

# Morphology and Flame-Retardancy Properties of Ternary High-Impact Polystyrene/Elastomer/Polystyrene-Encapsulated Magnesium Hydroxide Composites

Suqin Chang,<sup>1,2</sup> Tingxiu Xie,<sup>3</sup> Guisheng Yang<sup>1,3</sup>

<sup>1</sup>Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

<sup>2</sup>Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

<sup>3</sup>R&D Center, Shanghai Genius Advanced Materials Company, Limited, Shanghai 201109, People's Republic of China

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**ABSTRACT:** The effects of elastomer type on the morphology, flammability, and mechanical properties of high-impact polystyrene (HIPS)/polystyrene (PS)-encapsulated magnesium hydroxide (MH) were investigated. The ternary composites were characterized by cone calorimetry, mechanical testing, and scanning electron microscopy. Morphology was controlled with poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) triblock copolymer or the corresponding maleinated poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS-*g*-MA). The HIPS/SEBS/PS-encapsulated MH composites exhibited separation of the filler and elastomer, whereas the HIPS/SEBS-*g*-MA/PS-encapsulated MH composites exhibited encapsulation of the filler

by SEBS-*g*-MA. The flame-retardant and mechanical properties of the ternary composites were strongly dependent on microstructure. The composites with an encapsulation structure showed higher flame-retardant properties than those with a separation structure at the optimum use level of SEBS-*g*-MA. Furthermore, the composites with a separation structure showed a higher modulus and impact strength than those with an encapsulation structure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2488–2493, 2008

**Key words:** fillers; flame retardance; microstructure; polystyrene

## INTRODUCTION

Ternary-phase composites consisting of a polymer matrix, elastomer inclusion, and particulate filler have become attractive materials for numerous engineering applications. The properties of such composites are determined not only by composition but also by the phase morphology present, in particular, the relative dispersion of additive components. Two cases of composite morphology may be found,<sup>1–15</sup> either elastomer and filler particles dispersed separately in the polymer matrix or elastomer-encapsulated filler particles forming an encapsulation structure.

Various methods have been applied to control these phase structures. For example, in polypropylene (PP)/ethylene propylene rubber (EPR)/CaCO<sub>3</sub> composites, a complete separation was extensively promoted by the addition of functionalized PP to the composite, whereas a complete encapsulation was

achieved by the use of functionalized elastomer.<sup>10,13</sup> These distinct morphologies gave significantly different tensile and impact properties. Ternary composites with a separation structure have been reported to have higher moduli and tensile yield stresses than those containing encapsulated filler,<sup>6,13–15</sup> whereas composites with an encapsulation structure exhibit a higher impact strength.<sup>9,13,14</sup> However, a contrasting result was reported by Kolarik and Jancar<sup>10</sup> for PP/EPR/CaCO<sub>3</sub> composites, in which composites containing encapsulated particles had a lower impact strength than composites with a separation structure.

In our previous work,<sup>16–19</sup> we mainly investigated the effects of polystyrene (PS)-encapsulated magnesium hydroxide (MH) on the mechanical, rheological, and flame-retardant properties of high-impact polystyrene (HIPS) composites. The main objective of this study was to investigate the effects of the type and composition of elastomer on the phase microstructure and flame-retardancy properties of HIPS/elastomer/PS-encapsulated MH ternary composites at a fixed concentration of MH, namely, 40 wt %. The mechanical properties are also discussed. The two elastomers examined were poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) and maleinated poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene]

Correspondence to: G. Yang (ygs@geniuscn.com).

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(SEBS-*g*-MA), which are representative of nonpolar and polar elastomers, respectively.

