Effect of Stearic Acid and Epoxy Silane on the Structure and Flame-Retardant Properties of Magnesium Hydroxide/ Ethylene Vinyl Acetate Copolymer/Very Low Density Polyethylene Composites

He Rong, Xu Man, Zhong Lisheng, Xie Darong, Tuo Xinlu, Wu Jingxuan

State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, China

ABSTRACT: Ethylene vinyl acetate copolymer (EVA) and very low density polyethylene (VLDPE) blends filled with magnesium hydroxide (MH) were compounded by melt blending. Two kinds of surface treatments were used in this research, including stearic acid and epoxy silane. The composites were analyzed by scanning electron microscopy, thermogravimetric analysis, differential scanning calorimetry, limiting oxygen index (LOI), and cone calorimeter testing to study the effects of stearic acid and epoxy silane on the structure and flame-retardant properties of the MH/EVA/VLDPE composites. The results indicate that stearic acid and epoxy silane had different effects on the interfacial interaction of the MH/EVA/VLDPE composites; this made a difference in the condensed phase of the physical process. Thus, the composites with different surface treatments had different flammability characteristics, thermal degradation processes, char yields, and LOIs. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: composites; flame retardance; structure; surface modification; thermal properties

INTRODUCTION

In recent years, the ecological green movement has paid extensive attention to the field of flame-retardant (FR) materials; thus, halogen-free FR materials have been widely researched and used. For example, inorganic fillers, such as alumina trihydrate and magnesium hydroxide (MH), are widely used as FRs with low smoke, offering low toxicity and low corrosion.[1,2] However, the FR efficiencies of MH/polymer or alumina trihydrate/polymer composites are very low. To achieve the required flame retardancy, high loadings of about 60 wt % MH are needed; this would lead to poor mechanical performance in the composites and difficult processing. To resolve these problems, researchers worldwide have focused on MH/polymer composites and have found that the surface treatment of MH and the addition of compatibilizers can be effective methods.[3–6] The surface modifiers are able to connect the two phases to improve the dispersion of fillers in the polymer matrix. Maleic anhydride grafted polymers based on polypropylene or polyethylene (PE) are effective coupling agents between polymers and a variety of inorganic fillers, and they provide significant property enhancements.[3]

Previous studies have indicated that some surface treatments of MH improve the flame retardancy but worsen other properties of the composites. For example, Wang and Qu[7] found that the presence of stearic acid improved the breaking elongation a lot but decreased the tensile strength and flame retardancy in MH/PE composite. In addition, stearic acid decreased the melt viscosity and improved the processing performance. In this investigation, we studied the effects of surface treatments on the flame retardancy of MH/ethylene vinyl acetate copolymer (EVA)/very low density polyethylene (VLDPE) composites and the cooperative effect of compatibilizers and surface treatments on the composites.

A study by Vaughan et al.[8] showed that the use of EVA/PE as the matrix could improve the dispersion of fillers. So, in this investigation, EVA with four different vinyl acetate (VA) contents and VLDPE was used as the matrix. FR MH was treated by stearic acid or epoxy silane, and maleic anhydride grafted polyethylene (PE-g-MAH) acted as the compatibilizer, so we could study the effect of stearic acid and epoxy silane on the structure and FR properties of the MH/EVA/VLDPE composites.

EXPERIMENTAL

Materials

The EVAs with four different VA contents were designated as follows: EVA[12] (containing 12 wt % VA,

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Correspondence to: Z. Lisheng (lszhong@mail.xjtu.edu.cn).

TABLE I
Compositions of the FR Samples

Sample number	EVA	Composition (wt %)		
		EVA/VLDPE	MH	PE-g-MAH
A1	EVA[12]	52.6	47.4	0.0
A2		38.5	57.7	3.8
A3	EVA[19]	51.3	46.1	2.6
A4		37.7	56.6	5.7
A5	EVA[28]	50.0	45.0	5.0
A6		40.0	60.0	0.0
A7	EVA[40]	48.8	43.9	7.3
A8		39.2	58.8	2.0
B1	EVA[12]	52.6	47.4	0.0
B2		38.5	57.7	3.8
B3	EVA[19]	51.3	46.1	2.6
B4		37.7	56.6	5.7
B5	EVA[28]	50.0	45.0	5.0
B6		40.0	60.0	0.0
B7	EVA[40]	48.8	43.9	7.3
B8		39.2	58.8	2.0

Melting Index (MI) = 3 g/10 min), EVA[19] (containing 19 wt % VA, MI = 0.65 g/10 min), and EVA[28] (containing 28 wt % VA, MI = 3 g/10min). All were produced by Exxon Mobil Corp. EVA[40] (containing 40 wt % VA, MI = 3 g/10 min) was produced by DuPont. VLDPE (MI = 0.9 g/10 min) was produced by Clearflex FGB0. MH, with an average particle size of about 10 μm and a surface area of 7.00m^2/g, was produced by Nuova Sima Srl. Epoxy silane (silan GLYMO DL70) was produced by Lehmann Voss Co. Stearic acid was produced by Uniqema. PE-g-MAH (MI = 1.2 g/10 min) was produced by Orevac.

