

Influence of Fumed Silica on the Flame-Retardant Properties of Ethylene Vinyl Acetate/Aluminum Hydroxide Composites

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Received 12 December 2009; accepted 4 August 2010

DOI 10.1002/app.33126

Published online 22 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The flammability and synergistic flame-retardant effects of fumed silica (SiO_2) in ethylene vinyl acetate (EVA)/aluminum hydroxide (ATH) blends were studied with limiting oxygen index measurements, UL 94 testing, cone calorimeter testing (CONE), and thermogravimetric analysis (TGA). The results show that the addition of a given amount of fumed SiO_2 can apparently improve UL 94 rating. The CONE data indicated that the addition

of fumed SiO_2 greatly reduced the heat release rate. The TGA data showed that this synergistic flame-retardant mechanism of fumed SiO_2 in the EVA/ATH materials was mainly due to the physical process. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1285–1289, 2011

Key words: additives; composites; flame retardance; thermogravimetric analysis (TGA)

INTRODUCTION

Ethylene vinyl acetate (EVA) copolymers with different acetate contents are used extensively in many fields, especially in the cable industry as excellent insulating materials with their good physical and mechanical properties.¹ However, EVA copolymers are particularly flammable and emit a large amount of smoke while burning; this restricts their practical applications. Therefore, it is very important to improve the flame retardance in applications of EVA materials.

In recent years, the development of halogen-free flame-retardant polymeric materials has become a potential trend. Many investigations have demonstrated that aluminum hydroxide (ATH) is a non-toxic and smoke-suppressing halogen-free flame-retardant additive in flame-retardant polymeric materials. However, ATH has an essential disadvantage, that a greater than 60% ATH loading is required to meet flame-retardant properties; this could be detrimental to the mechanical properties of flame-retardant materials. Many investigations have been done on ATH incorporated with other halogen-free flame-retardant synergistic agents^{2–10} to enhance

flame resistance and decrease the high loading level of ATH. Ramazani et al.³ reported the synergistic effect of zinc borate with ATH in the flame retardance and physicomaterial properties of propylene composites. Schartel et al.⁶ studied the flame-retardant effect of phosphonium-modified layered silicate with ATH in epoxy resin nanocomposites. Beyer¹⁰ investigated the synergistic flame-retardant effect between ATH and modified layered silicate (montmorillonite) EVA copolymer composites synthesized by a melt-blending process.

Fumed silica (SiO_2) is usually used as an enhancing agent in thermoplastic polymers to increase their mechanical properties, such as the tensile strength and toughness. Kashiwagi et al.¹¹ reported the flame-retardant mechanism of SiO_2 in polypropylene blends. Fu and Qu¹² studied the synergistic flame-retardant mechanism of fumed SiO_2 in EVA/magnesium hydroxide blends. Nelson and coworkers^{13,14} investigated the impact of fumed nano- SiO_2 on the decomposition process of polymer nanocomposites and elucidated the relationships between the decomposition process and fire behavior. As far as we are aware, however, no work has been done on the synergistic effect of fumed SiO_2 in EVA/ATH blends. This study was mainly devoted to the investigation of the flammability and synergistic mechanism of fumed SiO_2 with ATH in EVA/ATH blends with limiting oxygen index (LOI) testing, UL 94 testing, cone calorimeter testing (CONE), and thermogravimetric analysis (TGA).

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Contract grant sponsor: Outstanding Young Scientist Research Award Fund of Shandong Province; contract grant number: BS2009CL015.

TABLE I
Results of LOI and UL 94 Testing of the EVA/ATH/SiO₂
Compositions

Sample code	EVA (%)	ATH (%)	SiO ₂ (%)	LOI	UL-94
EVA-0	45.0	55.0	—	35.2 ± 0.2	No rating, dripping
EVA-1	45.0	53.0	2.0	33.2 ± 0.3	No rating, no dripping
EVA-2	45.0	50.0	5.0	32.6 ± 0.2	No rating, no dripping
EVA-3	45.0	47.0	8.0	32.5 ± 0.3	No rating, no dripping
EVA-4	45.0	45.0	10.0	32.3 ± 0.2	No rating, no dripping

EXPERIMENTAL

Materials

EVA with 28 wt % vinyl acetate was bought from Sumitomo Chemical Co., Ltd. (Japan). ATH (Martin Corp., Germany), with a decomposition temperature of about 220°C and an average particle size of about 2 μm, was activated with fatty acids. Fumed SiO₂ (Degussa Co., Germany), with a specific surface area of 150 m²/g and an average particle size of 14 nm, was modified with the silane coupling agent KH-550. The formulations are given in Table I.

