Effect of Particle Size on Flame Retardancy of $Mg(OH)_2$-Filled Ethylene Vinyl Acetate Copolymer Composites

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ABSTRACT: Four kinds of magnesium hydroxide ($Mg(OH)_2$) with different particle sizes are chosen and mixed with ethylene vinyl acetate copolymer (EVA) to investigate the effect of particle size on the flame retardancy of composites, which is evaluated by limiting oxygen index (LOI) testing, horizontal fire testing, and cone calorimeter. When $Mg(OH)_2$ filling level changes from 35 to 70 wt %, the composites filled with nano-$Mg(OH)_2$ do not always possess the best flame retardancy, and among the composites filled with micro-$Mg(OH)_2$, the composites filled with 800 mesh $Mg(OH)_2$ show the best flame retardancy; however, the composites filled with 1250 mesh presents the worst one. So the effect of particle size on the flame retardancy of micro-$Mg(OH)_2$-filled EVA is not linear as expected. All the differences are thought to result from both particle size effect and distributive dispersion level of $Mg(OH)_2$. To prepare the composites with better mechanical properties and flame retardancy, authors suggested that $Mg(OH)_2$ of smaller size should be chosen as flame retardant, and good dispersion of $Mg(OH)_2$ particles also should be assured. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4461–4469, 2006

Key words: EVA; magnesium hydroxide; particle size; distributive dispersion; flame retardancy; cone calorimeter

INTRODUCTION

The use of polymeric materials has increased sharply over the past decades, but their flammability has become an obstacle from expanding their application in many fields, such as electrical products, decorating products, even packing products, etc. Theoretically, it is desirable for all the polymer materials to possess certain flame retardance, but the fact is that most polymer materials burn easily. Generally, nonflammable polymer materials are made by the joint use of halogen-type flame retardant and antimony trioxide, whose effect is satisfactory in flame retardance. This method, however, brings up problems such as toxicity of flame retardants, emission of corrosive, toxic, and smoky halogen compounds in fire.[1] In the past time, more attentions had been paid to this problem and many techniques were applied into this field. Among them, using halogen-free flame retardants, such as aluminum hydroxide and magnesium hydroxide ($Mg(OH)_2$) in place of traditional flame retardants, is a practical and promising way to overcome the aforementioned difficulties. These flame retardants tend to decrease the amount of fumes and the toxicity of smoke generated during combustion, but it is necessary to fill more than 60% by weight $Mg(OH)_2$ or $Al(OH)_3$ in matrix to obtain excellent flame retardancy, because of their low flame retarding efficiency. As a consequence, this method (i.e., extremely high loading of filler) easily causes processing difficulties and marked deterioration in mechanical performances of nonflammable composites.[2]

Though there are many investigations on the properties of polymer composites filled only with $Mg(OH)_2$ or $Al(OH)_3$,[3,4] it is still difficult to compromise among the mechanical properties of composites, the modified combustion characteristics, and processing properties when preparing halogen-free flame retarding composites. Therefore, it becomes very active and important to enhance the flame retarding efficiency of $Mg(OH)_2$ or $Al(OH)_3$, aiming at reducing their loading amount by using many methods, such as, to find some synergists of $Mg(OH)_2$,[3,5] to highly exert the retarding effect by adjusting geometry parameter of $Mg(OH)_2$,[6] to improve the dispersion of filler,[7] etc. It is well-known that particle size is an important structural parameter of flame retardant additives, which not only probably affect the mechanical properties and fluid properties of composites,

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but also might influence the flame retardancy. A natural question is whether the mechanical property and flame retardancy of composites filled with $Mg(OH)_2$ or $Al(OH)_3$ at the high loading level would increase with the reduction of particle size, and fluid property of composite becomes unbearable. Some researches have more or less involved this interesting question.[7–13] Some of them disagreed to the presence of particle size effect[8,9] and ascribed the difference of flame retardancy of composites to the degree of dispersion of filler in matrix.[7] It was said that the better the degree of dispersion, the more evenly the heat generation of the resin and the heat absorption of $Mg(OH)_2$ balance throughout the composites. To the contrary, some researchers reached the expected conclusions that small particle size of $Mg(OH)_2$ or $Al(OH)_3$ could improve the flame retardancy of composites.[10–13] However, the systemic research works are less, and no convinced and consistent conclusions were made. Authors had ever investigated the particle size effect of $Mg(OH)_2$/ethylene–propylene copolymer rubber composites and found that the nano-sized $Mg(OH)_2$-filled rubber exhibited the best flame retardancy,[14] while for the micro-sized $Mg(OH)_2$-filled rubbers, they had shorter ignition time (IT) and higher peak value of Rate of heat release (RHR).

In this work, to give a comprehensive evaluation about the effect of particle size on the flame retardancy of $Mg(OH)_2$/ethylene vinyl acetate (EVA) composites, four kinds of $Mg(OH)_2$ with different particle sizes, including nano-$Mg(OH)_2$, are chosen as the flame retardants of EVA, which is a popular polymer matrix (at least partly) of fire-resistant and halogen-free cable materials. The limiting oxygen index (LOI), horizontal fire testing, and cone calorimeter testing are employed to present the flame retarding results. This research is expected to be useful for the preparation of halogen-free flame retarding polymer materials.

EXPERIMENTAL

Materials

EVA copolymer (*Elvax 460*$^{(R)}$, with vinyl acetate of 18% and melt flow index of 2.5 dg/min) was bought from DuPont Corp. Three kinds of micro-$Mg(OH)_2$ and one kind of nano-$Mg(OH)_2$ were provided by Beijing Fine Chemical Plant of BUCT.

