

# Study on fire retardant mechanism of nano-LDHs in intumescent system

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**This paper investigated the fire-retardant mechanism of the nano-LDHs in the intumescent system by the temperature programmed oxidation (TPO). Researches were also conducted to explore the function of the nano-LDHs in the composite fire-retardant agents in air and nitrogen atmosphere, respectively. The results indicated that the nano-LDHs species were responsible for the catalytic oxidation of the rich-carbon compound in oxygen atmosphere. In addition, the nano-LDHs species and their calcinated products at high temperature could increase the carbonaceous residue-shield of the carbon-rich materials, improve the quality and the graphitization degree of the formed char-layer, and accelerate the intumescence and expansion of the melting carbon-rich materials to a certain degree under the oxygen-free condition, leading to the carbonization and expansion of the intumescent layer.**

nanometer, layer double hydroxides (LDHs), fire-retardant mechanism, intumescent system

Since the layered double hydroxides (LDHs) were firstly published to be used as precursors of new catalysts by Miyata S<sup>[1]</sup> in 1971, many issues on their potential applications were increased year after year. The interstitial layers of LDHs were analogous to the molecular sieve, leading to their direct application to a rigidity support framework for the intumescent coat of the fire-retardant coating with an increasing fire-retardant performance. Moreover, the complex metal oxides, formed by calcination of LDHs at different temperature, exhibited an improvement on the carbonization of intumescent layer of fire-retardant coating in fire. Therefore, the LDHs gradually became an ideal fire-retardant auxiliary agent. It should be noticed that the nanometer layered double hydroxides (nano-LDHs) had received considerable interests owing to their comprehensive applications as fire-retardants in recent years. The thermal stability and thermal degradation process of nano-LDHs were analyzed by Yang W et al.<sup>[2-4]</sup>, and their fire-retardant performance were also investigated by Xu Jianghua et al.<sup>[5-7]</sup>, however, there were few studies on their fire-

retardant mechanism. The present work mainly purposed to firstly study the fire-retardant mechanism of nano-LDHs by the temperature programmed oxidation, and investigate their fire-retardant function in the intumescent fire-retardant system.

## 1 Experimental

### 1.1 Reagent and instruments

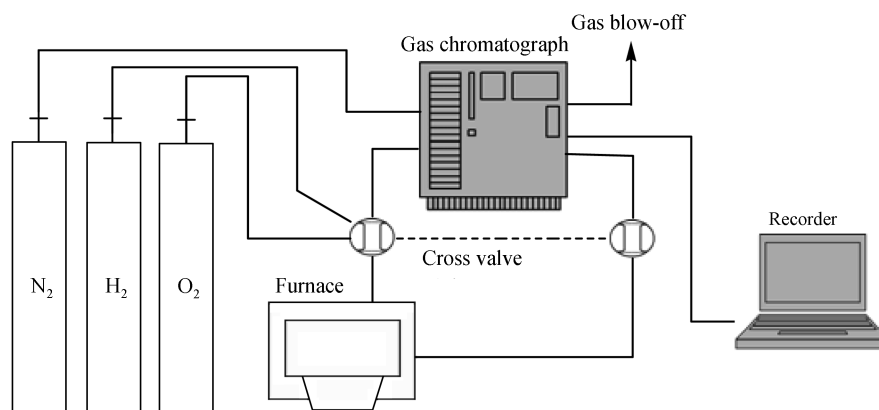
The preparation of the purposed products was carried out on the QM planet-style ball mill (Instrument Factory of Nanjing University). The self-manufactured temperature programmed oxidation (TPO) equipment, whose temperature control was carried out on an AI-708PA artificial intelligence industry adjuster (ÜGU Company), was recorded on the produced gas quantity (Figure 1).

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**Figure 1** Program heat equipment plot to test the removal of gas quantity during the charring of the fire-retardant reagents.

