

# Synergistic Effects of Exfoliated LDH with Some Halogen-Free Flame Retardants in LDPE/EVA/HFMH/LDH Nanocomposites

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Received 30 July 2007; accepted 13 October 2007

DOI 10.1002/app.27526

Published online 5 December 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The synergistic effects of exfoliated layered double hydroxides (LDH) with some halogen-free flame retardant (HFFR) additives, such as hyperfine magnesium hydroxide (HFMH), microencapsulated red phosphorus (MRP), and expandable graphite (EG), in the low-density polyethylene/ethylene vinyl acetate copolymer/LDH (LDPE/EVA/LDH) nanocomposites have been studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermal analysis (TGA and DTG), mechanical properties, limiting oxygen index (LOI), and UL-94 tests. The XRD results show that EVA as an excellent compatilizer can promote the exfoliation of LDH and homogeneous dispersion of HFMH in the LDPE/EVA/HFMH/LDH nanocomposites prepared by melt-intercalation method. The TEM images demonstrate that the exfoliated LDH layers can act as synergistic compatilizer and dispersant to make the HFMH particles dispersed homogeneously in the LDPE matrix. The results from the mechanical, LOI, and UL-94 tests show

that the exfoliated LDH layers can also act as the nano-enhanced and flame retardant synergistic agents and thus increase the tensile strength, LOI values, and UL-94 rating of the nanocomposites. The morphological structures of charred residues observed by SEM give the positive evidence that the compact charred layers formed from the LDPE/EVA/HFMH/LDH nanocomposites with the exfoliated LDH layers play an important role in the enhancement of flame retardant and mechanical properties. The TGA and DTG data show that the exfoliated LDH layers as excellent flame retardant synergist of MRP or EG can apparently increase the thermal degradation temperature and the charred residues after burning. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3694–3701, 2008

**Key words:** synergistic effect; layered double hydroxide; hyperfine magnesium hydroxide; halogen-free flame retardant; polymeric nanocomposites

## INTRODUCTION

In recent years, a great deal of attention has been paid to the application of halogen-free flame retardant (HFFR) polyolefin (PO) insulated wire and cable because halogen-containing PO materials give rise to toxic gas and smoke that can choke people exposed to the toxic and acidic fumes and can damage costly equipment. Magnesium hydroxide (MH) as an environmentally friendly HFFR additive has been extensively used in PO materials. But many studies show that more than 60% MH loading in the PO blends is required to obtain an adequate level of flame retard-

ant properties. Such high loadings lead to great losses in the mechanical properties of the flame retardant PO materials, because of the poor compatibility between inorganic additives and polymer resin.<sup>1</sup> To minimize this effect, surface treatment of MH by coupling agents has been widely used to improve their compatibility.<sup>2–4</sup> However, this kind of improvement of mechanical properties is not only very limited, but also this surface modification brings the deterioration of flame retardant properties, because most of organic coupling agents are flammable.<sup>5</sup> On the other hand, many studies show that the synergistic effects of some HFFR agents, such as microencapsulated red phosphorus (MRP), zinc borate (ZB), and expandable graphite (EG) with MH, can enhance flame retardancy and reduce the high loading level of MH and thus improve the mechanical properties of the flame retardant materials.<sup>5–7</sup> The hyperfine and/or nanoscaled MH has been verified to be very effective to improve the flame retardant and mechanical properties of polymeric materials, but its dispersion in polymer matrix is very difficult.<sup>8</sup>

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Contract grant sponsor: China National Natural Science Foundation; contract grant number: 50373039.

Contract grant sponsor: China NKBRFSF project; contract grant number: 2001 CB409600.

*Journal of Applied Polymer Science*, Vol. 107, 3694–3701 (2008)  
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In the past two decades, polymer/layered inorganic nanocomposites (PLN) have attracted considerable attention because a few (<5 wt %) amount of nano-fillers added into the composites can apparently enhance mechanical, thermal, dimensional, and barrier performance properties.<sup>9</sup> Recently, Ristolainen et al.<sup>10</sup> and Bourbigot et al.<sup>11</sup> reported the nanoscaled cationic clay layers (MMT) have the ability to improve the dispersion of inorganic additions in the polymer matrix. As far as we are aware, however, there are few studies on the effects of nanoscaled anionic clay called as layered double hydroxides (LDH) on the polymer flame retardant materials.

