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Flame retardant mechanism of an efficient flame-retardant polymeric synergist with ammonium polyphosphate for polypropylene

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An efficient flame retardant polymeric synergist poly[*N*^{4}-bis(ethylenediamino)-phenyl phosphonic-*N*^{2}, *N*^{6}-bis(ethylenediamino)-1,3,5-triazine-*N*-phenyl phosphonate] (PTPA) was designed and synthesized from cyanuric chloride, ethylenediamine and phenylphosphonic dichloride. It was characterized by Fourier Transform Infrared (FTIR), ^{1}H NMR and ^{31}P NMR, Elemental Analysis (EA) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Combined with ammonium polyphosphate (APP), a new intumescent flame retardant (IFR) was obtained. The flammability behaviors of polypropylene (PP)/IFR system were investigated by limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimetry. With 25 wt% of IFR (APP:PTPA = 2:1), the PP/IFR system could achieve a LOI value of 34.0% and UL-94 V-0 rating, and the heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR) and smoke production rate (SPR) were considerably reduced, especially HRR and SPR were decreased by 85% and 79%, respectively. The results indicate that there is an excellent synergism between APP and PTPA, which endows PP with both good flame retardancy and good smoke suppression. Furthermore, the thermal degradation mechanism of IFR and the flame-retardant mechanism of PP/IFR system were investigated by thermogravimetric analysis (TGA), FT-IR, TG-FTIR and scanning electron microscope (SEM). The study on the flame-retardant mechanism of IFR indicated that a structure containing −CN was formed due to the reaction between APP and PTPA.

1. Introduction

Polypropylene (PP) is widely used in apparel, floor covering, upholstery, medical, geotextile and automobile due to its low cost, light weight, good mechanical properties and excellent resistant to many chemicals. However, PP is a highly combustible material, which restricts its application in many fields. Therefore, it is essential to endow PP with good flame retardancy [1].

In the research for environmentally friendly flame retardants for PP, intumescent flame retardants (IFR) have attracted considerable attention [2–19]. However, there are some shortcomings with traditional IFR, such as not high enough flame-retardant efficiency, low thermal stability and low water resistance [20]. In the efforts to improve the flame-retardant efficiency of IFR system, the synthesis and application of the phosphorus-nitrogen containing intumescent flame retardants become a trend for the synergistic effect between phosphorus and nitrogen. Among them, triazine and its derivatives attracted the interest of scientists due to its high thermal stability and structure of tertiary nitrogen [4,17,21–24]. Cyanuric chloride is an excellent raw material to design and synthesize different flame retardants because of its high selectivity [4,21,24]. Some phosphorus-nitrogen containing IFR systems with low molecular weights have been synthesized from cyanuric chloride [25,26]. They might endow polymer with flame retardancy alone or together with APP. Literature indicated that some reactive phosphonic amides were used as the curing agents for epoxy resins and showed good thermal stability and charring ability [27,28]. It was shown that phosphorus oxynitride structure was helpful for the formation of stable char layer [29].

However, the research of the compound containing both triazine ring and phosphorus oxynitride structure is not reported. To further improve the flame-retardant efficiency of IFR, it deserves more efforts to design and prepare new IFRs. In the present article, we mainly aim to design and synthesize a novel polymeric flame retardant named PTPA containing triazine ring, benzene ring and phosphorus oxynitride structure, which might exhibit better thermal stability and charring ability. Combining this polymeric flame

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retardant with APP, a new high-efficient IFR for PP is obtained. The structure of PTPA is characterized by FT-IR, ^{1}H NMR, ^{31}P NMR, EA and ICP-AES. The flame-retardant properties, thermal degradation mechanism and flame-retardant mechanism are investigated in detail.

2. Experimental

2.1. Materials

Cyanuric chloride was purchased from the Yingkou Sanzheng Organic Chemical Industry Co., Ltd., China. Ethylenediamine, sodium hydroxide and chloroform were supplied by Changzheng Chemical Reagent Co., China. Phenylphosphonic dichloride was provided by Weili Flame Retardant Chemicals Industry Co., Ltd (Chengdu, China). Ammonium polyphosphate (APP) was supplied by Sichuan Shifang Chuanhong Phosphorus Chemical Co., Ltd. China. Polypropylene (PP) resin (T30S) used in this work was purchased from Lanzhou Petroleum Chemical Co., China.

2.2. Preparation of poly[N^4-bis(ethylenediamino)-phenyl phosphonic-N^2, N^6-bis(ethylenediamino)-1,3,5-triazine-N-phenyl phosphonate] (PTPA)

The synthesis route of PTPA is shown in Scheme 1.