The nano-LDHs,  $\text{Mg}_{6.14}\text{Al}_{2.17}(\text{OH})_{16.78}\text{CO}_3 \cdot 4.74\text{H}_2\text{O}$  with a particle size of 10–40 nm was synthesized according to the literature<sup>[8]</sup>. Polyethylene (99 grade of PE, the pentaerythritol content  $\geq 98\%$ , Yunnan Yun Tian Hua Company, Ltd.), Ammonium Polyphosphate (APP, polymerization degree  $\geq 63$ , Changfeng Chemical Industry Company of Shifang City, Ltd.), and Melamine (Mel, Sichuan Chemical Industry Group) were used without any further purification.

## 1.2 Synthesis of the composite fire-retardants

A desired amount of pentaerythritol, APP, Mel, and nano-LDHs were well-proportioned mixed and grinded to obtain a well-distributed composition with a particle size of less than 80  $\mu\text{m}$  (Table 1).

## 1.3 Measurement of the produced gas quantity by TPO

A desired quantity of composite fire-retardant reagent was added to the U quartz tube lying in the center of the calcination furnace. Then, oxygen gas flowed into the U quartz tube at a rate of 17 mL/min until the baseline of the graphic instrument become stable. In the present study, the curve about the produced gas quantity was recorded on a TPO instrument by heating the sample in an  $\text{O}_2$  atmosphere from 28 to 1028°C at a heating rate of 10°C/min. The remains were weighted.

## 1.4 Carbonization

0.1 g of the composite fire-retardant reagents was added to the U quartz tube. Then,  $\text{N}_2$  flowed into the tube at a rate of 34 mL/min until the baseline of the recorder was even and level. In this study, the curve about the produced gas quantity was recorded on a TPO instrument by heating the sample from 28°C to a desired temperature at a heating rate of 20°C/min and then holding on a constant temperature in an  $\text{O}_2$  atmosphere. After 1 h, the samples were forcibly cooled to the room temperature at a rate of 20°C/min, resulting in a charring product. The remains were weighted in order to calculate mass loss.

## 1.5 Measurement of produced gas quantity of carbonized products by TPO

$\text{O}_2$  flowed into the U quartz tube at a rate of 17 mL/min until the baseline of the graphic instrument was even and level. The curve about the produced gas quantity was recorded on a TPO instrument by heating the sample from 28 to 1028°C at a rate of 10°C/min and in an  $\text{O}_2$  atmosphere. The remains were also weighted.

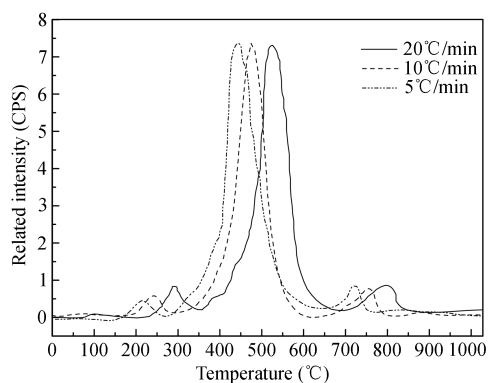
## 2 Results and discussion

### 2.1 The TPO curves at the different heating rates

The curves of gas quantity produced from the heated nano-LDHs are shown in Figure 2 at the different heat-

**Table 1** The content of composite fire-retardants

No.	Sample	$m(\text{Mel})$ (g)	$m(\text{PE})$ (g)	$m(\text{APP})$ (g)	$m(\text{nano-LDHs})$ (g)
S-1	PE	–	0.600	–	–
S-2	APP+PE	–	0.600	1.4994	–
S-3	nano-LDHs	–	–	–	1.5026
S-4	nano-LDHs+PE	–	0.600	–	1.5026
S-7	APP	–	–	1.4994	–
FR-0	APP+PE+Mel	0.6	0.9	2	–
FR-1	APP+PE+Mel+nano-LDHs	0.6	0.9	2	0.3



**Figure 2** The thermal decomposition condition of the purposed nano-LDHs, at the varied heating rate, under O<sub>2</sub> atmosphere at a flow rate of 17 mL/min.

ing rates. From these curves, we can elementarily see that (1) the initial time of the decomposed and overflowed volatile gas is different with continuous heating; (2) the quicker the heating rate, the higher the peak temperature of overflowed volatile gas will be; otherwise lower. This is the same as the result of the thermogravimetric analysis. In the temperature range of 309–589°C, there is a big gas flow peak.