The LDH are anion clays, which consist of a stacking of positive hydroxylated layers separated by interlayered anionic species and water molecules. Its highly tunable properties and unique anion exchange properties has been considered as a new emerging layered crystals for the preparation of multifunctional PLN.<sup>12,13</sup> Many studies showed that LDH layers could enhance the thermal stability of polymer and promote the charring process during the thermal degradation process of polymer. So LDH is considered as a promising flame retardant of polymeric material.<sup>14</sup> Recently a series of intercalated or exfoliated polymer/LDH nanocomposites have been prepared by several methods such as *in situ* polymerization, solution intercalation, and melt-intercalation, and so on.<sup>15–22</sup> Among these existing methods, the melt-intercalation method is a nonsolvent, environment-friendly, and convenient process and has been extensively used to prepare polymer/MMT nanocomposites.<sup>23</sup> Heinrich and coworkers<sup>22</sup> reported the melt intercalation of low-density polyethylene (LDPE) in the organomodified MgAl-LDH. But they found that even the maleic anhydride-grafted polyethylene was unable to intercalate into the interlayers of organomodified LDH to obtain the exfoliated structure, which could give some more enhanced properties than the intercalation nanocomposites and microdispersed composites. This might be due to the high branched structure of LDPE, which leads the LDPE chains not to intercalate into the interlayers of LDH easily. Ethylene vinyl acetate (EVA) as a copolymer of ethylene and vinyl acetate or its blends with LDPE is often used as cable sheaths and insulated materials. EVA is also used to improve the compatibility of inorganic metal hydrates with polyethylene and cable flexibility.<sup>24</sup> Our previous work has reported polar polymer can intercalate more easily into the interlayers of LDH than nonpolar polymer such as PE.<sup>19</sup> So EVA could be used as a compatilizer of PE and inorganic flame retardants to improve their dispersion in the polymer matrix.

In the present work, the effects of exfoliated LDH layers and some HFFRs on the morphological struc-

tures, mechanical, flame retardant, and thermal properties of the LDPE/EVA/HFMH/LDH nanocomposites have been studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), mechanical properties measurements, thermal analysis (TGA and DTG), limiting oxygen index (LOI), and UL-94 tests. The main interesting of the present work is to develop new PO/HFMH/LDH nanocomposites that can be used in the manufacture of HFFR wires and cables.

## EXPERIMENTAL

### Materials

Two kinds of POs used in this work were LDPE supplied by Qilu Petro chemical (China) and ethylene vinyl acetate copolymer (EVA containing 18 wt % vinyl acetate) supplied by Sumitomo Chemical.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , NaOH, and sodium dodecyl sulfate (SDS) were obtained from China Medicine (Group) Shanghai Chemical Reagent Corporation. The hyperfine magnesium hydroxide (HFMH) with a particle size of 0.1–1.0  $\mu\text{m}$  used in this work was supplied by Jingjiang Kexing nanomaterials., China. MRP was prepared in our laboratory. The EG with an expansion ratio of 40 was supplied by Hebei Maoyuan Chemical Industry. The particle size of EG is 100 mesh. All the above chemicals were used as received without further purification. Distilled water was used throughout.

### Preparation of samples

#### Organomodification of MgAl-LDH

The organomodification of MgAl-LDH (OM-LDH) was prepared by coprecipitation method.<sup>24</sup> The pH values of 300 mL aqueous solution containing  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.03 mol),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.01 mol), and SDS (0.01 mol) was adjusted to about pH = 10 with 1 mol  $\text{L}^{-1}$  NaOH aqueous solution. The obtained slurry was aged for 3 days at 80°C, then filtered, and washed by distilled water. The white power OM-LDH was obtained by drying at 60°C in an oven for 24 h.