## EXPERIMENTAL

### Materials

HIPS (PH-88HT, melt flow index = 4.5 g/10 min at 200°C and 5 kg) with a density of 1.04 g/cm<sup>3</sup> was provided by Zhenjiang Chimei Corp. (Jiangsu, China) MH, used as a filler, was a high-purity untreated grade (Magnifin H5) supplied by Martinswerk (Germany) GmbH. The average volume particle size was 1.5 μm, and the specific surface area 5.0 m<sup>2</sup>/g. MH was encapsulated with PS by an *in situ* encapsulation method developed in our laboratory before compounding. The SEBS triblock copolymer, Kraton G1652, was supplied by Shell Chemicals (USA) (29%styrene, molecular weights: styrene block = 7000, EB block = 37,500). The corresponding SEBS-*g*-MA triblock copolymer, Kraton FG1901X, was supplied by Shell Chemicals (29% styrene, nominal weight of grafted maleic anhydride = 1.8 ± 0.4%, quoted at 1.84%, as measured by elemental analysis<sup>20</sup>). Hydrochloric acid was purchased from Shanghai Chemical Reagents Co. (Shanghai, China) and was used without further treatment.

### Preparation of PS-encapsulated MH

MH was dried at 120°C for 6 h and was then put into a high-speed mixer and heated to 70°C at a rotation speed of 1200 rpm. Then, acetone solutions of 3-(methacryloxy)propyltrimethoxy silane with water and acetic acid were added under stirring for 20 min. The modified powder was dried at 80°C for 12 h. Finally, modified powder, monomer (styrene),

and additional initiator (2,2'-azobisisobutyronitrile) were placed in the mixer with the agitation fixed at 1200 rpm and heated in an oil bath at 80°C for 45 min. The crude product at the end of polymerization was dried. The charge rate of PS/MH was 6.0 wt %. The charge rate of PS/MH was selected on the basis of earlier experimental results on the flame retardancy of HIPS/PS-encapsulated Mg(OH)<sub>2</sub> composites.<sup>19</sup> PS-encapsulated Mg(OH)<sub>2</sub> is designated MH-T in the following discussion.

### Material preparation

The 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 Co., Ltd., Nanjing, Jiangsu, China) with a length/diameter 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 mechanical testing were molded with an injection-molding machine (CJ80M2V, Zhende Plastics Machinery Co., Ltd., Foshan, Guangdong, China), and the injection temperature was 210°C.

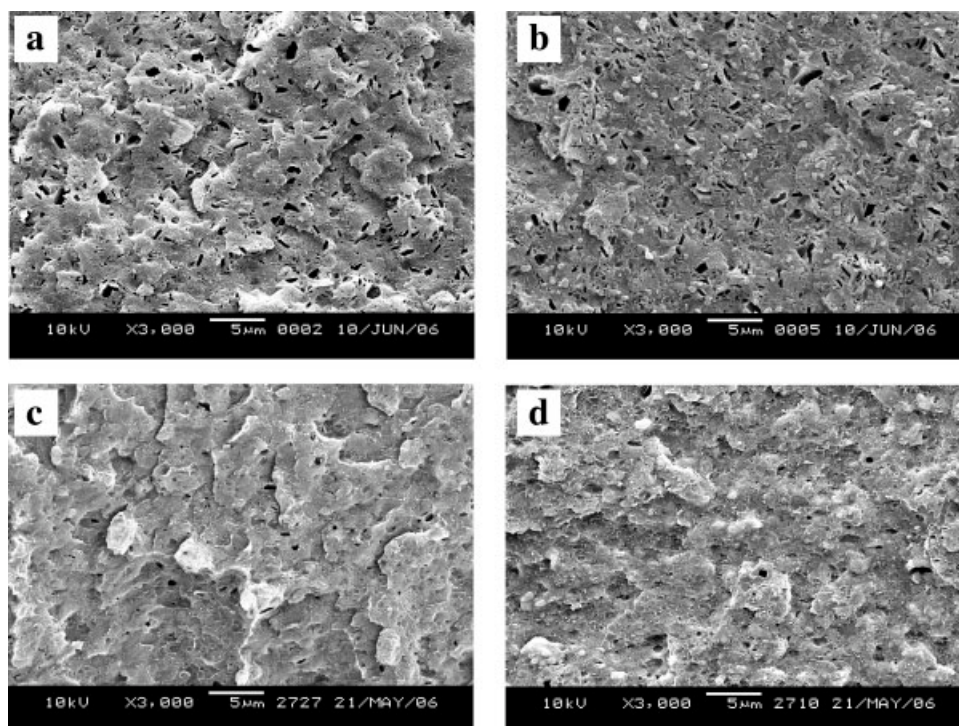
### Characterization of the composites

The cryogenic fractured surfaces of the specimens were etched with hydrochloric acid for 2 h to remove the naked MH particles and were then gold-sputtered. The surfaces of the specimen images were observed with a scanning electron microscope (JSM-6360LV, JEOL Inc., Tokyo, Japan) with an accelerating voltage of 10 kV.