Sample preparation

All of the samples were prepared with a mixer with the same procedures. EVA was added to the mixer with a rotational speed of 20 rpm at 120°C. ATH filler and SiO₂ were added after the EVA polymer was melted, and the mixing was carried out at 50 rpm for 10 min. The obtained composites were finally compression-molded at 120°C for 10 min under 10 MPa into sheets of suitable thickness. Samples for testing were cut from the compressed sheets according to the standards mentioned in the following section.

Measurements

LOI

LOI was measured according to ASTM D 2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China). The specimens used for the test had dimensions of 100 × 6.5 × 3 mm³.

UL 94 testing

Vertical testing was carried out on a CFZ-2 instrument (Jiangning Analysis Instrument Co.) according to the UL 94 test standard. The specimens used had dimensions of 130 × 13 × 3 mm³.

CONE

CONE (Stanton Redcroft, United Kingdom) was performed according to ISO 5660 standard procedures. Each specimen, with dimensions of 100 × 100 × 4 mm³, was wrapped in aluminum foil and exposed horizontally to an external heat flux of 50 kW/m².

TGA

TGA was carried out in nitrogen on a STA 409C TGA apparatus (Netzsch Co., Germany) at a heating rate of 10°C/min. About 5 mg of sample, placed in a TGA pan, was heated from ambient temperature to 700°C.

RESULTS AND DISCUSSION

LOI and UL 94 testing

Table I presents the LOI values and UL 94 testing results of the flame-retarded EVA composites. The LOI values of the composites decreased slightly with increasing SiO₂ (EVA-0 to EVA-4). This phenomenon could be explained by the fact that there was a decrease in the loading of ATH. When the flame-retardant samples were heated, ATH decomposed to form water, which could dilute the flammable gases and oxygen and decrease the temperature.

The results obtained from the UL 94 tests show that SiO₂ improved the antidripping properties of the flame-retardant composites, although all samples did not pass the UL 94 test. Sample EVA-0, without SiO₂, dripped greatly in the UL 94 test. However, the samples with SiO₂ had no dripping phenomena in the process of the UL 94 test. The addition of fumed SiO₂ also increased the polymer melting viscosity, which favored the UL 94 test.^{12,15}

CONE

Heat release rate (HRR)

Although the LOI and UL 94 tests are widely used to evaluate the flame retardation of materials, especially for screening flame-retarded formulations of polymers, CONE provides a wealth of information on the combustion behavior.¹⁶ Some CONE results have been found to correlate well with those obtained from large-scale fire tests and can be used to predict the behavior of materials in real fires.¹⁷ For example, the peak heat release rate (PHRR) is an important parameter, which can be used to evaluate the intensity of fires.¹⁸

The fire performance of flame-retardant EVA composites was tested with CONE. In CONE, the data of thermally thin samples cannot be compared with that of thermally thick samples. Pure EVA is thermally thin at a fixed thickness (4 mm), and thus, the

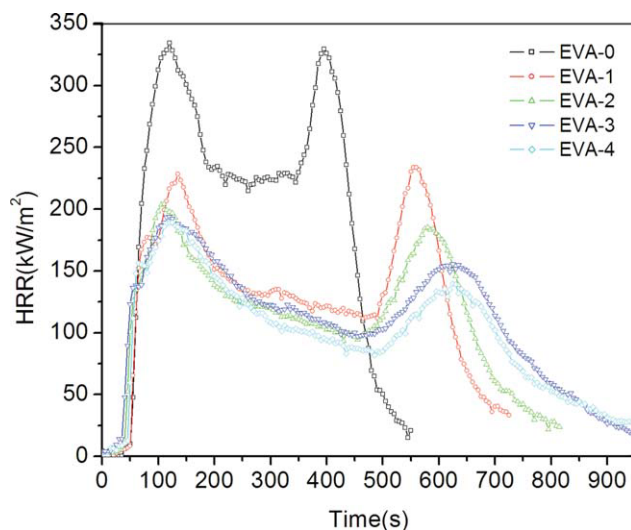


Figure 1 HRR curves of EVA/ATH/SiO₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONE results of pure EVA are not shown in this article.