#### LDPE/EVA/HFMH/LDH nanocomposites

The LDPE/EVA/HFMH/LDH samples were prepared with different LDPE/EVA ratio and some HFFR synergists by melt compounding at 140°C in an XSS-300 torsion rheometer (made in China). After the samples with a given ration of LDPE and EVA and 5 phr OM-LDH were blended for 10 min, the small amount of sample was collected for the XRD and TEM determinations. Then the desired amount

**TABLE I**  
**Formulations of LDPE/EVA/HFMH Samples with Different Halogen-Free Flame Retardant Synergistic Agents**

Sample code	LDPE	EVA	MH (phr)	LDH (phr)	MRP (phr)	EG (phr)
A	100	–	100	–	–	–
B	100	–	95	5	–	–
C	80	20	100	–	–	–
D	95	5	95	5	–	–
E	90	10	95	5	–	–
F	80	20	95	5	–	–
G	80	20	95	–	5	–
H	80	20	90	5	5	–
I	80	20	95	–	–	5
J	80	20	90	5	–	5

of HFMH, MRP, and EG compounds were added into the remained samples and continued the melt compounding for another 5 min. After blending, the samples were hot-pressed under 10 MPa to sheets of suitable thickness for 10 min at 140°C. The formulations of various samples are summarized in Table I.

### Measurements

#### X-ray diffraction

The X-ray diffraction (XRD) patterns were recorded at room temperature on a Philips X' Pert PRO SUPER apparatus (Nicolet Instrument, USA) using Cu K $\alpha$  tube and Ni filter ( $\lambda = 0.1542$  nm) at a scan rate of 0.0167°/s.

#### Transmission electron microscopy

The transmission electron microscopy (TEM) images were obtained on a JEOL-2010 transmission electron microanalyzer with an accelerate voltage of 200 kV. The samples were ultramicrotomed with a diamond knife on an LKB Pyramitome to give 100 nm thick slices. The slices were transferred from water to a Cu grid.

#### Scanning electron microscopy

The scanning electron microscopy (SEM) of the char layers were analyzed by a JEOL JSM-6700F Field emission scanning electron microscope. The specimens were previously coated with a conductive layer of gold.

#### Thermogravimetric analysis

Thermogravimetric analysis (TGA) were performed on a Shimadzu TGA-50H thermoanalyzer at a scan rate of 10°C/min under the air flow rate of  $2 \times 10^{-5}$  m<sup>3</sup>/min.

#### Mechanical properties measurements

The mechanical properties were measured with a universal testing machine (DCS5000, Shimadzu) at temperatures 25°C  $\pm$  2°C. The crosshead speed was 25 mm/min. The dumb-bell shaped specimens were prepared according to ASTM D412-87.

#### Limiting oxygen index measurements

Limiting oxygen index (LOI) measurements were carried out using a HC-2 type instrument (made in China) in accordance with ASTM D2863-77. The samples used for the test were of dimensions 100  $\times$  6.5  $\times$  3 mm<sup>3</sup>.

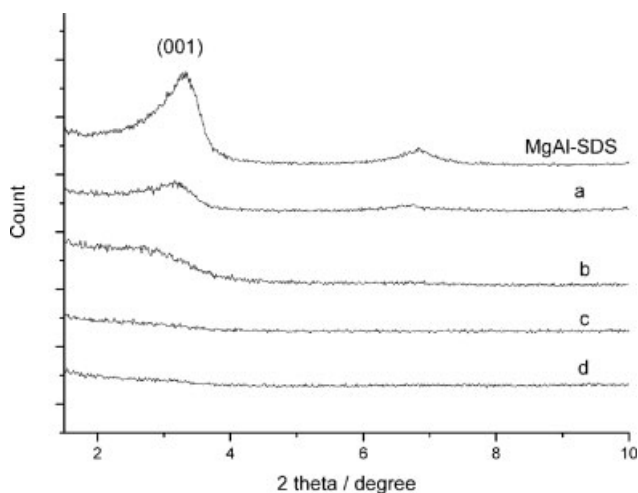
#### The UL-94 vertical test

The UL-94 vertical test was carried out using a CZF-1 type instrument (made in China) on sheets of 127  $\times$  12.7  $\times$  3 mm<sup>3</sup> according to ASTM D635-77.

