



Effects of surface acid-activated kaolinite on the fire performance of polypropylene composite



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ARTICLE INFO

Article history:

Received 21 July 2016

Received in revised form

17 November 2016

Accepted 11 December 2016

Available online 15 December 2016

Keywords:

Kaolinite

Acid-activated

Flammability

Thermostability

Polypropylene

Catalysis

ABSTRACT

Modified kaolinite containing Lewis acidic sites (Acid-Kaol) was prepared by calcination of kaolinite (Kaol) and successive acid treatment. Acid-Kaol was then introduced into polypropylene (PP) with intumescent flame-retardant (IFR). The flammability and thermostability of PP/IFR/Acid-Kaol were studied by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter test (CCT) and thermogravimetric analysis (TGA). LOI value of PP/25 wt.% IFR composite was 31.1%, it increased to 34.9% by 1.5 wt.% Acid-Kaol substitution with IFR. Moreover, the peak of heat release rate (PHRR) of PP/IFR/Acid-Kaol decreased 46.8% compared with that of PP/IFR composite. The residues after CCT were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectrometer (XPS) and FTIR. It was indicated that Acid-Kaol accelerated crosslinking during combustion and promoted char formation, which will act as insulating barrier to protect the matrix from further decomposed.

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1. Introduction

PP is highly combustible with severe dripping and no char left, its LOI is only 18%, which restricts its application in flame-retarded field. To face these problems, much work has been done, such as intumescent flame retardants (IFR) with inorganic clay are often considered to be the most effective way [1–6].

Synergism between nature clay and IFR has been documented by many researchers [1–10], such as montmorillonite (MMT) and halloysites (HNTs) are obtained more attentions. Comparatively, kaolinite (Kaol) or modified kaolinite received less attention [11,12]. Kaol is an abundant nature clay mineral, and it is a 1:1 layer sheet structured hydrated aluminum silicate with a very fine particle size with one silicon oxygen (SiO_4) tetrahedral layer and one alumina $[\text{Al}(\text{O},\text{OH})_6]$ octahedral layer (or expressed in other way, $[\text{Si}_2\text{O}_5]^{2-}$ sheet and $[\text{Al}_2(\text{OH})_4]^{2+}$ sheet) with pseudo-hexagon asymmetry, bonded together through sharing of apical oxygen and exists alternately, with the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ [13–15]. The stacked layers are linked by strong hydrogen bonding, and the asymmetric structure can create large superposed dipoles. This structure makes Kaol resistant to acid leaching; however,

metakaolinite is generally used because of its higher susceptibility to acid activation [16,17], resulting in increasing surface area, porosity and number of acid centers, as well as leaching of Al, Mg, and Fe cations with respect to the parent clays. Acid-activated clays are considered as efficient solid catalysts that can provide acid sites, and a wide range of pore sizes to extend the surface area [16,18,19]. In addition, Dong et al. proposed that the introduction of the acid-activated objects can promote cross-linking reactions and char formation during burning of polystyrene [20]. However, the effect of acidic site changes in acid-activated metakaolinite for the flame retardancy of polymer has not yet been reported so far. In this work, Lewis acidic sites on the surface of Kaol (Acid-Kaol) was increased via high temperature calcinations and acid treatment, and then the Acid-Kaol was used as catalytic synergists with IFR to improve crosslinking and char formation in PP. The flame retardancy and thermal stability were investigated by LOI, UL-94, CONE and TGA. The char residue after combustion was also examined by SEM, XPS and FTIR. Meanwhile, the mechanism of char promoting effect of acid-activated metakaolinite during the burning of PP composite was proposed.

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2. Experimental

2.1. Materials

A commercial PP (Sinopec Group) with melt flow index of 3 g/10 min was used. Ammonium polyphosphate (APP) was purchased from Jin Ying Tai chemical Co., Ltd (Jinan, China). Melamine (MA) was obtained from Jin Tong Le Tai chemical product Co., Ltd (Beijing, China). Pentaerythritol phosphate (PEPA) was a product of victory chemistry Co., Ltd (Zhangjiagang, China). Sulfuric acid was supplied by Beijing chemical factory (Beijing, China). The raw kaolinite was provided from Xing Yi mineral processing plant (Shijiazhuang, China).

2.2. Preparation of acid-activated kaolinite

Kaol was calcined at 850 °C for 2 h, providing metakaolinite that was labeled as C8. Then C8 was activated at 90 °C for 1 h with 4 mol/L sulfuric acid solutions, and then washed with distilled water before dried at 100 °C for 24 h (named as C8S4). Finally, C8S4 was calcined at 400 °C for 2 h (the final product was designated as Acid-Kaol). The synthetic process was listed in [Scheme 1](#).

