

SHORT COMMUNICATION

Effect of particle size on the flame retardancy of poly(butylene succinate)/Mg(OH)₂ composites

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SUMMARY

Poly(butylene succinate)/magnesium hydroxide (PBS/Mg(OH)₂) composites were prepared by melt compounding to investigate the effect of particle size on the flame retardancy of PBS. Their flammability properties were investigated by limiting oxygen index, UL-94, and cone calorimeter tests, which suggested that the medium-sized Mg(OH)₂-5 μm displayed the best flame retardancy. The residual char structure were analyzed and indicated that Mg(OH)₂-5 μm could form a better protective layer than other sized particles, leading to the better flame retardancy to PBS. © 2016 The Authors. Fire and Materials published by John Wiley & Sons, Ltd.

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KEY WORDS: poly(butylene succinate); magnesium hydroxide; composites; particle size; flame retardancy

1. INTRODUCTION

Poly(butylene succinate) (PBS), as a typical aliphatic polyester, is one of the most promising biodegradable materials [1, 2]. However, the inherent flammability of PBS restricts its wide applications in many fields. Consequently, there is a sustained interest in improving its flame retardancy to meet various endues applications.

On the heels of growing environmental awareness and stringent legislation for textile addition agents, to seek alternatives for the halogen flame retardants has been an urgent task. Hitherto, the halogen-free flame retardants mainly include inorganic hydroxides (magnesium hydroxide (Mg(OH)₂), Al(OH)₃, etc.) [3, 4], intumescent flame retardants [5], nano-sized flame retardants [6], and phosphor-containing flame retardants [7]. Among them, Mg(OH)₂ is a good candidate because of its abundant source, relatively high decomposition temperature, and low cost [8, 9]. Much effort for polymer/Mg(OH)₂ composites is focused on the decrease of filler loading [10], the compatible modification [11, 12], and the exploration of new synergists [13, 14]. Actually, the structural parameters for Mg(OH)₂ itself were also important to the combustion properties of polymer composites [15], such as particle size [16]. Some researchers have more or less involved the effect

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of particle size on the flame retardancy. For example, Huang *et al.*[16] prepared poly(ethylene-co-vinyl acetate)/Mg(OH)₂ composites with different particle size (800 mesh, 1250 mesh, 2500 mesh, and nanometer) and concluded that smaller particle size resulted in better flame retardancy. But, nonetheless, no convinced explanation was made for the relationship between particle size and flame retardancy; especially, the effect of particle size on the resultant char structure was omitted.

In this study, PBS/Mg(OH)₂ composites were prepared with the particle size from 20 to 500 nm. The flame retardancy properties of PBS composites were estimated by the limiting oxygen index (LOI), vertical fire testing (UL-94), and cone calorimeter testing. Moreover, the residual char structure was analyzed to investigate the relationship between particle size and improved flame retardancy.

2. EXPERIMENTS

2.1. Materials and preparation of PBS/Mg(OH)₂ composites

Poly(butylene succinate) (GS PLA, Japan) was a commercial product of Mitsubishi Chemical Corp. The melt flow index was 4.5 g/10 min at 190 °C under 2.16 kg of weight. Three types of Mg(OH)₂ were prepared via direct precipitation method by changing pH value [17]. The average particle diameter was 20 μm, 5 μm, and 500 nm, respectively. They were dried at 120 °C for 12 h before usage. Maleic anhydride-grafted PBS was synthesized via reactive melt-grafting process [18], and the degree of MA was 4.2 wt%.

Poly(butylene succinate)/Mg(OH)₂ composites were prepared via melt compounding at 135 °C in a Haake batch intensive mixer (Haake Rheomix 600; Haake, Karlsruhe, Germany) at a rotor speed of 80 rpm for 6 min. The content of maleic anhydride-grafted PBS (as a compatibilizer) was kept constant as 15 wt% in the composites, and the content of Mg(OH)₂ was changed from 10 to 60 wt%.

2.2. Characterization

The particle morphology was examined with scanning electron microscope (SEM) (XL30 FESEM FEG; FEI Co., Hillsboro, Texas, USA). The samples were adhered to a conductive tape, and they were coated with gold before SEM observation.

The limited oxygen index (LOI) was measured on a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, Jiangning, China) with sheet dimensions of 130 × 6.5 × 3.2 mm³, according to ISO 4589-1984. The vertical burning rating was tested according to the UL-94 (ANSI/ASTMD635-77) with sheet dimensions of 125 × 12.7 × 3.2 mm³.