## RESULTS AND DISCUSSION

### Structural characterization of LDPE/EVA/HFMH/LDH nanocomposites

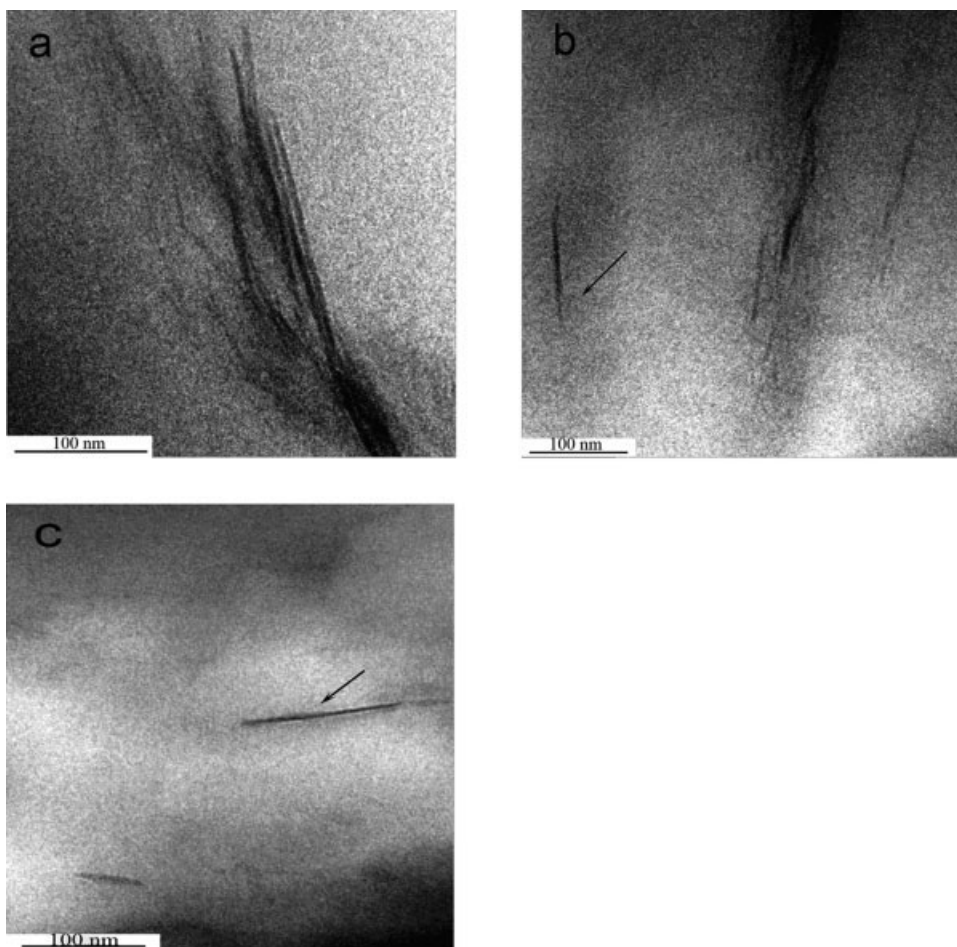
Figure 1 gives the low-angle XRD patterns of the OM-LDH and LDPE/LDH samples with 5 phr OM-LDH, and different amount of EVA as a compatilizer under kept the total amount of 100 phr resins constant. The diffractogram of OM-LDH sample in Figure 1 has a maximum (001) peak at  $2\theta = 3.36^\circ$  corresponding to a basal spacing of 2.63 nm. The diffraction peak of sample B without EVA at  $2\theta = 3.36^\circ$  [see curve (a) in Fig. 1] is the same as that of OM-LDH sample except for its intensity, which indicates that no intercalation occurs during the melt compounding process of OM-LDH with LDPE. The sample D with 5 phr EVA shows a broad diffraction peak at about  $2\theta = 2.4^\circ$  corresponding to the basal spacing of 3.8 nm, as shown in Figure 1 (see curve b), which means that EVA has intercalated into the