Sample preparation

MH was treated by epoxy silane and stearic acid separately via a high-speed blender. Then, the raw materials were compounded on a rheometer (HAAKE RC-90, Germany) at 170°C and then were put in a double-roll mixer at 120°C for 5 min. The mixtures were hot-pressed into sheets of about 1 mm at 180°C via a plate vulcanizer. The prepared samples are listed in Table I. The polymeric matrix of EVA and VLDPE were in a ratio of 9 : 1. Samples A1–A8 were treated by epoxy silane, and samples B1–B8 were treated by stearic acid. The surface treatments and MH were in a ratio of 1 : 100. The MH content of each sample marked by an odd number was 90 phr, and the MH content of each of the other samples was 150 phr.

Characterization

Scanning electron microscopy (SEM)

The samples were cooled by liquid nitrogen and then broken. The fracture surfaces, coated with a conductive gold layer, were observed on a model S-2700 scanning electron microscope (Hitachi, Japan).

Thermal analysis

The thermogravimetric analysis (TGA) data were obtained with an SDTA851 thermogravimetric analyzer (Mettler Toledo, Switzerland) at a heating rate of 10°C/min from 25 to 600°C under a nitrogen atmosphere. Differential scanning calorimetry (DSC) data were obtained using a 822^e differential scanning calorimeter (Switzerland) at a heating rate of 10°C/min from 20 to 500°C in air.

Limiting oxygen index (LOI)

The LOI values were undertaken within samples with dimensions of $120 \times 6.5 \times 3 \text{ mm}^3$ with an HC-2 type instrument (Nanjing Analytical Instrument Factory Co., Ltd., China) according to ISO 4589-1996.

Cone calorimeter testing (CCT)

Cone calorimeter tests were carried out according to the procedures indicated in the ISO 5660 standard with an FTT cone calorimeter (Fire Testing Technology, Ltd., United Kingdom). Square specimens ($100 \times 100 \times 4 \text{ mm}^3$) were irradiated with a heat flux of 50 kW/m. Several combustion parameters were determined: the heat release rate (HRR) as a function of time; the peak heat release rate (PHRR), which is considered as the parameter that best expresses the maximum intensity of a fire and indicates the rate and extent of fire spread; the time to ignition (TTI); and the fire performance index (FPI), which is defined as the ratio of TTI to PHRR and is a parameter related to the time available to escape in a real fire situation. The mass loss rate (MLR) was also investigated.

RESULTS AND DISCUSSION

Effect of the surface treatments on the morphological structures of the MH/EVA/VLDPE composites