Figure 1 shows the HRR curves of the flame-retardant EVA composites obtained from CONE, and the correlated data are listed in Table II. As shown in Figure 1, EVA-0 burns fast after ignition. A sharp HRR curve with two peaks appeared in the range 80–500 s, whereas EVA-1 with 2% SiO₂ showed a dramatic decline in the HRR curve, and its combustion was prolonged to 650 s from the 500 s of the control EVA-0. With the addition of SiO₂, the burning time was prolonged. In the sample with 10% SiO₂ addition, the combustion time was prolonged to 860 s. The PHRR decreased with the addition of SiO₂; this indicated that SiO₂ contributed to the decrease in the flammability of the materials. When the HRR curve of EVA-1 was compared with that of EVA-0, we observed that the incorporation of 2% SiO₂ into the EVA/ATH blends caused a decrease in HRR. To our surprise, a further reduction in HRR (the EVA-2 to EVA-4 curves) was obtained when the same amount of ATH premixed with SiO₂ was increased. When the SiO₂ content was raised to 10%, the PHRR decreased to 189.3 kW/m² (EVA-4) from 334.1 kW/m² (EVA-0). SiO₂ did not act as a component that accelerated the burning of EVA but as a synergistic retardant of ATH to reduce the burning rate of EVA. EVA-4 showed the lowest HRR, which indicated that the incorporation of SiO₂ into the ATH flame-retardant system helped to improve the flame retardancy of EVA. The HRR of all of the samples showed two separate peaks during burning; this indicated the gradual burning of the specimen through the thickness after the initial charred layers were formed. This combustion feature of multiple HRR peaks was also reported by Fu.¹² Furthermore, the second peak of HRR decreased

more obviously than the first one with the addition of SiO₂. It is important to determine the reason that the SiO₂ improved the flame retardancy of the EVA/ATH composites.

Fumed SiO₂ is usually considered to be an inert additive in flame-retardant systems. However, the previous data indicated that the flame-retardant performances of the EVA/ATH blends were enhanced by the partial substitution of ATH with SiO₂. The mechanism of the reduction in HRR was mainly due to the physical processes instead of chemical process in the condensed phase, as reported in the literature.^{11,12} Fumed SiO₂ has a large surface area and low density and tends to accumulate near the regressing sample surface without sinking through the polymer melt layer during the gasification/burning process. The accumulated SiO₂ consequently formed a charred layer by collaborating with ATH, which acted as a heat insulation barrier. This charred layer prevented heat transfer and the transportation of degraded products between the melting polymer and the surface; it, thus, reduced HRR and related parameters.

Mass

Figure 2 shows the mass loss curves from CONE. During combustion, a compact char may occur on the surface of the burning sample. Also, the compact char can be seen as a physical protective barrier. The physical process of the char can act as a protective barrier in addition to the compact shield and can, thus, limit the oxygen diffusion to the substrate. In this study, the compact char residue of EVA-1 to EVA-4 formed on the surface of the sample. Fumed SiO₂ tended to accumulate near the surface without sinking through the polymer melt layer during the gasification/burning process.^{19,20} The accumulated SiO₂ consequently formed a charred layer by collaboration with ATH, which acted as a heat insulation barrier.

Total heat release (THR)

Figure 3 presents the THR for all of the samples. The slope of the THR curve was assumed to be representative of fire spread.²¹ As shown in Figure 3, THR

TABLE II
CONE Data

Sample code	PHRR (kW/m ²)	THR (MJ/m ²)	Time to ignition (s)	Time to PHRR (s)
EVA-0	334.1 ± 10	106.7 ± 8	43 ± 1	120 ± 2
EVA-1	228.2 ± 5	93.6 ± 7	44 ± 1	135 ± 2
EVA-2	204.3 ± 5	91.6 ± 7	36 ± 2	110 ± 1
EVA-3	193.7 ± 4	103.5 ± 9	30 ± 2	120 ± 3
EVA-4	189.3 ± 5	93.2 ± 6	41 ± 1	125 ± 2