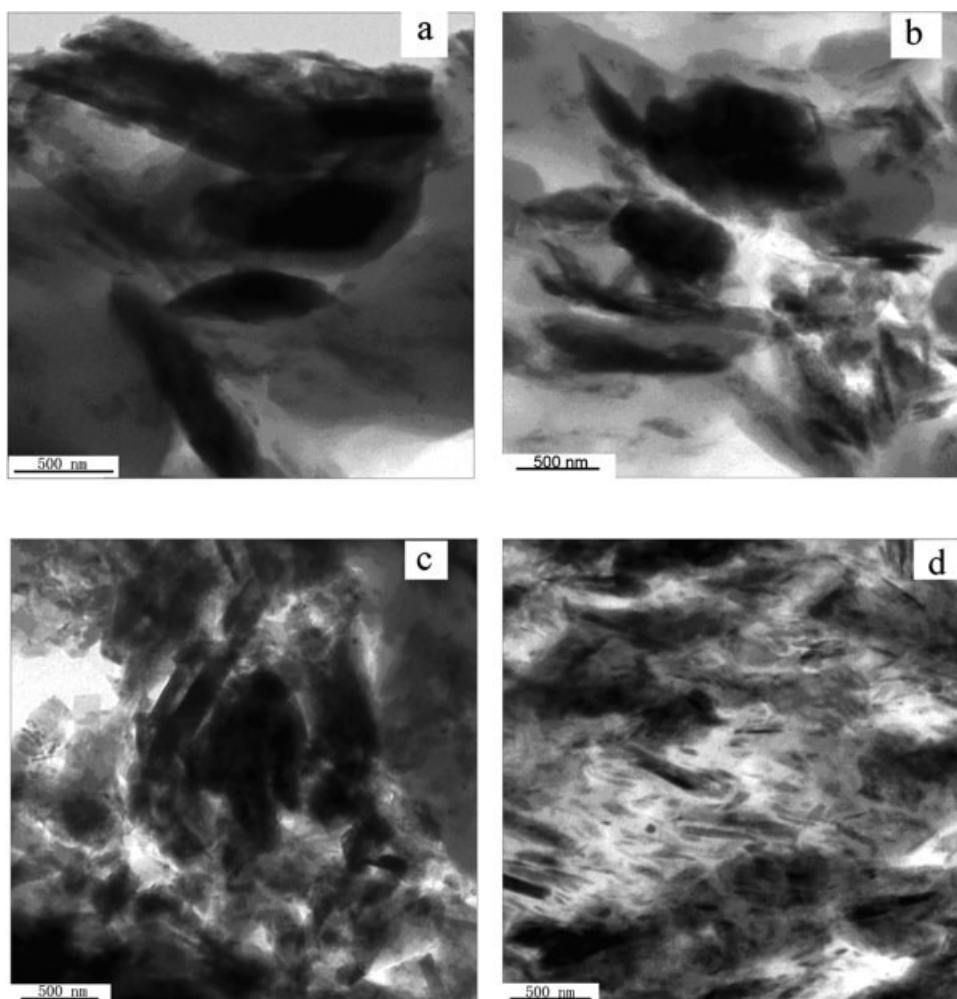
**Figure 1** XRD patterns of OMLDH and various LDPE/LDH samples with 5 phr OMLDH and different amount of EVA listed in Table I: (a) 0 phr (sample B); (b) 5 phr (sample D); (c) 10 phr (sample E); and (d) 20 phr (sample F).

OM-LDH layers to form the intercalation structure and thus expands the spacing of LDH layers. When the amount of EVA increases to 10 and 20 phr (sample E and F), no diffraction peak can be observed at the range of  $2\theta = 1.5\text{--}10^\circ$ , as shown in Figure 1(c,d), respectively. This indicates that the OM-LDH layers have been exfoliated in the LDPE/EVA matrix. The above results give the positive evidence that the addition of EVA is beneficial to the exfoliation of OM-LDH layers in the LDPE matrix.

Figure 2 presents the TEM images of LDPE/EVA/LDH samples with 5 phr LDH and different EVA loadings. It can be seen from Figure 2(a) that some face-face groups of LDH fillers (darker lines) are separated by about 2–3 nm spacing, which means that the LDH layers are intercalated by polymers. Figure 2(b,c) show the exfoliated structures of LDH layers (as pointed by the arrows) dispersed relatively homogeneously in the polymer matrix (bright part), in which the thickness and lateral sizes of the exfoliated LDH layers can be calculated as being about 1–2 nm and 80–180 nm, respectively. These results



**Figure 2** TEM images of the LDPE/LDH samples with 5 phr OMLDH and different amount EVA listed in Table I: (a) 5 phr (sample D); (b) 10 phr (sample E); and (c) 20 phr (sample F).



**Figure 3** TEM images of various LDPE/HFMH samples: (a) Sample A without LDH and EVA; (b) Sample B only with 5 phr LDH; (c) Sample C only with 20 phr EVA; and (d) Sample F with both 5 phr LDH and 20 phr EVA.

obtained from TEM are in good agreement with those from XRD, which indicates that EVA as a compatilizer can promote the exfoliation of LDH in LDPE to form the intercalated or exfoliated structures of LDPE/LDH nanocomposites.