It is generally known that surface treatments can decrease the surface energy of inorganic fillers and improve the dispersion of an inorganic filler in a polymer matrix. The mechanical performance and flame retardancy of the composites largely depend on the dispersion of fillers in the polymer matrix and the adhesion between the filler particles and polymer matrix. Different surface treatments obviously affect interactions between fillers and the polymer matrix. In this study, epoxy silane [$CH_2OCH-CH_2O(CH_2)_3Si(OCH_3)_3$], which was reaction type, and stearic acid ($CH_3(CH_2)_{16}COOH$), which was alkyl carboxylic type, were used for the surface treatments. The reactions between the surface treatments and fillers is shown in Scheme 1(a,b). The
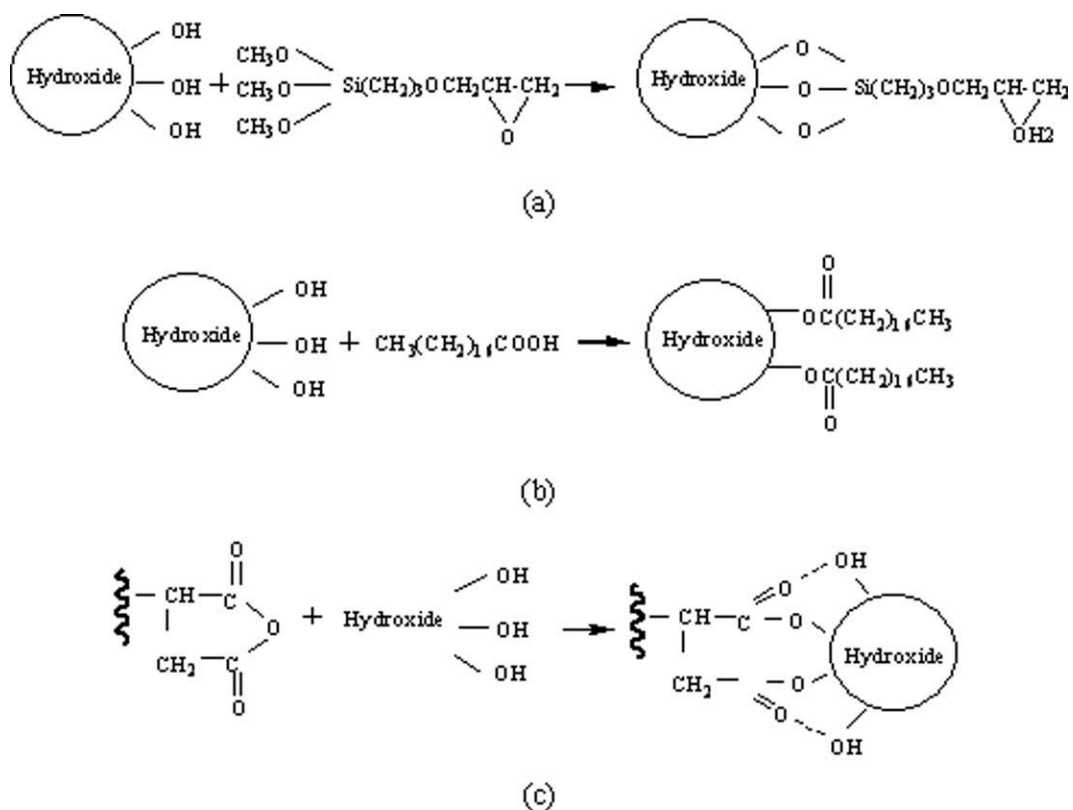
Scheme 1 Reactions between the (a) epoxy silane and fillers, (b) stearic acid and fillers, and (c) coupling agent and fillers.
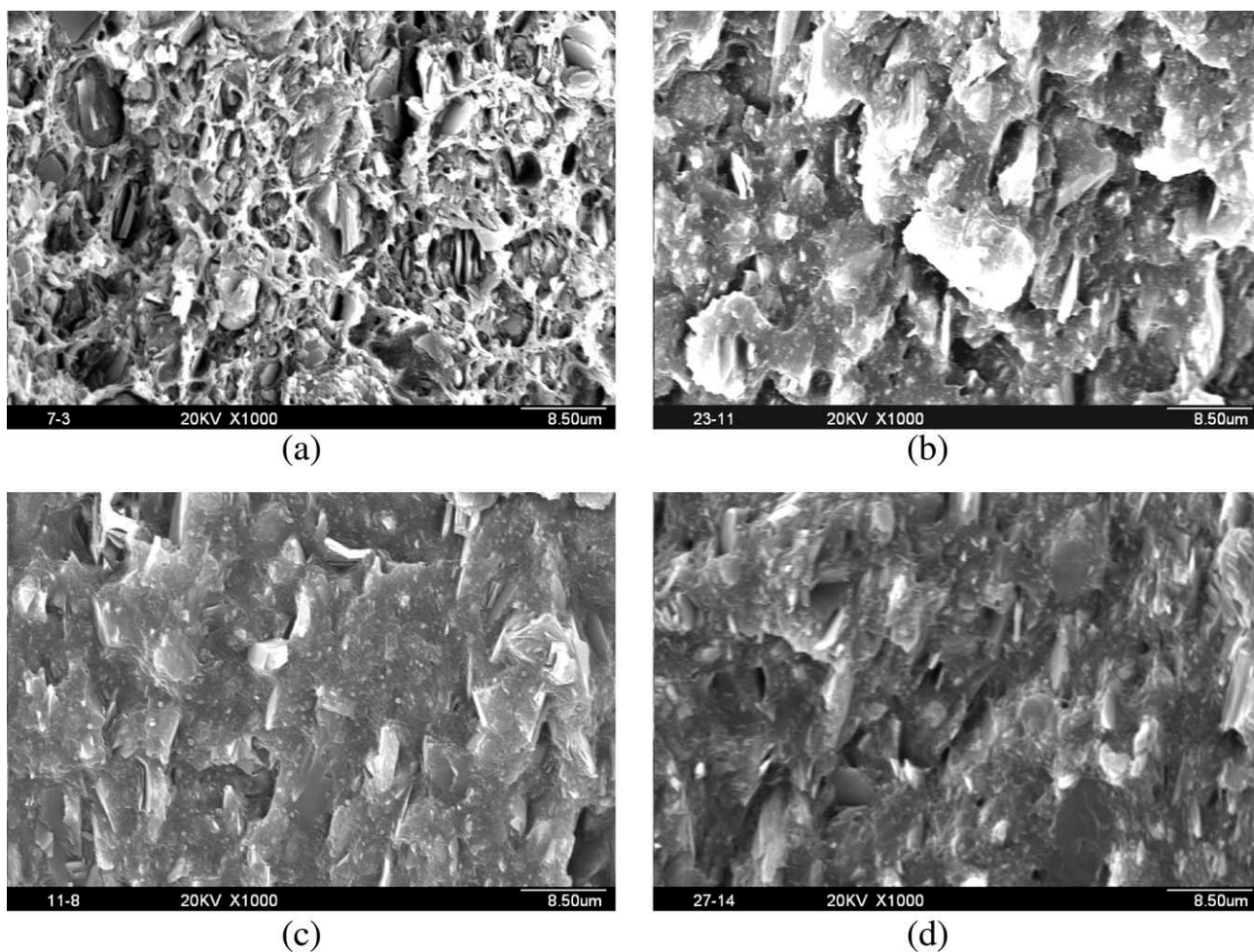

