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Flame retardation of polypropylene via a novel intumescent flame retardant: Ethylenediamine-modified ammonium polyphosphate

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ABSTRACT

Ammonium polyphosphate (form I APP) was modified via ion exchange reaction with ethylenediamine, and the resulting modified ammonium polyphosphate (MAPP) was used alone to prepare intumescent flame-retardant (IFR) polypropylene (PP) via melt blending. The flame retardancy of PP containing MAPP was investigated by limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter (CC). The LOI value of PP containing 40 wt% of MAPP reached 32.5%, which increased by 56.9% compared with that of PP with the same content of APP, and the UL-94 rating was V-0 in the case of specimen thickness of 1.6 mm, while the latter had no rating. CC test results showed that the heat release rate (HRR), the mass loss rate (MLR) and the smoke production rate (SPR) of PP/MAPP system decreased significantly compared with neat PP and PP/APP systems. Especially the fire growth rate (FGR) and SPR peak of PP containing 35 wt% MAPP decreased by 89.1% and 63.2% respectively compared with those of PP containing 35 wt% APP. These results demonstrated that only by incorporating the MAPP without additional charring agents, could PP be successfully flame retarded. Fourier transform infrared spectroscopy (FTIR) etc. were used to investigate the flame retardant mechanism of MAPP, and it was found that both the generation of carbon–carbon double bonds after the scission of C–N bonds and the residue consisting of some stable structures such as P–N–C and C–N etc. caused the charring ability to increase dramatically, which must be the principal reason for the much better flame retardancy of PP/MAPP system without any additional charring agent compared with APP.

1. Introduction

PP has been widely used in many fields due to its excellent properties, such as electrical insulation, chemical corrosion resistance, machinability and so on [1–4]. However, the flammability of PP restricts its application in flame-retarded material field [5,6]. In order to expand its application in this field, much work has been performed to improve the flame retardancy of PP [7,8], in which IFR is considered to be one of the most promising candidates for its merits, such as low damage to the properties of polymer matrix, low loading, environmental friend, low smoke etc. [9].

Generally, IFR is composed of an acid source, a charring agent and a blowing agent [10]. Ammonium polyphosphate (APP) and charring agent are the typical components of intumescent halogen-free flame retardant system. Ammonium polyphosphate (APP) is used as the experimental acid source and blowing source due to its high contents of phosphorus (P) and nitrogen (N). During the combustion process, the carbonization agent is engaged in charring process under the catalytic effect of acid source, and the char formed can be expanded under the action of blowing source to form an intumescent char layer. The char layer formed reduces heat transfer between the heat source and the polymer surface, and also limits fuel transfer from the polymer toward the flame as well as the diffusion of oxygen into the material, consequently promoting the flame retardancy of polymer composite. Almost in all IFR systems, the carbonization agent is necessary to form expandable char layer. However, as we all know, the preparation processes of carbonization agents are very complicated [11–13], and the solvent is harmful to the environment, so the ideal pathway is to find some new IFRs which are composed of a single material which gathers all the advantages of acid source, carbonization agent and blowing agent. At present, no was reported on how to apply a single material

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to prepare intumescent flame-retardant polymer composite. APP derivatives should be the best candidate since APP has gathered two advantages as acid source and blowing agent.

For APP, currently the most important method to enhance its application in IFR is microencapsulation at the surface. The main aim of this method focuses on enhancing the water resistance and thermal stability of APP, or improving the compatibility between APP and polymer matrix [9,14]. Hu et al. [15–18] found that microencapsulated ammonium polyphosphate with melamine–formaldehyde resin, urea–formaldehyde resin, polyurethane or epoxy resin shell, etc. could lead to a decrease in the water solubility of APP particles. Lei et al. [4] had studied microencapsulated ammonium polyphosphate with hydroxyl silicone oil (HSO) and melamine formaldehyde (MF) resin, and found that the compatibility of HSO–MFAPP with PP was better than that of unmodified APP besides the better water resistance. Bourbigot et al. [19] found the replacement of APP by a coated APP (APP-THEIC) was enhancing the performances of the epoxy based intumescent coating. However, no literature reported that APP modified through chemical reaction could act as an efficient charring agent besides the acid source and blowing agent, consequently might promote the flame retardancy of polymer composite. Based on the idea that APP can be involved in charring during the combustion process, a novel kind of modified APP was prepared by incorporating ethylenediamine in our experiment. So far, it has been found that ethylenediamine phosphate (EDAP) could enhance the flame retardancy of PP [20]. However, no literature reported that ethylenediamine could contribute to improve the flame retardant effect of APP in polymer matrix. So ethylenediamine was incorporated into APP through chemical reaction to enhance the flame retardant effect of APP in this work.

In current experiment, the flame retardancy of PP/MAPP composite was studied with the aid of different combustion tests, and the flame retardant mechanism of MAPP as a separate IFR was also investigated in detail.