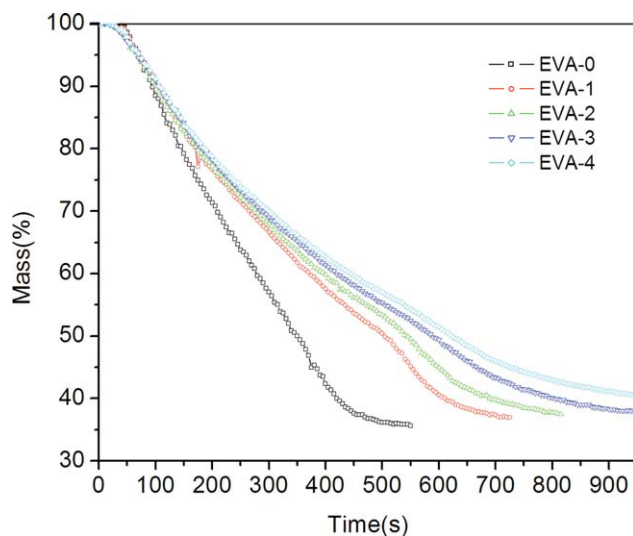


Figure 2 Mass curves of EVA/ATH/SiO₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased with the addition of SiO₂. It is very clear that the flame spread of the samples (EVA-0 to EVA-4) decreased, and the flame spread of EVA-4 was comparatively the lowest. This phenomena could also be explained by the fact that the migration of SiO₂ onto the surface of the sample, which could have been a barrier from the flame zone to the underlying materials, restrained the flammable gases to the flame zone.¹² We also suggest that there was a synergistic effect of flame retardance between ATH and SiO₂.

TGA

Thermogravimetric curves for EVA and its composites are shown in Figure 4. Pure EVA underwent two

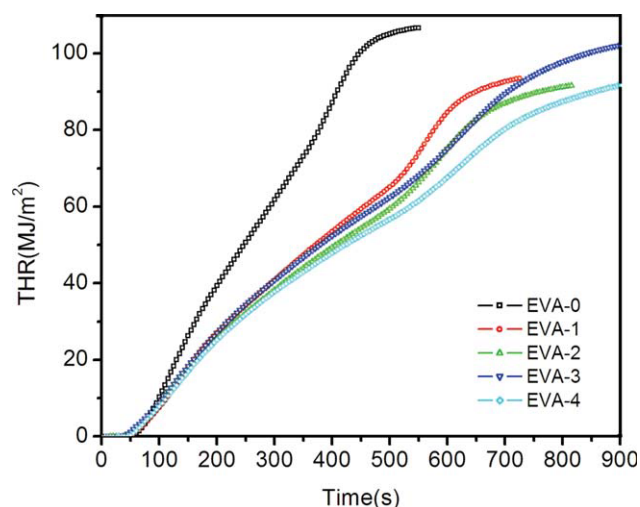


Figure 3 THR curves of EVA/ATH/SiO₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation steps, as shown in Figure 4. The first decomposition step was due to the loss of acetic acid, and the second involved random chain scission of the remaining material, which formed unsaturated vapor species, such as butene and ethylene.^{22,23} As shown in Figure 4, the incorporation of ATH lowered the decomposition rate of the second step but accelerated the loss of acetic acid. The —OH groups on the fillers could assist β -hydrogen leaving.²⁴ That is, the loss of acetic acid could be catalyzed by ATH. Polymer/clay nanocomposites have been studied widely,^{25,26} and Costache²³ reported a similar catalyzing function of —OH groups on the edges of montmorillonite layers. To our surprise, ternary composites, which contain both SiO₂ and ATH, showed high thermal stability at high temperatures. This should have been the main reason that the ternary composites had better flame retardancy than EVA/ATH had at the same ATH loading. This result correlated well with the CONE results. The analogous weight loss curves of the flame-retardant composites also reflected the synergistic mechanism by SiO₂, which was mainly due to the physical process in the condensed phase.²⁷

CONCLUSIONS

SiO₂ had a synergistic effect on the flame retardancy with ATH in EVA. The synergistic mechanism of SiO₂ with ATH was mainly due to its physical effect in the condensed phase, as revealed by thermogravimetric data showing that the addition of SiO₂ led to the formation of a more thermally stable barrier, and the residual char of the system with SiO₂ was higher than that of the system without SiO₂. A more compact barrier produced by SiO₂ collaborating with ATH consequently led to decreases in HRR, mass, and THR, as detected by CONE.

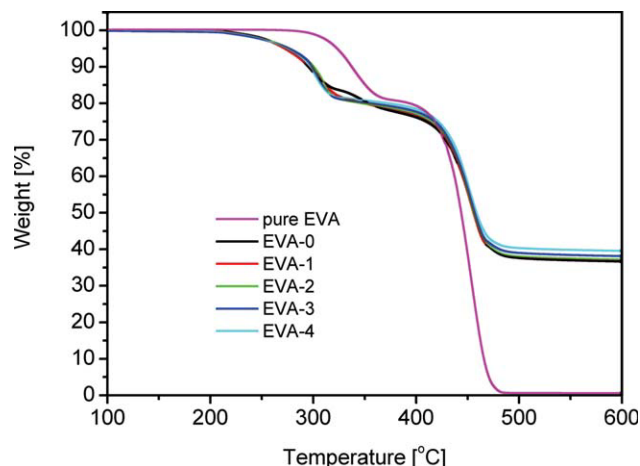


Figure 4 TGA curves of EVA/ATH/SiO₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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