TABLE I  
Formulations of All of the Ternary Composites

Sample formulation	Composition (wt %)			
	HIPS	MH-T <sup>a</sup>	SEBS	SEBS- <i>g</i> -MA
a A	100	0	0	0
B	57.6	42.4	0	—
C	80	0	20.0	—
D	53.6	42.4	4.0	—
E	49.6	42.4	8.0	—
F	45.6	42.4	12.0	—
G	41.6	42.4	16.0	—
H	37.6	42.4	20.0	—
b I	80	0	—	20.0
J	53.6	42.4	—	4.0
K	49.6	42.4	—	8.0
L	45.6	42.4	—	12.0
M	41.6	42.4	—	16.0
N	37.6	42.4	—	20.0

<sup>a</sup> MH-T represents Mg(OH)<sub>2</sub> particles encapsulated with 6.0 wt % PS by *in situ* polymerization [i.e., charge rate of PS/Mg(OH)<sub>2</sub> = 6/100 w/w].



**Figure 1** SEM micrographs of the etched surfaces of the ternary composites: (a) HIPS/MH-T/SEBS (49.6/42.4/8.0), (b) HIPS/MH-T/SEBS (37.6/42.4/20.0), (c) HIPS/MH-T/SEBS-g-MA (49.6/42.4/8.0), and (d) HIPS/MH-T/SEBS-g-MA (37.6/42.4/20.0).

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 flux was maintained at 35 kW/m<sup>2</sup>. The real irradiation sample area was 0.007854 m<sup>2</sup>. Exhaust flow was set at 24 L/s, and the spark was continuous until the sample ignited. All samples were run in triplicate, and the average value is reported; the results from the cone calorimeter were generally considered to be reproducible to  $\pm 10\%$ .

The tensile testing was performed on a universal testing machine (SANS, Shenzhen, China) according to ASTM D 638 with a crosshead speed of 50 mm/min. The Izod notched impact strength was measured with an impact testing machine (XJU-22, Chengde Testing Machine Corp., Chengde, China) according to ASTM D 256. All experiments were conducted at room temperature and at a relative humidity of 50%.

## RESULTS AND DISCUSSION

### Scanning electron microscopy (SEM) observation

In ternary polymer/elastomer/inorganic filler composites, the dispersion states of the elastomer and filler play an important role in the determination of the properties of composites. Therefore, microstruc-

tural characterization of the ternary composites was carried out in detail with the aid of SEM.

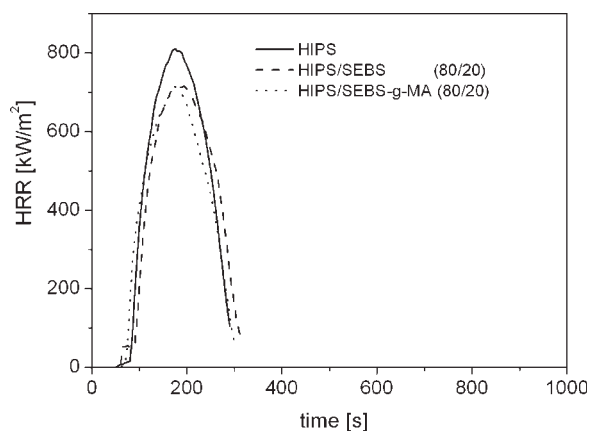
SEM micrographs of the etched cryogenic fracture surfaces of the HIPS/SEBS/MH-T and HIPS/SEBS-g-MA/MH-T composites are shown in Figure 1(a–d). The dark holes represent the etched MH particles. The dark holes of the HIPS/SEBS/MH system shown in Figure 1(a,b) were evenly distributed in the matrix, whereas there was no evidence of SEBS encapsulation around the filler, which resulted in a separate dispersion of SEBS and MH particles in the HIPS matrix.