Basic formula (phr): EVA, 100; Antioxidant 1010 (Tetrakis [β-(3,5-ditertiary-butyl-4′-hy-droxyphenyl) propionate] pentaerythritol ester): 1.6 phr; $Mg(OH)_2$, varied from 55, 83, 120 phr to 230 phr, corresponding to the weight percentage of $Mg(OH)_2$ in the composites from 35, 45, 55 to 70 wt %.

Preparation of composites

EVA copolymer and $Mg(OH)_2$ were blended together in the two-roll mixer at 130°C for 20 min. The resulting compound was compressed for 10 min at 15 MPa and at 160°C, and then was transferred to another pressing machine and pressed for 10 min at 15 MPa and at an ambient temperature. For different testing, the molds with different dimension were applied. The relative mechanical properties and flame retardance test were conducted.

Measurements

Mechanical properties measurement

The molded samples of all the composites were died into dumbbell-shaped specimens. Mechanical properties of the composites were measured at a tensile speed of 250 mm/min, according to ASTM standard.

Analysis of particle size

Three kinds of micro-$Mg(OH)_2$ were analyzed by Mastersize 2000 particle-sizing instrument (Malvern Instruments Ltd., Malvern, UK), which can provide the average particle size and particle size distribution.

Scanning electron microscopy

S-250-III SEM (Cambridge, UK) was employed to observe the particle morphology of three kinds of micro-$Mg(OH)_2$ particles.

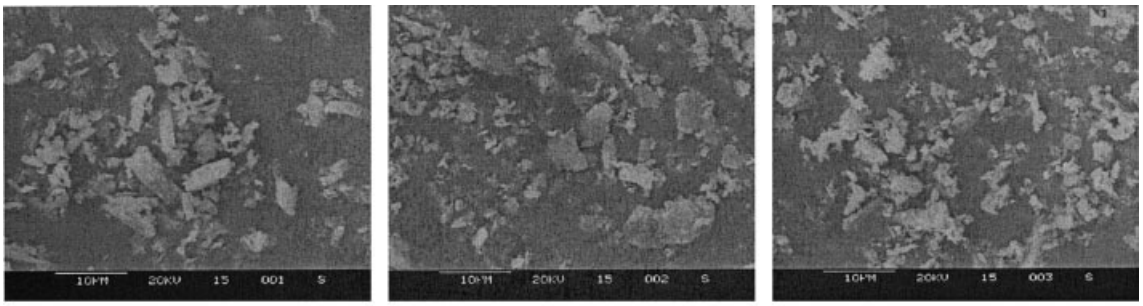

Figure 1 SEM micrographs of three kinds of micro-$Mg(OH)_2$.

Environmental scanning electron microscopy (ESEM)

ESEM experiment was performed using a XL-30 environmental scanning electron microscope (PET company, USA) to acquire a direct visualization of nano-$Mg(OH)_2$ particles.

Thermal analysis

Thermogravimetry analyses were carried out by a Netzsch TG 209C (German) instrument. About 10 mg sample was positioned in silica pans, and the samples were heated at 10°C/min from ambient temperature to 900°C. The thermal analyses were performed under a nitrogen purge (10 mL/min).

Rheological property measurement

Rheological properties of the composites were measured at 200°C by an Instron Capillary Viscometer INSTRON-3211 (Instron, UK). The dimension of the capillary is 1.196 mm in diameter and 51.11 mm in length.

Flame retardance testing

Three standard test methods were utilized to evaluate the flame retardance of composites.

LOI is an indicator of the minimum oxygen concentration that is needed to cause the material combusting in an oxygen–nitrogen atmosphere through downward burning of a vertically mounted specimen. Test specimen is required of 70–150 mm in length, 6.5 mm in width, and 3 mm in thickness, according to Chinese state standard GB/T 2406–93, using a Jiangning Analyzer Plant instrument JF-3, China.

Horizontal fire test and vertical fire test of the specimen ($125 \times 13 \times 3$ mm^3) is conducted in ambient atmosphere, according to the Chinese state standard GB/T 2408–1996, using a Jiangning Analyzer Plant instrument CZF-3, China. For the horizontal fire test, there are two marks on the specimen: one lying at 25 mm to the left end, and the other lying at 100 mm to the left end. During testing, the specimen is kept in a horizontal position, and the left end of the specimen is burned for 30 s. Then, fire may spread from the left to the right, passing the two marks. Four levels (FH-1, FH-2, FH-3, FH-4) are defined by whether fire spreads the two marks or not and the spread speed. If the fire does not pass the first mark, it is identified as FH-1, standing for the best. If the fire passes the first sign but does not pass the second sign, it is identified as FH-2. If the fire passes the second mark, then there must be a spread speed through the two marks. If the speed is less than 40 mm/min, it is identified as FH-3, or it is FH-4 rating. FH-4 is the worst rating. Three specimens are needed at least in each experiment.

Cone calorimeter is a kind of novel instrument to comprehensively evaluate the flame retardancy of composites.[15] The cone calorimeter produced by FTT Company of UK uses a truncated conical heater element to irradiate test specimen at heat fluxes from 10 to 100 kW/m^2 to simulate a range of fire intensities. In the present work, cone calorimeter tests were carried out according to ISO 5600–93, using the incident heat flux of 35 kW/m^2. The bottom and edges of each specimen with a dimension of $100 \times 100 \times 3$ mm^3 are wrapped with an aluminum foil. RHR, IT, residual mass of the composite, and the fire performance index

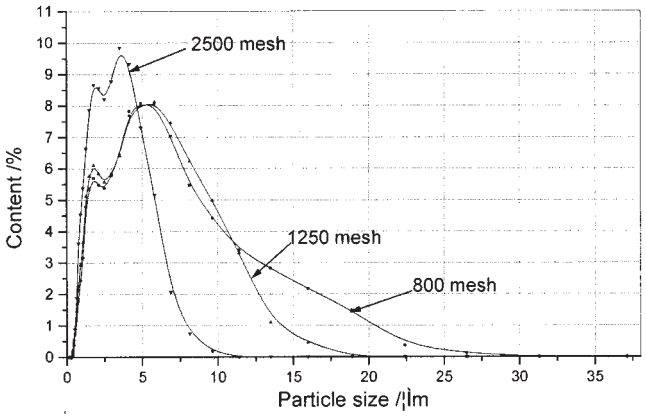

Figure 2 The particle size scatter of micro-$Mg(OH)_2$.

