

SYNERGISTIC EFFECTS OF LAYERED DOUBLE HYDROXIDE WITH PHOSPHORUS-NITROGEN INTUMESCENT FLAME RETARDANT IN PP/EPDM/IFR/LDH NANOCOMPOSITES

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Abstract Synergistic effects of layered double hydroxide (LDH) with intumescent flame retardant (IFR) of phosphorus-nitrogen (NP) compound in the polypropylene/ethylene-propylene-diene/IFR/LDH (PP/EPDM/IFR/LDH) nanocomposites and related properties were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), limiting oxygen index (LOI), UL-94 test, cone calorimeter test (CCT) and thermo-gravimetric analysis (TGA). The XRD and TEM results show that the intercalated and/or exfoliated nanocomposites can be obtained by direct melt-intercalation of PP/EPDM into modified LDH and that LDH can promote the IFR additive NP to disperse more homogeneously in the polymer matrix. The SEM results provide positive evidence that more compact charred layers can be obtained from the PP/EPDM/NP/LDH sample than those from the PP/EPDM/LDH and PP/EPDM/NP samples during burning. The LOI and UL-94 rating tests show that the synergetic effects of LDH with NP can effectively increase the flame retardant properties of the PP/EPDM/NP/LDH samples. The data from the CCT and TGA tests indicate that the PP/EPDM/NP/LDH samples apparently decrease the HRR and MLR values and thus enhance the flame retardant properties and have better thermal stability than the PP/EPDM/LDH and PP/EPDM/NP samples.

Keywords: Synergistic effect; Intumescent flame retardant; Layered double hydroxides; Flame retardant and thermal stability properties; PP/EPDM nanocomposites.

INTRODUCTION

Polypropylene (PP) is one of the major commodity polymeric materials having excellent physical properties, such as high stiffness and tensile strength^[1]. However, due to its relatively high glass transition temperature (about 0°C^[2]), PP is quite brittle at low temperatures. In order to improve its impact strength at low temperatures, several elastomers have been blended with PP as modifiers, in which ethylene-propylene-diene copolymer (EPDM) is most important^[3]. In the last decades, PP/EPDM blends have been extensively applied in many fields, such as cars, electric casings, interior decoration and insulation materials.

Like other polymeric materials, PP/EPDM blends are particularly flammable and emit a large amount of smoke while burning, which limits their practical applications. However up to now, there are little reports on flame retardant PP/EPDM materials. Therefore, studies on flame retardant PP/EPDM should be interesting and fascinating^[4–6]. The flame retardants as additives have been widely used to decrease the flammability of polymer materials, in which the intumescent flame retardants (IFR) have been proved to be quite efficient. Usually the intumescent flame retardant system comprises three active ingredients of an acid source as a catalyst, a carbonization compound and a blowing agent. The IFR mechanism is proposed that the foamed cellular charred

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layers formed on heating act as a physical barrier, which slows down heat and mass transfer between gas and the condensed phase and thus protects the underlying material from heat flux or flame^[7]. According to our previous studies^[7], the phosphorus-nitrogen compound NP containing 15.6 wt% P and 27.5 wt% N is an excellent IFR additive that can provide the acid source, carbonizing and blowing agents in the intumescent flame retardant polyolefin.

As a relatively new kind of inorganic layered crystalline materials, layered double hydroxides (LDHs) have attracted great interest in the field of polymer material science since the intercalated and/or exfoliated polymer/LDH nanocomposites often have the improved mechanical and electrical properties, enhanced thermal stability and optical properties^[8–11]. Moreover, LDHs being very similar to magnesium hydroxide and aluminum hydroxide are reasonably considered as a potential replacement of metal hydroxides in preparing environment friendly flame retardant composites with better dispersibility through polymer intercalation. Bourbigot *et al.* have reported the potential synergistic effects that can be achieved by combining inorganic fillers with conventional flame retardants from theory analysis^[12, 13]. However, as far as we are aware, there are few studies on the synergistic effects of LDH with IFR additive for the flame retardancy and thermal stability of the PP/EPDM/IFR/LDH nanocomposites.

