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Synthesis of a novel charring agent containing pentaerythritol and triazine structure and its intumescent flame retardant performance for polypropylene

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ABSTRACT

A novel charring agent (PEPAPC) containing pentaerythritol and triazine structure, was successfully prepared via the nucleophilic substitution reaction of cyanuric chloride, 2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane-4-methanol (PEPA), and piperazine. Then, different proportions of PEPAPC and ammonium polyphosphate (APP) were added into polypropylene (PP) at a 20% total loading via melt blending. The results of limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis (TGA) and cone calorimeter test revealed that PEPAPC/APP system could effectively enhance the thermal stability and flame retardance of PP. When the weight ratio of APP to PEPAPC was 3:1 with a 20% loading (PP6), the PP composite achieved the highest LOI value of 28% and passed the vertical burning test (UL-94) V-0 rating. Meanwhile, PP6 showed the highest amount of char residues via TGA test and the lowest PHRR (253 kW/m^2) via cone calorimeter test. Moreover, Scanning electron microscopy (SEM) also indicated that PEPAPC/APP system benefited to the formation of more compact char layer which hindered the transfer of volatiles and heat during burning. The investigation of their water resistance demonstrated that the PP6 still obtained a UL-94 V-0 rating after 72 h dipping in hot water.

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1. Introduction

Polypropylene (PP), as an important polyolefin, has been extensively used in various fieds such as electric and electronic, transportation, and construction owing to its superior mechanical capacity, easy processability and low cost. However, the application of PP is strongly restricted owing to its easy combustibility and dripping tendency, thus it is very necessary to enhance the flame retardance of PP [1–6].

In recent years, intumescent flame retardant (IFR) systems have been extensively employed to improve the flame resistance of polyolefins as a sort of halogen-free flame retardant. Compared with halogen-containing flame retardants, IFR system shows less smoke, low toxic released during the burning and environmental friendly, etc [7–9]. In general, an IFR system basically includes an acid source, a charring agent and a blowing agent [10]. During combustion process, the IFR system undergoes a series of chemical reactions such as esterification and carbonization. Therefore, a swollen char layer is generated as a shield to restrain heat and mass transfer between gas and condensed phases, and to protect the inside material [11,12]. Ammonium polyphosphate (APP as acid source), pentaerythritol (PER as charring agent) and melamine (blowing agent) form a traditional IFR system together. However, micromolecular PER and melamine easily ooze from the surface of the samples due to their poor compatibility with polymer matrix [13]. Besides, APP and PER are not durable because of their water soluble, so the flame retardant polymer composites are easily attacked by water and spilt. Moreover, the additive amount of the IFR compound in polymer is too much, and the flame retardancy of PP is always weakened due to the poor thermal stability with the

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polymer. To get rid of these drawbacks, two main ways have been widely studied [14,15]. One is modification of the acid source, such as microencapsulation of APP [16,17]. The other is the development of a more efficient charring agent which may generate a synergistic effect with APP to improve the flame retardancy of PP [18–20]. At present, the research for a novel char foaming agent has attracted more attention.

The previous works have demonstrated that the triazine-based polymeric charring foaming agents possess excellent charring ability, high thermal stability, a relatively high flame-retardant efficiency at low loading, and antidripping during combustion in comparison with conventional IFRs [21,22], which could be attributed to the abundant nitrogen element and stable triazine rings structure. They can get rid of the defects of traditionally micromolecular flame retardants, such as physical loss through ooze from the surface of the samples. Li and his coworkers [23–25] synthesized a range of triazine-based linear polymeric charring agents and it was found that these charring agents exhibited remarkable synergistic effect with APP in polypropylene. A novel charring agent containing triazine ring, benzene ring and phosphorus oxynitride structure (PTPA) was synthesized by Zhao et al. [26] and combinated with APP, which was a new high-efficient IFR for PP. Xie et al. [27] synthesized a novel hindered amine phosphorous-nitrogen macromolecular charring agent (HAPN) with free-radical quenching capability, which was used to impart flame retardancy for PP. The results showed that when the total addition content was maintained at 25 wt%, PP/HAPN/APP could self-extinguish at 36 s after igniting in the oxygen concentration of 29.5% and pass a UL-94 V-0 rating. Furthermore, a caged phosphorus-containing compound, 2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane-4-methanol (PEPA), is composed of a phosphorus compound and pentaerythritol [28]. A range of charring agents based on PEPA have been synthesized and applied owing to its high phosphorus content, remarkable thermal stability, and water resistance [29–31]. Since both PEPA-based derivatives and triazine-based derivatives have a prominent charring effect in intumescent flame retardants, the synthesis of a novel charring agent containing PEPA and triazine and its application in PP are worthy of research.