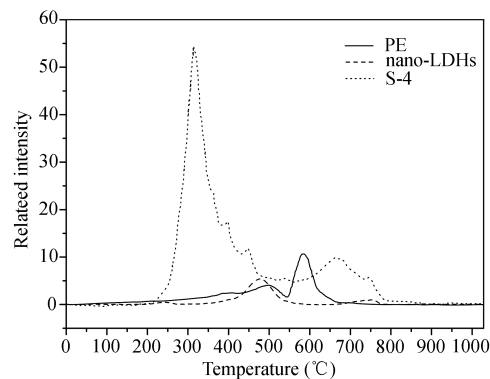
## 2.2 Improvement of nano-LDHs on PE carbonization

2.2.1 In O<sub>2</sub> atmosphere. The mass loss of the S-1, S-3, and S-4 are shown in Table 2. From these data, we can conclude that mass loss of S-4, prepared by co-mixing nano-LDHs and PE, is lower than that of pure PE.

**Table 2** The removal gas of Sample PE, nano-LDHs and S-4 at 10°C/min under O<sub>2</sub> atmosphere

No.	Samples	Initial mass (g)	Mass loss (%)
S-1	PE	0.0060	76.8
S-3	Nano-LDHs	0.0154	54.8
S-4	PE+nano-LDHs	0.0214	67.5

From Figure 3, it is seen that two gas flow peaks of S-4 are observed in the temperature range of 170–557°C and 560–825°C, respectively. Furthermore, both peaks are different with those of PE raw materials. The first gas-producing temperature of S-4 appears in 314.1°C and is lower than that of PE. Since the area of removal peak represents the removal quantity of gas, the first removal amount of gas for the heating S-4 is more than that of PE or nano-LDHs in the temperature region of 170–557°C. Additionally, The second gas peak temperature of S-4 is observed in 666.2°C, which is higher than that of pure PE in the temperature range of 560–



**Figure 3** The removal gas of sample PE, nano-LDHs and S-4 at 10°C/min under O<sub>2</sub> atmosphere. Flowing rate = 20 mL/min, during 28–1028°C.

825°C. The reasons are as follows: (1) The nano-LDHs can catalyze the oxidation of the organic substance in presence of O<sub>2</sub>, resulting in the fact that PE produces much gas and simultaneously releases a great deal of H<sub>2</sub>O, CO and CO<sub>2</sub> in lower temperature<sup>[2]</sup>. (2) The second peak of S-4 in 666.2°C should be attributed to the contribution of removal CO and CO<sub>2</sub> from oxidization of the produced graphite layer with a high crystallinity, which comes from the oxidization and carbonization of PE. When heated, the surface layer of a heap of the S-4 power will be melted and then carbonized, and then the inner of the purposed power will be coated and wrapped, therefore leading to an anoxic status in the inner fine particle. Under the anoxic condition, the nano-LDHs and the produced oxide (such as Al<sub>2</sub>O<sub>3</sub> and MgO) can accelerate the PE carbonization to obtain a graphite layer with a high degree graphitization, resulting in above-mentioned second gas peak under higher temperature. This point is different with that of the pure PE without the nano-LDHs, which can hardly produce the graphite layer at the high temperature region.

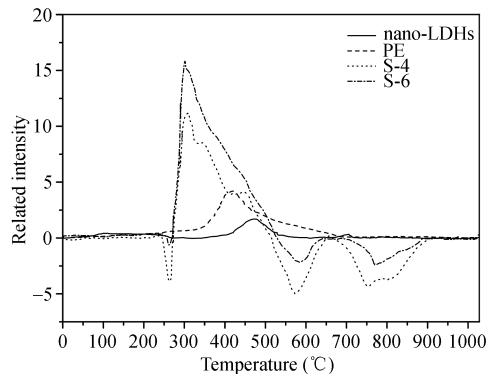
In contrast, the catalytic oxidization of nano-LDHs is obvious; however, the carbonization-accelerated effect of the inner nano-LDHs as well as their produced oxides is comparatively weaker.

