Polymer Degradation and Stability 126 (2016) 117–124

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Study on inorganic modified ammonium polyphosphate with precipitation method and its effect in flame retardant polypropylene

Zhaolu Qin, Dinghua Li*, Rongjie Yang

National Engineering Research Center of Flame Retardant Materials, School of Materials, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, PR China

ARTICLE INFO

Article history:
Received 5 September 2015
Received in revised form
11 January 2016
Accepted 29 January 2016
Available online 2 February 2016

Keywords:
Ammonium polyphosphate
Aluminum chloride
Inorganic modification
Polypropylene
Flame retardancy

ABSTRACT

A novel inorganic modified ammonium polyphosphate (IMAPP) is prepared by the chemical deposition reaction which proceeds on the particle surface of APP. IMAPP is characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), water solubility, water contact angle (WCA) and thermogravimetric analysis (TGA). Results show that the chemical deposition reaction produces aluminum hydroxide and aluminum phosphate on the particle surface, which has improved its water resistance and reduced its thermal decomposition rate. Then IMAPP is incorporated with dipentaerythritol (DPER) in the flame retarded polypropylene (FR-PP). The flame retardancy of FR-PP is investigated by means of limiting oxygen index (LOI), UL 94 and cone calorimeter tests. Compared with PP/DPER/APP composite, the PP/DPER/IMAPP has higher LOI value and can reach the V-0 rating easily. Studies on the char-forming behaviour of PP/DPER/IMAPP demonstrate that IMAPP has contributed to the formation of compact intumescent char during combustion. The formation of ceramic, continuous and homogeneous surface shielding over the PP matrix protects the underlying matrix and enhances the thermal stability of condensed phase, thereby reducing the heat release rate (HRR), total heat release rate (THR) and mass loss (ML) of FR-PP significantly. Finally, TGA coupled with Fourier transform infrared spectrometry (TG-FTIR) is used to analyze the thermal degradation process of PP/DPER/IMAPP composite. Based on the above results, the flame retardant mechanism is discussed.

1. Introduction

The fire protection of flammable materials by an intumescence process has been known for several years [1]. Intumescent flame retardants (IFR), with characters of non-halogen, lower toxicity and less smoke release, has been a hotspot in flame retardant field, considered as green environmentally friendly flame retardant [2–4]. Flame retarded materials by IFR are essentially a special case of condensed phase mechanism [5–7]. These flame retarded materials, upon heating, promote the formation of intumescent char which protects the underlying polymer matrix [8–15].

Unfortunately, the application of IFR in PP is restricted because of its poor water resistance and compatibility with PP matrix. For this purpose, many additives are employed to modify the surface of APP particles. So far, the surface modification techniques about APP particles mainly include: (1) surface modification with coupling agents [16,17]; (2) microencapsulation technologies [18–25]; (3) modification with surfactants [26–29]; (4) activated modification with melamine [30–32]; (5) other methods [33–36]. As can be seen, all these surface modification methods involve in the use of organic modifiers.

To the best of our knowledge, the surface modification of APP with inorganic modifiers has not been reported until now. On the other hand, aluminum hydroxide (ATH) is a commonly-used inorganic flame retardant, releasing water to the gas phase with the in-situ formation of a thermally stable ceramic material (alumina-Al_2O_3) during combustion [37]. However, the flame retardant efficiency of ATH is poor so that high loading is usually needed to meet suitable flame retardant requirement. In most cases, ATH is usually mixed with other flame retardants to improve flame retardant efficiency.

In this work, a novel inorganic modified APP (IMAPP) is prepared through the chemical reaction between aluminum chloride and ammonia, which proceeds on the surface of APP particles. IMAPP is characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), water solubility, water

* Corresponding author.
E-mail address: dli@bit.edu.cn (D. Li).

http://dx.doi.org/10.1016/j.polymdegradstab.2016.01.022
0141-3910/

contact angle (WCA) and thermogravimetric analysis (TGA). Then the flame retardancy of IMAPP in PP/DPER system is evaluated by means of limiting oxygen index (LOI), UL-94 vertical burning and cone calorimeter tests. Furthermore, TGA coupled with Fourier transform infrared spectrometry (FTIR) is used to discuss the flame retardant mechanism of IMAPP in PP/DPER system.

2. Experimental

2.1. Materials

PP (S1003) with a melt flow index (MFI) of 3.2 g/10 min^{-1} (230 °C/2.16 kg) was provided by Yanshan Petroleum Chemical Company. APP-II with an average degree of polymerization, n > 1,000, was provided by Zibo SaiDa Flame Retardant New Materials Co., Ltd. Aluminum chloride, aluminum phosphate and aluminum hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Dipentaerythritol (DPER) was provided by Jiangsu Ruiyang Chemical Co., Ltd. Anhydrous ethanol and ammonium hydroxide (NH_3: 25%) were purchased from Beijing Chemical Reagents Company. The antioxidant 1010 [Pentaerythritol tetrakis (3-(3, 5-di-*tert*-butyl-4-hydroxyphenyl) propionate)] and antioxidant 168 [Tris-(2,4-di-*tert*-butyl)-phosphite] were supplied by Ciba Specialty Chemicals Company, Switzerland. All chemicals were used without further purification.