#### Effects of LDH and EVA on dispersion of HFMH in polymer matrix

Figure 3 shows the effects of LDH and EVA on the dispersion of HFMH particles in the LDPE/HFMH samples observed by TEM images. It can be seen that the HFMH particles in Sample A without LDH and EVA show the obvious agglomerations, as shown in Figure 3(a). The dispersion of HFMH particles in Sample B only with 5 phr LDH seems no apparent improvement [Fig. 3(b)]. Sample C only with 20 phr EVA shows much better dispersion of HFMH, as seen in Figure 3(c). However, Sample F with both 5 phr LDH and 20 phr EVA shows apparently homogeneous dispersion of HFMH particles

in the LDPE matrix, as seen in Figure 3(d). This is because EVA resin has good compatibility with PE, LDH, and HFMH, which promotes the LDH to be exfoliated and homogeneous dispersion of HFMH particles. These results indicate that the exfoliated LDH layers can act as a synergistic compatilizer and dispersant of HFMH particles during the melt blending with LDPE and EVA and apparently improve both the dispersion of HFMH in polymer matrix and compatibility between the HFMH and the polymer matrix.

#### Synergistic effects of LDH with MRP and EG in LDPE/EVA/HFMH/LDH nanocomposites

The LOI and UL-94 tests are widely used to evaluate the flame retardant properties of materials. The comparison of LOI, UL-94, and tensile strength (TS) of related samples in Table I is listed in Table II. It can be seen by comparison of samples A, B, and C that the addition of 20 phr EVA (Sample C) increases 2%

**TABLE II**  
**Comparison of Flame Retardant, Mechanical Properties, and Char Residue of Related Samples in Table I**

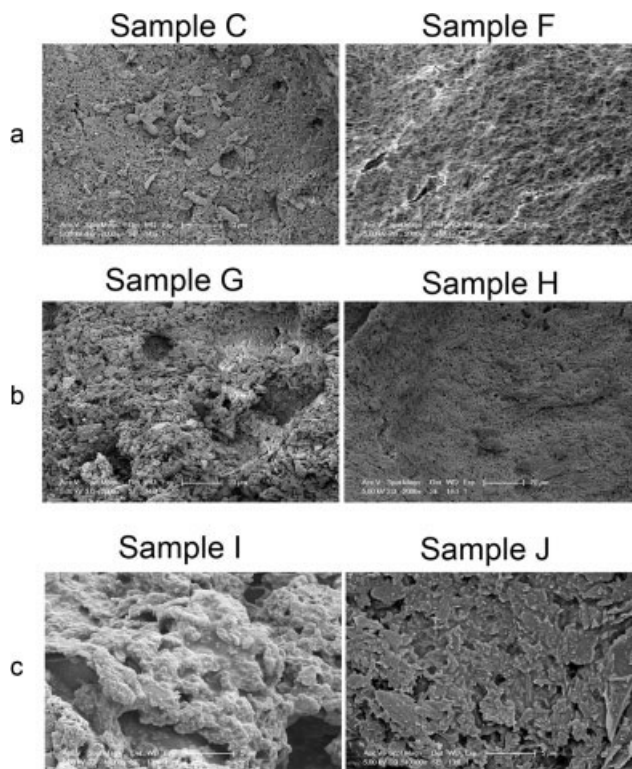
Sample code	LOI (%)	UL-94 rating	Observation phenomena	Char residue weight (%) at 600°C	Tensile strength (MPa)
A	29	Fail	Dripping	—	9.7
B	29	Fail	Dripping	—	9.8
C	31	Fail	Dripping	34.6	8.9
F	33	Fail	No dripping	36.5	11.2
G	34	V-0	Dripping	35.8	8.7
H	36	V-0	No dripping	37.3	11.4
I	34	V-0	Dripping	36.8	9.1
J	38	V-0	No dripping	38.1	12.1

LOI values, which is in good agreement with the results reported in the literature.<sup>25,26</sup> But Sample C also failed to pass V-0 rating in UL-94 vertically burning test. Sample F only with 5 phr LDH further increases the LOI values to 33, but still cannot pass the UL-94 V-0 rating. Sample G only with 5 phr MRP and Sample I only with 5 phr EG can increase the LOI values to 34 and pass the V-0 rating, but can observe their dripping in the LOI and UL-94 tests. However, Sample H with both 5 phr LDH and 5 phr MRP and Sample J with 5 phr LDH and 5 phr EG not only show the highest LOI values 36 and 38, but also can pass the V-0 rating without dripping in the LOI and UL-94 tests. Apparently MRP and EG have synergistic effects with LDH in the LDPE/EVA/HFMH blends.