In the past years, a series of polymer/LDH nanocomposites have been prepared in our laboratory^[14–20]. The studies showed that the LDH layers dispersed in polymer matrix can promote the charring process during the thermal degradation process of polymer. More recently, the synergistic effects of exfoliated LDH with hyperfine magnesium hydroxide (HFMH) in ethylene vinyl acetate copolymer (EVA)/HFMH/LDH (EVA/HFMH/LDH) nanocomposites, as well as that of LDH with HFMH in low-density polyethylene nanocomposites have been reported^[19]. The organically modified LDH (OM-LDH) can act as compatibilizer and flame retardant synergist to promote the HFMH particles to disperse homogeneously in the polymer matrix, and thus increase the LOI values and UL-94 rating of the nanocomposites.

In the present work, the synergistic effects of OM-LDH as compatibilizer and synergist with the IFR additive NP as main flame retardant in the PP/EPDM/ IFR/LDH nanocomposites have been studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), cone calorimeter test, thermo-gravimetric analysis (TGA), limiting oxygen index (LOI) and the UL-94 tests.

EXPERIMENTAL

Materials

Commercial polypropylene (PP F401) was purchased from Yangzi Oil Company with a melt index of 2.0 g/min (230°C/2.16 kg). EPDM 4045 (60 wt% ethylene, 3 wt% 5-ethylidene-2-norbornene) was supplied by Mitsubishi Petrochemical Co. Ltd., Japan. The intumescent phosphorus-nitrogen flame retardant NP containing 15.6 wt% P and 27.5 wt% N with a particle size of 400 mesh was supplied by Weizheng Fine Chemicals Co (China). $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Shanghai Zhenxing Chemicals No.1 Plant. Sodium dodecyl sulfate (SDS) and NaOH were obtained from China Medicine (Group) Shanghai Chemical Reagent Corporation. All the above commercial chemicals were analytically pure and used as received without further purification.

Preparation of Samples

Organically modified MgAl LDH

Organically modified MgAl LDH (OM-LDH) was synthesized by coprecipitation method according to our previous work^[17]. The pH value of 500 mL aqueous solution containing $\text{Mg}(\text{NO}_3)_2$ (0.15 mol), $\text{Al}(\text{NO}_3)_3$ (0.05 mol), and SDS (20 g) was adjusted to about pH 9–10 by drop-wisely adding 1 mol L⁻¹ NaOH aqueous solution. The obtained slurry was aged for 3 days at 60°C, and then washed for four times by ultrasonic and then filtrated. The obtained white powder OM-LDH was dried at 60°C in a vacuum oven.

PP/EPDM/IFR blends

The PP/EPDM/IFR samples were prepared by two-step blending. First, a desired amount (weight %) of PP/EPDM was melt-blended at 170°C for 8 min by a SXX-300 two-roll mill with a rotor speed of 64 r/min. Secondly, IFR additive NP was dispersed into the PP/EPDM blends by blending for another 5 min. After that, the mixture was compression-moulded into sheets with appropriate thickness. The compositions and some flame retardant properties of various PP/EPDM/NP samples are summarized in Table 1.

Table 1. Compositions and some flame retardant properties of PP/EPDM/IFR samples

Sample No.	FR properties			
	PP/EPDM	NP	LOI (%)	UL-94 rating
1	70/30	–	18	Fail
2	70/30	10	23	Fail
3	70/30	20	32	Fail
4	70/30	22	32	Fail
5	70/30	24	33	Fail
6	70/30	25	33	V-0
7	70/30	30	37	V-0

PP/EPDM/IFR/LDH nanocomposites

The PP/EPDM/IFR/LDH samples were prepared by melt intercalation of two-step blending. At first, a desired amount of PP/EPDM and OM-LDH powders were melt-intercalated at 170°C for 8 min by a SXX-300 two-roll mill with a rotor speed of 64 r/min. Then IFR additives were dispersed into the PP/EPDM/LDH nanocomposites by blending for another 5 min. At last, the obtained mixture was compression-moulded into sheets of 1 mm to 3 mm thickness. The formulation of various PP/EPDM/IFR/LDH samples with different compositions and their flame retardant properties are given in Table 2.