Cone calorimeter testing was performed using an FTT device (icone, UK) according to ISO 5660 at an incident flux of 50 kW m⁻², and the size of specimens was 100 × 100 × 6 mm³; each sample was tested three times. The photographs of the residual chars after the cone calorimeter tests were collected by a digital camera.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of three synthesized Mg(OH)₂ with different particle size. Clearly, the particles presented similar sheet-like structure, but their geometric shape was irregular. The morphology of Mg(OH)₂-20 μm was block shaped, while the Mg(OH)₂-5 μm was petal like. By contrast, the Mg(OH)₂-500 nm was approximately an ellipsoid. In this situation, it was difficult to evaluate their accurate particle size distribution. Consequently, three Mg(OH)₂ particles were sifted with different mesh sizes of sifter to make sure the filler size is in a suitable range as required.

The effect of three Mg(OH)₂ on the flame retardancy of PBS matrix was firstly investigated by LOI and UL-94 tests. As shown in Figure 2, the LOI value was gradually increased with the addition of filler from 10 to 60 wt%. Moreover, with the same Mg(OH)₂ loading, the LOI value was as follows: Mg(OH)₂-20 μm < Mg(OH)₂-5 μm < Mg(OH)₂-500 nm. Despite these, the increased trend was quite different. For Mg(OH)₂-20 μm and Mg(OH)₂-500 nm, the LOI was almost linearly increased with the addition of filler loadings. But for Mg(OH)₂-5 μm, when its content was more than 40 wt%, a suddenly substantial increase for LOI appeared, and the LOI value was very close to