TABLE I
The Average Particle Size of Micro-$Mg(OH)_2$

	800 mesh	1250 mesh	2500 mesh
Average specific area (m^2/g)	2.03	2.47	2.93
Average particle size (D_{50}) (μm)	3.89	2.90	2.33

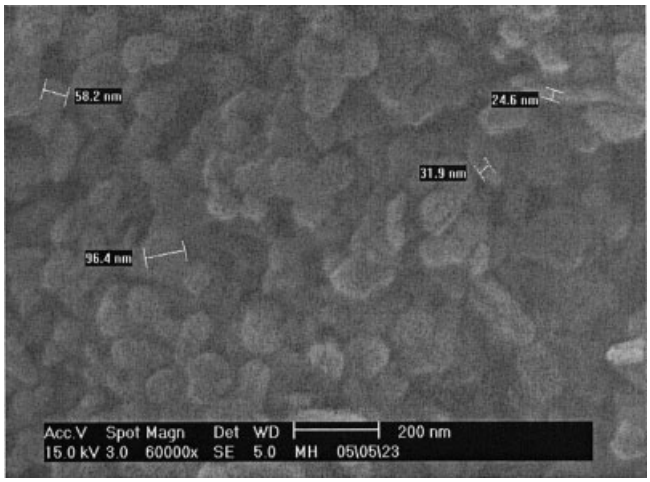

Figure 3 ESEM image of nano-$Mg(OH)_2$.

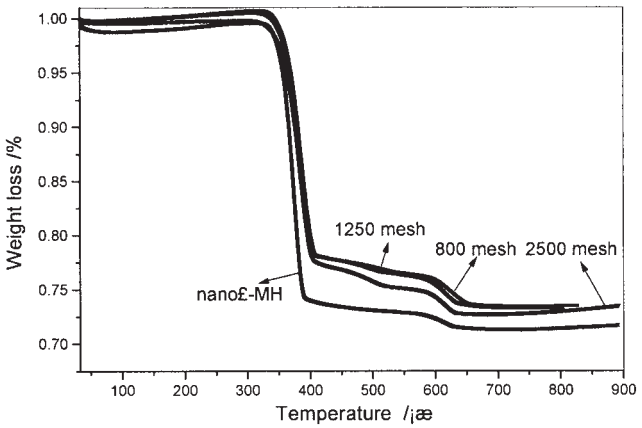

Figure 4 TG curves of four kinds of $Mg(OH)_2$ with different particle dimension under N_2 flow.

(FPI), defined as the ratio of IT to Peak RHR (FPI = IT/Peak RHR), can be obtained through the test at one time. It has been suggested that FPI value relates to the time to flashover (or the time available for escape) in a full-scale fire situation.

RESULTS AND DISCUSSION

Morphology and particle size of $Mg(OH)_2$

Figure 1 shows the scanning electron photomicrographs of three kinds of micro-$Mg(OH)_2$ with different particle size. They clearly demonstrate that the $Mg(OH)_2$ samples are similar sheet-like particles and some particles are even irregular rectangular pieces, and the particle size distribution is pretty wide. However, because of the wide distribution of particle size and self-aggregation of $Mg(OH)_2$ particles, the accurate particle diameters cannot be attained from the scanning electron photomicrographs. Therefore, a particle-sizing instrument is used to measure the particle diameters, and the results are summarized in Table I and Figure 2. From Table I, it can be seen that the average particle sizes of three kinds of commercial micro-$Mg(OH)_2$, 800, 1250, and 2500 mesh, are 3.89, 2.90, and 2.33 μm, respectively. More difference among the particle sizes could be observed in their distributions, as shown in Figure 2. The particle size distribution of 2500 mesh $Mg(OH)_2$ is the narrowest and no particle is larger than 9.64 μm. However, the distributions of 1250 and 800 mesh are very wide, especially the latter. It could be seen from Figure 2 that 800 mesh $Mg(OH)_2$ has considerable amounts of big particles, around the size beyond 20 μm.

Figure 3 is the environmental scanning electron micrograph of nano-$Mg(OH)_2$, which shows that the nano-$Mg(OH)_2$ particle is a kind of sheet-like particle. The dimension of nano-$Mg(OH)_2$ particles is less than 100 nm, and the thickness of most particles is less than 50 nm.

Thermogravimetry analysis of $Mg(OH)_2$

As we all know, the flame retarding mechanism of $Mg(OH)_2$ is that in which when $Mg(OH)_2$ is heated, it decomposes to magnesium oxide with the release of water, and both the decomposition reaction and evaporation of water will absorb a great deal of heat to lessen the temperature on the surface of the materials, which hence retards the decomposition of polymer and reduces the formation of combustible compounds. Accompanying with those, the released vapor can dilute the concentration of oxygen on the surface of materials to reduce the burning rate, and the generated magnesium oxide can as a barrier layer protect the composites from burning. Apparently, during the above process, the decomposition characteristics of metal hydroxide are very important and strongly correlated to the flame retardance of composites. Figure 4 compares the thermogravimetric curves of four kinds of $Mg(OH)_2$ with different particle sizes. Interestingly, it can be found that the decomposition temperature of nano-$Mg(OH)_2$ is slightly lower and content of crystal water of nano-$Mg(OH)_2$ is higher compared with micro-$Mg(OH)_2$. While for three kinds of micro-$Mg(OH)_2$, there is no distinct difference existing in decomposition temperature and residual amount.