N, *N*′-bis(2-aminoethyl)-phenyl phosphorodiamidate (BPPA) was synthesized according to literature [28]. Ethylenediamine (126 g) and chloroform (400 ml) were added in a 1000 ml four-necked reaction vessel provided with a stirrer, a thermometer, and a constant pressure dropping funnel, followed by simultaneously dropwise adding a solution of phenylphosphonic dichloride (117 g) dissolved in chloroform while keeping the temperature at −5 °C to 5 °C with stirring. After the completion of the dropwise addition, the mixture was further agitated at the same temperature for 6 h, then filtered to remove ethylenediamine hydrochloride and got the solution of BPPA which would be used immediately in the following reaction.

Cyanuric chloride (92 g) and chloroform (500 ml) were added into a 1000 ml four-necked reaction vessel with a stirrer, a thermometer and two constant pressure dropping funnels, followed by simultaneous dropwise addition of half of the BPPA solution and an aqueous solution of sodium hydroxide (20 g), while keeping the temperature at −5 °C to 5 °C with stirring. After completion of the dropwise addition, the mixture was further agitated at the same temperature for 6 h, followed by heating it up to room temperature, dropwise adding the other half of the BPPA solution and sodium hydroxide (20 g) dissolved in water. After the completion of the reactant addition, the mixture was agitated under reflux for 8 h at 61 °C. The intermediate was filtered and dispersed in the aqueous solution of BPPA and keeping pH at 6 to 8 by adding sodium hydroxide for 8 h at 100 °C. The mixture was then cooled down to room temperature, followed by filtration, washing the product with water, drying it to a constant weight in vacuum at 80 °C, and 150 g of yellowish solid was obtained. Its solubility in 100 g water at 70 °C was 0.09 ± 0.01 g.

2.3. Preparation of flame-retardant PP samples

All samples with different compositions of PP/flame retardants (FR) were prepared in a parallel co-rotating twin-screw extruder with a length/diameter ratio of 40 and a screw diameter of 25 mm. The PP/FR samples were extruded at 190 °C at the screw speed of 80 rpm. Then, the specimens for LOI and UL-94 tests were compression-molded by means of a vulcanizing press at 200 °C under 10 MPa for 3 min to obtain 3.2 mm thick plaques. Finally, the compressed sheets were cut into standard testing bars.

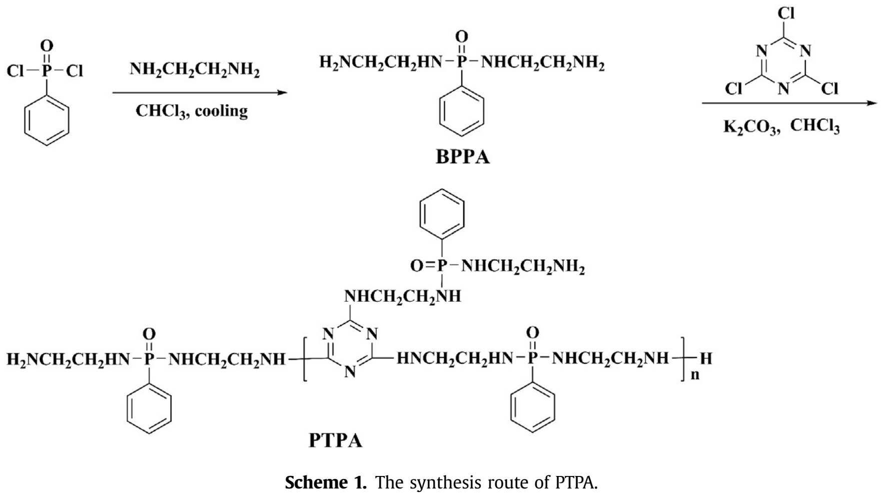
2.4. Characterization

The structures of BPPA and PTPA were characterized by NMR (^{1}H NMR, ^{31}P NMR, Bruker FT-80A NMR), FT-IR (Nicolet FTIR 170SX infrared spectrophotometer, KBr powder) and Elemental Analysis (EA). The phosphorus content of PTPA was analyzed using an IRIS ADV Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES). Thermogravimetry (TG) was carried out on an SDT Q600 thermal analyzer in a 60 ml/min flowing N_2 at a heating rate of 10 °C/min. The flame retardancy and burning behaviors were determined by LOI test (JF-3 oxygen index meter, Jiangning, China; using sheet dimension of 130 mm × 6.5 mm × 3 mm according to ASTM D2863-97), UL-94 measurement (CZF-2-type, Jiangning, China; using sheet dimension of 130 mm × 13 mm × 3 mm according to ASTM D3801) and cone calorimetry test (FTT cone calorimeter; square specimens, 100 mm × 100 mm × 3 mm were irradiated at a heat flux of 50 kW/m^2 according to ISO 5660 standard procedures).

3. Results and discussion

3.1. Characterization of BPPA and PTPA

Fig. 1 shows the FT-IR spectra of BPPA (a) and PTPA (b). For the spectrum of BPPA, the absorptions of N–H (primary) at 3440 and



Scheme 1. The synthesis route of PTPA.