



# Improvement of flame retardancy and thermal stability of polypropylene by P-type hydrated silica aluminate containing lanthanum



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## ABSTRACT

Raw kaolinite (kaol) was experimentally transformed to P-type hydrated silica aluminate (HSA-P). After treated by  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  solution, the final product of La-loaded for P-type hydrated silica aluminate (HSA-P-La) was obtained. The middle and final products were characterized using fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM). Kaol, HSA-P, HSA-P-La was introduced into PP with intumescent flame retardants (IFR), respectively. And their effect on the flame retardant and thermal properties of PP composites was studied by limiting oxygen index (LOI), vertical burning test, cone calorimeter test (CCT) and thermogravimetric analysis (TGA). The LOI increases from 18.0% of neat PP to 31.2 in composite of 75 wt% PP/25 wt % IFR, further increases to 32.5, 35.1, 37.5 in 75 wt% PP/23.5 wt % IFR/1.5 wt% Kaol, HSA-P or HSA-P-La, respectively. CCT results show heat release content and rate is best controlled in PP/IFR/HSA-P-La composite. Morphology observation indicates the char layer of PP/IFR/HSA-P-La composite is most compact and thick, which guarantees excellent fire resistance. At same time the effect of HSA-P/HSA-P-La was also compared with generally used A-type hydrated silica aluminate (HSA-A)/HSA-A-La. Anyway HSA-P/HSA-P-La exhibited higher efficiency than HSA-A/HSA-A-La in both flame retardancy and thermostability.

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## 1. Introduction

Hydrated silica aluminate (HSA) is a porous tridimensional aluminosilicate and generally used as catalyst/adsorbent/ions exchange [1–3]. After Bourbigot proposed that HSA can be used as synergistic flame retardant in polymer [4], more and more research focused on its application and mechanism [5–10]. In all the application, the most common structure, HSA -A was widely used. Nie [11] and Demir [12] reported that only 1–5 wt% HSA adding in polymer/intumescent flame retardant (IFR) will obviously lifted LOI and decrease heat release. Feng [13] found that introduction of HSA

into Polypropylene (PP)/IFR promoted the formation of compact and homogeneous carbonaceous char layer on the outer surface of the material during burning. Further research found HSA -P, with more open, flexible and adaptable crystal structure than popular A-type hydrated silica aluminate (HSA-A), showing better catalytic efficiency, absorbability and ion exchange capacity [14–16]. And some rare earth metal, especially those light elements such as La/Ce embedded in HSA will also accelerate efficiency of HSA [13–21].

Kaolinite (kaol) is a natural mineral with rich deposit. In recent years, kaol [22,23] and modified kaol [24–31] were used as synergistic in PP/IFR in our work. Several kinds of modified kaol at different steric configuration were designed and prepared. And their synergistic effect in PP/IFR was studied in detail. In our work, raw kaol was treated by different way to form one-dimensional nanorolls [24], two-dimensional exfoliated/intercalated plates [25–29] and tri-dimensional HSA structure [30,31]. Many literature found HSA fabricated from kaol exhibited excellent flame retardant [32–39]. In our work we also found all the modified kaol showed

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improved synergistic flame retardant in PP/IFR but HSA fabricated from kaol was the most potential way.

Based on previous work, we tried to prepare HSA-P from kaol and also embed  $\text{La}^{3+}$  ions. Its synergistic flame retardant efficiency in PP/IFR was compared with HSA-A. At last the flame retardant mechanism was inferred according to all the experimental results.

## 2. Experimental

### 2.1. Materials

PP (melt flow rate of 3 g/10 min) used in this work was produced by Sinopec Maoming Company (Maoming, China). The raw kaol with the average particle size about 20  $\mu\text{m}$  was friendly offered by Xing Yi Mineral Processing Plant (Shijiazhuang, China). Ammonium polyphosphate (APP) was purchased from Shandong Jin Ying Tai Company, China. Melamine (MEL) was obtained from Henan Zhong Yuan Da Hua Company, China. Pentaerythritol phosphate (PEPA) was provided by Zhejiang Victory Chemistry Co., Ltd, China. In this work, Microencapsulation of APP (MCAPP) was obtained by the reaction between APP and MEL [30].

Formaldehyde solution (concentration of 36%) and lanthanum chloride ( $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ) were purchased from Tianjin Fu Chen chemical reagent factory, China. Urotropin was purchased from Xi Long Chemical Company, China. Ammonium chloride ( $\text{NH}_4\text{Cl}$ ) was provided by Tianjin Guang Fu Technology Development Company, China.

### 2.2. Characterization

X-ray diffraction (XRD) patterns were obtained with D/max-2500 diffraction. It was operating at 40 KV and 20 mA, using filtered Cu Ka radiation ( $\lambda = 0.154 \text{ nm}$ ). For all the samples, the scan rate is  $10^\circ/\text{min}$  with the angle  $2\theta$  varying from 3 to  $50^\circ$ .

Fourier transform infrared (FTIR) spectra were recorded on an instrument of Thermo Nicolet IS 5 in the range of  $400\text{--}4000 \text{ cm}^{-1}$  by using KBr pellet.

Thermogravimetric analysis (TGA) was conducted under  $\text{N}_2$  atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  from room temperature to  $700^\circ\text{C}$  using a thermal analyzer (STA449C, Netzsch). The mass of each sample is about 4–5 mg.