For the HIPS/SEBS-g-MA/MH-T system, a contrasting morphology is shown in Figure 1(c,d). Voids were almost not observed. This result demonstrates that the introduction of SEBS-g-MA could further encapsulate MH particles due to the strong interaction between the maleic anhydride groups of SEBS-g-MA and the MH particles unencapsulated by PS.<sup>17</sup> The complete encapsulation of MH particles prevented them from being etched by hydrochloric acid. Thus, the encapsulation structure in the SEBS-g-MA based ternary composites was obtained.

### Flammability of the composites

The flame-retardancy properties of the polymer/elastomer/filler ternary composites were determined not only by composition but also by the phase mor-



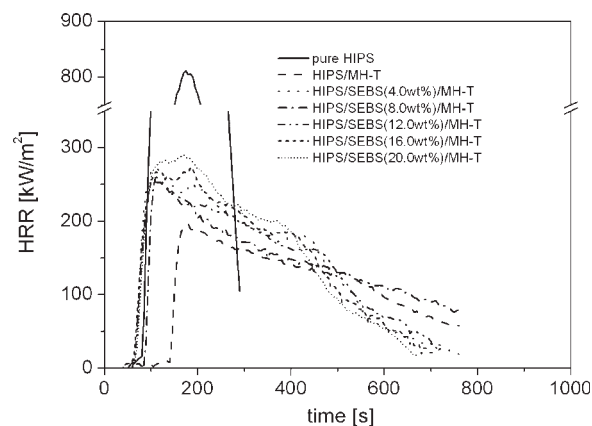


**Figure 2** HRR for HIPS and the HIPS/elastomer blends.

phology present, in particular, the relative dispersion of additive components. To investigate the effect of the phase structure on the flammability of the ternary composites, the flame retardant was fixed at the same concentration. At the same time, the flammabilities of HIPS, HIPS/SEBS, and the HIPS/SEBS-g-MA blends were investigated by cone calorimetry, as shown in Figure 2. The various parameters that may be evaluated with cone calorimetry, including the time to ignition; the heat release rate (HRR) curve, especially its peak value; the peak heat release rate (PHRR); mean heat release rate from ignition to 180 s (MHRR<sub>180s</sub>); and the specific extinction area (SEA), are tabulated in Table II. The incorporation of elastomer into HIPS led to a slight reduction in the HRR of the binary blends of both HIPS/SEBS and HIPS/SEBS-g-MA. Furthermore, the HRR curves of both HIPS/SEBS and HIPS/SEBS-g-MA were very similar, and the PHRR values was the same. Conclusions can be made from the previous results that the

**TABLE II**  
Cone Calorimetry Data of the Flame-Retarded HIPS Composites

Sample code	Time to ignition (s)	PHRR (kW/m <sup>2</sup> )	MHRR <sub>180s</sub> (kW/m <sup>2</sup> )	SEA (m <sup>2</sup> /kg)
A	65	806	320	907
B	129	196	35	775
C	76	715	268	919
D	59	272	145	782
E	60	260	155	779
F	57	253	135	765
G	54	274	148	780
H	59	290	153	809
I	56	715	311	999
J	65	92	44	740
K	65	75	34	619
L	65	143	73	656
M	68	247	106	654
N	63	324	142	553

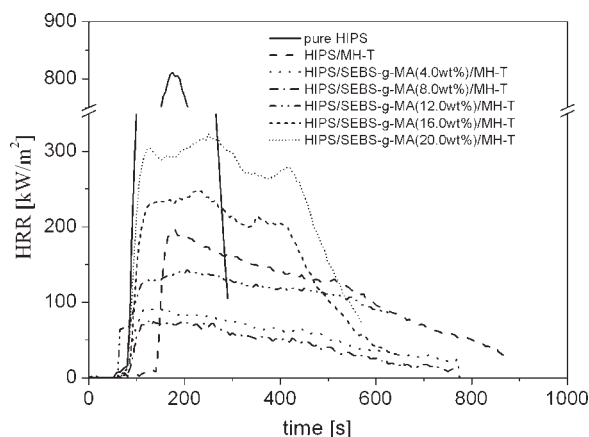


**Figure 3** HRR for the HIPS/MH-T composites containing SEBS.

elastomer polarity had little influence on the flame-retardancy properties of the HIPS/elastomer blends. That is, there was no difference in PHRR values between SEBS and SEBS-g-MA.