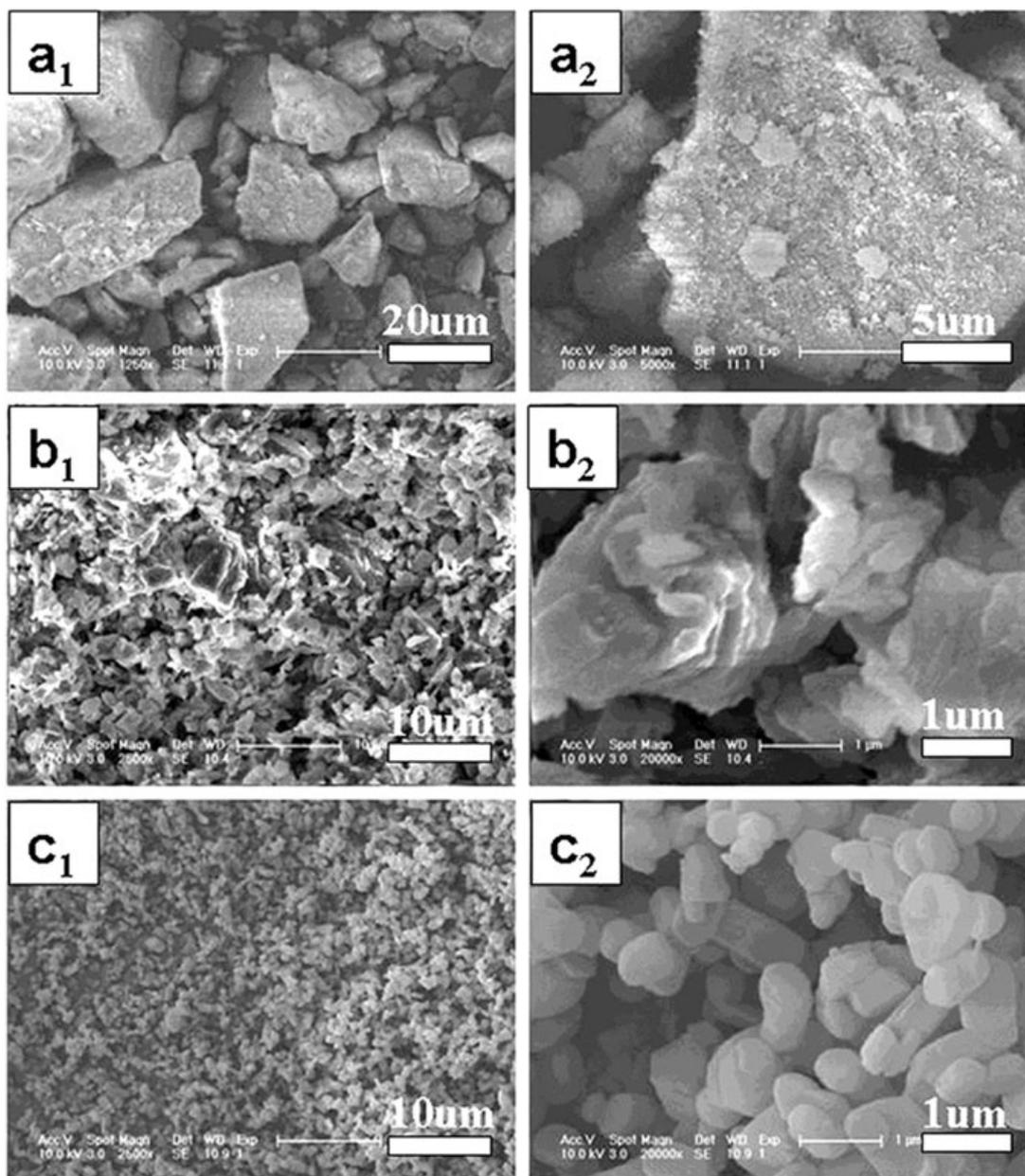


Figure 1. SEM images for the magnesium hydroxide (Mg(OH)₂) with different particle sizes: (a₁,a₂) Mg(OH)₂-20 μm; (b₁,b₂) Mg(OH)₂-5 μm; and (c₁,c₂) Mg(OH)₂-500 nm.

that of Mg(OH)₂-500 nm. Coincidentally, the dependence of vertically burning rating on Mg(OH)₂ content was also different. When the filler was 30 wt%, all the samples could reach to V-1. For approaching V-0 rating, the required content for Mg(OH)₂-20 μm was as high as 60 wt%, but that for Mg(OH)₂-5 μm and Mg(OH)₂-500 nm was only 40 wt%. These results indicated that the effect of Mg(OH)₂-5 μm and Mg(OH)₂-500 nm on flame retardancy of PBS was similar, which is more efficient than that of Mg(OH)₂-20 μm. Furthermore, the char structure after LOI test was investigated by SEM. As shown in Fig. S1, the char from Mg(OH)₂-20 μm was loose, while that from Mg(OH)₂-5 μm and Mg(OH)₂-500 nm was compact. The difference in charring during combustion may result in the different dependence on Mg(OH)₂ loadings.

The effect of particle size of Mg(OH)₂ on the flame retardancy of PBS was further investigated by cone calorimeter testing. The heat release rate–time curves for PBS samples (the content of Mg(OH)₂ was kept constant as 40 wt% in PBS composites) are shown in Figure 3a, and detailed combustion

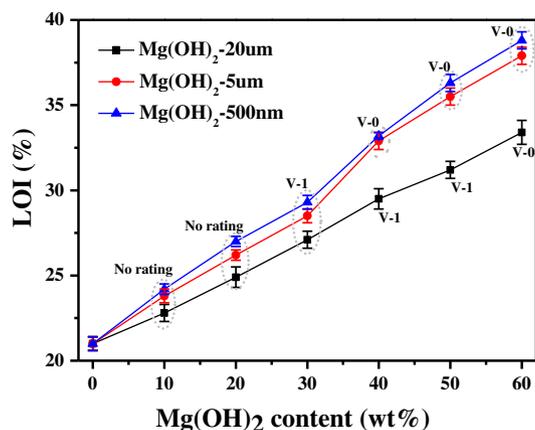


Figure 2. Effect of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) content on the flame retardancy of poly(butylene succinate) by limiting oxygen index (LOI) and UL-94 tests.

