Effects of Silicon Additive as Synergists of Mg(OH)$_2$ on the Flammability of Ethylene Vinyl Acetate Copolymer

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ABSTRACT: The present work dealt with the effects of nine kinds of silicon additives on flame retardancy of ethylene-vinyl acetate copolymer (EVA)/magnesium hydroxide [Mg(OH)$_2$] composites, as well as mechanical properties. The limiting oxygen index (LOI) test, horizontal fire test, vertical fire test, and cone calorimeter test were employed to evaluate flame retardancy of the composites. It was found that different silicon additives had different synergistic effects with Mg(OH)$_2$ on flame retardancy of the EVA matrix and exerted different influences on mechanical properties of the composites. The incorporation of organic montmorillonite (MMT) clay or silicone rubber not only made the composite reach FH-1 rating in the horizontal fire test and FV-1 rating in the vertical fire test, respectively, but also dramatically reduced the peak rate of heat release (Peak RHR) and increased the fire performance index (FPI) and ignition time (IT). The composites filled with precipitated SiO$_2$ exhibited the longest IT, the highest FPI, and FV-1 rating. However, only the composites filled with silicone rubber could attain a balance between mechanical properties and flame retardancy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3203–3209, 2006

Key words: ethylene-vinyl acetate copolymer; flame retardancy; magnesium hydroxide; silicon additive

INTRODUCTION

Since the emergence of synthetic polymer materials, they have been substituting for metallic material in more and more fields due to their low density, good processing properties, electrical insulation, erosion resistance, and so forth. However, the flammability of most polymers is an obvious obstacle to expanding and extending their application, especially in cases such as electrical products, decorating products, even packing products, and so on. Theoretically, it is good for all polymer materials to possess a certain flame retardancy. Therefore, the flame retarding science and technology of polymer materials is very significant, becoming more and more important and necessary. As is well known, flame-retarded polymers can be prepared by adding some flame retardants into the matrices, and as a result, many types of flame retardants have been developed. Although halogen-containing flame retardants have been widely used owing to their excellent flame retarding effect, the composites filled with them release toxic gases and smokes once they are heated and fired. So it is difficult to save people or protect costly equipment from being destroyed. Consequently, it is a trend to apply and develop halogen-free flame retardants (HFFR) instead of halogen-containing flame retardants.

Magnesium hydroxide is one kind of widely used halogen-free flame retardant, as well as aluminum hydroxide. Compared with aluminum hydroxide, its processing safety and smoking suppressing capability are better. Generally, the mechanical properties of composites filled with Mg(OH)$_2$ deteriorate with the Mg(OH)$_2$ filling level increasing. To endow polymer/Mg(OH)$_2$ composites with an excellent flame retardancy, for instance, to get to the UL-94 standard V-0 rating, the loading level of Mg(OH)$_2$ is usually required to reach over 60 wt % in total, which easily results in processing difficulties and marked deterioration in mechanical performances.[1] It is very difficult to compromise among the mechanical properties of composites, the modified combustion characteristics, and the processing properties when preparing halogen-free flame retarding composites. Therefore, it is effective and even necessary to use some synergists to improve the flame retarding efficiency of Mg(OH)$_2$ and subsequently reduce its filling amount to keep a balance of processing and mechanical properties. In addition, many researchers showed that when the filling level of Mg(OH)$_2$ is around 55 wt %, the compos-

ites will attain better mechanical properties and appropriate flame retardancy.[2,3]

Silicon additive is a good synergist and it can partially replace $Mg(OH)_2$ in halogen-free flame retarded polymeric materials.[4–6] Many researchers have focused on organic silicon compounds.[7–10] When some of them were used together with $Mg(OH)_2$, it was found that they helped to enhance the dispersion of $Mg(OH)_2$ in the host polymer and improved the flame retardancy of the composite. Further, it was thought that organic silicon compounds accelerated the formation of carbonaceous char on the surface of burning polymer materials so that the material underlying was insulated from the fire outside.[11] Moreover, other silicon additives, such as silicon gel, organically modified layered silicate, talc, and so on, were also found to improve flame retardancy of the composite to some extent.[12,13]

The main purpose of the present work is to investigate the synergistic flame-retardant effect of nine different kinds of silicon additives with $Mg(OH)_2$ in their EVA-based composites under the condition of 55 wt % $Mg(OH)_2$ loading, including organic silicone powder, silicone rubber, and other inorganic silicon additives; and the effects of these silicon additives on the mechanical properties of the composites are also of interest. It is worthy of pointing out that EVA is well used as the matrix of electrical cable insulation covering. Some interesting and important results are found in this work, and the relative mechanisms are suggested.