The changes in HRR as a function of burning time for the HIPS/MH-T composites with different contents of SEBS are shown in Figure 3. The various parameters that may be evaluated with cone calorimetry are also tabulated in Table II. The pure HIPS resin burned very fast after ignition, and a sharp HRR peak appeared with a PHRR of 907 kW/m<sup>2</sup>. In the case of the HIPS/MH-T composites, PHRR values were greatly reduced, as shown in Table II. Moreover, the HIPS/MH-T/SEBS series showed a slight increase in PHRR (from 196 to 270 W/m<sup>2</sup>) compared with the value of the HIPS/MH-T composites without SEBS at the same additive level (42.4 wt %). In addition, the time to ignition of the ternary composites with SEBS varied from 54 to 60 s, and PHRR varied from 253 to 290 kW/m<sup>2</sup>. This result shows that there was no change in PHRR with the increase in the content of SEBS; it must be remembered that the usual spread of values in a cone experiment is  $\pm 10\%$ , so any change that was less than 10% was considered to be no change.

Figure 4 shows the HRR curves of the HIPS/MH-T composites containing different contents of SEBS-g-MA. As shown by the data listed in Table II, the HIPS/MH-T/SEBS-g-MA series showed a further decrease in PHRR (from 196 to 75 kW/m<sup>2</sup>) compared with the value of the HIPS/MH-T composites without SEBS-g-MA at the same additive level (42.4 wt %) when the content of SEBS-g-MA was no more than 8.0 wt %. However, with the continuous increase of SEBS-g-MA, PHRR began to increase obviously (from 75 to 324 kW/m<sup>2</sup>). This result shows that there existed a critical SEBS-g-MA content, 8.0 wt %, for optimum flame-retarding properties of the HIPS/SEBS-g-MA/MH-T composites.



**Figure 4** HRR for the HIPS/MH-T composites containing SEBS-g-MA.

From Figures 2–4, it was interesting to find that the pure HIPS, the binary HIPS/SEBS and HIPS/SEBS-g-MA blends, and some ternary composites with no more than 12 wt % elastomer only had a single peak, whereas there were two or three HRR peaks for some ternary composites containing more than 12 wt % elastomer, which had worse flame retardation (a higher HRR). Bourbigot and co-workers<sup>21,22</sup> also found this phenomenon in exploring ammonium phosphate (APP)/melamine (MEL)/pentaerythritol (PER) intumescent systems. The one HRR peak was easily understood because the sample was gradually burnt. In the second case, the first peak was assigned to the development of the protective char. After the first peak, the HRR curve formed a plateau in some cases, in which the increase in HRR was suppressed because of the presence of the efficient protective char. The second peak was due to the degradation of the protective layer gradually, as the sample was continuously exposed to the heat,

and the formation of a new protective char in some formulations, which then gave rise to the third HRR peak (the whole char degraded). The conclusion can be made from the previous results that in the ternary HIPS/MH-T/SEBS-g-MA composites, only a suitable ratio of SEBS-g-MA to MH-T was needed to form an efficient protective char, and this resulted in a decrease in PHRR. However, with the increase in the content of SEBS-g-MA, the flame retardancy of the composites declined somewhat.