In the current work, we designed and synthesized a novel linear polymeric charring agent (PEPAPC) containing cyanuric chloride, PEPA and piperazine via the nucleophilic substitution reaction. As mentioned above, both triazine-based derivatives and PEPA-based derivatives possess outstanding charring effect and high thermal stability. Moreover, the piperazine ring structure also shows outstanding thermal stability compared to the straight-chain, which may be due to its structural features similar to a benzene ring. And piperazine was cheap and easily available. This polymeric charring agent was expected to have good thermal stability, excellent char formation ability owing to the presence of triazine rings, piperazine rings and PEPA. The chemical structure and thermal properties of the charring agent were analyzed by fourier transform infrared (FTIR), elemental analysis, ^{31}P nuclear magnetic resonance (^{31}P NMR), solid-state ^{13}C NMR, and thermogravimetric analysis (TGA). Then, it was combined with APP to prepare various intumescent flame retardant PP samples. The thermal properties and combustion properties of IFR-PPs have been investigated in detail by thermogravimetric analysis, limiting oxygen index (LOI), UL-94 test, and cone calorimetry. The surface morphology and structure of the char residue were studied by scanning electron microscopy (SEM) and Raman spectroscopy. In addition, the effect of PEPAPC on the water resistance of PP composites was also studied. Through this research, we hope to provide efficient intumescent flame retardants with excellent water resistance ability.

2. Experimental

2.1. Materials

Cyanuric chloride and piperazine were bought from Aladdin Industrial Corporation (China). PEPA was supplied from Shanghai D&R Fine Chemical Co. (China). Other chemicals were obtained from China National Pharmaceutical Group (Shanghai, China). PP resin (F401) was supplied by Yangzi Petrochemical Co. (China). The commercial products APP (phase II, the degree of polymerization >1000) was supplied from Shandong Shi'a chemical Engineering Corp (China).

2.2. Synthesis of PEPAPC

A novel charring agent containing pentaerythritol and triazine was prepared according to one-pot method. Cyanuric chloride (0.2 mol) and acetonitrile (200 ml) were poured into a 1000-ml, three-necked, round-bottomed flask outfitted with a reflux condenser. A solution of PEPA (0.2 mol) and triethylamine (0.2 mol) in 200 ml of acetonitrile was added dropwise into the flask over 1 h and the mixture was kept at 10–15 °C for 3 h. Thereafter, a solution of piperazine (0.1 mol) and triethylamine (0.2 mol) in 50 ml of acetonitrile was added dropwise into the flask, followed by stirring at 40–50 °C for another 3 h. Then, another solution of piperazine (0.1 mol) and triethylamine (0.2 mol) in 50 ml of acetonitrile was added dropwise into the above reactive system. The mixture was kept under solvent reflux temperature for 6 h, followed by cooling to room temperature. The precipitate was filtered and washed with distilled water five times. It was dried at 80 °C at reduced pressure for 24 h. The char forming agent (PEPAPC, yield: 70.4%) was obtained (Scheme 1).

2.3. Preparation of flame-retardant PP

PP, APP and PEPAPC were dried in vacuum drier at 80 °C for 8 h before use. Afterwards, pure PP filled with different ratios of APP or PEPAPC were mixed for 15 min through a two-roll mixing mill (Rheomixer XSS-300, Shanghai Ke Chuang China) at 180 °C and 60 rpm. After mixing, the composite were hot-pressed for 4 min at 190 °C to make a sample of suitable thickness and size. A range of samples were on the list of Table 1.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were measured by using a Nicolet MAGNA-IR 750 spectrophotometer.

Elemental analysis was investigated via the Vario EL III elemental analyzer.

^{31}P Nuclear Magnetic Resonance (NMR) spectra were recorded by an Avance 300 Bruker spectrometer using DMSO-d_6 as a solvent.

^{13}C solid-state NMR spectra were recorded on a Bruker AVANCE III 400 WB.

Thermogravimetric analysis (TGA) was obtained by using a Q5000IR thermo-analyzer instrument (TA Co., USA) (2–10 mg sample, 20 °C/min heating rate).

The Limiting oxygen index (LOI) was carried out by an HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China) according to standard of ASTMD 2863. All specimens of $100 \times 6.5 \times 3.2$ mm^3 dimensions for the LOI test were applied.

The vertical burning test (UL-94) was determined with a CFZ-2 type instrument according to ASTM D3801-1996 standard and purchased from Jiangning Analysis Instrument. All specimens

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