Performance of halogen-free flame retardant EVA/MH/LDH composites with nano-LDHs and MH

DING YanYan^{1*}, XU Liang² & HU GengSheng¹

¹ College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, China;

² Jinhua Fire Detachment of Zhejiang Province, Jinhua 310014, China

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The flammability properties of three series of Ethylene-Vinyl Acetate/Magnesium Hydroxide/Layered Double Hydroxide (EVA/MH/LDH) composites as well as the flame retardance effect between LDH and the conventional flame retardant additive MH are investigated. In addition to acting as an insulating barrier, LDH assists the dispersion of MH particles in the EVA matrix, and promotes the formation of the char residues because of its abundant interlayer hydroxyl groups. Composites containing LDH show good flame retardancy in Cone and LOI testings. This means that the combustion properties of the composites have decreased, which may lessen the fire hazard when this materials are used.

layered double hydroxide, cone calorimeter, flame retardancy, EVA, synergistic effects

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Ethylene-vinyl acetate copolymers (EVA) with different vinyl acetate (VA) contents are extensively used in many fields, especially in the cable industry as excellent insulating materials with good physical and chemical properties [1]. However, EVA resins are particularly flammable and emit a large amount of smoke when burnt. Magnesium hydroxide is a conventional non-toxic, smoke-suppressing halogen-free flame retardant additive with a high decomposition temperature that is used in flame retardant polymeric materials. However, its flame retardant efficiency is low, so very large amounts must be used, leading to a sharp drop in the mechanical properties of the flame retardant materials. To minimize this effect, the dispersion of MH and its compatibility with the polymer matrix must be improved. The use of very small (hyperfine) particles and surface treatment of MH are two important methods to achieve this. The usual surface modifiers for MH are organic reagents or polymers, which could be detrimental to combustion properties such as the limiting oxygen index (LOI). Hyperfine magnesium

hydroxide has been very effective at improving the flame retardance and mechanical properties of polymeric materials, but its dispersion in polymer matrices is very difficult [2].

In recent years, the intercalated or exfoliated polymer/LDH nanocomposites have attracted great interest in the field of materials science, because of their excellent thermal stability, flame retardance, and physico-chemical properties [3–6]. In the present work, we use MH and organic modified LDH layers as a flame retardant system and study their synergistic effects on the morphology and structure, flame retardant properties and mechanical properties of EVA/MH/LDH nanocomposites. X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), LOI, dynamic mechanical thermal analysis (DMTA), and cone calorimetry (Cone) tests are performed. The aim is to study the effects of adding LDH and MH to EVA resin (in particular its flame retardant and mechanical properties), and also to explore three difference synergistic systems containing MgAl-LDH, ZnAl-LDH, or MgFe-LDH. The main purpose of this study is to develop a new type of low smoke, halogen-free flame retardant

*Corresponding author (email: yyding@mail.ustc.edu.cn)

polymeric composite which can then be applied to create halogen-free flame retardant EVA insulated wire and cable.

1 Materials and methods

1.1 Materials

EVA (containing 28 wt% vinyl acetate, 28-05) was purchased from Beijing Organic Chemical Plant. Magnesium hydroxide (MH, HV5M) was kindly supplied by Wuhu Keyan Chemical Material Technology Development Co., Ltd. LDH was chemically synthesized in our laboratory. All chemicals were obtained from China Medicine (Group) Shanghai Chemical Reagent Corporation including magnesium nitrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], aluminum nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], sodium hydroxide [NaOH] and sodium dodecyl sulfate (SDS). All were analytically pure and used without further purification.

1.2 Preparation

MgAl-LDH was synthesized by co-precipitation. A mixed solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a $\text{Mg}^{2+}/\text{Al}^{3+}$ mol ratio of 3:1 was added dropwise under N_2 to a vigorously stirred solution of SDS until the pH reached 10.0. The resulting suspension was aged at 80°C for 8 h under N_2 . The slurry was washed thoroughly with de-ionized water and dried under vacuum at 70°C for 24 h, to give MgAl-LDH.

ZnAl-LDH was also synthesized by co-precipitation. A mixed solution containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a $\text{Zn}^{2+}/\text{Al}^{3+}$ mol ratio of 3:1 was added dropwise under N_2 to a vigorously stirred solution of SDS until the pH reached 10.0. The suspension was aged and the resulting slurry washed and dried as above to give ZnAl-LDH.

MgFe-LDH was synthesized by ion-exchange. A reddish-brown solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with $\text{Mg}^{2+}/\text{Fe}^{3+}$ mol ratio of 3:1 was added dropwise under N_2 to a vigorously stirred solution of 2 mol/L NaOH until the pH reached 9.5. The resulting reddish-brown suspension was aged at 100°C for 6 h under N_2 . The pristine LDH was then obtained by thoroughly washing and drying the slurry. Then a desired amount of SDS aqueous solution was added into an aqueous solution which containing 2.5 g pristine LDH. This solution was stirred mechanically at 100°C for 7 h under N_2 , and the solid obtained was washed thoroughly and dried under vacuum for 48 h, to give the

final MgFe-LDH, which was a pale yellow solid.