The influence of flame retardant on the flammability of composites must be considered from two aspects, that is, the flame-retardant dispersion state in the matrix and the flame-retardant concentration. In this study, the fire-resistance performances of the HIPS/MH-T composites were enhanced by partly the substitution of HIPS with SEBS-g-MA, when the SEBS-g-MA was no more than 8 wt %, which was due to the better dispersion of filler in the matrix and which led to an enhancement in the flame-retardant efficiency of MH-T. However, the fire-resistance performances of the HIPS/MH-T composites were reduced by the partial substitution of HIPS with SEBS-g-MA when the SEBS-g-MA content was over 8 wt %; this may be explained by the fact that the introduction of excessive SEBS-g-MA accelerated the degradation of the composites. The major factor of influence on the fire retardancy of the samples was not the dispersion degree of the filler but the excessive SEBS-g-MA coating, which acted as a heat and mass transfer barrier due to the formation of the encapsulation structure.

In conclusion, the ternary composites with the encapsulation structure showed higher flame retardation than those with the separation structure containing no more than 16 wt % elastomer in this study.

**TABLE III**  
Tensile Strength, Elongation at Break, Flexural Modulus, Flexural Strength, and Izod Impact Performance Values of the Specimens of the HIPS Ternary Composites

Composite code	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Notched Izod impact strength (J/m)
A	29.0	36.0	48	2.1	220
B	30.3	3.2	55	4.6	31
C	23.7	61	37	1.4	410
D	25.1	4.5	45	3.2	36
E	24.8	5.2	44	3.2	37
F	21.5	5.9	39	2.7	44
G	18.3	12.8	34	2.2	73
H	16.5	20.0	30	1.8	130
I	23.0	85.0	36	1.4	350
J	21.3	5.9	40	1.9	33
K	21.2	6.9	39	1.8	37
L	19.3	8.6	35	1.3	38
M	18.3	9.2	33	1.3	39
N	17.4	14.0	29	1.0	44

### Mechanical properties

Table III lists the tensile strength, elongation at break, flexural modulus, flexural strength, and Izod impact strength of notched specimens for the HIPS ternary composites with elastomer contents of 4, 8, 12, 16, and 20 wt % at a fixed concentration of MH-T of 42.4 wt %. The tensile strengths of both systems were almost the same at the same content of elastomer. This result indicates that elastomer polarity had little influence on the tensile strengths of both ternary composites. However, the ternary system with SEBS had a higher elongation than those of the composites with SEBS-*g*-MA at a high concentration of elastomer.

The flexural properties of the ternary composites of HIPS/SEBS/MH-T and HIPS/SEBS-*g*-MA/MH-T are also shown in Table III. The ternary composites with SEBS-*g*-MA showed a much lower flexural modulus than the composites with SEBS. This indicated that the reinforcing efficiency of the filler in the HIPS/SEBS-*g*-MA/MH-T composites was suppressed by the encapsulation structure of MH with SEBS-*g*-MA. The decrease in modulus of composites with an encapsulation structure have been reportedly due to the volume of low-modulus elastomer extended by the rigid filler, which thus led to a decrease in the composite modulus.<sup>14</sup> However, elastomer polarity had little influence on the flexural strength of the ternary composites.

As shown in Table III, the notched Izod impact strength of composites with the encapsulation structure was lower than that of those with the separation structure. These results show that the separated dispersion of elastomer and filler in the matrix was much more effective for maintaining the impact strength than encapsulation structure at the same content of elastomer. A similar effect was observed by Kolarik and Jancar.<sup>10</sup>

### CONCLUSIONS

In this study, composites of HIPS/SEBS/PS-encapsulated MH exhibited separation of the filler and elastomer, whereas composites of HIPS/SEBS-*g*-MA/PS-encapsulated MH exhibited encapsulation of the fil-

ler by SEBS-*g*-MA. The flame-retardant and mechanical properties of the ternary composites were strongly dependent on microstructure. The composites with a separate dispersion structure showed higher moduli and impact strengths than those with the encapsulation structure. Furthermore, the composites with the encapsulation structure showed higher flame-retardant properties than those with the separation structure at optimum use levels of SEBS-*g*-MA. However, with increasing content of SEBS-*g*-MA, the flame retardancy of the composites declined somewhat, which could be explained by the fact that the SEBS-*g*-MA coating acted as a heat and mass transfer barrier due to the formation of the encapsulation structure.

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