2. Experimental section

2.1. Materials

Commercial APP (form I) was supplied by Changfeng Fire Retardants Co., Ltd. (Sichuan, China); ethylenediamine (AR, 99.0%) and ethanol (AR, 99.7%) were purchased from Kelong Chemical Reagent Co., Ltd. (Sichuan, China); polypropylene (T30S) was obtained from Petro China Lanzhou Petrochemical Co., Ltd. (Lanzhou China).

2.2. Preparation of MAPP

A certain volume ratio of ethanol and water (800 mL: 30 mL) was poured into a three-neck flask equipped with a stirrer under a nitrogen atmosphere. Half an hour later, ethylenediamine (18 g) was injected into the flask, and the solution was stirred. Then 100 g APP was added to the flask. After that, the mixture was heated up to 90 °C for 4 h. When the reaction completed, the reaction mixture was cooled down to room temperature. Then the white solid was filtered, washed with ethanol, and then dried to a constant weight. And the average sizes of APP and MAPP particles were investigated by Master Sizer 2000 (Malvern Instruments Ltd., UK), which are about 13.3 μm and 20.7 μm, respectively.

2.3. Sample preparation

2.3.1. Samples for combustion test

Both the Commercial APP and the prepared MAPP were dried in a vacuum oven at 80 °C for 12 h. Then the PP blends filled with different ratios of APP or MAPP were prepared via a twin-screw extruder (CTE 20, Kebeilong Keya Nanjing Machinery Co., Ltd, Nanjing, China) with the rotation speed of 150 rpm at the following temperature protocol from the feed zone to the die: 175, 180, 190, 185, 180 and 170 °C. Finally the extruded pellets were hot-pressed into different samples by plate vulcanizer (Qingdao Yadong Rubber Viachinery Co. Ltd. China).

2.3.2. Residual char samples for FTIR test and XPS test

The samples were heated to the corresponding temperature at a heating rate of 10 °C/min under a nitrogen atmosphere and retained 10 min at a series of temperature in TG 209 F1 (NETZSCH, Germany). Then the residual char samples were obtained.

2.4. Measurements

The FTIR spectra were recorded by a Nicolet FTIR 170 SX spectrometer (Nicolet, America) using the KBr disk, and the wave number range was set from 4000 to 500 cm^{-1}.

^1H NMR spectra were recorded on a Bruker AV II-400 MHz spectrometer (Bruker, Switzerland) by using D_2O as a solvent.

The XRD patterns using Cu Kα radiation ($\lambda = 1.542$ Å) were performed with power DX-1000 diffractometer (Dandong Fangyuan, China) at the scanning rate of 0.02° per second in the 2θ range of 5–50°.

The surface morphologies of the APP and MAPP were observed by using a JEOL JSM 5900LV scanning electron microscopy (SEM) (JEOL, Japan) at the accelerating voltage of 5 kV.

The contents of carbon (C), nitrogen (N) and hydrogen (H) in APP and MAPP were measured by elemental analysis (EA) on CARLO ERBA1106 instrument (Carlo Erba, Italy).

The LOI value was measured using an HC-2C oxygen index instrument (Jiangning, China) according to ASTM D2863-97 with a sheet dimension of 130 mm × 6.5 mm × 3.2 mm.

The UL-94 vertical burning level was tested on a CZF-2 instrument (Jiangning, China) according to ASTM D3801, the dimensions of samples were 130 mm × 13 mm × 3.2 mm and 130 mm × 13 mm × 1.6 mm, respectively.

The flammability of the sample was measured by a cone calorimeter device (Fire Testing Technology, UK). The samples with the dimension of 100 mm × 100 mm × 3 mm were exposed to a radiant cone at a heat flux of 50 kW/m^2.

Thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR) consists of TG 209 F1 (NETZSCH, Germany) coupled with 170 SX FTIR spectrometer (Nicolet). The sample (about 6 mg) was heating at a rate of 10 °C/min in the temperature range from 40 to 700 °C under the nitrogen flow of 50 mL/min. XPS spectra were recorded by a XSAM80 (Kratos Co, UK), using Al Ka excitation radiation (hv-1486.6 eV).

3. Results and discussion

3.1. Characterization of MAPP

The FTIR spectra of MAPP and APP are shown in Fig. 1. The peaks located at 3400–3030 cm^{-1} were ascribed to the NH_4^+ asymmetry stretching vibration [21], and the new absorption peaks appeared at the 2917 cm^{-1}, 2850 cm^{-1} and 1541 cm^{-1}, which are the characteristic stretching absorption peaks of $-CH_2-CH_2-$ and $-NH_3^+$. The appearance of the peaks corresponding to $-CH_2-CH_2-$ and $-NH_3^+$ in MAPP proved the EDA salt ($-NH_3^{+-}O-P-$) instead of ammonium salt ($-NH_4^{+-}O-P-$) was formed.

The ^1H NMR spectra of APP and MAPP are shown in Fig. 2. Obviously, there is no ^1H NMR peak other than the water peak at 4.80 ppm. But for MAPP, the peak attributed to $-CH_2-$ protons appeared at 3.40 ppm, indicating the structure of $NH_3^+-CH_2-CH_2-NH_3^+$ was