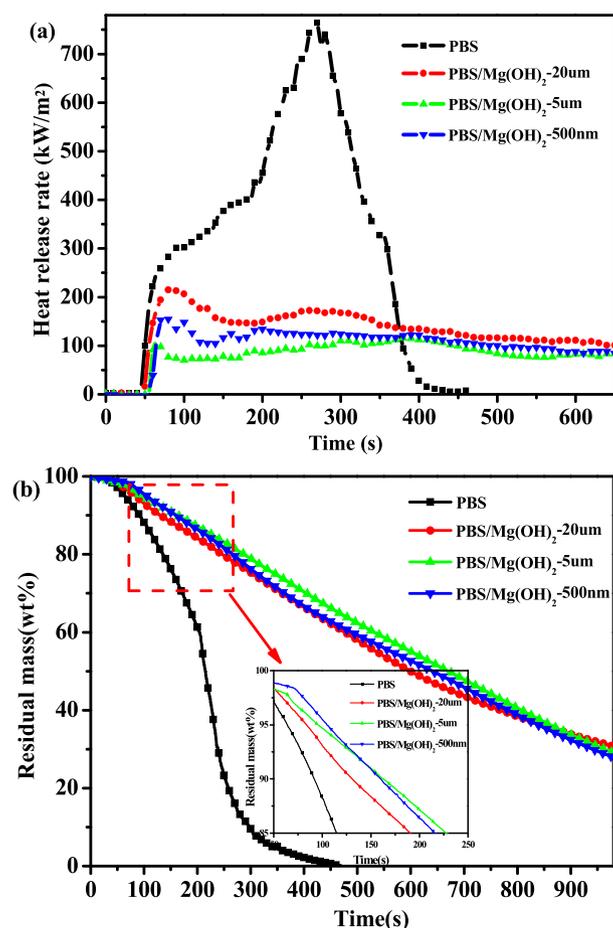


Figure 3. Heat release rate curves (a) and mass loss curves (b) of poly(butylene succinate) and its composites with 40 wt% $\text{Mg}(\text{OH})_2$ with different particle sizes measured by a cone calorimeter at an external radiant flux of 50 kW/m^2 . PBS/ $\text{Mg}(\text{OH})_2$, poly(butylene succinate)/magnesium hydroxide.

parameters are listed in Table S1. The ignition time (t_{ign}) for neat PBS was 48 s, while those for PBS composites were 53 s ($\text{Mg}(\text{OH})_2$ -20 μm), 58 s ($\text{Mg}(\text{OH})_2$ -5 μm) and 61 s ($\text{Mg}(\text{OH})_2$ -500 nm). It suggested that the addition of $\text{Mg}(\text{OH})_2$ could prolong the onset of combustion process, and the samples with smaller-sized $\text{Mg}(\text{OH})_2$ were more difficult to be ignited. These results are well

consistent with the previous report in poly(ethylene-co-vinyl acetate)-Mg(OH)₂ system [16]. The peak value of heat release rate and the total heat release (THR) of PBS composites were significantly decreased, which may be ascribed to the dehydration of Mg(OH)₂ during thermal decomposition. Interestingly, the lowest values for peak value of heat release rate and THR appeared in the PBS/Mg(OH)₂-5 μm, which were 117 kW/m² and 79 MJ/m², respectively. These observations demonstrated that Mg(OH)₂-5 μm was the optimal flame retardant in PBS/Mg(OH)₂ system.

The mass loss curves for PBS samples were also analyzed to evaluate their flammability properties. It is apparent that the presence of Mg(OH)₂ led to a dramatic decrease of the mass loss rate of PBS (Figure 3b). With the same filler loading, the mass loss rate of Mg(OH)₂-5 μm was slower than that of Mg(OH)₂-20 μm, while that for Mg(OH)₂-500 nm suddenly became fast after the combustion time was beyond 180 s (Figure 3b, inset). The aforementioned HRR results further indicated that Mg(OH)₂-5 μm exhibited the best flame retardant effect. Additionally, as shown in Table S1, the amount of residual char for PBS composites was different. According to theoretical calculation, the residual char should be 27.6 wt%. In fact, the corresponding char in PBS/Mg(OH)₂ system were 30.8, 27.9, and 26.9, respectively. Considering the decomposition process of Mg(OH)₂, there were two possible reasons. On one hand, it was ascribed to the 'cover effect'. With the decomposition of outside Mg(OH)₂, the MgO product may cover on its surface to resist the inside decomposition. As a consequence, the decomposition of innermost Mg(OH)₂-20 μm with larger particle size was not complete, resulting in a higher value for the residual char. On the other hand, although Mg(OH)₂ was prepared by the similar technology, the crystal water content might be different. The removal of the crystal water during combustion may lead to a lower amount of the residual char.

By carefully analyzing the LOI, UL-94, and cone calorimeter tests, it is still a puzzle why the medium-sized Mg(OH)₂-5 μm exhibits the best flame retardancy, but not for the smallest-sized one. It is well known that Mg(OH)₂ is implemented by multiple fire retardancy mechanisms in polymer