EXPERIMENTAL

Materials

Ethylene vinyl acetate copolymer (EVA Elvax 460[(R)], with vinyl acetate of 18% and melt flow index of 2.5dg/min) was bought from Dupont Corp. Magnesium hydroxide, with an average particle size of approximately 2.03μm, came from Fine Chemical Factory of BUCT. Nine kinds of silicon additives were used in the present work: organic MMT clay, from Nanocor Company; silicone rubber, from the Second Chemical Factory of Beijing; silicone powder, from Dow Corning Corp.; attapulgite, from Dalian Sanhuan Mining Company, Ltd; pottery clay, hydrated magnesium silicate, and hydrotalcites, from Fine Chemical Factory of BUCT; SiO_2, with an average particle size of approximately 20–40nm. from Nanji Chemical Technology Company, Ltd; and silicious clay (N85), from Hoffmann Mineral GmbH and Co. Germany.

Surface modification of magnesium hydroxide

Surface modification of magnesium hydroxide was the same as the traditional way. The coating of silane coupling agent was carried out by treating a stirred aqueous slurry of magnesium hydroxide at 80°C for an hour. Then, the coated product was filtered, washed, dried, and de-agglomerated in a high-speed mixer before it was used. The level of coupling agent applied is 3.0% of filler.

Preparation of composites

EVA copolymer, magnesium hydroxide, and silicon additives were blended together in the two-roll miller at 130°C in the general procedure. The resulting compound was compressed for 10 min at the 15MPa and 160°C, and then was transferred to another pressing machine and was pressed for 10 min at 15MPa and at the ambient temperature. For different testing, molds with different dimensions were applied. The relative mechanical properties and flame retardance test were conducted.

Mechanical properties measurement

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

Flame retardance testing

Four standard test methods were employed to evaluate the flame retardancy of the composites.

The limiting oxygen index (LOI) is an indicator of the minimum oxygen concentration that is needed to cause the material to combust in an oxygen-nitrogen atmosphere through downward burning of a vertically mounted specimen. A test specimen is required to be 70 to 150 mm in length, 6.5mm in width, and 3mm 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 × 13 × 3mm) is conducted in ambient atmosphere according to 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 lies in 25mm to the left end, and the other lies in 100mm 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 divided by whether fire spreads past 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, there must be a spread

speed through the two marks. If the speed is less than 40mm/min, it is identified as FH-3, but when the fire spreading speed is more than 40 mm/min, the FH-4 rating is reached, which is the worst rating. FH-4 is the worst rating. At least three specimens are needed in each experiment.

For the vertical fire test, the specimen is kept in a vertical position, and the bottom is exposed to the flame. During testing, the samples are burned for 10 s and then removed from the flame. Combustion time of samples and the experimental phenomena are observed. When the fire quenches, the samples are burned for 10 s again and the combustion time is recorded. Seeing about the sum of two-time combustion time after successive application of flame and burning drops from the burning samples, four ratings (FV-0, FV-0, FV-2 and -) are identified according to Chinese state standard GB2408-1996. If the total time is less than 10 s, it is identified as FV-0 rating. When the total time is more than 10 s, but less than 30 s, and the pledget under the sample isn't fired by the drops, it is identified as FV-1 rating. However, if the pledget is fired, the composites can only reach FV-2 rating. Finally, if the total time is more then 30 s, it is identified as "-" rating. FV-0 stands for the best rating, while "-" stands for the worst. The test result is equal to the UL-94 standard. For example, the FV-0 rating corresponds to UL 94 standard V-0 rating. At least five specimens are needed in each experiment.