Figure 1 SEM micrographs of different FR samples: (a) A4, (b) B4, (c) A6, and (d) B6.

reaction between the coupling agent and fillers is shown in Scheme 1(c).

SEM micrographs of fracture surfaces offer bulk information on the dispersion of fillers in a polymer matrix and the adhesion between fillers and the polymer matrix. Figure 1 shows the SEM micrographs of the fracture surfaces of several samples. Figure 1(a,b) shows the fracture surfaces of sample A4 and B4, respectively, which had the same compositions and different surface-treatment agents. The fracture surface of sample A4 [Fig. 1(c)] was quite rough and looked like knitting. Sample A4 was modified by epoxy silane. The reaction mechanism is shown in Scheme 1(a). The epoxy group reacted with PE-g-MAH in a ring-opening reaction, which led to stable chemical bonding between the fillers and the polymer matrix. Compared with that in Figure 1(c), the micrograph in Figure 1(d) shows that the fillers were surrounded by the matrix but did not look like knitting. This was because stearic acid was used as a surface-treatment agent in sample B4. The reaction mechanism is shown in Scheme 1(b). The short-chain alkyl of the stearic acid molecule acted as a lubricant of the matrix, softening the phase interface.[6] The long-chain alkyl of PE-g-MAH, by which MH was coated, was entangled with the polymer molecule chains, so the connections between the fillers and the matrix in sample B4 were not as strong as those in sample A4.

Figure 1(c,d) shows the fracture surfaces of samples A6 and B6, which had the same compositions and different surface-treatment agents. The fracture surfaces of samples A6 and B6 were similar. It is worth noting that both samples A6 and B6 did not have PE-g-MAH, so the connections between fillers and the matrix in samples A6 and B6 were weak. Also, the high VA content of 28% in samples A6 and B6 may have affected the dispersion of fillers in the polymer matrix.

Effect of the surface treatments on the thermal degradation behaviors of the MH/EVA/VLDPE composites

The thermal degradation behaviors of FR composites could be evaluated by TGA and DSC. Figure 2(a) shows the TGA curves of the matrix and some filled samples. In Figure 2(a), we observed that EVA/VLDPE decomposed in two steps. The first one took place mainly between 300 and 380°C and corresponded to the deacylation of the VA groups of EVA and the release of acetic acid. The second step was due to the decomposition of the PE chains between 380 and 500°C. For the filled samples, there were also two steps in the degradation process. The first one was between 305 and 380°C and corresponded to the deacylation of VA and the dehydration of MH, and the second step was attributed to the decomposition of the PE chains and the dehy-
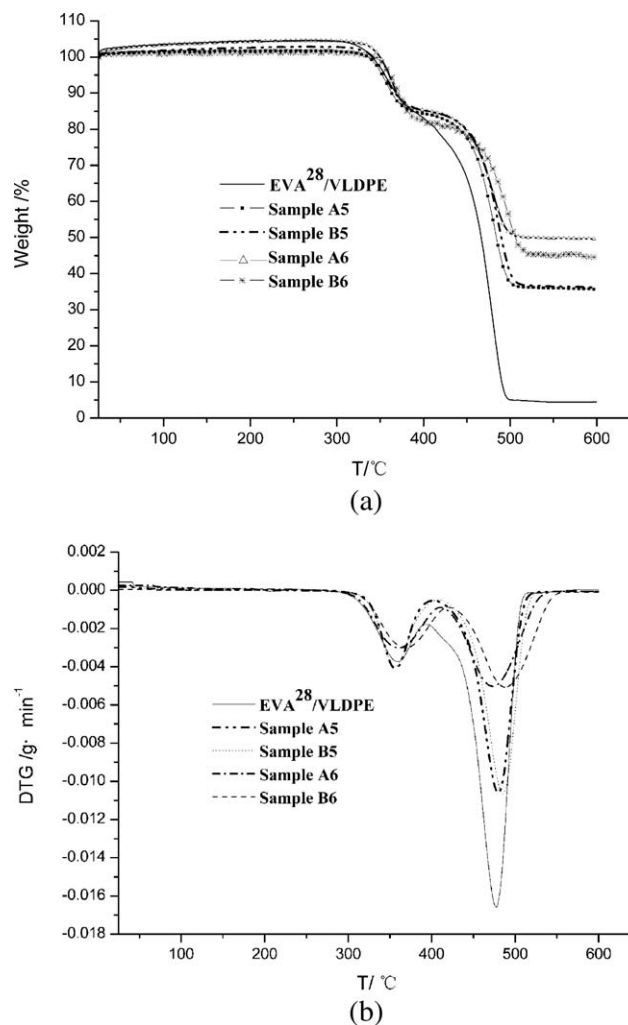