Effect of particle size on properties of composites

Composites filled with 55 wt % $Mg(OH)_2$

Generally, the 55–60% by weight of $Mg(OH)_2$ loaded in polymer matrix is a popular case to prepare halo-

TABLE II
Effect of $Mg(OH)_2$ Dimensions on Properties of EVA Composites

Particle size of $Mg(OH)_2$	Tensile strength (MPa)	Elongation at break (%)	LOI (%)	Horizontal fire rating	Vicat softening point (°C)
3.89 μm	12.0	116	35.2	FH-2–20 mm	70.6
2.90 μm	13.1	124	35.0	FH-1[a]	71.6
2.33 μm	12.8	116	37.3	FH-1[a]	71.2
Nanometer	12.1	108	34.6	FH-1	73.8

[a] The specimen extinguished because of drops during being fired.

gen-free flame retarding polymer composites. Therefore, the effect of particle size of $Mg(OH)_2$ is firstly investigated in such a filling system.

Table II, which summarizes the properties of composites loaded with $Mg(OH)_2$ of different particle sizes, clearly indicates that the horizontal fire rating of composites improves with the reduction of particle size. Concretely speaking, the horizontal fire rating of composites filled with nano-$Mg(OH)_2$ can reach FH-1 rating, the highest rating, and the rating of composites filled with 800 mesh $Mg(OH)_2$ is only FH-2–20 mm rating. Though the composites filled with 1250 mesh $Mg(OH)_2$ and 2500 mesh $Mg(OH)_2$ can also approach the FH-1 rating, they extinguished because of drops during being fired. However, Table II shows that there is little difference of EVA composites in terms of LOI values and mechanical properties.

Effect of particle sizes on the Vicat softening temperatures of EVA containing $Mg(OH)_2$ is also shown in Table II. The nano-$Mg(OH)_2$ endows EVA with the highest Vicat softening temperature, 73.8°C, among the four kinds of $Mg(OH)_2$. There is a slight rise trend of Vicat softening temperature with the reduction of particle size of $Mg(OH)_2$. Higher heat-resistance of composites is believed to benefit the flame retardancy through the resistance to heat-distortion and heat-flow.[16]

On comparing the two flame retardancy test methods, the situation of horizontal fire test is more like an actual full-scale fire situation, and so the results gained from horizontal fire test are more believable. Therefore, a conclusion that the nano-$Mg(OH)_2$/EVA composites possess the best flame retardancy can be initially drawn. It is also suggested that the nano-$Mg(OH)_2$ with small particle size has high surface activity and specific area, which strongly constrains the macromolecular chain motion, and suppresses the dropping of melted composites. As a consequence, the Vicat softening temperature and horizontal fire rating are improved.

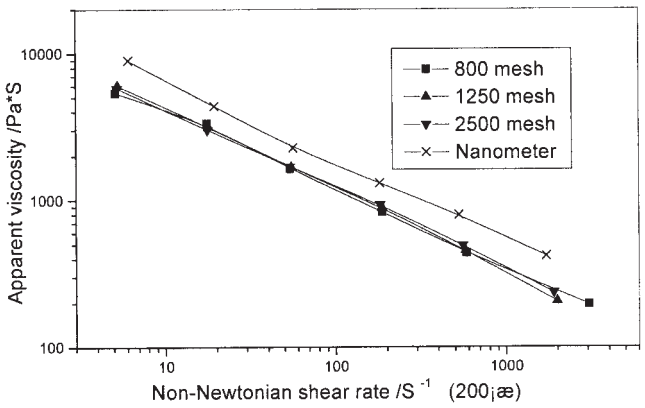

Figure 5 Effect of particle sizes on the rheological property of the composites.

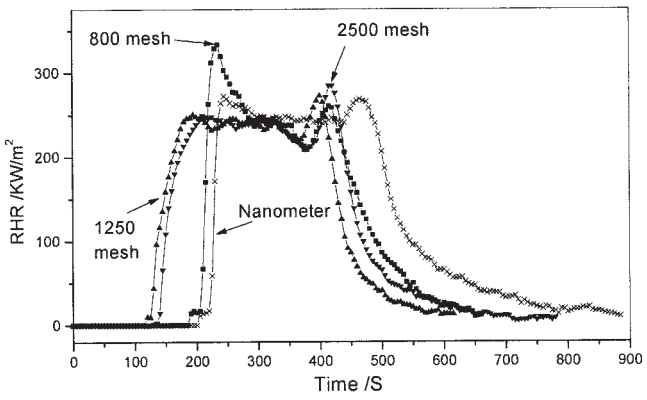

Figure 6 RHR curves of EVA/$Mg(OH)_2$ with different particle sizes, at 55 wt %.

Figure 5 further illustrates the effect of particle size on the flowability of $Mg(OH)_2$/EVA particulate composites. It can be seen that the apparent viscosity of the nano-$Mg(OH)_2$-filled composites is higher than that of composites filled with micro-$Mg(OH)_2$. Again, the rheological experiments of composites testify the advantages of heat-resistance of nano-$Mg(OH)_2$-filled composites. There is no difference in the flowability of three kinds of micro-$Mg(OH)_2$-filled composites, which is partly attributed to their close particle size. However, it is worthy of pointing out that over-high viscosity of composites is not practical when composites is extruded to form a cable or line.

