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Flame-retardant mechanism of a novel polymeric intumescent flame retardant containing caged bicyclic phosphate for polypropylene

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ABSTRACT

A novel polymeric intumescent flame retardant, named poly(ethanediamine–1,3,5-triazine-*o*-bicyclic pentaerythritol phosphate) (PETBP), was synthesized and characterized by Fourier transform infrared spectroscopy (FTIR), solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR), ^{31}P NMR and elemental analysis (EA). The effects of PETBP on the flame retardancy and thermostability of polypropylene (PP) were investigated by limiting oxygen index (LOI), vertical burning test (UL-94V), cone calorimetric test (CCT), thermogravimetric analysis (TGA) and TG-FTIR, respectively. The results showed that PETBP could significantly improve the flame retardancy and thermostability of PP. When the content of PETBP was 25.0 wt%, the PP/PETBP mixture could achieve a LOI value of 29.5% and a UL-94 V-0 rating, and its peak heat release rate (PHRR), total heat release (THR), average mass loss rate (av-MLR), smoke production rate (SPR) and total smoke production (TSP) were considerably decreased. The flame-retardant mechanism of PETBP was investigated by TGA, FTIR, TG-FTIR and scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDXS). The results revealed that during the combustion PETBP could quench the free radicals of PP chain scission, and form a continuous and compact intumescent char on the substrate, thus effectively retard the degradation and combustion of PP.

1. Introduction

Polypropylene (PP) is a widely used thermoplastic in many fields due to its easy processing capability, excellent mechanical performance and low cost. However, the inherent flammability is a major drawback of PP and severely restricts its application in some aspects required high flame retardancy. Therefore, it is imperative to improve the flame retardancy of PP. In recent years, intumescent flame retardant (IFR) is considered to be one of the most promising flame retardants to replace halogen-containing ones, because of them being environmental-friendly, having high efficiency, anti-dripping and low smoke [1–3]. Typically, IFR consists of three ingredients, including an acid source, a charring agent and a blowing agent. The most commonly reported IFR is ammonium polyphosphate/pentaerythritol/melamine (APP/PER/MEL), which has been systematically investigated by Camino's and Bourbigot's groups [1,4–6]. Their researches revealed that the IFR could form a multicellular swollen char on the surface of the polymer when being heated beyond a critical temperature, which protected the substrate from burning. However, the traditional IFRs are mainly composed of small molecule compounds, such as PER and MEL, which are moisture sensitive and easily attacked by water and exuded out of the mixtures, leading to a severe deterioration of the flame retardancy [7,8].

One solution to these problems is to employ microencapsulation technology by enveloping the IFR particles in a thin film of polymer which serves as a solid wall [7–11]. The other one is to synthesize polymeric IFRs with high molecule weight, which possess low water solubility and better resistance to extraction [12–14]. Song and Co-workers [14] synthesized an oligomeric intumescent flame retardant, named PDBPP, and employed it to flame retard PP. The results showed that the incorporation of PDBPP could improve both the flame retardancy and thermostability of PP. However, in order to achieve a limiting oxygen index (LOI) value of 28.0%, more than 30wt% PDBPP was necessary. The relatively low flame retardant efficiency limited its further application. In recent years, triazine derivatives have aroused more and more attention because of their high reactivity and good char-forming performance [15–17]. Our

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group [18] had reported a novel charring agent triazine-based macromolecule (TBM), which showed a superior char-forming capability and little water solubility. Nevertheless, owing to the absence of acid source, TBM was still needed to combine with melamine pyrophosphate (MPP) to obtain good flame retardancy, which required more complicated processing condition to achieve uniform dispersion of the IFR particles in the polymer.

In this work, a novel single-component polymeric IFR containing caged bicyclic phosphate, named poly(ethanediamine-1,3,5–triazine-*o*-bicyclic pentaerythritol phosphate) (PETBP), was synthesized by using phosphorus oxychloride, pentaerythritol, cyanuric chloride and ethylenediamine. The chemical structure of PETBP was characterized by Fourier transform infrared spectroscopy (FTIR), solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR), ^{31}P NMR and elemental analysis (EA). The flame retardancy, thermal properties and flame-retardant mechanism of the PP/PETBP mixture were investigated by limiting oxygen index (LOI), vertical burning test (UL-94V), cone calorimetric test (CCT), thermogravimetric analysis (TGA), thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR), and scanning electron microscopy-energy dispersive spectra (SEM-EDXS).