Table 2. Formulations of various PP/EPDM/NP/LDH samples with different compositions and their flame retardant properties

Symbols of samples	Compositions, phr			FR properties	
	PP/EPDM	NP	LDH	LOI (%)	UL-94 rating
PP/EPDM/LDH5	70/30	–	5	18	Fail
PP/EPDM/NP25	70/30	25	–	33	V-0
PP/EPDM/NP20/LDH5	70/30	20	5	35	V-0
PP/EPDM/NP19/LDH5	70/30	19	5	34	V-0
PP/EPDM/NP18/LDH5	70/30	18	5	33	V-0
PP/EPDM/NP17/LDH5	70/30	17	5	32	Fail
PP/EPDM/NP20/LDH4	70/30	20	4	34	V-0
PP/EPDM/NP19/LDH4	70/30	19	4	33	Fail
PP/EPDM/NP18/LDH4	70/30	18	4	32	Fail
PP/EPDM/NP20/LDH3	70/30	20	3	32	Fail

Measurements

The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MaxrA rotating anode X-ray diffractometer equipped with a Cu K α tube and Ni filter ($\lambda = 0.1542$ nm) at a scan rate of 0.0167 (°)/s.

The transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microanalyzer with an accelerated voltage of 200 kV. The sample was ultramicrotomed with a diamond knife on an LKB Pyramitome to give about 100 nm thick slices. The slices were transferred from water to a 200-mesh Cu grid for TEM observation.

The surface morphologies of intumescent charred samples were observed by a scanning electron microscope (SEM) (Hitachi X560 scanning electron microanalyzer, Japan). Before observation, the surface was coated with a conductive gold layer.

The cone calorimeter tests were carried out using a Redcroft Cone Calorimeter following the procedure defined in ISO 5660, on 3 mm thick 100 mm $\times$ 100 mm plaques. Each specimen was wrapped in aluminum and

exposed horizontally to an external heat flux of 35 kW/m^2 . The experimental error from the cone calorimeter was about 5%.

Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50H thermoanalyzer under flowing air environment from room temperature to 700°C and at a heating rate of 10 K/min .

The limiting oxygen index (LOI) values were measured using an HC-2 type instrument (made in China) on the specimens of $12 \text{ mm} \times 6.5 \text{ mm} \times 4 \text{ mm}$ according to the standard oxygen index test ASTM D2863-77.

The UL-94 vertical burning tests were carried out using a CZF-1 type instrument (made in China) on the sheets of $127 \text{ mm} \times 12.7 \text{ mm} \times 3 \text{ mm}$ according to the standard UL-94 test ASTM D635-77.

RESULTS AND DISCUSSION

Structure Characterization of PP/EPDM/NP/LDH Nanocomposites

Figure 1 gives the low-angle XRD patterns of the OM-LDH, PP/EPDM/LDH5, and PP/EPDM/NP18/LDH5 samples. The basal spacing of the OM-LDH sample is measured to be 2.45 nm from the (001) maximum diffraction peak at around 3.6° (2θ) (see curve a). The PP/EPDM/LDH5 sample with 5 phr LDH shows a diffraction peak at around 2.1° (2θ) corresponding to the basal spacing of 4.37 nm , as shown in curve (b), which indicates that PP/EPDM has been intercalated into the OM-LDH layers to form the intercalated structure and thus to expand the basal spacing of LDH layers. When 18 phr NP was added into the PP/EPDM/LDH5 sample, the (001) diffraction peak of the LDH layers appears at $2\theta = 2.5^\circ$ and the basal spacing decreases to 3.60 nm , as shown in curve c of Fig. 1. The above results indicate that the addition of NP does not change the intercalation structures of the PP/EPDM/NP/LDH sample, and the decrease of basal spacing is probably due to the replacement of some macromolecular chains in the LDH layers by small molecular NP.

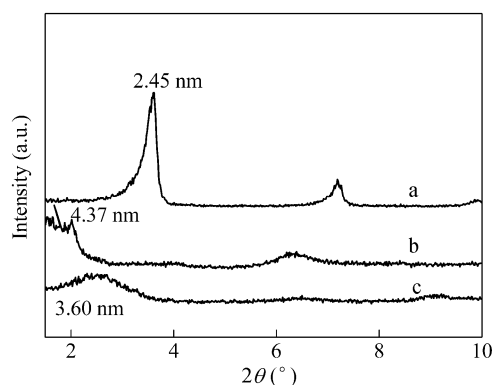


Fig. 1 Low-angle XRD patterns: (a) OM-LDH, (b) PP/EPDM/LDH5, (c) PP/EPDM/NP18/LDH5