Further study of the effects of particle size on flame retardancy of composites is investigated by cone calorimeter, shown in Figure 6 and Table III. An important result obtained from RHR to time curve is that the maximum rate of heat release (Peak RHR) of nano-$Mg(OH)_2$-filled composites is less than that of micro-$Mg(OH)_2$-filled composites, and the IT of nano-$Mg(OH)_2$-filled composites is the longest one, as presented in Figure 6 and Table III. The FPI value of nano-$Mg(OH)_2$/EVA composites is the highest one. It has been suggested that FPI of composites relates to the time to flashover (or the time available for escape) in a full-scale fire situation.[3] This index can well reflect the potential danger of composites in fire. The higher the FPI value, the longer the time to flashover, and the longer time available for people in fire situation to

TABLE III
Values of IT, Peak RHR, and FPI of EVA/$Mg(OH)_2$ with Different Particle Sizes

Particle size	IT (s)	Peak RHR (kW/m^2)	FPI (m^2 s/kW)
3.89 μm	199	333.054	0.60
2.90 μm	120	272.389	0.44
2.33 μm	133	284.497	0.47
Nanometer	216	271.946	0.79

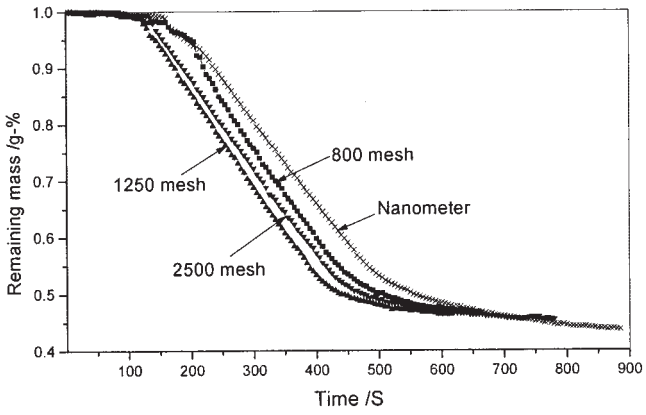

Figure 7 The relation between the residue mass of EVA/$Mg(OH)_2$ with different particle size and time, at 55 wt %.

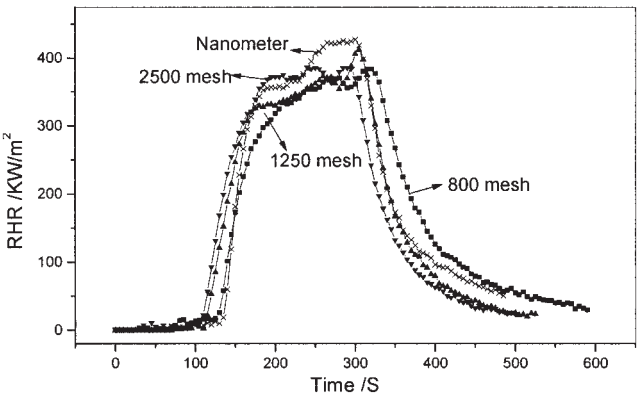

Figure 9 RHR curves of composites filled with 45 wt % $Mg(OH)_2$, with different particle sizes.

escape. Therefore, these results strongly confirm that the flame retardancy of composites filled with nano-$Mg(OH)_2$ is excellent at a filling level of 55 wt % among four kinds of composites.

Figure 7 reveals the relation between remaining mass of composites filled with different particle sized $Mg(OH)_2$ and time under the heat flux 35 kW/m^2. It can be seen that the composites filled with nano-$Mg(OH)_2$ and 800 mesh $Mg(OH)_2$ have no weight loss before 170 s, and the nano-$Mg(OH)_2$/EVA composites displays more remaining mass than the other three microcomposites at any time between 170 and 700 s. It is postulated that nano-$Mg(OH)_2$ may have good dispersion, and has stronger interaction with the macromolecular chain, and then retards the decomposition of composites.

Combining horizontal fire rating, flowability, Vicat softening point, and cone calorimeter testing results, we can draw the conclusion that the composites filled with nano-$Mg(OH)_2$ possesses the best flame retardancy among the four kinds of $Mg(OH)_2$/EVA composites, which is in agreement with the particle size effect as reported in some literatures.[10–14]

However, the effect of particle size on the flame retardancy of micro-$Mg(OH)_2$-filled EVA is not linear and even confused. Typically, the comprehensive flame resistance, FPI values of 800 mesh $Mg(OH)_2$-filled EVA seems to be the best, and that of 1250 mesh $Mg(OH)_2$-filled EVA is the worst.

Composites filled with 35, 45, and 70 wt % $Mg(OH)_2$

To get more accurate and overall conclusion, i.e., to find out whether the particle size effect occurs or not at other filling level of $Mg(OH)_2$, the cone calorimeter measurement of four kinds of different particle-sized $Mg(OH)_2$-filled EVA composites at the filling level of 35, 45, or 70 wt % are carried out, respectively. RHR and remaining mass curves for these samples are presented in Figures 8-10 (RHR series) and Figures 11-13 (remaining mass series).