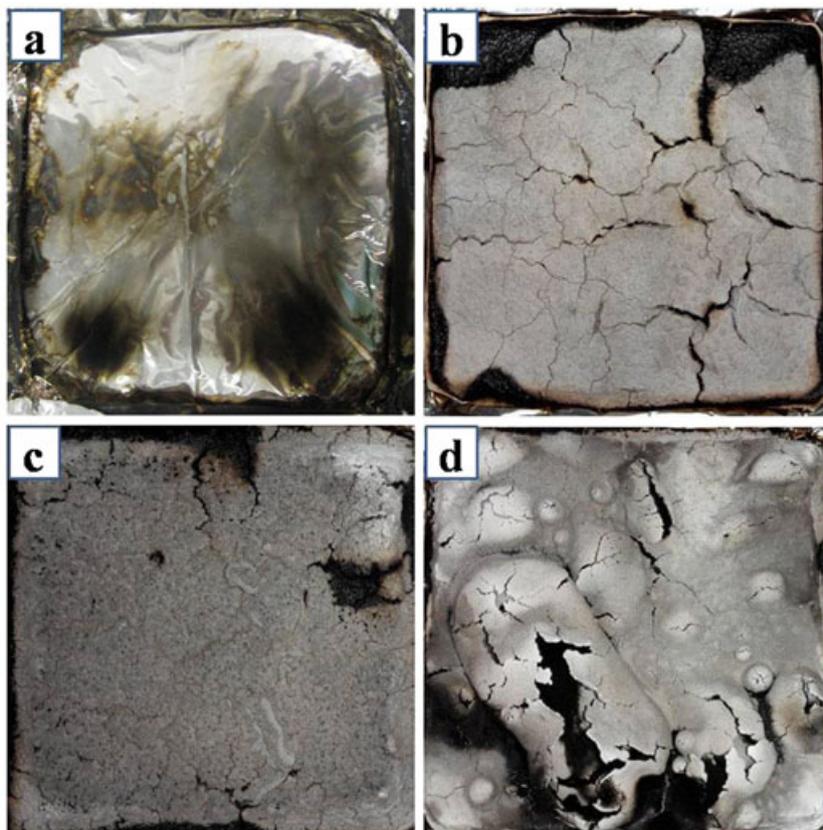


Figure 4. Photographs of the residues after the cone calorimeter test from (a) neat poly(butylene succinate); (b) magnesium hydroxide (Mg(OH)₂)-20 μm; (c) Mg(OH)₂-5 μm; and (d) Mg(OH)₂-500 nm.

composites [19]. When heated above 340 °C, it decomposes to form MgO and water vapor with an absorbed heat of 1300 J/g. The evolved water vapor acts as a fire inhibitor and diluent in the gas phase. Meanwhile, the inert MgO may form protective layer, to inhibit the spread of fire and the transport of decomposed volatiles and air. In our PBS/Mg(OH)₂ composites, we assumed that the absorbed heat has no appreciable difference at the same filler content, so the different flame retardancy effect may be associated with the residual char structure [20]. Figure 4 shows photographs of the residues after cone testing. Neat PBS was completely decomposed without any residue (Figure 4a), whereas PBS/Mg(OH)₂ composites left a mass of gray-white chars. The char from Mg(OH)₂-20 μm was compact, but it presented many big cracks (Figure 4b). For Mg(OH)₂-5 μm, the char was also compact, but only a small amount of cracks appears in the marginal zone (Figure 4c). To our surprise, the char from Mg(OH)₂-500 nm exhibited a number of cracked holes and bubbles (Figure 4d), leading to a worse char protected layer. It should be mentioned that the cone calorimeter tests were carried out at 765 °C (50 kW m⁻²), which is much higher than the decomposition temperature of Mg(OH)₂. In this case, the decomposition rate for Mg(OH)₂-500 nm with the smallest particle size should be much faster than those for other larger-sized Mg(OH)₂, so it released large amounts of water vapor within a very short time. The water vapor would strongly break through the surface char layer and resulted in these cracked holes and bubbles. In contrast, Mg(OH)₂-20 μm and the Mg(OH)₂-5 μm with larger particle size would gradually decompose from outside to inside, and the release rate for water vapor was slower, so they could remain a complete protected layer. According to these results, it is indicated that the combustion properties of PBS composites were significantly influenced by the Mg(OH)₂ size and only the medium-sized Mg(OH)₂ could form good protective char layer resulting in better flame retardancy.

4. CONCLUSIONS

Poly(butylene succinate)/Mg(OH)₂ composites with different-sized fillers were prepared by melt compounding with the Mg(OH)₂ loading varied from 10 to 60 wt%. The Mg(OH)₂-5 μm with a medium particle size resulted in the best flame retardancy. Besides the absorbed heat mechanism, the better flame retardancy from Mg(OH)₂-5 μm was mainly ascribed to forming good protected char layer. The further work will turn to reduce the filled Mg(OH)₂ content, explore effective synergists, optimize the mechanical properties of PBS composites, and so on. These results will be reported in the future.

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