The TEM images of the PP/EPDM/LDH5, PP/EPDM/NP25, and PP/EPDM/NP18/LDH5 samples are presented in Fig. 2. It can be seen clearly from the marked ellipse in Fig. 2(a) that the LDH layers in the PP/EPDM/LDH5 sample have been well dispersed in the PP/EPDM matrix, which is in good agreement with the results obtained from XRD analysis. However, the NP particles in the PP/EPDM/NP25 sample are badly agglomerated as dark (or gray) platelets pointed by the arrow in Fig. 2(b). In contrast, the well-dispersed NP particles as pointed by arrows can be observed from the TEM image of PP/EPDM/NP18/LDH5 sample. The LDH layer can improve the homogeneous dispersion of NP inorganic particles in the PP/EPDM/NP/LDH blends because of their electrostatic interaction between the metal cations from the LDH layers and the negative ions of PO_3 from NP. These results show that LDH can act as an efficient compatibilizer and synergist and promote the NP inorganic particles to disperse homogeneously in the PP/EPDM/NP/LDH nanocomposites.

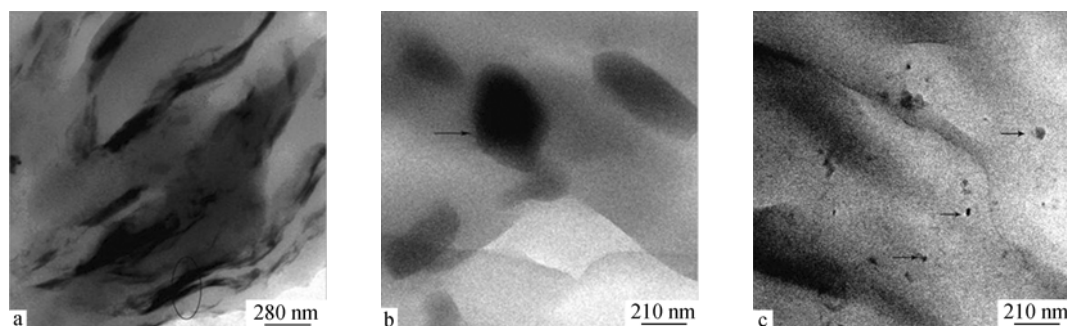


Fig. 2 TEM images of (a) PP/EPDM/LDH5, (b) PP/EPDM/NP25 and (c) PP/EPDM/NP18/LDH5 samples

Synergistic Effect of LDH with NP on Flame Retardant Properties

The LOI and UL-94 tests are widely used to evaluate the flame retardant properties of materials and to screen flame retardant formulations^[11]. The LOI and UL-94 data of the PP/EPDM samples with different amounts of IFR additive NP are listed in Table 1. It can be seen that only when the amount of NP reaches above 25 phr, the sample No. 6 and No. 7 can pass the UL-94 V-0 rating. Based on the total amount 25 phr of flame retardant the synergistic effects of LDH with NP were observed by replacing the IFR additive NP with LDH in the following section.

Table 2 lists the UL-94 and LOI data of the PP/EPDM/NP/LDH samples with different contents of NP and LDH. It can be seen that the four samples, PP/EPDM/NP20/LDH5, PP/EPDM/NP19/LDH5, PP/EPDM/NP18/LDH5 and PP/EPDM/NP20/LDH4 samples can pass the UL-94 V-0 rating, and their LOI values reach 33% to 35%. Among them, the PP/EPDM/NP18/LDH5 sample is the best one because of the least amount of additives. The result shows that 5 phr LDH can replace 7 phr NP, which means the synergistic effect of LDH with NP leads to decrease the total loading of the flame retardant additives while the sample keeps the similar flame retardant properties. It can be seen from Table 1 and Table 2 that the LOI value of PP/EPDM/NP20/LDH5 sample is 35%, whereas the LOI values of PP/EPDM, PP/EPDM/LDH5, and PP/EPDM/NP25 samples are 18%, 18%, and 33%, respectively, which indicates that 5 phr LDH instead of 5 phr NP can increase the LOI value from 33% to 35%. Apparently, the LOI value increase of 2% is due to the synergistic effect of LDH with NP.