2.2.2 In N<sub>2</sub> atmosphere. In order to measure the carbonization-accelerated effect of nano-LDHs, the composite samples containing nano-LDHs were decomposed under N<sub>2</sub> atmosphere.

In N<sub>2</sub> atmosphere, on the one hand, the organic substances will be carbonized and decomposed to give off many small molecule volatile substances, leading to the presence of “positive value” gas peak; on the other hand, the nano-LDHs can accelerate the melted PE to produce

a heat-insulated carbon layer with excessive microporous, which will be filled and detained by the flow gas (such as inert carrier gas and the produced gas), leading to the presence of “negative value” gas peak.

From Figure 4, a “negative value” peak in the temperature range of 240–270°C can be observed in the curve of S-4. It indicates that the surface of PE system has been quickly carbonized and swelled, thus the more inert carrier gas and the produced gas are detained and left behind.



**Figure 4** The removal gas of Sample PE, nano-LDHs, S-4 and S-6 at 10 °C/min under N<sub>2</sub> atmosphere. Flowing rate = 20 mL/min, during 28–1028°C.

A “positive value” peak in 270–520°C can also be observed in the curve of S-4, which shows that the PE is carbonized and decomposed to give off a great deal of volatile gas which is far more than the detained gas. However, this peak area is yet far less than that of the composite PE burned in O<sub>2</sub>. It is perhaps because the nano-LDHs cannot bring into play a catalytic oxidization in N<sub>2</sub>.

When the temperature is up to 520–640°C and 650–920°C, respectively, the curve of the purposed sample also shows a “negative value” peak. Since the melting inner layer of the above-mentioned sample particles have instantly been carbonized and swelled to produce a number of compact and multiporous carbonaceous-layer, the more inert carrier gas and the produced gas are detained and left behind.

With the increasing of temperature, the remanent OH<sup>-</sup> of the nano-LDHs can rapidly decompose into water, and the interlayer CO<sub>3</sub><sup>2-</sup> can also give off CO<sub>2</sub>, so that the nano-LDHs form the multiporous Al<sub>2</sub>O<sub>3</sub> and MgO, which makes up a removal passage of gas. Simultaneously, the char-rich compound PE will melt to form a flow pattern, then further crack and carbonate to emit water vapour and incombustible gas, so that the above

melted system is boiled. It turns out that the melted PE is coated on the surface of nano-LDHs, resulting in a reaction with each other to form the Al—C and Mg—C bonds<sup>[9]</sup>, the decrease of mass loss, and the increase of remains mass in the intumescent system (Table 3).

**Table 3** The removal gas condition of sample PE, nano-LDHs and S-4 at 10°C/min in N<sub>2</sub> atmosphere

No.	Samples	Initial mass (g)	Mass loss (%)
S-1	PE	0.0061	70.7
S-3	nano-LDHs	0.0154	54.4
S-4	PE+nano-LDHs	0.0214	56.4
S-6	PE+LDHs	0.0214	57.7

Therefore, the nano-LDHs can improve the formation of an intumescent and heat-insulating carbonaceous layer into polymer to some extent, which can be explained by the “Hotspot Nucleation” mechanism. That is to say that the molten mass near the hotspot will firstly melt to become a low potential energy point, leading to formation of nucleation of the molten mass.

