Polymer Degradation and Stability 134 (2016) 179–185

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Hyperbranched phosphorus/nitrogen-containing polymer in combination with ammonium polyphosphate as a novel flame retardant system for polypropylene

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ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form
27 September 2016
Accepted 9 October 2016
Available online 15 October 2016

Keywords:
Hyperbranched
Phosphorus/nitrogen-containing
Thermal stability
Flame-retardancy
Synergy
Polypropylene

ABSTRACT

A novel phosphorus/nitrogen-containing hyperbranched polymer (PN-HBP) was synthesized via esterification reaction of 2-carboxyethyl (phenyl) phosphinic acid (CEPPA) and tris (2-hydrooxyethyl) isocyanurate (THEIC). PN-HBP was characterized by Fourier transform infrared (FTIR) spectrometry and ^{1}H nuclear magnetic resonance (^{1}H NMR) spectrometry. Its initial decomposition temperature ($T_{-5wt\%}$) is around 300 °C as the thermogravimetric analysis (TGA) showed. The flame-retardant polypropylene (PP) composites were prepared with the combination of PN-HBP and ammonium polyphosphate (APP) via melt blending. A higher limiting oxygen index (LOI) and a V-0 rating in the UL-94 vertical burning test were realized, indicating an apparent synergistic effect. The peak heat release rates (PHRR) of composites were reduced significantly compared with that of PP. The structure of the char residue was tested by Raman spectroscopy, indicating that the combination of PN-HBP and APP can prompt the formation of graphitized carbon layers and therefore improves the flame-retardancy of the PP composite.

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1. Introduction

In recent years, eco-friendly halogen-free flame retardants (FRs) have attracted considerable attention due to the ban of traditional halogenated FRs [1–3]. However, compared with the traditional halogenated FRs, the flame-retardant efficiency of halogen-free FRs was relatively lower. Therefore, developing high effective, halogen-free and eco-friendly flame-retardant materials and technology has been an important subject.

Intumescent flame retardants (IFRs) [4–6], a new generation of flame retardants, are mainly composed of an acid source, a carbon source and blowing agents, which possess several advantages including less smoke and lower toxicity. A typical and widely studied IFR system is the mixture of APP, pentaerythritol and melamine [7]. However, traditional IFRs have some shortcomings when applied into thermoplastics, e.g. lower flame-retardant efficiency and thermal stability. To solve the problem, a lot of researches have been done. Bourbigot et al. [8] have reviewed several strategies, for example, the substitution of classical polyols (char-forming agents) by char-forming polymers (polyamides and thermoplastic polyurethane), the synergy between nanocomposites and intumescent systems, and the microencapsulation of acid sources by char-forming membranes. Li et al. [9] synthesized a series of triazine derivatives as charring agents, which showed high thermal stability and a good synergistic effect with APP in flame-retardant PP.

Recently, hyperbranched polymers have attracted considerable attention for their unusual structure and properties. Combining with APP, Ke et al. [10] introduced a hyperbranched polyamine charring agent (HPCA) to prepare flame-retardant PLA. Li et al. [11] also synthesized a hyperbranched polyamine charring agent (HPCA) containing triazine and adopted it in ABS resin. The results showed a good synergistic effect between HPCA and APP. Qian and co-workers [12] synthesized a hyperbranched derivative of triazine group by the elimination reaction between ethylenediamine and cyanuric chloride, and found that it showed a good synergistic effect with APP in PP. Schartel et al. [13] also summarized several triazine-phosphorous flame retardants. Shi et al. [14] synthesized a

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.10.004
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hyperbranched polyphosphate ester (HPPE) and applied it into flame-retardant epoxy resin, while Zang et al. [15] synthesized a novel star-shaped flame retardant and also used in the epoxy resin, both of them found satisfactory results. Täuber et al. [16] applied the hyperbranched poly(phosphoester)s as flame retardants into engineering polymers, which was a promising work. However, all these reactions needed organic solvents and the dehydrochlorination process. Thus, new environment-friendly synthetic processes or new charring agents are in urgent requirement.

In this work, a novel phosphorus/nitrogen-containing hyperbranched polymer (PN-HBP) was synthesized by the esterification reaction of tris (2-hydrooxyethyl) isocyanurate (THEIC) and 2-carboxyethyl (phenyl) phosphinic acid (CEPPA) and added into PP together with APP. The synergistic effect on flame-retardant and thermal properties of PP was investigated.

2. Experimental

2.1. Materials

APP (average diameter 10 μm) was provided by Hefei Anjuda New Material Technology Co., Ltd. (Hefei, China). THEIC was provided by Xinxiang Weiye Chemical Co., Ltd. (Xinxiang, China). CEPPA was received from Jinan Kerry Flame Retardant Technology Co., Ltd. (Jinan, China). The CEPPA and THEIC are chemically pure. PP (F401, melt index = 2.5 g/10min) was supplied as pellets by Yangzi Petrochemical Co., Ltd. (Nanjing, China).