The cone calorimeter produced by FTT Company of UK uses a truncated conical heater element to irradiate the test specimen at heat fluxes from 10 to 100kW/m^2 to simulate a range of fire intensities. In the present work, cone calorimeter tests are carried out according to ISO 5600, 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 aluminum foil. The rate of heat release (RHR), ignition time (IT), residual mass of the composite, and fire performance index (FPI), defined as the ratio of IT to Peak RHR (FPI = IT/Peak RHR), can be measured through the test at one time.

RESULTS AND DISCUSSION

Effect of silicon additives on mechanical properties of composite

To obtain more practical and high leveled flame retardancy of composites, more Mg(OH)$_2$ or other flame retardant, such as synergists, should be incorporated into the polymer matrix. Since Mg(OH)$_2$ is a very good and important halogen-free flame retardant compared with other flame retardants and synergists, the most practical recipes for halogen-free flame retarded polymer composites choose it as a main component.[3,14] The authors first chose 55 wt % Mg(OH)$_2$ as a basic

TABLE I
Effects of Different Silicone Additives on Mechanical Properties of the Composites

Samples	Yield strength/MPa	Elongation at break/%
Mg(OH)$_2$*	12.1	136
Organic MMT clay	13.1	116
Silicone powder	11.6	156
Silicone rubber	10.4	164
Attapulgite	11.5	96
Pottery clay	12.4	100
Silicious clay	11.1	152
SiO$_2$	11.5	72
Hydrated magnesium Silicate	12.2	140
Hydrotalcites	11.2	76

*The control composite.
EVA/Mg(OH)$_2$ = 100/110; silicon additives: 10 phr.

comparing point, and then introduced more synergists into composites to investigate the synergistic effect with Mg(OH)$_2$. Nine different kinds of silicon additives were chosen to improve the flame retardancy of Mg(OH)$_2$/EVA composites, including organically modified montmorillonite (MMT) clay, organic silicone powder, silicone rubber, attapulgite, pottery clay, silicious clay, precipitated SiO$_2$, hydrated magnesium silicate, and hydrotalcites.[15]

It is well known that the tensile strength or yielding strength and elongation at break of retarded polyolefin composites are two critical mechanical indexes for their application. In Table I, it is clearly and interestingly shown that the incorporation of 10 phr silicon additives has a marked influence on elongation at break of the Mg(OH)$_2$/EVA composite, but little effect on its yield strength, compared with the 10 phr Mg(OH)$_2$. Among the nine silicon additives, organic silicone powder and silicone rubber belong to organic compounds with long organic chains, which are more compatible with the polymer compared with other kinds of silicon additives. Due to the lower surface tension, organic silicone powder tends to weaken the interactions of polymer macromolecules and, therefore, is often used to improve the flow property of the polymer. Linear (i.e., uncrosslinked) silicone rubber, on the other hand, has a very low strength and high elongation at break due to its intrinsic elastomeric polymer characteristics. As a result, the composites filled with these two silicon additives instead of an equal amount of Mg(OH)$_2$ have increased elongation at break and decreased yield strength of composites.

The other seven kinds of silicon additives are inorganic silicon compounds, and all of them possess higher surface tension and consequently have a poor compatibility with polyolefin materials. Their effects on the mechanical properties of the composites mainly depend on the dispersion level and the interfacial

interaction between them and the polymer matrix, which further are affected by their original particle sizes, shapes, surface activity, and surface modification, as well as processing. Generally, elongation at break of the composites will be lowered if inorganic filler is added in at high loading, especially for a crystal polymeric matrix like EVA. In the opinion of the authors, the more irregular the shape is, the stronger the interfacial interaction is[16]; and the poorer the dispersion is, the lower the elongation at break of the composites is. Specifically, compared with the spherical filler, the filler with irregular shape easily causes a stress concentration in the polymer matrix near its edge, tip, and corner; the stronger interfacial interaction tends to decrease the elongation at break of composites through the stronger restriction to deformation of macromolecule chains; the poor dispersion of the filler in the polymer matrix generally results in the decrease of tensile strength and elongation at break due to the defect effect and stress concentration effect. Since the emphasis of this article is on the synergistic effect in flame retardancy of silicon additives with $Mg(OH)_2$, and distinguishing the dispersion of different fillers is difficult due to the close morphology of different fillers and the high loading, detailed research on the morphology and interfacial interaction of all silicon additive filled composites was not conducted.