All compositions were melt compounded using a two-roll mill at about 120°C for 15 min. After mixing, the mixtures were then compression molded at about 120°C into sheets (1 and 3 mm thickness) under a pressure of 10 MPa for 10 min. The 3-mm sheets were cut into specimens of suitable size for fire testing, while dumbbell-shaped samples for mechanical property tests were cut from the 1-mm sheets. The formulations used in the present work are listed in Table 1.

1.3 Analyses and characterization

X-ray powder diffraction (XRD) analysis was performed on a Rigaku Japan K/max- γ A X-ray diffractometer with Cu K α radiation (Tokyo, Japan) ($\lambda = 1.54178 \text{ \AA}$) at a scan rate of $0.02^\circ/\text{s}$.

The transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope (Tokyo, Japan) with an accelerating voltage of 200 kV. The sample was ultramicrotomed with a diamond knife on an LKB Pyramitome (Stockholm, Sweden) to give 80–100 nm thick slices.

An scanning electron micrograph (SEM) was used. The specimens were cryogenically fractured in liquid nitrogen, and then sputter-coated with a conductive layer.

The limiting oxygen index (LOI) measurements were carried out using an HC-2 instrument (China) according to ASTM D 2863.

A cone calorimeter (Stanton Redcroft Type, made in England) was used to measure the flammability characteristics of EVA and its blends under a heat flux of 35 kW/m^2 according to ISO5660. The parameters used for flammability characterization include the heat release rate (HRR), the time to ignition, etc.

Dynamic mechanical thermal analyses (DMTA) were performed on a Perkin Elmer Diamond DMA (Massachusetts, USA) at a constant frequency of 5 Hz and a heating rate of $5^\circ/\text{min}$.

2 Results and discussion

2.1 Morphological characterization

The XRD patterns in the range of $2\theta = 2^\circ\text{--}10^\circ$ for four composite samples are shown in Figure 1. The (003) and (006) characteristic diffraction peaks characteristic of the

Table 1 Details of the samples

Sample	EVA	EM0	EM1	EM2	EM3
Composition	EVA	EVA/MH	EVA/MH/MgAl	EVA/MH/ZnAl	EVA/MH/MgFe
Content (%)	100	50/50	50/45/5	50/45/5	50/45/5

Figure 1 Small angle X-ray diffraction of composite samples.

nano-LDHs have completely disappeared, which indicates that the long range order in the inorganic phases has been completely destroyed and that the MgAl-LDH, ZnAl-LDH and MgFe-LDH layers have been completely exfoliated into the EVA matrix [7,8].

SEM images of EM0, EM1, EM2, and EM3 samples are shown in Figure 2. The MH particles in the sample EM0 are obviously badly agglomerated. Although the MH particles and LDH layers are difficult to discern in the SEM images, relatively well-dispersed MH particles as opposed to agglomerates are seen in the EM1, EM2, and EM3 samples, with sample EM1 being the most evenly distributed. The TEM images in Figure 3 also show that the distribution of inorganics in sample EM1 (Figure 3(b)) is more homogeneous than the distribution in sample EM0 (Figure 3(a)), which means that the addition of LDH improve to the distribution of MH into EVA. This may be because of the SDS

within the LDH, which has hydrophobic functional groups that might help MH to disperse evenly in the EVA matrix. The LDHs could then act as dispersants during the melt blending of MH with EVA and thus help MH particles to disperse homogeneously in the EVA [9].

It is well known that dispersion of inorganics in the polymer matrix will influence the properties of nanocomposites. Sample EM1 with more uniform dispersion should also perform best. It will be examined in the following tests.

2.2 Dynamic mechanical thermal analysis

DMTA gives accurate T_g (glass transition temperature) values of polymer. The effects of LDH on the T_g of the polymer composites are shown in Figure 4. The T_g values of three composite samples are lower than the T_g of EM0. It seems that the addition of LDH actually enhances the mobility of the polymer chain segments compared to the control EM0 sample. This is because the LDHs which contain SDS reduce the agglomerations of the MH particles, dispersing them more evenly in the EVA matrix [10]. The homogeneously dispersed MH particles make the composites more flexible with a lower T_g . The curves of storage modulus of samples vs the temperature are shown in Figure 5. The storage modulus of sample EM0 is much larger than that of the pure EVA sample due to the high stiffness of the MH filler. It has been reported that the storage modulus of poly(propylene) also increased with increasing MH content [11]. However, the storage modulus of the EVA/MH/LDH samples is lower than that of EM0. This is also a result of better dispersion of MH in the presence of the LDH, making EVA/MH/LDH samples more flexible than that of the EM0 sample without LDH.