2.2. Synthesis of PN-HBP

PN-HBP was synthesized through the esterification reaction of THEIC and CEPPA, and the corresponding ratio was set 2:3 to keep their functional groups equal moles. (Fig. 1). THEIC (0.1mol), CEPPA (0.15mol) and H_2O (100 ml) were added into a 250 mL flask with mechanical stirring. The temperature was raised to 180 °C and continued for about 8 h until most of water steamed out. With the application of a vacuum (0.098 MPa), the temperature was further raised to 200 °C and kept for 2 h. After that, the transparent viscous liquid was poured out and cooled down, and the transparent solid PN-HBP was obtained with a yield of 88.9% (51.89/58.35*100%).

2.3. Preparation of flame-retardant PP composites

PP, APP and PN-HBP were dried in vacuum oven at 80 °C overnight before using. All samples were prepared on a two-rotator mixer at a temperature range of 180–190 °C for 10 min. The composites were then hot-pressed (under 10 MPa) into sheets of suitable thickness and size for tests. The composition of the PP composites is listed in Table 1.

2.4. Measurements

Fourier transform infrared (FTIR) spectra were obtained by a Nicolet 6700 spectrometer with 4 cm^{-1} resolution (Nicolet Instrument Company, USA) using KBr pellets method. ^1H nuclear magnetic resonance (^1H NMR) measurement was performed on an AVANCE 400 Bruker spectrometer with dimethyl sulfoxide-d_6 as the solvent. Limiting oxygen index (LOI) results were obtained by an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ASTM D2863. The sample size was 100*6*3 mm^3. The UL-94 test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 test standard. The sample size was 100*13*3 mm^3.The cone calorimetry test was performed on a JCZ-2 type instrument (Jiangning Analysis Instrument Company, China)

Table 1
The composition of the PP composites.

Samples	PP (wt%)	APP (wt%)	PN-HBP (wt%)
PP	100	0	0
PP/APP20	80	20	0
PP/APP10/PN-HBP10	80	10	10
PP/PN-HBP20	80	0	20

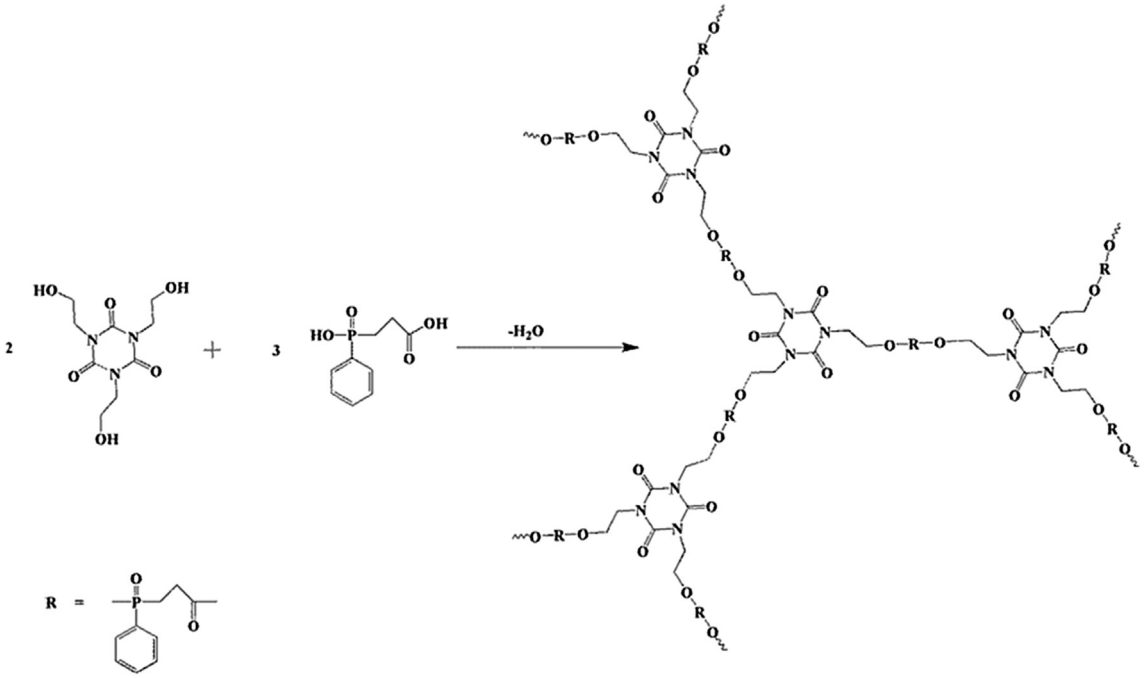

Fig. 1. Synthesis of the novel phosphorus/nitrogen-containing polymer (PN-HBP).

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