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Synergistic effect between a novel triazine charring agent and ammonium polyphosphate on flame retardancy and thermal behavior of polypropylene

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ABSTRACT

A novel oligomeric charring agent (PTCA) containing triazine and diphenyl group was synthesized by cyanuric trichloride, diphenylamine and ethylenediamine through nucleophilic reaction. The structure and thermal stability of PTCA were characterized by Fourier transform infrared spectrometry (FT-IR), element analysis testing and thermogravimetric analysis (TGA). The effectiveness of the novel intumescent flame retardant system (ammonium polyphosphate and PTCA, abbrev. IFRs) on fire retardancy and thermal stability of polypropylene (PP) was investigated through UL-94, limiting oxygen index (LOI) tests, cone calorimeter tests and thermogravimetric analysis (TGA). UL-94 vertical burning test revealed that the addition of 20 wt% IFRs into neat PP was enough to reach V-0 rating. LOI value of PP by addition of 20 wt% IFRs rose from 17.5 to 31 vol%. Moreover, a remarkable decrease in peak heat release rate (PHRR: −90%), total heat release (THR: −54%) and total smoke release (TSR: −51%) was revealed when the loading of IFRs was 20 wt%. TGA results showed that PTCA presented good char formation ability, and it would greatly increase the thermal stability of PP when combined with APP. The Fourier transformed infrared spectra (FTIR) revealed that the flame retardant mechanism might be ascribed to aromatic and phosphoric char formed during combustion. Additionally, the structure and morphology of char residues were further studied by SEM and Raman spectra.

1. Introduction

In recent years, intumescent flame retardant (IFR) additives have been widely used to enhance the flame resistance of polymers, such as polypropylene (PP), polyethylene (PE) and other polyolefin [1,2]. Intumescent flame retardant (IFR) system is a promising way to improve the fire resistance of polymer materials. Compared with halogenated flame retardant additives, IFR system presents several advantages including less smoke, low toxic and environmental friendly, etc. The most widely reported IFR system is composed of three basic components, i.e. acid source, carbon source and blowing agent [3–5]. However, traditional IFR additives exhibit low flame retardant efficiency in PP. According to the exhaustive research [6–8] and references cited within, it is revealed that IFR is efficient at large amounts (25–30 wt%) which entail a relatively high cost. Therefore, continuous effort is carried out to develop new high efficiency intumescent systems. Furthermore, traditional IFR additives ammonium polyphosphate (APP)/pentaerythritol (PER) are susceptible to migrate onto the polymer surface during the processing owing to their low molecular weight, therefore, the fire resistance decrease. To overcome the shortcomings, high molecular weight oligomeric or polymeric IFR have been developed, which provide a good strategy to solve the above problems [9–11]. Among these, triazine derivatives as a charring agent in IFR have been paid great attention due to their stable triazine rings and easily charring characteristics during burning [12–16]. Intumescent systems containing triazine derivatives as flame retardants have been widely used in various polymers [3,17–20]. Li and coworkers [12,16] synthesized a series of triazine derivatives as charring agents and it was found that the charring agents showed good synergistic effect with APP in flame retardant PP. Ke et al. [3] synthesized one kind of hyperbranched polyamine charring agent containing triazine which presented good flame retardant and anti-dripping abilities for polylactide, the limiting oxygen index (LOI) could reach 36.5 with 30 wt% additives and V-0 rating was obtained. A novel intumescent flame retardant containing spiral and triazine structure

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(PSPTR) was synthesized by Hu et al. [17] and a new intumescent flame retardant (IFR) system, which was composed of PSPTR and Phenol Formaldehyde Resin (PF), was used to impart flame retardancy for ABS. The results showed that when the total addition content was 30 wt%, the weight ratio of PSPTR to PF was 1:1, the LOI value of ABS/IFR reached 28.2, and UL-94 reached V-1 rating. A distinct synergistic flame retardant effect exists between PSPTR and PF. Yang et al. [18] have synthesized a hydrophobic triazine-containing macromolecule (ETPC) via two step reactions. A detailed study of ETPC revealed that ETPC could act as an effective charring and foaming agent in the IFR, due to its high thermal stability, good char formation ability and excellent hydrophobicity. Moreover, the novel intumescent flame retardant consisting of ETPC, ammonium polyphosphate (APP) and silica was applied to investigate the flame retardancy and water resistance of polypropylene (PP). A comprehensive study indicated that IFR showed very effective flame retardancy and water resistance in PP, and the hot water treatment had a little influence on LOI values, UL-94 ratings, the heat release rate (HRR) and the smoke production rate (SPR).