The SEM micrographs in Fig. 3 show the morphological structures of the intumescent char layers obtained from the PP/EPDM/LDH5, PP/EPDM/NP25, and PP/EPDM/NP18/LDH5 samples, respectively. As we can see from two different scales of Fig. 3, the charred surfaces of the PP/EDPM/LDH5 and PP/EPDM/NP25 samples (Fig. 3I and Fig. 3II) are irregularly swollen and broken, whereas the PP/EPDM/NP18/LDH5 sample shows more homogenous and compact ceramic structures with some white draff of oxides (Fig. 3III). These results imply that the above enhanced flame retardant properties of PP/EPDM/NP18/LDH5 can be attributed to the more homogeneous dispersion of NP and formation of more compact charred layers after being burned of PP/EPDM/NP/LDH sample. This kind of charred layers can slow down the heat and mass transfer between the gas and the condensed phase and prevent the underlying polymeric substrate from further attack by heat flux in flame. The results observed from SEM further give the evidence that the synergistic effect of LDH with NP can promote more homogeneous dispersion of NP and formation of more compact charred layers and thus improve the flame retardant properties and thermal stability of the PP/EPDM/NP/LDH samples. Similar effects of LDH with hyperfine magnesium hydroxide (HFMH) in EVA/ HFMH /LDH nanocomposites have also been reported in our previous work^[19].

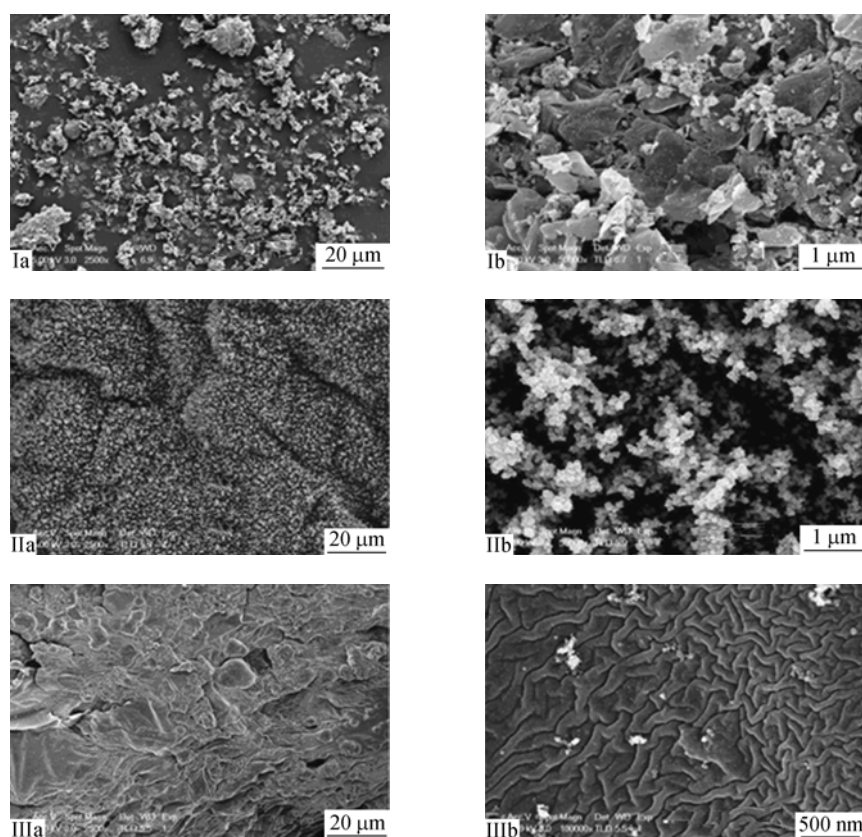


Fig. 3 SEM micrographs of the charred layers obtained from (I) PP/EPDM/LDH5, (II) PP/EPDM/NP25 and (III) PP/EPDM/NP18/LDH5 samples

Dynamic Flammability Characterization of PP/EPDM/NP18/LDH5 Sample

The cone calorimeter test based on the oxygen consumption principle has been widely used to evaluate the flammability characteristics of materials. Although the cone calorimeter test is a small-scale test, the obtained results have been found to correlate well with those obtained from a large-scale fire and can be used to predict the combustion behavior of materials in a real fire^[20–22]. The heat release rate (HRR) measured by cone calorimeter is a very important parameter as it expresses the intensity of a fire, which in turn determines other parameters, such as mass loss rate (MLR), specific extinction area (SEA) and fire growth rate. The peak HRR (pk-HRR) value is often used to express the intensity of a fire, and a highly flame retardant system normally shows a low average HRR (av-HRR)^[18, 22, 23].