However, based on the effects of silicone rubber and organic silicone powder, the authors suggest that forming a lower surface tension organic layer to cover the surface of the inorganic silicon filler will benefit the elongation at break of the composites.

In Table I, it can also be found that yield strength of the composites filled with organically modified MMT goes up a little. This may be due to the partial exfoliation and intercalation of MMT in the matrix, which will greatly limit the movement of the polymeric chain and provide an evident reinforcement.

Effects of silicon additives on flame retardancy of composites

LOI test, horizontal fire test, and vertical fire test

Fire tests, including the LOI test, horizontal fire test, and vertical fire test, are often used to evaluate flame retardancy of the composites. Although the limiting oxygen index (LOI) test cannot reflect the actual combustion situation of a material in fire, the data from the test can be well repeated and give a primary and relative comparison of the flammability of all kinds of material. So it is still employed to estimate flame retardancy of composites in this study.

As shown in Table II, compared with the composite only filled with $Mg(OH)_2$, the four composites filled with organic silicone powder, silicone rubber, pottery clay, or hydrotalcites, respectively, present a higher

TABLE II
Effect of Silicon Additives on LOI, Horizontal Fire and Vertical Fire Rating of the Composites

Samples	LOI%	Horizontal fire rating	Vertical fire rating
$Mg(OH)_2$	36.8	FH-3—23.8mm/min	"-"
Organic MMT clay	35.2	FH-1	FV-1
Silicone powder	40.5	FH-3—20.1mm/min	"-"
Silicone rubber	42.8	FH-1	FV-1
Attapulgite	36.6	FH-3—24.7mm/min	"-"
Pottery clay	38.6	FH-3—19.8mm/min	"-"
Silicious clay	33.7	FH-3—20.6mm/min	FV-1
SiO_2	34.8	FH-3—18.2 mm/min	FV-1
Hydrated magnesium silicate	36.2	FH-3—18.1 mm/min	"-"
Hydrotalcites	39.9	FH-3—17.8 mm/min	"-"

LOI value; while the composites filled with organic MMT, silicious clay, or SiO_2 exhibit a slightly decreased LOI value; and the other composites showed no change. On the other hand, almost all the composites filled with silicon additives burn more slowly in the horizontal fire test except the composite filled with attapulgite. Moreover, the composites containing organic MMT clay or silicone rubber show an FH-1 rating in the horizontal fire test, which is much better than the other composites. As for the vertical fire test, four kinds of silicon additives, that is, organic MMT, silicone rubber, silicious clay, and precipitated SiO_2, effectively improve the combustion resisting level of the composites, specifically, from "-" rating to FV-1 rating.

According to these results, there are two phenomena that deserve some attention. One is the result that the LOI experiment, horizontal fire test, and vertical fire test do not parallel and even contradict each other. Therefore, it is suggested that these three tests should be used together to assess flame retardancy of the composites. Another one is that the incorporation of organic MMT clay or silicon rubber indeed redounds to retard the combustion of the composites since the results of three kinds of experiments consistently illustrate the obvious positive effect, while the other seven kinds of silicon additives more or less improve the flame retardancy of the $Mg(OH)_2$/EVA composite, or at least do not deteriorate flame retardancy.