Microtopography was observed on a Hitachi S-4700 scanning electron microscopy (SEM) with the voltage of 10 kV.

Limiting oxygen index (LOI) was tested with a JT-30 limited oxygen index instrument (Jiangning instrument, Nanjing, China), the samples size is  $120 \times 6.5 \times 3 \text{ mm}^3$ . The experiments were repeated five times.

Vertical burning test were performed on a CZF-3 apparatus (Jiangning, China) to obtained UL-94 grade. The sample dimension is  $125 \times 13 \times 3 \text{ mm}^3$ . The experiments were repeated five times.

The fire behavior was performed using cone calorimeter (FFT Co., Ltd) according to ISO 5660 standard. A  $100 \times 100 \times 3 \text{ mm}^3$  plate was exposed to a heat radiant flux density of  $50 \text{ kW}/\text{m}^2$ .

### 2.3. Sample preparation

#### 2.3.1. Synthesis of HSA-P/HSA-P-La

Raw kaol was calcined at  $1000^\circ\text{C}$  for 2 h and metakaolinite with higher activity was obtained. 4.5 g of metakaolinite powder was added into 30 mL of 3 mol/L NaOH solution. The mixture was then stirred and heated at  $90^\circ\text{C}$  for 10 h. The reacted mixture was washed three times with ethanol, and then filtrated before being dried at  $60^\circ\text{C}$  for 12 h. The product is referred as HSA-P.

About 7.5 g HSA-P was mixed with 150 mL of 2 mol/L  $\text{NH}_4\text{Cl}$  solution under magnetic stirring at  $80^\circ\text{C}$  for 1 h, after washing with

**Table 1**

Formulations of PP composites (weight percentage, wt%).

|                       | PP   | IFR   |      | Synergistic FR <sup>a</sup> |
|-----------------------|------|-------|------|-----------------------------|
|                       |      | MCAPP | PEPA |                             |
| PP                    | 100  |       |      |                             |
| PP/Synergistic FR     | 98.5 |       |      | 1.5                         |
| PP/IFR                | 75   | 16.7  | 8.3  |                             |
| PP/IFR/Synergistic FR | 75   | 15.7  | 7.8  | 1.5                         |

<sup>a</sup> Synergistic FR: kaol, HSA-P; HSA-P-La; HSA-A; HSA-A-La.

ethanol three times, filtration and drying, the obtained intermediate was named as HSA-P- $\text{NH}_4^+$ . Subsequently, 3 g HSA-P- $\text{NH}_4^+$  was added into 100 mL of 0.5 mol/L  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  solution with stir at  $100^\circ\text{C}$  for 1 h, after washing with ethanol three times, filtration and drying, obtained product of HSA-P-La- $\text{NH}_4^+$ . After calcination at  $650^\circ\text{C}$  for 2 h, the final product was named as HSA-P-La.

#### 2.3.2. Preparation of composites

Compositions were extruded using a micro twin-screw extruder (Wuhan Rui Ming Plastics Machinery Co., Ltd) with the rotational speed of 40 rpm. The processing temperatures of different section were maintained at 160, 180, and  $185^\circ\text{C}$ , respectively. The formulations are showed in Table 1. The IFR used in this experiment is composed by MCAPP/PEPA = 2:1.

The preparation of HSA-A/HSA-A-La and PP/IFR composite containing HSA-A/HSA-A-La has been introduced in the earlier work [31].

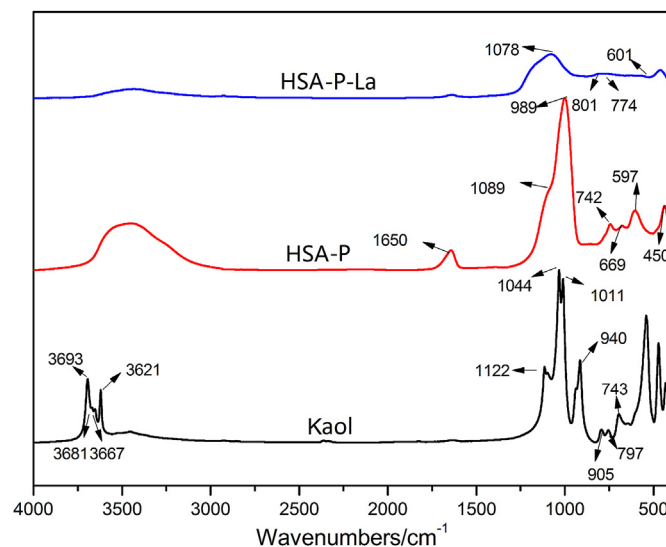
## 3. Results and discussion

### 3.1. Characterization of HSA-P and HSA-P-La

#### 3.1.1. FTIR

The FTIR spectra of kaol, HSA-P and HSA-P-La are showed in Fig. 1. In the spectrum of kaol, several separated bands in  $3600\text{--}3700 \text{ cm}^{-1}$  are ascribed to the outer or inner -OH groups respectively. Several bands in the lower wavenumber at  $800\text{--}1200 \text{ cm}^{-1}$  are attributed to Si-O/Al-O [31].

The spectrum of HSA-P is obviously different from that of kaol. The separated -OH group bands are merged into a diffuse peak in  $3000\text{--}3700 \text{ cm}^{-1}$  accompanied with the peak emerged at



**Fig. 1.** FTIR spectra of kaol, HSA-P and HSA-P-La.

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