Different from Figure 6, it is an interesting result that all the composites filled with nano-$Mg(OH)_2$ ex-

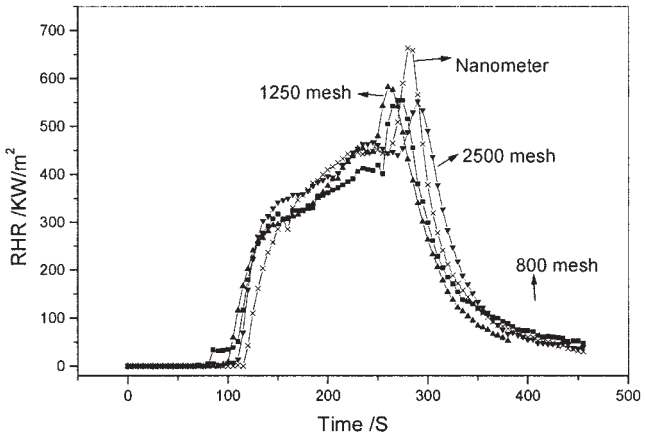

Figure 8 RHR curves of composites filled with 35 wt % $Mg(OH)_2$, with different particle sizes.

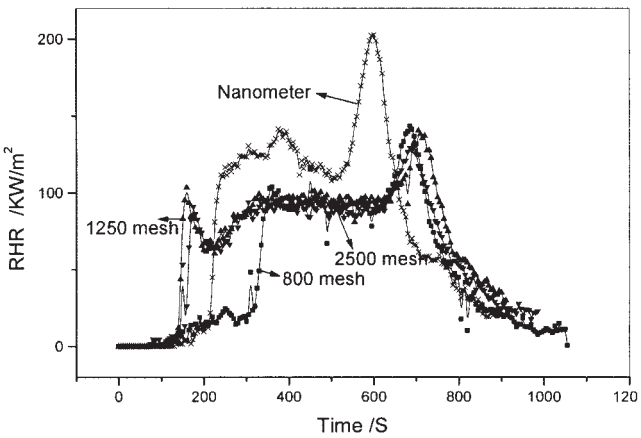

Figure 10 RHR curves of composites filled with 70 wt % $Mg(OH)_2$, with different particle sizes.

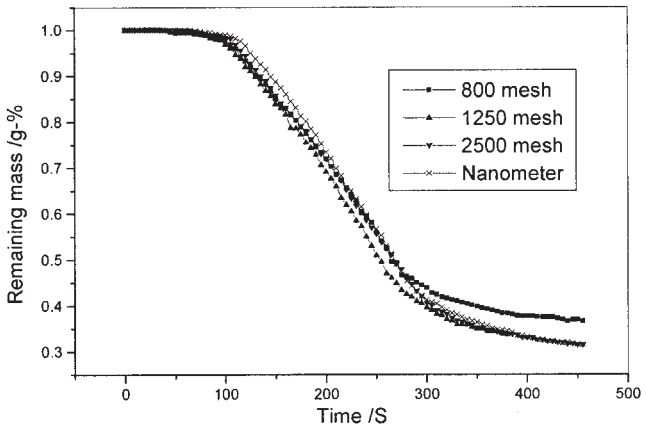

Figure 11 Residue mass of composites filled with 35 wt % $Mg(OH)_2$, with different particle sizes.

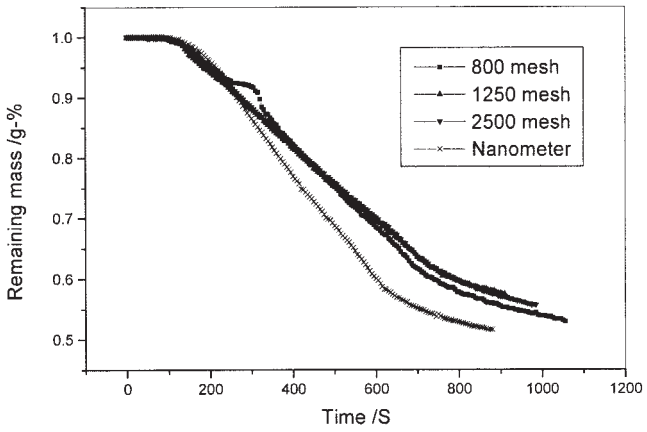

Figure 13 Residue mass of composites filled with 70 wt % $Mg(OH)_2$, with different particle sizes.

hibit higher Peak RHR values than the micro-$Mg(OH)_2$-filled composites, shown in Figures 8–10, which is never mentioned in previous papers. In the systems filled with 70 wt % $Mg(OH)_2$ by weight, the Peak RHR value of composites filled with nano-$Mg(OH)_2$ is even far higher than that of composites filled with micro-$Mg(OH)_2$. Moreover, when the filling level of $Mg(OH)_2$ varies from 35 to 45 wt %, the gaps of Peak RHR between composites filled with nano-$Mg(OH)_2$ and micro-$Mg(OH)_2$ lessen.

On the other side, the composites filled with 35 wt % nano-$Mg(OH)_2$ and 45 wt % nano-$Mg(OH)_2$ have the longest IT values, but the composites filled with 70 wt % nano-$Mg(OH)_2$ has a shorter one, compared with the systems filled with micro-$Mg(OH)_2$.

The relation between the residual mass and heat radiation time of composite is depicted in Figures 11–13. It is found that the nano-$Mg(OH)_2$-filled EVA always have a longest decomposition-starting time, but its advantage in remaining mass gradually diminishes and even transforms into a disadvantage, with the increase of filling amount. Especially at the filling level of 70 wt %, the composites filled with nano-$Mg(OH)_2$ have the lowest remaining mass. It is possible that the nano-$Mg(OH)_2$ particles can easily form tight agglomerates because of strong filler–filler interaction and large specific area. As a result, it will be hard to disperse them into polymer matrix, and the dispersed particles tend to flocculate in polymer melt, which leads to the poor dispersion of the nano-$Mg(OH)_2$, compared with micro-$Mg(OH)_2$.