The mechanical properties of related samples are also listed in Table II. It can be seen that the LDPE/EVA/HFMH samples with 5 phr LDH show highest TS of above 11.2 MPa. Among them, Sample J with both 5 phr LDH and 5 phr EG reach the highest TS value of 12.1 MPa. Apparently, the exfoliated LDH layers in the nanocomposites can act as the disperser and compatilizer of HFMH, and nano-reinforced function and thus greatly enhance the TS of materials. The above reinforcing effect was also observed in the FR system with the nano MMT layers.<sup>27,28</sup>

The SEM images of the char samples obtained from the surfaces of various fire samples with and without LDH are given in Figure 4. It can be seen from Figure 4(a) that many cracks exist on the surface of Sample C without LDH, but the char structures of Sample F with 5 phr LDH are relatively smooth and compact compared with Sample C. Many holes and irregular swollen char structures are formed after burning of Sample G with 5 phr MRP and Sample I with 5 phr EG, as shown in Figure 4(b,c), which are due to the intumescence effect of release gases during burning of MRP or EG. However, the char structures of Samples H and J with 5 phr LDH show much smaller microholes, more homogeneous and compact structures, as shown in Fig-

ure 4(b,c). These results imply that the exfoliated LDH layers can promote the homogeneous dispersion and form more compact charred structures. This kind of homogeneous and compact charred layers slow down heat and mass transfer between the gas and condensed phase and prevent the underlying polymeric substrate from further attack by heat flux in flame. The results observed from SEM are in good agreement with those of LOI and UL-94 tests in Table II.

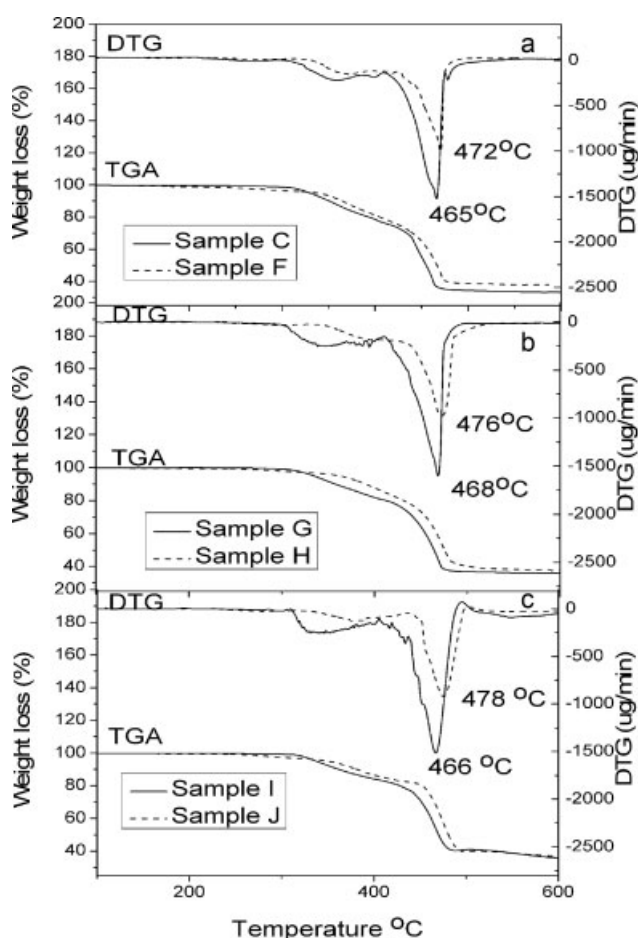


**Figure 4** SEM images of the char samples obtained from the LDPE/EVA/HFMH, LDPE/EVA/HFMH/MRP, and LDPE/EVA/HFMH/EG samples with and without LDH: (a) samples C and F; (b) samples G and H; and (c) samples I and J listed in Table I.