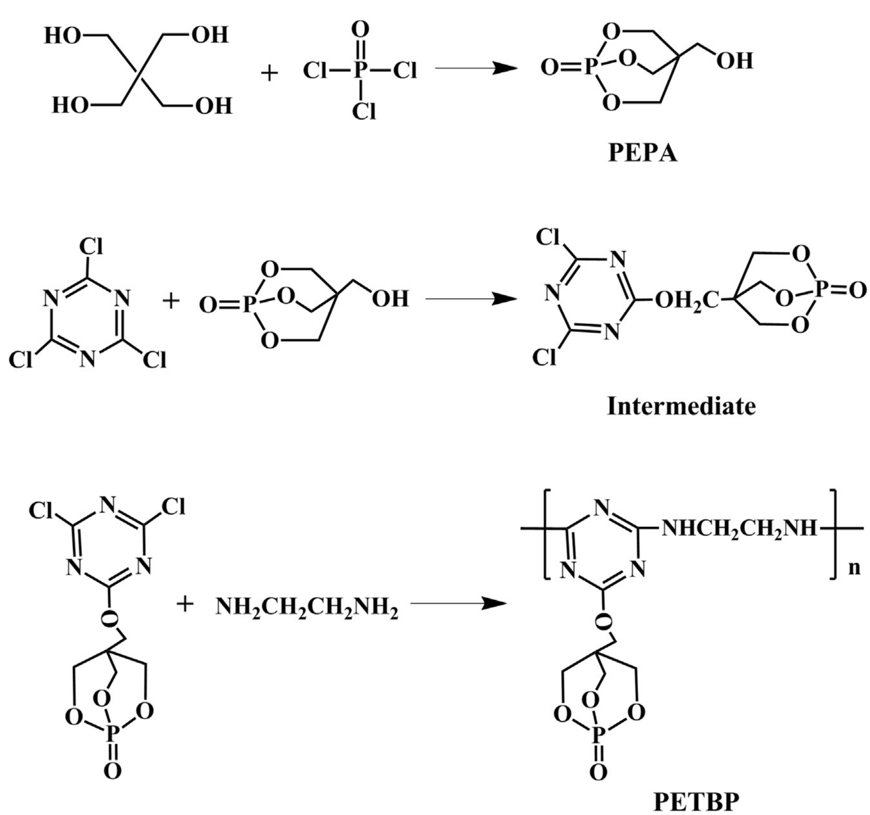
2. Materials and experimental

2.1. Materials

Phosphorus oxychloride ($POCl_3$) was provided by Guangzhou Chemical Reagent Co., Ltd., China. $POCl_3$ was distilled under atmospheric pressure before use. Pentaerythritol (PER, water solubility at 70 °C: 15.0 g/100 mL H_2O) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd., China. Ammonium polyphosphate (APP, water solubility at 70 °C: 2.5 g/100 mL H_2O) and melamine pyrophosphate (MPP, water solubility at 70 °C: 1.3 g/100 mL H_2O) was obtained from Jiangmen Topchem Technology Co., Ltd., China. Triazine-based macromolecule (TBM, water solubility at 70 °C: 0.7 g/100 mL H_2O) was synthesized according to the reference [18]. Cyanuric chloride (CNC) was obtained from Yingkou Sanzheng Organic Chemical Industry Co., Ltd., China. Ethanediamine was obtained from Chinasun Specialty Products Co., Ltd., China. Acetonitrile and triethylamine were obtained from China National Pharmaceutical Group, China. Polypropylene (PP, T30S), a granulated product with a melt flow index of 3.0 g/10 min (230 °C, 2.16 kg), was supplied by Maoming Petrochemical Co., Ltd., China. Antioxidant (IRGANOX B215) was provided by Ciba Specialty Chemicals Inc., Switzerland. 2,6,7-Trioxa-1-phosphabicyclo-[2,2,2] octane-4-methanol-1-oxide (PEPA, as shown in Scheme 1) was synthesized according to the reference [19] and recrystallized in alcohol. All the commercial materials except $POCl_3$ were used directly without further purification.

2.2. Synthesis of poly(ethanediamine-1,3,5–triazine-o-bicyclic pentaerythritol phosphate) (PETBP)

Exactly 36.9 g (0.2 mol) cyanuric chloride and 150 mL acetonitrile were added in a 500 mL round bottom flask under nitrogen, and stirred at room temperature until a transparent solution was formed. Then, 36.0 g (0.2 mol) PEPA and 27.8 mL (0.2 mol) triethylamine were dissolved in another 100 mL acetonitrile. The mixture solution was dropped slowly into the flask. The pH value of the solution was monitored in real time by a pH measuring apparatus (SX723, Shanghai San-Xin Instrumentation, Inc.) and kept at 7–8. The reaction was continued for 4 h after the mixture solution was dropped completely. Afterwards, the temperature was increased to 45–50 °C. 6 g (0.1 mol) ethanediamine and 27.8 mL



Scheme 1. Synthetic route of PETBP.