Figure 2 (a) Thermogravimetric and (b) DTG curves of the EVA/VLDPE and samples (T = temperature).

dration of MH between 380 and 510°C. In a comparison of the matrix and the filled samples, we observed that there was almost no difference under 380°C, but the weight loss processes above 380°C and the residual masses were different.

The derivative thermogravimetric (DTG) curves, reflecting the weight loss rate (v; the absolute value) in the heating process, are depicted in Figure 2(b). Compared with v of the matrix, the v values of the FR samples decreased a lot. As the filler content of the samples increased, v decreased. The type of surface treatments had an effect on v.

To further investigate the thermal decomposition of samples, TGAs of all of the samples in Table I were performed, and the characteristic values are listed in Table II. T_i represents the initial degradation temperature, and T_{max1} and T_{max2} are the temperatures corresponding to the first peak and the second peak, respectively.

It can be seen in Table II that the T_i and T_{max1} values of the samples modified by stearic acid were

TABLE II
Characteristic Values of TG and DTG
for Different Samples

Sample number	T_i (°C)	T_{max1} (°C)	T_{max2} (°C)	Char yield (%)
A1	345.51	365.33	483.33	3.95
A2	368.02	382.33	498.33	6.80
A3	343.11	362.50	482.50	4.27
A4	364.90	378.17	490.83	9.23
A5	336.86	357.67	481.33	4.93
A6	344.68	363.17	480.00	8.59
A7	337.85	360.67	483.50	4.59
A8	338.71	357.67	473.67	7.68
B1	342.37	359.50	489.17	4.33
B2	327.08	347.56	478.37	4.28
B3	336.59	356.50	487.33	5.52
B4	342.93	365.00	488.00	6.44
B5	339.01	356.50	486.33	5.46
B6	347.91	369.67	495.17	3.89
B7	337.54	357.67	486.17	5.69
B8	317.00	341.08	471.13	6.02

Char yield (%) = Residual weight (%) − MgO content (%).

of the char structures. Stearic acid softened the phase interface and made the transport of heat and flammability gases easier and the char structure loose. Therefore, the char yield of the sample without the PE-g-MAH was smallest [Fig. 3(b)]. Also, the addition of the compatibilizer could have made the interfaces strong and increased the char yield.

The DSC curve shows that FR polymers decomposed endothermically in the range 305–406°C in Figure 4. The main decomposition was assigned to the deacylation of VA and the dehydration of MH. They provided the FR properties of the samples, so the greater the endothermic character of the samples was, the better the FR properties were.

The characteristic values of DSC of all of the samples in Table I are listed in Table III. T_p represents the temperature of the exothermic peak. ΔH and ΔH_T are the experimental and theoretical heat absorptions, respectively. When we compared ΔH and ΔH_T, we found that the ΔH_T values of the

almost lower than those of the samples modified by epoxy silane, and this phenomenon was even more obvious for samples with low VA contents, such as samples A2, B2, A4, and B4. This was because the lubrication effect of the stearic acid softened the phase interface, which made heat transport easier. So the deacylation of VA and the dehydration of MH were easier and quicker at lower temperatures; this was better for the flame retardancy in the endothermal hydroxide/polymer system.[9]