2.2. Preparation of IMAPP

APP (50 g) was first dispersed in 200 mL anhydrous ethanol and then transferred into a 500 mL three-neck flask with a stirrer, a thermometer and reflux condenser. 1 g aluminum chloride was cautiously dissolved in 10 mL distilled water and stirred for 10 min. Then, the aluminum chloride solution was added into the above three-neck flask, dropwise. The mixture was adjusted to pH 8–9 with ammonium hydroxide, heated to 60 °C and kept at this temperature for 2 h. After that, the mixture was filtered, washed with a mixed solution of ethanol and distilled water (volume ratio 1:1), and dried at 100 °C. Finally, IMAPP was obtained.

2.3. Preparation of FR-PP composites

The FR-PP composites were prepared by melt blending in a twin-screw extruder (SHJ-20) with the screw length/diameter ratio of 20. The temperature of each section is 170 °C, 175 °C, 180 °C, 185 °C, 180 °C and 175 °C. The feed rate is 12 rpm and the screw speed is 25 rpm. The test specimens were prepared using an injection molding machine (HTF80X1). The temperature of each section for injection molding is 200 °C, 200 °C, 190 °C and 170 °C. To compare the flame retardancy of ATH-modified APP with the merely mixture of ATH and APP at the same dosage of ATH, the PP/DPER/APP/ATH composites were also prepared. The formulations of FR-PP composites were described in Table 1.

2.4. Characterization and measurements

X-ray photoelectron spectroscopy (XPS) data were obtained through a Perkin Elmer PHI 5300 ESCA system at 250 W (12.5 kV at 20 mA) under vacuum better than 10^{-6} Pa. Typical results from XPS were reproducible within ±3%, and the reported results are the average of three measurements. To compensate for sample charging, all binding energies were referenced to C_{1s} at 284.9 eV.

The morphology of APP, IMAPP and the fracture surfaces of FR-PP composites were observed by S4800 Scanning Electron Microscope (SEM).

The water contact angle (WCA) was measured by a drop-shape analysis system (KRUSS DSA100) at three different points for each sample. Typical results from WCA were reproducible within ±3%, and three replicate specimens were tested for each sample.

Water solubility was measured according to the Chemical Industry Standard of the People's Republic of China (Ammonium polyphosphate for industrial use, HG/T 2770-2008). Results are the averages of three measurements.

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyzer. To detect gas species, the TGA was coupled with Fourier transform infrared spectrometry (TGA-FTIR, Nicolet 6700), and the measurements were carried out under air atmosphere at a heating rate of 10 °C/min from 40 °C to 800 °C. The sample weight was 10 mg for each measurement. TGA was performed at a gas flow rate of 60 mL/min. The typical results from TGA were reproducible within ±1%, and the reported data are averages of three measurements.

Limiting oxygen index (LOI) was measured according to ASTM D2863. The apparatus used was an FTA-II oxygen index meter (Rheometric Scientific Ltd, British). The specimens used for the test were of dimensions 118 × 6.5 × 3 mm^3.

The vertical burning test was carried out on a CZF-5A-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 test standard. The specimens were of dimensions 125 × 13 × 3.2 mm^3.

Cone calorimeter measurements were performed according to ISO 5660 protocol, using a Fire Testing Technology apparatus (FTT 0007) with a truncated cone-shaped radiator. The specimen (100 × 100 × 3 mm^3) was measured horizontally without any grids under a heat radiant flux of 50 kW/m^2. Typical results from cone calorimeter were reproducible within ±10%, and the reported results are the average of three measurements.

Table 1
The formulation design of FR-PP composites (wt%).

Sample	PP	APP	ATH	IMAPP	DPER	1010	168
PP Control	99.7	–		–	–	0.1	0.2
PP/DPER/APP	74.7	17.2		–	7.8	0.1	0.2
PP/DPER/APP/ATH	74.7	16.2	1	–	7.8	0.1	0.2
PP/DPER/IMAPP	74.7	–		17.2	7.8	0.1	0.2

3. Results and discussion

3.1. XPS analysis of APP and IMAPP

XPS was used to investigate the surface chemical state of neat APP and IMAPP and determine the evidence of surface modification. The XPS spectra of APP and IMAPP are shown in Fig. 1. APP signals show the presence of oxygen (530.6 eV, O_{1s}), nitrogen (400.8 eV, N_{1s}), and phosphorus (134.5 eV, P_{2p} and 190.9 eV P_{2s}) atoms. For IMAPP, the characteristic peaks of Al_{2p} (74.38 eV) and Al_{2s} (117.75 eV) verify the presence of Al element on the surface of IMAPP particles. Moreover, Table 2 shows the surface elemental compositions of APP and IMAPP. It should be noted that the N/P ratio of APP (0.95) is much higher than that of IMAPP (0.71). It indicates that the surface elemental composition of the IMAPP has changed because of modification.

To verify the specific components of the surface coating, the Al_{2P} spectra of IMAPP was studied by means of XPS-peak-differentiation-imitating analysis. At the same time, the Al_{2p} spectra of two commercial aluminum compounds (ATH and $AlPO_4$), which are considered the most likely to be formed on the IMAPP surface, were also analyzed for comparison. The Al_{2p} spectra curves (ATH, $AlPO_4$, IMAPP and fitted curve of ATH/$AlPO_4$) are shown in Fig. 2. The Al_{2p} spectra curve of IMAPP matches perfectly with the fitted Al_{2p} curve