The FPI values of the above systems are summarized in Table IV, which indicates that the nano-$Mg(OH)_2$ does not show the expected advantage over the other micro-$Mg(OH)_2$, too, which is consistent with the above results.

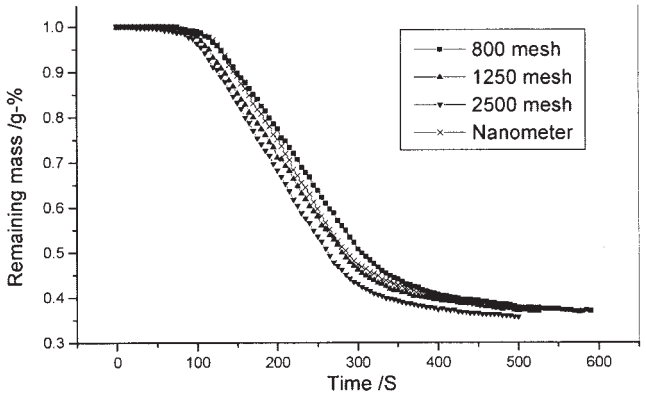

Figure 12 Residue mass of composites filled with 45 wt % $Mg(OH)_2$, with different particle sizes.

Analysis

To more clearly demonstrate the effect of particle size on the flammability of composites, all the data are summarized and depicted in Figure 14-16, including IT values, Peak RHR values, and FPI values. From these results, it can be seen that to all the composites, as the content of $Mg(OH)_2$ increases, the IT values and FPI values increase and the Peak RHR values decrease. However, change of flame retardancy of composites with the loading amount of $Mg(OH)_2$ shows different regulation due to the influence of particle size and dispersion of $Mg(OH)_2$.

TABLE IV
FPI Values of Composites Filled with 35, 45, and 70 wt % $Mg(OH)_2$

Filling level	35 (wt %)	45 (wt %)	70 (wt %)
3.89 μm	0.18	0.28	2.20
2.90 μm	0.16	0.22	0.93
2.33 μm	0.18	0.22	1.14
Nanometer	0.16	0.27	1.01

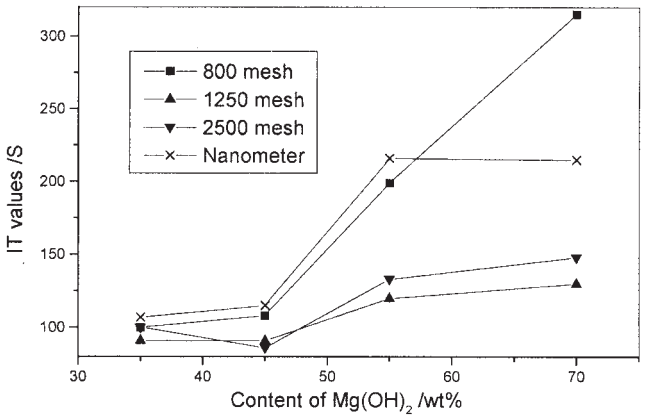

Figure 14 The relationship of IT values of composites and $Mg(OH)_2$ content.

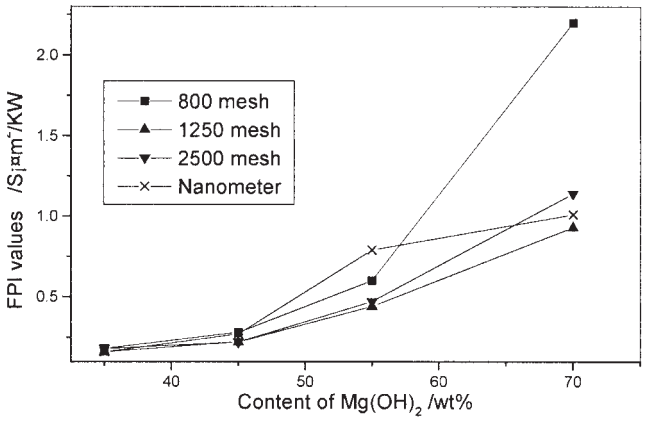

Figure 16 The relationship of FPI values of composites and $Mg(OH)_2$ content.

From above results, it can be seen that the advantage of nano-sized $Mg(OH)_2$ in flame retarding particulate composites does not always occur. More precisely, the particle size effect appears only when the $Mg(OH)_2$ filling level reaches an appropriate content, for example, about 55 wt % in EVA filled with $Mg(OH)_2$. More surprisingly, unlike that expected, 800 mesh $Mg(OH)_2$ endows EVA with a higher flame-resistant property in most cases.

In the opinion of authors, decomposition-characteristics, particle size, interfacial interaction, and dispersion of $Mg(OH)_2$ probably are the four main factors to influence the flame retardancy of composites. The decomposition-characteristic is mainly decided by its chemical composition, crystal structure, and water content, etc. The particle size is suggested to have a little effect through change of surface area on the decomposition-characteristic of $Mg(OH)_2$. The dispersion of $Mg(OH)_2$ is also assured to affect the fire-resistance by the changing of resistance-efficiency, and the higher the dispersion level, the higher the flame retardancy efficiency might be. This is because the dispersion phase is the main body of fire-resister, and a nonuniform distributive dispersion of $Mg(OH)_2$ in matrix possibly results in a early burning in the micro-region where the $Mg(OH)_2$ is less loaded. Theoretically, the smaller particle may be dispersed everywhere in polymer matrix; however, aggregation of smaller particle is also stronger. These probably cause a competitive effect. The improvement of interfacial interaction between $Mg(OH)_2$ and polymer matrix may improve the flame retardancy of composites by the enhancement of dispersion level and heat-flow resistance. But, some interface modifiers, for example stearic acid, may benefit the burning and weaken this positive effect. In this paper, to make the question simple, we did not modify the surface of $Mg(OH)_2$.