It is clear in Table II that char yield values of the samples modified by epoxy silane increased with increasing MH content. The plot of char yield versus the VA content of samples with MH contents of 90 and 150 phr are depicted in Figure 3. For samples with an MH content of 90 phr, the char yield of the samples modified by epoxy silane were smaller than that of the samples modified by stearic acid, as shown in Figure 3(a). The changes in T_{max2} listed in Table II were the same as those of the char yield. When the content of MH was 90 phr, the MH treated by stearic acid slowed down the decomposition of the matrix's main chains and promoted the char-forming course. The reason may have been that the acidity of the systems modified by stearic acid increased,[6] and so, the OH⁻ groups were easier to capture; this terminated the chain transitive. However, for samples with an MH content of 150 phr, the result was just the opposite. It could be clearly seen that the char yield increased with increasing PE-g-MAH content, as shown in Figure 3(b). At a high loading level of MH, the problems of interfaces between the fillers and the matrix were more important. The interaction between the fillers and the matrix affected the char formation and the stability
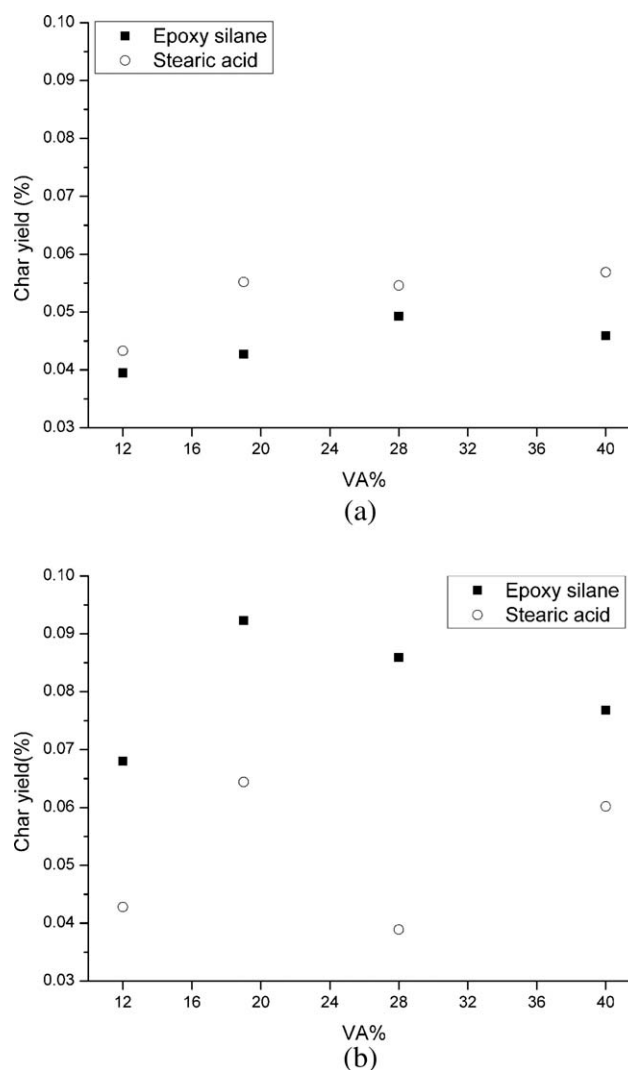

Figure 3 Plot of char yield versus VA (%) of samples with MH contents of (a) 90 and (b) 150 phr.

Figure 4 DSC curves of the EVA/VLDPE and samples (P = Power, W = watt, T = temperature).

TABLE III
Characteristic Values of the DSC and LOI Values for Different Samples

Sample number	T_p (°C)	ΔH (J/g)	ΔH_T (J/g)	LOI (%)
A1	361.17	350.87	381.49	24.60
A2	361.33	422.31	464.64	27.20
A3	365.67	350.98	371.71	25.90
A4	371.67	513.64	455.87	31.10
A5	358.50	370.51	362.42	27.40
A6	362.83	480.66	483.22	32.00
A7	350.50	365.11	353.58	25.90
A8	354.17	524.82	473.75	32.00
B1	353.17	305.85	381.49	25.40
B2	352.83	439.60	464.64	28.90
B3	346.67	373.83	371.71	27.20
B4	352.67	461.53	455.87	31.10
B5	340.33	374.11	362.42	25.40
B6	348.33	513.62	483.22	32.50
B7	360.33	471.22	353.58	26.30
B8	353.50	522.29	473.75	34.20

samples were smaller than the ΔH values, except for those containing EVA.[12] ΔH_T values were just calculated according to the heat release of the dehydration of MH, but ΔH contained the decomposition of EVA and led to an endothermic effect. Therefore, the differences between ΔH and ΔH_T became bigger with increasing VA content. When these samples were modified by epoxy silane, the ΔH values of the samples modified by stearic acid were bigger, and the T_p values of those samples were smaller. The reason may have been that stearic acid could have catalyzed the decomposition of EVA.[10] The reaction is shown in Scheme 2.

In addition, other conclusions obtained from Table III were as follows.

1. When the matrices of the samples were the same, the LOI values increased with the filler content.
2. The LOI values of the samples modified by stearic acid were almost higher than those of the samples modified by epoxy silane.
3. It is known that there is a certain relation between the heat of decomposition and the LOI values. For samples containing high VA contents, the increase of the LOI values with MH content was bigger.

These phenomena indicated that the flame retardancy for the MH/EVA/VLDPE systems could not be just explained by the heat release of the dehydration of MH and the dilution flammability of gases but also by the specific reactions between MH and EVA.