Figure 2 SEM photographs of EM0 and composite samples (scale = 10 μm).

Figure 3 TEM photographs of EM0 (a) and EM1 (b) composites.

The LOI values of various samples with and without LDH are listed in Table 2. Substitution of LDH for MH increases the LOI values slightly compared with sample EM0 [12], with the greatest increase shown for sample EM1. These results are consistent with the TEM and SEM analyses and are further evidence that LDH can act as a synergistic flame retardant agent in the presence of MH. Not only are the LDH layers effective barriers themselves, they also help the MH additive disperse more evenly in the EVA matrix and thus increase the LOI values compared to sample EM0.

Table 2 The LOI values of EVA, EM0 and nanocomposite samples

Sample	EVA	EM0	EM1	EM2	EM3
LOI	22	32	35	33	32

A cone calorimeter is used to evaluate the fire properties of materials. The time to ignition (t_{ign}), the heat release rate (HRR), the peak heat release rate (PHRR), and mass loss rate (MLR) were measured and are given in Table 3. The fire development test can be followed by plotting the HRR values as a function of time (Figure 6). The PHRR value of pure EVA is around 1860 kW/m². The PHRR of sample EM0 containing MH only is 553 kW/m², while the PHRRs of EM1, EM2 and EM3 samples decrease to 228, 403 and 281 kW/m², respectively. Sample EM1 displays a remarkable reduction in the PHRR of almost 60% relative to EM0. Composites containing of LDH show good flame retardancy based on Cone analysis with very different fire behavior relative to EM0 with only MH. This means that the good dispersion of flame retardant in these samples and the synergistic effects of LDH and MH are efficient in inducing significant fire retardancy.

This differences can be easily understood from the appearance of the residues (Figure 7). While pure EVA is entirely burnt out, a thin layer of carbonaceous species is recovered after the combustion of EM0. Much more char is present after combustion of the LDH-containing composite samples, suggesting that the synergetic system helps char

Table 3 Cone calorimetry data for the samples

Cone calorimetry data	EVA	EM0	EM1	EM2	EM3
t_{ign} (s)	55	113	128	105	122
PHRR (kW/m ²)	1860	553	228	403	281
t_{PHRR} (s) ^{a)}	183	318	436	330	418
MLR (g/s, average value)	0.153	0.098	0.07	0.095	0.07

a) t_{PHRR} : Time at PHRR.

Figure 4 Loss tangents ($\tan\delta$) of various samples vs. temperature.

Figure 5 Storage modulus (E') of various samples vs. temperature.

Figure 6 Heat release rate curves of EVA, EM0, and composites.

Figure 7 Digital photos of the char residues for EM0 and composite samples.

formation as the matrix degradation. The masses of char formed from the EM0, EM1, EM2, and EM3 samples are 1.1, 2.7, 1.6, and 2.5 g, respectively. Thus LDH has promoted the formation of the char residues due to the abundant hydroxyl groups in its interlayer space. Sample EM1 which contains very well dispersed LDH and MH (as shown by SEM and TEM analyses), formed a particularly homogeneous and cohesive char with some cracks and also gave the lowest HRR value.

As already discussed in the literature [13], the mechanism of the fire retardancy increase by the addition of nanolayers is believed to be a combination of barrier effects which retard the diffusion of the volatile products arising from polymer degradation and physical protection which keeps the material away from the flame. This mechanism will be most effective if the layers are homogeneously dispersed at the nanometer scale to form a cohesive char. In addition, the LDHs which contained SDS, help MH particles to disperse evenly in the EVA matrix and participate in the formation of char residue, further improving the flame retardancy.

3 Conclusion

The synergistic effects of organic-modified LDH with MH in flame retardant EVA/MH/LDH composites have been studied by XRD, TEM, SEM, LOI, DMTA, and Cone Calorimetry. The XRD data show that exfoliated LDH structures have been prepared in the EVA/MH/LDH composites. The SEM and TEM images reveal that the LDHs can help disperse the MH particles evenly in the EVA matrix. The DMTA shows that the T_g values of the composites decrease

(relative to sample EM0 without LDH) with the introduction of LDH and approach the T_g of pure EVA. In other words, the introduction of LDHs makes the EVA/MH/LDH samples more flexible than sample EM0. The Cone calorimeter shows that EM1 displays a remarkable reduction in the PHRR of almost 60% relative to that of EM0. LDHs can promote not only the distribution of MH in composites, but also the formation of char residues to improve the flame retardant properties of composites in addition to the flame retardancy of LDH itself. The combustion properties of the composites are reduced, which may lessen the fire hazard of the materials in use.

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