### Thermal behaviors of LDPE/EVA/HFMH/LDH nanocomposites

Figure 5 presents the TGA and DTG curves of six kinds of LDPE/EVA/HFMH, LDPE/EVA/HFMH/MPR, and LDPE/EVA/HFMH/EG samples with and without LDH. The thermal decomposition behaviors of all the LDPE/EVA/HFMH samples mainly take place in two-step process. The first step involves the dehydration of MH and the loss of acetic acid in the range of 300–360°C, whereas the second degradation step in the temperature range of 360–550°C is due to the degradation of polyethylene chains and volatilization of the residual polymer. It can be seen from Figure 5 that samples F, H, and J with 5 phr LDH show a slight weight loss at about 120–300°C, which is due to the evaporation of physically absorbed water in the intercalated layers, the loss of hydroxide in the LDH layers and the decomposition of the SDS, as reported in the literature.<sup>16</sup> The samples F, H, and J with LDH show much

slower degradation rate at the range of 300–360°C and higher thermal stability than the samples C, G, and I without LDH, respectively. This beneficial effect can be ascribed to the fast charring process brought from the first slight weight loss at the low temperature of 120–300°C, because the charred layers can enhance the thermal stability of samples at higher temperature. The maximum peaks of the DTG curves at the range of 450–500°C can be assigned to the thermal oxidative degradation temperature of samples. The thermal oxidative degradation temperatures of samples C, G, and I without LDH are 465, 468, and 466°C, respectively. However, the thermal oxidative degradation temperatures of the corresponding samples F, H, and J with LDH increase to 472, 476, and 478°C, respectively, which are 7–12°C higher than those of samples C, G, and I. Moreover, the maximum weight loss rates of samples F, H, and J represented by the peak intensities are much smaller than those of samples C, G, and I. Meanwhile it can be seen from Table II that the samples F, H, and J with LDH give more residues than samples C, G, and I without LDH, and it is worth noting that a higher residual weight is associated with higher flame retardancy and thermal stability. These results indicate that the samples with LDH possess higher thermal stability. This is because the exfoliated LDH layers can promote the formation of charred layers efficiently and hinder the diffusion of oxygen and flammable volatile products. It has been reported<sup>16,17</sup> that an efficient charring process in flame retardant polymeric materials must occur at a temperature higher than the processing temperature of the polymer but much lower than the decomposition temperature of polymer. Therefore, the weight loss produced by the decomposition of LDH layers at about 120–300°C is highly advantageous for promoting charring process and enhancing the thermal stability of polymer in matrix. This similar observation in polymer/MMT and some other polymer/LDH nanocomposites.<sup>29,30</sup>



**Figure 5** TGA and DTG curves of six kinds of LDPE/EVA/HFMH, LDPE/EVA/HFMH/MPR and LDPE/EVA/HFMH/EG samples with and without LDH: (a) samples C and F; (b) samples G and H; and (c) samples I and J listed in Table I.

### CONCLUSIONS

The synergistic effects of exfoliated LDH with some HFFR additives, such as HFMH, MRP, and EG in LDPE and ethylene acetate copolymer blends, have been studied successfully by XRD, TEM, SEM, TGA-DTG, flame retardant (LOI and UL-94), and mechanical properties measurements. The XRD results demonstrate that EVA as excellent compatilizer can promote the exfoliation of LDH in the LDPE/EVA/HFMH/LDH nanocomposites prepared by melt-intercalation method. The TEM images give the evidence that the exfoliated LDH layers can also act as compatilizer and synergistic disperser of EVA to

disperse the HFMH particles homogeneously in the LDPE matrix. The results from the LOI, UL-94, and mechanical tests show that the exfoliated LDH layers as flame retardant synergistic agent and nano-reinforced agent of MRP and EG increase the LOI values and UL-94 rating and enhance the TS of the nanocomposites. The structures of charred residues observed by SEM give the positive evidence that the exfoliated LDH layers promote the formation of the compact charred layers in the LDPE/EVA/HFMH nanocomposites, which can efficiently protect the underlying polymeric materials to be burning. The TGA and DTG data show that the thermal-oxidation degradation temperatures of the LDPE/EVA/HFMH/MRP or EG samples with LDH layers are 7–12°C higher than those from the corresponding samples without LDH, indicating LDH can enhance the thermal stability of the nanocomposites.

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