym Degrad Stab* 2003, 82, 357.
- Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J. M.; Dubois, Ph. *Mater Sci Eng: R* 2009, 63, 100.
- Oishi, S.; Youshi, M.; Hiraishi, W. U.S. Pat. 6,676,920 (2004).
- Yamauchi, K.; Matsuoka, H.; Matsumoto, H.; Inoue, T. U.S. Pat. 6,136,892 (2000).
- Chen, L.; Wang, Y. Z. *Polym Adv Technol* 2010, 21, 1.
- Ringkagaku Kogyo Co Ltd. U.S. Pat. 4,879,087 (1989).
- Ringkagaku Kogyo Co Ltd. Eur. Pat. 0,638,608 A1 (1994).
- Wu, Q.; Lu, J. P.; Qu, B. *J Polym Int* 2003, 52, 1326.
- Hu, Z.; Chen, L.; Zhao, B.; Luo, Y.; Wang, D. Y.; Wang, Y. Z. *Polym Degrad Stab*, to appear.
- Wei, P.; Wu, D.; Zhong, H. F.; Du, J. X. *J Wuhan Technol-Mater Sci Ed* 2009, 24, 235.
- Zhong, H. F.; Wei, P.; Jiang, P. K.; Wang, G. L. *Fire Mater* 2007, 31, 411.
- Iji, M.; Serizawa, S. *Polym Adv Technol* 1998, 9, 593.
- Liu, S. M.; Ye, H.; Zhou, Y. S.; He, J. H.; Jiang, Z. J.; Zhao, J. Q. *Polym Degrad Stab* 2006, 91, 1808.
- Zhong, H. F.; Wei, P.; Jiang, P. K.; Wu, D.; Wang, G. L. *J Polym Sci Part B: Polym Phys* 2007, 45, 1542.
- Zhou, W. J.; Yang, H. *Therm Acta* 2007, 452, 43.
- Hatanaka, H.; Shiromoto, K.; Ueki, H.; Morita, Y. Eur. Pat. 1,094,093 (2002).
- Iji, M.; Serizawa, S.; Yamamoto, A.; Yamaya, M.; Yamamoto, K.; Kobayashi, Y. U.S. Pat. 6,284,824 (2001).
- Satio, A.; Kitamura, T.; Ishida, H.; Takezawa, Y.; Horie, Y.; Zenbayashi, M. U.S. Pat. 6,451,906 (2002).
- Satio, A.; Kitamura, T.; Ishida, H.; Takezawa, Y.; Horie, Y.; Zenbayashi, M. Eur. Pat. 1,272,565 (2003).
- Asano, T.; Shimizu, K. U.S. Pat. 6,649,680 (2003).
- Hu, Y.; Ni, J. X. China Pat. 101,376,812 A (2008).
- Li, Q.; Jiang, P. K.; Su, Z. P.; Wei, P.; Wang, G. L.; Tang, X. Z. *J Appl Polym Sci* 2005, 96, 854.