2.3. Preparation of MCAPP

40 g APP and 100 mL anhydrous alcohol were mixed with 200 mL distilled water in a 500 mL beaker under vigorous stirring at 25 °C. Then 10 g of formaldehyde solution (36% mass fraction), 0.03 g of urotropin and 6 g melamine were added to a three-necked glass flask equipped by vigorous stirring. The mixtures were stirred for 5 min under 25 °C. Next the reaction system was heated up to 80 °C. When the mixtures changed from muddy to clear and the precipitation ratio was moderate, the pH value was adjusted to 8 by using 5 wt% Na₂CO₃ solutions. The obtained sample was denoted as MF. Subsequently, the pH value was adjusted to 5 by using HAC solution after MF was transferred to the beaker containing APP mixtures. Finally, the mixtures were transferred into a 500 mL three-necked glass flask equipped with a stirrer. The mixtures were stirred for 2 h at 80 °C. The experimental products were filtered and washed with ethyl alcohol and distilled water two times, respectively, and dried for 12 h at 80 °C and the final product MCAPP was obtained. The synthetic process of MCAPP was listed in below [Scheme 2](#).

2.4. Preparation of PP composites

The PP composites were prepared by melt blending with a micro twin-screw extruder (Wuhan Rui Ming Plastics Machinery Co. Ltd). The processing temperatures of different section were maintained at 160, 180 and 200 °C, respectively.

[Table 1](#) presents the weight percentages of PP and additives.

Table 1
Formulation of PP composites.

Samples	PP (wt%)	IFR (wt%)	Kaol (wt%)	Acid-Kaol (wt%)
PP	100.0	–	–	–
PP/IFR	75.0	25.0	–	–
	75.0	24.5	0.5	–
PP/IFR/Kaol	75.0	23.5	1.5	–
	75.0	22.0	3.0	–
	75.0	24.5	–	0.5
PP/IFR/Acid-Kaol	75.0	23.5	–	1.5
	75.0	22.0	–	3.0

2.5. Measurements

XRD was performed with a D/max-2500 diffractometer. The Cu K α radiation source was operated at 40 kV and 20 mA ($\lambda = 0.154$ nm). The interlayer space of clay was calculated according to Bragg's equation.

$$\lambda = 2d\sin\theta$$

Where d was the basal spacing, θ was the diffraction angle.

FTIR spectra were recorded in 4000–500 cm⁻¹ spectral region using a Nicolet IS5 under the resolution of 1 cm⁻¹ in 32 scans.

LOI was tested according to the standard oxygen index test method of ISO 4589-2. The dimension of all samples is 50 × 6.5 × 3 mm³. The vertical burning was tested according to UL 94 test standard. The specimen dimension was 130 × 13 × 3 mm³. The results presented an average of five replicates.

Evaluation of flammability of the composites was performed using cone calorimeter (FFT Co., Ltd) according to the standard ISO 5660. The samples with a dimension of 100 × 100 × 3 mm³ were tested at horizontal position with heat radiant flux density of 50 kW/m². Specimens were wrapped in aluminum foil, leaving the upper surface exposed to the radiator, and then placed on ceramic backing board at a distance of 25 mm from cone base. The experiments were repeated two times. Relative parameters such as heat release rate (HRR), time to ignition (TTI), total heat released (THR), mass loss rate (MLR) and smoke production rate (SPR), were obtained.

TGA was conducted using a synchronous thermal analyzer (STA449C, Netzsch) from 30 to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

The micrographs of scanning electron microscopy (SEM) were obtained by a Hitachi S-4700 SEM under the voltage of 20 kV.

X-ray photoelectron spectrometer (XPS) spectra were recorded with an ESCALAB 250 (Thermo Fisher Scientific, UK), using Al K α excitation radiation ($h\nu = 1486.6$ eV) and calibrated by assuming the binding energy of carbonaceous carbon to be 284.8 eV.

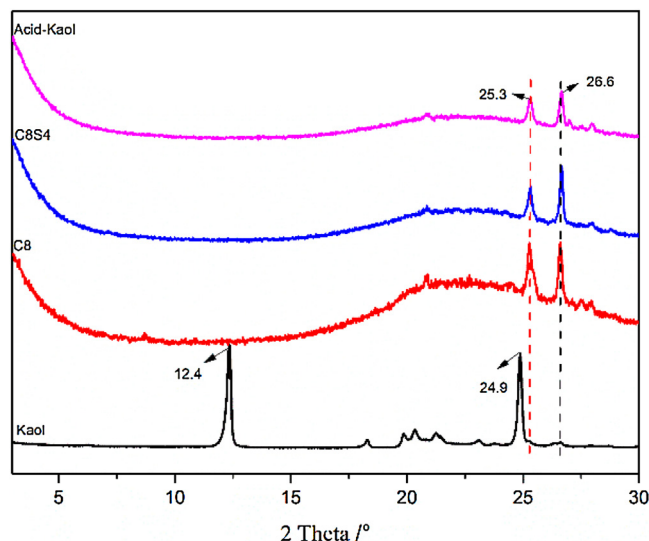


Fig. 1. XRD patterns of Kaol and its modified products.

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