Effect of the surface treatments on the combustion behaviors of the MH/EVA/VLDPE composites

The HRR curves of the samples are shown in Figure 5. From Figure 5, it can be observed that the HRR curve of the matrix was very sharp, appearing in the
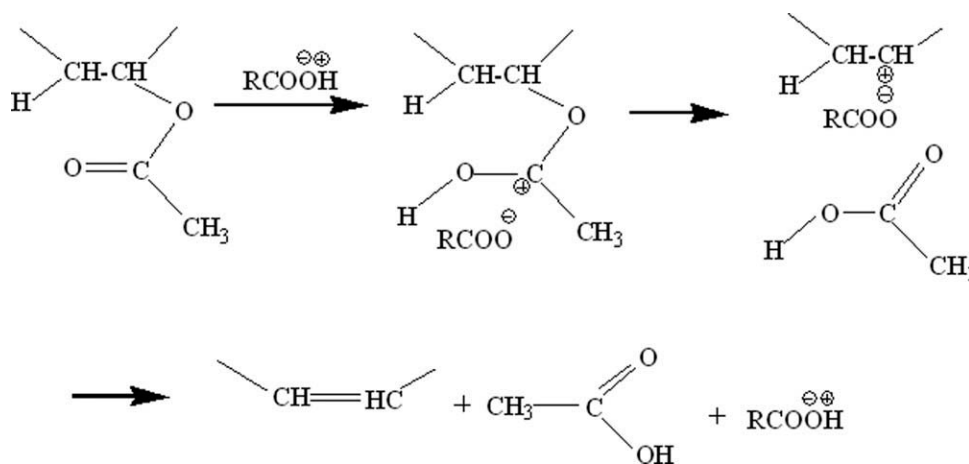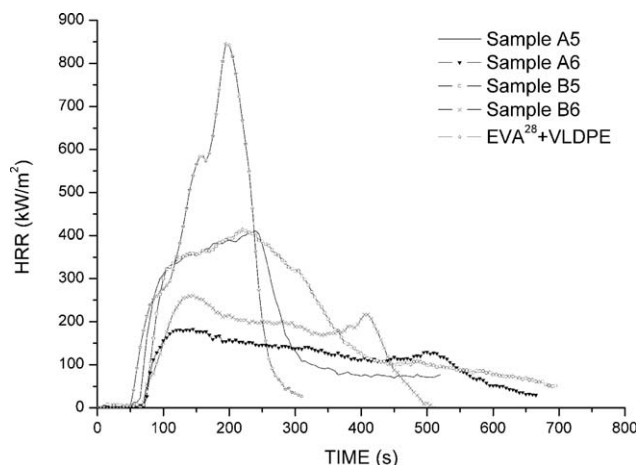

Scheme 2

Figure 5 HRR curves of the samples.

range 50–310 s. However, samples A5 and B5 had HRR curves with lower intensity, and their combustions were prolonged to 500 s (sample A5) and 700 s (sample B5). Sample B5 had the longest flameout time of 700 s. The result was consistent with the con-
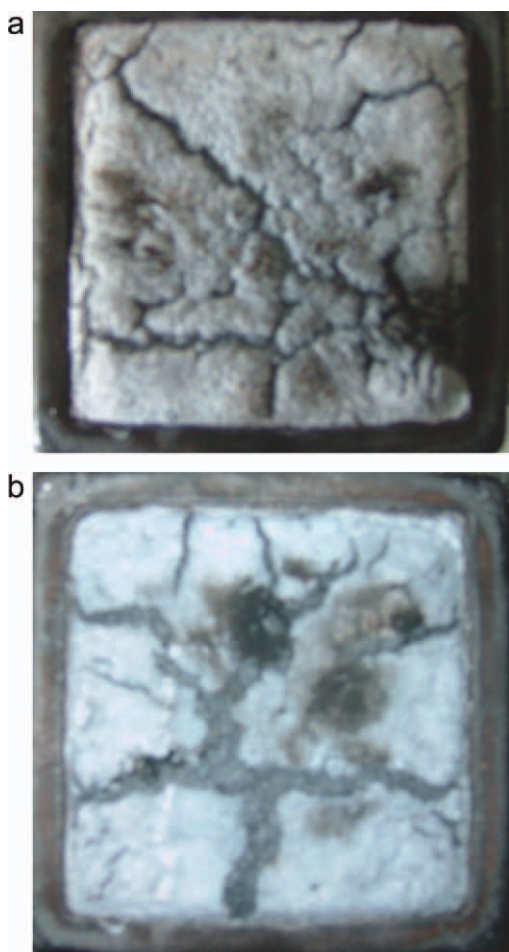