In this work, an oligomeric triazine charring agent (PTCA) was synthesized and characterized. The effects of PTCA combined with APP on flame retardancy and thermal degradation of PP were investigated. Moreover, the flame retardant performance and thermal stability of this novel IFR system were compared with that of traditional IFR system.

2. Experimental

2.1. Materials

All the starting materials and solvents were commercially available and were used without further purification. Cyanuric chloride (CYC) was purchased from Tokyo Chemical Industry Co., Ltd. N-Phenylaniline, ethylenediamine, acetone, Na_2CO_3 and NaOH were supplied by Nanjing Chemical Reagent Co., Ltd. The matrix polymer used in this study was polypropylene, PP (1215C, particle products). Ammonium polyphosphate (APP) was supplied by Xingxing Flame Retardant Co., Ltd.

2.2. Preparation of samples

2.2.1. Synthesis of PTCA

Firstly, the intermediate (4, 6-dichloro-N, N-diphenyl-1, 3, 5-triazin-2-amine) was prepared as follows: CYC (0.05 mol), Na_2CO_3 (0.1 mol) and 100 ml acetone were fed into a 500 ml glass flask equipped with a mechanical agitator. 0.042 mol N-phenylaniline dissolved in 50 ml acetone, and the obtained solution was added dropwise into the flask. The reaction temperature was kept at 0 °C, and the mixture was stirred for about 2 h until yellowish precipitate formed. The product was washed several times by cold water until no chloride could be detected, then the intermediate was obtained (yield: 91.2%).

Secondly, intermediate (0.05 mol), NaOH (0.06 mol) and 150 ml deionized water were added into a glass flask and the mixture was stirred constantly. Then the temperature was raised to 40 °C, 0.06 mol ethylenediamine was added dropwise to the flask within 2 h. Thereafter, the mixture was heated up to 100 °C and refluxing for another 12 h. The precipitate formed was collected and washed several times with deionized water and ethanol to remove the unreacted reagents. The product was dried under vacuum at 80 °C, then the novel charring agent PTCA was obtained (yield: 90%). The synthesis route was shown in Scheme 1.

2.2.2. Preparation of PP composites

All flame retarded PP composites were prepared using the CM reciprocating single-screw (CM-30). The temperature range of the single-screw extruder was set at 160–200 °C. The resulting compounds were subsequently dried in an oven, and then molded into testing bars with plate vulcanization machine for fire property characterization.

2.3. Characterization

2.3.1. Characterization of PTCA

The ^1H NMR spectra were recorded at 300 MHz on an ARX-300 Bruker spectrometer, using DMSO-d_6 as a solvent. The Fourier transform infrared (FT-IR) spectra were obtained with a spectrophotometer (NEXUS 670) in the range from 390 to 3700 cm^{-1}. Elemental analysis (EA) was performed with a VarioEL III elemental analyzer (Elementar, GM). Mass spectrum was obtained using a Finnigan-4570 mass spectrometer.

2.3.2. Thermal gravimetric analysis

Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409 PC instrument at a heating rate of 10 °C/min. In each case, 5–10 mg sample was examined under a nitrogen flow rate of 20 ml/min from 30 to 700 °C.

2.3.3. Flame retardancy tests

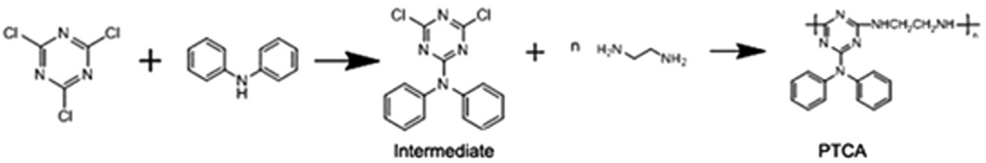
Limiting oxygen index (LOI) was carried in an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) with samples measurement 120 × 10 × 4 mm, following the procedure described in the ASTM D2863 standard. UL94 tests were performed on vertical testing apparatus (CZF-2, Jiangning Analysis Instrument Factory, China), with sample dimensions of 130 × 13 × 3 mm according to UL-94 test standard.

2.3.4. Cone calorimetry

All cone data were taken from a low oxygen standard cone calorimeter (manufactured by fire testing technology) at an incident heat flux of 50 kW/m^2 according to ISO 5660-1 standard. All samples (100 × 100 × 3 mm^3) were laid on a horizontal sample holder.

2.3.5. Raman diffusion

Laser Raman spectroscopy measurements were carried out at room temperature with a JY HR800 laser Raman spectrometer (JY Co., French).



Scheme 1. Synthesis route of PTCA.