The changes of HRR as a function of burning time for the PP/EPDM, PP/EPDM/NP25, and PP/EPDM/NP18/LDH5 samples are shown in Fig. 4. It can be found that the PP/EPDM sample without the IFR additive burns out in 277 s after ignition. A very sharp HRR peak appears at the range of 45–270 s with a pk-HRR value of 1198 kW/m², while the other two samples with flame retardant additives show dramatic decline of the HRR peaks and their combustion times prolong to 667 s and 682 s, respectively. The pk-HRR values of the PP/EPDM/NP25 and PP/EPDM/NP18/LDH5 samples at the range of 450 s to 670 s decrease drastically to 409 and 249 kW/m², respectively. This indicates the synergistic effect of LDH with NP greatly enhances the flame retardant efficiency of the PP/EPDM/NP18/LDH5 nanocomposites (Fig. 4), and the corresponding data are listed in Table 3.

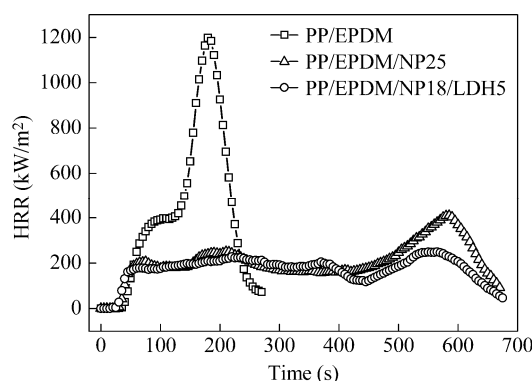


Fig. 4 Dynamic curves of the HRR versus burning time for the PP/EPDM, PP/EPDM/NP25 and PP/EPDM/NP18/LDH5 samples

Table 3. Related data of PP/EPDM, PP/EPDM/NP25 and PP/EPDM/NP18/LDH5 samples measured by the cone calorimeter test

CCT parameters	PP/EPDM	PP/EPDM/NP25	PP/EPDM/NP18/LDH5
pk-HRR (kW/m ²)	1198	409	249
av-HRR (kW/m ²)	414	205	173
av-MLR (g/s)	0.0974	0.0456	0.0419
TTI (s)	26	23	18
Combustion time (s)	277	667	682
FPI (m ² s/kW)	0.0217	0.0562	0.0723

Fire performance index (FPI) is defined as the ratio of time to ignition (TTI) to pk-HRR, which is independent of the tested sample thickness and is often used to predict whether a material can easily develop drastic combustion after ignition^[23]. Therefore, the greater the FPI value, the better the fire resistance. It can be seen from Table 3 that the FPI values of PP/EPDM, PP/EPDM/NP25, and PP/EPDM/NP18/LDH5 samples are 0.0217, 0.0562, and 0.0732 m²s/kW. Apparently, the PP/EPDM/NP18/LDH5 sample has the greatest value, which means that the PP/EPDM/NP18/LDH5 sample is the most difficult one in developing a combustion among the above three samples.

Another important parameter obtained from the CCT test is the mass loss rate (MLR). Figure 5 shows the MLR curves versus time for the PP/EPDM, PP/EPDM/NP25, and PP/EPDM/NP18/LDH5 samples. It can be seen that the MLR curves of the three samples have the similar features as the HRR curves. The av-MLR value of the PP/EPDM/NP18/LDH5 sample is the lowest among the 3 samples, as listed in Table 3. This means that the PP/EPDM/NP18/LDH5 sample is most difficult to lose its mass due to degradation.

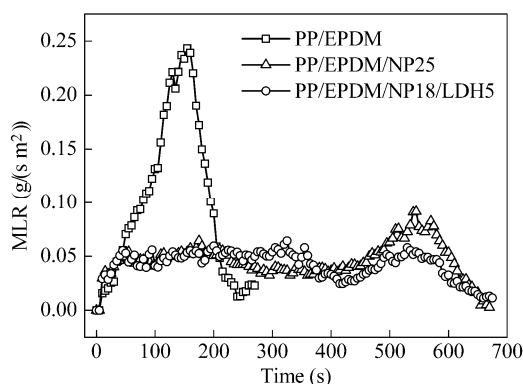


Fig. 5 Dynamic curves of the MLR versus burning time for the PP/EPDM, PP/EPDM/NP25 and PP/EPDM/NP18/LDH5 samples