According to the heterogeneous nucleation mechanism, we can obtain the following formula:

$$\Delta G_{\text{het}}^x = \Delta G_{\text{hom}}^* S(\theta).$$

Thereinto,  $\Delta G_{\text{het}}^x$  is critical free energy of heterogeneous nucleation;  $\Delta G_{\text{hom}}^*$  is critical free energy of homogeneous nucleation;  $S(\theta)$  is interface entropy. Because of  $0 < S < 1$ , the left  $\Delta G_{\text{het}}^x$  of the above formula is always less than  $\Delta G_{\text{hom}}^*$ . It can be inferred that the formation of the nucleation agent and bubble nucleus is of great advantage to production of a number of air bubbles. According to this theory, we can derive the conclusion as follows: The nano-LDHs and the produced Al<sub>2</sub>O<sub>3</sub> and MgO can be uniformly dispersed into the molten system to become a low potential energy point, namely the nucleation agent and bubble nucleus. Then, the gas and liquid phase will be directly blent to form a superfine air bubble nucleus, which will be affected by the purposed incombustible gas from the decomposition of polymer and nano-LDHs. It is worth the whistle that the nano-particles (such as the nano-LDHs) will play a key role on improving the quality of the formed superfine bubble, whose denseness and minuteness will play a fatal role on determining the compaction degree and distribution of the final intumescent carbonaceous layer.

According to requirement of free energy during the

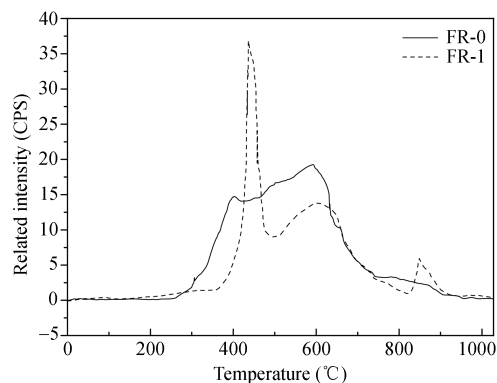
formation of bubble nucleus, we can also derive further the formula as follows:

$$\Delta F = rA.$$

Thereinto,  $\Delta F$  is interface free energy;  $r$  is surface tension;  $A$  is total interface area of air bubble. Therefore, it can be inferred that  $A$  will be increased and corresponding  $r$  must be decreased if the nucleus density of air bubble is increased. Increases of temperature and interface can decrease the surface tension ( $r$ ), which will be of great advantage to the formation of a number of bubble nucleus, so the nano-LDHs with a bigger specific surface will be in favor of the formation of bubble nucleus, and the great stiff and thick molten-mass containing the nano-LDHs particles will be beneficial to the growth, stabilization, and shaping of the formed carbonaceous layer. These results are similar to the catalytic carbonization of the molecular sieve in polypropylene according to ref. [10].

### 2.3 Influence of nano-LDHs to intumescent system

Figure 5 shows that FR-0 without the nano-LDHs continuously decomposes into and gives off the small molecule gas in the temperature range of 260–940°C, whereas FR-1 containing nano-LDHs is firstly carbonized and subsequently pyrolyzed into CO and CO<sub>2</sub> in the higher temperature range of 823–925°C. This indicates that the composite fire-retardant system containing the nano-particles produces a graphite layer with a high crystallinity at the carbonaceous stage, which should be attributed to the contribution of the nano-LDHs. In other words, the nano-LDHs can make the surface layer of the composite fire-retardant system containing App, Mel, and PE catalyzed and oxidized, and simultaneously, the inner layer of this composite fire-retardant system is



**Figure 5** The removal gas of the charring samples at the varied temperatures.

carbonized to obtain an intumescent and heat-insulating carbonaceous layer.

## 3 Conclusions

From the above analysis, we can obtain the following conclusions: (i) The quicker the heating rate of the purposed nano-LDHs, the higher the peak temperature of overflowed volatile gas will be; otherwise lower. (ii) The nano-LDHs have a capacity to catalytically oxidize the char-rich compound in the presence of O<sub>2</sub>; and under this anoxic condition, the nano-LDHs can accelerate the carbonization of the char-rich compound to obtain a more remnant char, improve the graphitization degree of the formed char, and further encourage the formation of an intumescent and heat-insulating carbonaceous layer to some extent. (iii) The nano-LDHs can make the surface layer of the composite fire-retardant system containing App, Mel, and PE catalyzed and oxidized, and simultaneously, the inner layer of this composite fire-retardant system can be carbonized to obtain an intumescent and heat-insulating carbonaceous layer.

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