Figure 6 Photos of the samples after CCT: (a) A6 and (b) B6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
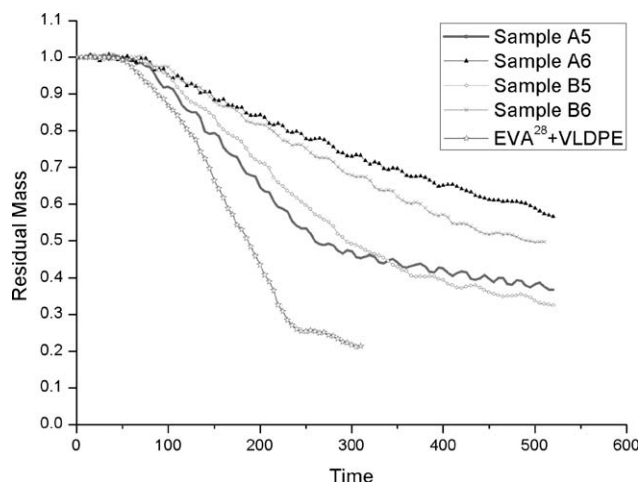

Figure 7 Residual mass curves of the EVA/VLDPE and different samples.

clusion obtained from TGA, which was the second step of degradation for sample B5, which took place at a higher temperature. The reason may have been that MH treated by stearic acid slowed down the degradation of the matrix's main chains at a lower loading level of MH. The HRR curves of the samples showed a strong dependence on the filler loading. This could be observed as a change in the aspect of the curve between samples with different loading levels. The HRR peaks of samples A6 and B6 containing 150 phr MH were lower than those of samples A5 and B5. Samples A6 and B6 also slowed the combustion behavior. Also, the HRR curves of samples A6 and B6, which had the same loading level and different surface treatments, are shown in Figure 5. Sample A6, modified by epoxy silane, had lower HRR values than sample B6, which was modified by stearic acid, and exhibited a slower decrease of the curve slope until 670 s. The reason may have
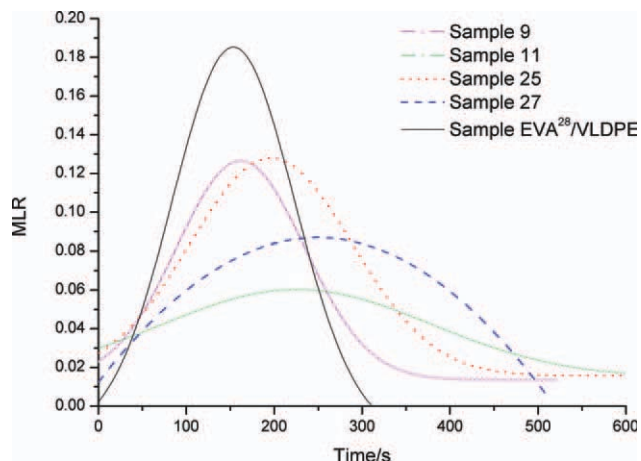

Figure 8 MLR curves of EVA/VLDPE and different samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sample	TTI (S)	PHRR (kW/m^2)	FPI (m^2 s/kW)
A5	66	410.90	0.161
A6	74	127.49	0.580
B5	74	413.31	0.179
B6	70	205.18	0.341
EVA + VLDPE	46	845.42	0.054

been that epoxy silane enhanced the interaction between the fillers and the matrix and increased the stability of the char-promoting mechanical cohesion of the crust. The aspects of the crust of samples A6 and B6 after CCT are shown in Figure 6. The crust appeared broken in sample B6, whereas it did not occur in sample A6. The residual mass curves of the samples after CCT are shown in Figure 7. The residual masses of the samples from CCT were consistent with the results of TGA, shown in Figure 2(a). The MLR curve is shown in Figure 8 and was consistent with the results of DTG, shown in Figure 2(b).

The parameters obtained from CCT are summarized in Table IV. Compared with the matrix, a reduction in PHRR and a higher TTI and FPI were found for the FR samples. The results of PHRR and FPI revealed a strong dependence on the filler loading. Samples with an MH content of 150 phr had a lower PHRR and greater FPI. At the same loading of MH, FPI depended on the type of surface treatment.

CONCLUSIONS

Stearic acid and epoxy silane affected the interfaces of MH/EVA/VLDPE systems differently. Stearic acid softened the interfaces of the composites, making the transportation of heat and flammability gases easier. On the contrary, epoxy silane enhanced the interfaces of the composites, forming a barrier for the transportation of heat and flammability gases, and slowed down the decomposition of the matrix's main chains.

When stearic acid was used as the surface modifier in the MH/EVA/VLDPE composites containing low MH content, it could accelerate the dehydration of MH and slow down the decomposition of the matrix's main chain; thus, it increased the char yield and improved the flame retardancy. When stearic acid was used as the modifier in these composites containing a high MH content, a compatibilizer (e.g., PE-g-MAH) was needed to enhance the interfaces and obtain better flame retardancy and processing properties.

The CCT data revealed that T_i, PHRR, and FPI of the MH/EVA/VLDPE composites depended not only on the MH loading levels but also on the type of surface treatments. The effect of the surface treatments was more obvious at high loading levels. Sample A6, treated by epoxy silane, showed a lower PHRR value, a greater FPI value, and a longer flameout time than sample B6, treated by stearic acid.

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