Thermogravimetric Behavior of PP/EPDM/NP/LDH Samples

Figure 6 compares the TGA and DTG curves of the PP/EPDM, PP/EPDM/LDH5, PP/EPDM/NP25 and PP/EPDM/NP18/LDH5 samples. There is almost one major weight loss stage for the PP/EPDM and PP/EPDM/LDH5 samples. The degradation process occurs at the range of 240°C to 420°C and 230°C to 500°C, respectively, as shown in Fig. 6(a). The main differences of the two samples are their different residues after 500°C. The corresponding largest degradation rates occur at temperatures of 395°C and 404°C, respectively, as shown in Fig. 6(b). Two degradation stages are observed from the PP/EPDM/NP25 and PP/EPDM/NP18/LDH5 samples in Fig. 6(a). The first step occurs at the temperature range of 250°C to 400°C and 440°C to 470°C, whereas the second step occurs at 400°C to 490°C and 470°C to 500°C, respectively. The corresponding thermal degradation temperatures of the PP/EPDM/NP25 sample occur at 387°C and 463°C, while the corresponding thermal degradation temperatures of the PP/EPDM/NP18/LDH5 sample occur at 400°C and 609°C, respectively, as shown in Fig. 6(b). These results show that the thermal degradation temperatures of the PP/EPDM/NP18/LDH5 sample are much higher than those of the PP/EPDM/NP25 sample. The molecular structure of LDH is very similar to those of flame retardants magnesium hydroxide and aluminum hydroxide, as reported in our previous work^[20]. The synergistic effect of LDH with NP can enhance the thermal stability of the PP/EPDM/NP/LDH samples. This is because the nano-structural LDHs with large surface area are of high thermal capacity and their decomposition will release large amount of water and absorb the heat that can raise the thermal degradation temperature of polymer materials. Besides, LDH can promote the formation of compact charred layer structures, which can further increase the thermal stability and flame retardant properties of PP/EPDM/NP/LDH nanocomposites.

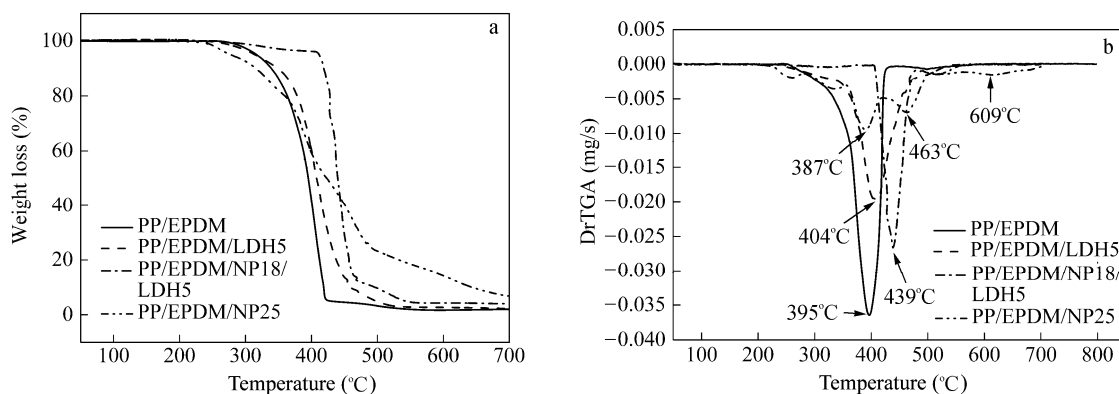


Fig. 6 TGA (a) and DTG (b) curves of the PP/EPDM, PP/EPDM/LDH5, PP/EPDM/NP25 and PP/EPDM/ NP18/LDH5 samples

CONCLUSIONS

The synergistic effects of LDH with the phosphorus-nitrogen intumescent flame retardant NP in the PP/EPDM/NP/LDH nanocomposites and related properties have been studied by XRD, TEM, SEM, CCT, TGA, LOI and UL-94 tests in this work. The LOI and UL-94 data show that a suitable amount of LDH combined with NP can obtain the highest flame retardant properties of the PP/EPDM/IFR/LDH nanocomposites. The results from XRD, TEM and SEM show that LDH can act as efficient compatibilizer and synergist, which improve the homogeneous dispersion of NP and promote the formation of compact charred layers in the PP/EPDM/NP/LDH nanocomposites during burning. The data from CCT give further evidence that the synergistic effects of LDH with NP apparently decrease the HRR and MLR values and thus enhance the flame retardant properties of the PP/EPDM/NP/LDH samples. The TGA results also show that the thermal degradation temperatures of the PP/EPDM/NP18/LDH5 sample are much higher than those of the PP/EPDM/NP25 sample because of the synergistic effect of LDH with NP.

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