Cone calorimeter test

The cone calorimeter test has been shown to provide useful data that correlate well with those from a full-scale fire test.[17] Ignition time (IT) is taken as the time required for the entire surface of the sample to burn. The longer IT is, the more difficult the material is fired. Peak rate of heat release (Peak RHR) is taken as the maximal value of the curve of the heat release rate
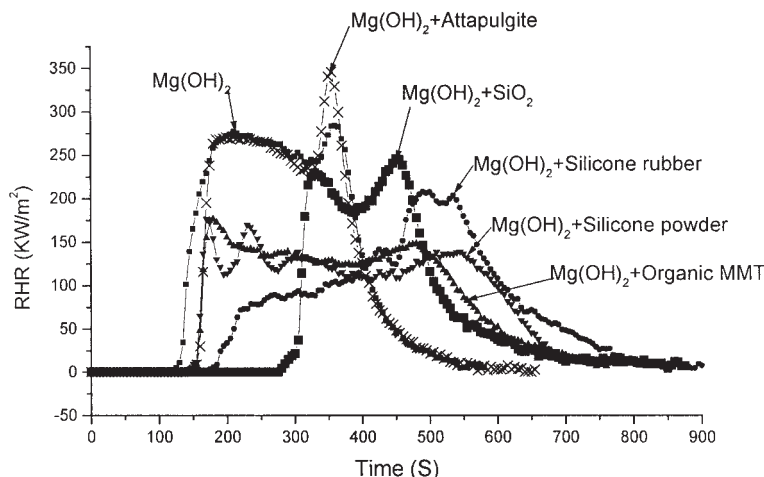
Figure 1 The relation between the RHR value of the composites and time.

versus time, indicating the extent of fire spread. Generally, the lower the Peak RHR of a burning material is, the better flame retardancy it has. Fire performance index (FPI) is defined as the ratio of IT to Peak RHR (FPI = IT/Peak RHR). It has been suggested that this parameter relates the time to flashover (or the time available for people to escape) in a full-scale fire situation.[18]

The RHR versus time curve of five chosen composites is presented in Figure 1; while IT, Peak RHR, and FPI of the composites are summarized in Table III. Obviously, compared with the control composites, all the composites filled with silicon additives possess longer IT. The existence of organic MMT, silicone powder, or silicone rubber in EVA/Mg(OH)$_2$ composites dramatically decrease the Peak RHR and prominently increase the FPI value and IT value. It is thought that burnable volatiles resulted from the degradation of the polymer matrix reduce and char layers is more easily formed to prevent burning due to their presence. Based on Figure 1 and Table III, it seems true that the composites with SiO$_2$ may possess the best flame retardancy due to the longest IT and the highest FPI value but exhibits higher peak RHR value, the

most important parameter to evaluate the flame retardancy of composites. However, the specific reason is not very clear, and future detailed research needs to be conducted. From the data of composites filled with silicone rubber and SiO$_2$, we can see that there is some relationship between the vertical fire test rating and the IT value. Certainly, the composite with attapulgite possesses poor flame retardancy although its IT increases a little. Summarily, we can reach the conclusion that silicon fillers have good synergistic effect with Mg(OH)$_2$ on the flame retardancy of the composites, except for attapulgite. This result is almost consistent with that drawn by the combination of the LOI, horizontal fire test, and vertical fire test.

Figure 2 presents the mass loss of the composite versus time curve. The weight of composites filled with silicon additives drops with time slower than the control composites except attapulgite. The composites with silicone rubber exhibit the lowest decreasing rate and highest mass residue, while the composites with attapulgite give the least residue and fastest decomposing rate close to the control composites. The composites filled with organic silicon powder or organic MMT have a little bit higher residue than that of the composite filled with SiO$_2$ after about 310 s. But before 300 s, it is reversed. This behavior, combined with its much longer IT, may be the reason why the composites filled with SiO$_2$ can keep an FV-1 rating in the vertical fire test. The results demonstrated by the relation between the residue mass of the composites and time are basically consistent with that by the relation between RHR values of the composites and time.

Based on all the discussion above, apparently, the composites with silicone rubber exhibit a good balance between mechanical properties and overall flame retardancy, while the attapulgite has little synergistic effect with Mg(OH)$_2$.