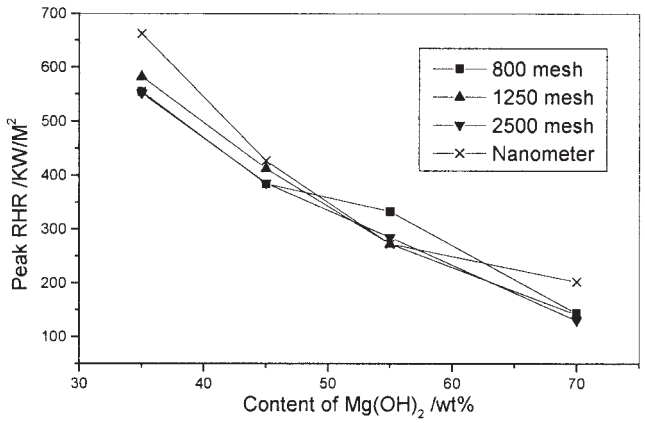

Figure 15 The relationship of Peak RHR of composites and $Mg(OH)_2$ content.

Generally, the particle with small size can easily form tight agglomerates due to strong filler–filler interaction and large specific area. As a result, on the one hand they are hard to be dispersed and on the other hand the dispersed particles tend to flocculate in polymer melt, especially when the content of filler is extremely high. So the distributive dispersion of small particle at high filling in polymer is poor. The appearance images of composites filled with 800 mesh $Mg(OH)_2$ [Fig. 17(a)] and nano-$Mg(OH)_2$ [Fig. 17(b)], at a filling level of 70 wt %, are shown in Figure 17. Through it, an evident dispersion difference is observed. In the EVA sample filled with 70 wt % nano-$Mg(OH)_2$ [Fig. 17(b)], its surface exposes a great deal of white flecks, which can be easily observed by bare eyes, compared with micro-$Mg(OH)_2$-filled composites [Fig. 17(a)].

Therefore, though the particle size of nano-$Mg(OH)_2$ is very small, the composites loaded with it do not display the best flame retardancy in some case, probably because of poor distributive dispersion. While for 800 mesh $Mg(OH)_2$-filled EVA, it always produces good flame retardancy, which is possibly

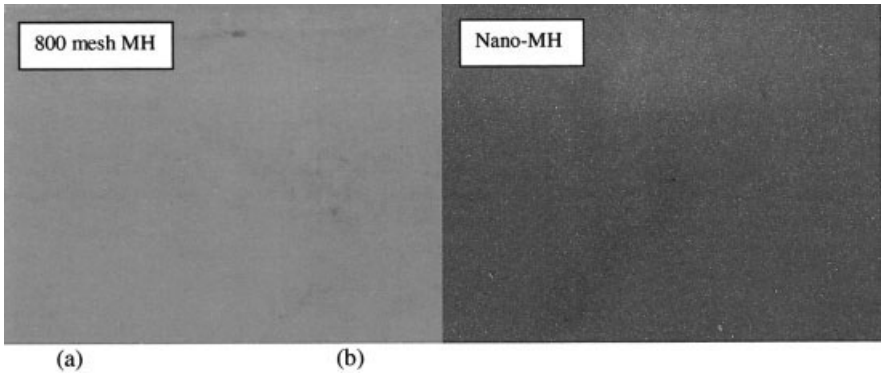

Figure 17 The appearance of composites filled with 70 wt % $Mg(OH)_2$.

ascribed to the best dispersion of $Mg(OH)_2$. As for 1250 mesh $Mg(OH)_2$ and 2500 mesh $Mg(OH)_2$, on the one hand they do not possess the advantages of small sized particles, and on the other hand, their dispersion are worse than that of 800 mesh $Mg(OH)_2$. As a consequence, their flame retardancy is in the middle level or the worst. The effect of dispersion of $Mg(OH)_2$ on the flammability of $Mg(OH)_2$/EVA composites will be discussed in another paper.

Synthesizing above results and analysis and considering the need of mechanical properties and flame retardancy of composites, authors suggested that the smaller sized $Mg(OH)_2$ should be chosen as flame retardant, but the appropriate surface modification must be conducted to improve the dispersion of smaller particle.

CONCLUSIONS

In this paper, the flame retardancy and mechanical properties of EVA containing $Mg(OH)_2$ have been investigated with reference to the particle size of $Mg(OH)_2$. At a filling level of 55 wt %, there is little difference in mechanical properties and LOI values among four composites; however, the composites filled with nano-$Mg(OH)_2$ possesses the best flame retardancy, and the effect of particle size on the flame retardancy of micro-$Mg(OH)_2$-filled EVA is not linear and even confused. Typically, the comprehensive flame retardancy of 800 mesh $Mg(OH)_2$-filled EVA seems to be the best and that of 1250 mesh $Mg(OH)_2$-filled EVA to be the worst, whereas at the other filling level of 35, 45, and 70 wt %, the expected effect of particle size does not exist, and the composites filled with nano-$Mg(OH)_2$ present bad flame retardancy, sometimes because of the poor distributive dispersion.

The flame retardancy of particulate composites ascribes the fact that particle size of inorganic flame retardants strongly influences its dispersion in polymer matrix. The good distributive dispersion and the small particle size tend to result in a better flame-retardency. Hence, the above regulations are determined by the interaction of both the particle size effect and distributive dispersion of $Mg(OH)_2$. However, considering the need of mechanical properties and flame retardancy of composites, authors suggested that the smaller sized $Mg(OH)_2$ should be chosen as flame retardant, but the appropriate methods must be conducted to improve the dispersion of smaller particles.

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