TABLE III
Effect of Silicon Additives on IT, Peak RHR, and FPI of EVA/Mg(OH)$_2$ blends

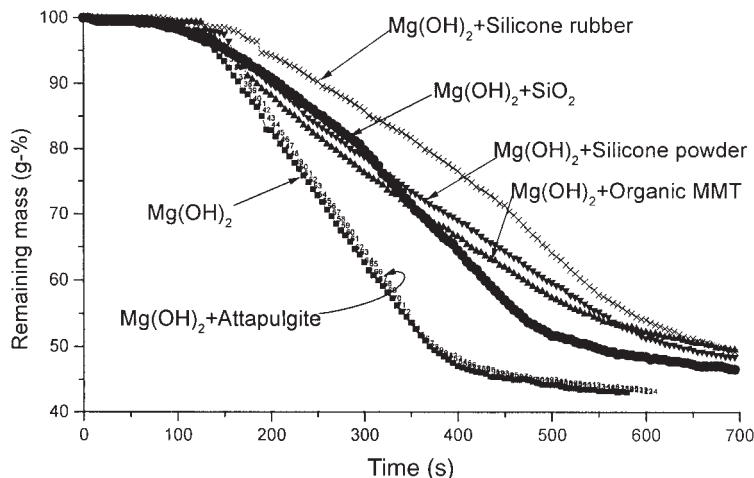| Samples	IT/s	Peak RHR/ kW/m^2	FPI
Mg(OH)$_2$	126	283.365	0.44
Organic MMT clay	150	172.455	0.87
Silicone powder	148	176.301	0.84
Silicone rubber	175	207.619	0.84
Attapulgite	152	345.193	0.44
SiO$_2$	298	245.497	1.21

Figure 2 The relation between the residue mass of the composites and time during the cone calorimeter test.

Effect of the loading of silicone rubber on mechanical properties

Since silicone rubber obviously favors the elongation at break and comprehensive flame retardancy but decreases the tensile strength of composites filled with it, it is desirable to investigate the loading of silicone rubber on the mechanical properties of the composites.

Figure 3 presents the effect of filling levels of silicone rubber on the mechanical properties of the composites. Surprisingly, after 10 phr loading, the elongation at break of the composites doesn't continue rising; while after 20 phr loading, the tensile strength of the composite doesn't decrease any more. Silicone rubber is extremely harmful to the comprehensive mecha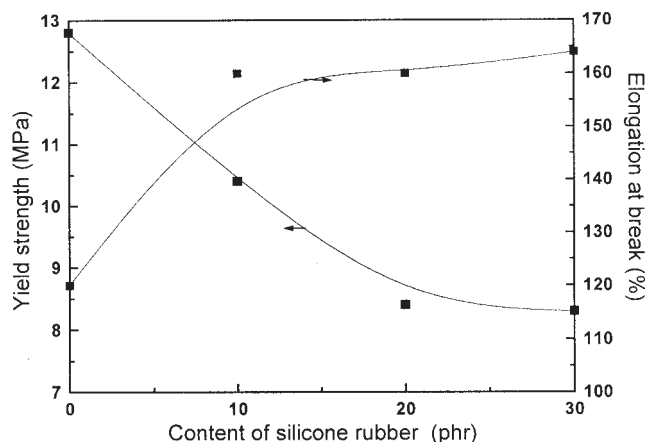nical property of plastic polymers, so its loading must be limited to a small amount. Therefore, to keep a balance between elongation at break and yield strength for practical application, the loading level of silicone rubber should not be more than 10 phr.

CONCLUSIONS

Different silicon additives have different synergistic effects with $Mg(OH)_2$ on the flame retardancy of an EVA matrix, and also produce different influences on the mechanical properties of the composites. Incorporation of organic MMT clay or silicon rubber is indeed in favor of retarding the combustion of the composites, while the other seven kinds of silicon additives more or less improve the flame retardancy of $Mg(OH)_2$/EVA composites or at least don't deteriorate flame retardancy. Only the composite filled with silicone rubber can achieve a good balance between mechanical properties and flame retardancy.

Figure 3 Mechanical properties of the composites with different content of silicone rubber. (EVA/$Mg(OH)_2$ = 100/150).

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