



Synthesis of *N*-methyl triazine-ethylenediamine copolymer charring foaming agent and its enhancement on flame retardancy and water resistance for polypropylene composites



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ARTICLE INFO

Article history:

Received 9 May 2016

Received in revised form

26 June 2016

Accepted 2 July 2016

Available online 2 July 2016

Keywords:

Triazine charring agent

Hydrophobic property

Intumescent flame retardant

Polypropylene

Water resistance

ABSTRACT

A novel charring foaming agent *N*-methyl triazine-ethylenediamine copolymer defined as MTEC was synthesized from cyanuric chloride, methylamine and ethylenediamine through nucleophilic reaction. Its chemical structure was well characterized by Fourier transform infrared spectroscopy, elemental analysis and ¹³C solid-state nuclear magnetic resonance. The wettability of flame retardant was evaluated by water contact angle (CA) tests, and the synthesized MTEC present excellent hydrophobic property with the water CA of 117°. Meanwhile, the water CA of the prepared intumescent flame retardant (IFR) system containing MTEC, ammonium polyphosphate and silica reached 104° and also presented hydrophobic property. The obtained IFR was incorporated into polypropylene (PP) resin to prepare flame retardant PP composites, and the flame retardancy, thermal degradation behavior, water resistance and flammability behavior for IFR-PP were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter and thermogravimetric analysis (TGA) tests. Water resistant properties of IFR-PP composites were evaluated by soaking the samples into distilled water at 70 °C for 168 h. The results demonstrated that IFR-PP samples both passed UL-94 V-0 flammability rating before water treated and after hot water soaking and drying when the loading amount of IFR was 22 wt %, the LOI value of IFR-PP only decreased from 29.6 to 29.3% and the mass loss percent was only 0.17 and 0.69% for 3.2 and 1.6 mm samples after water soaking and drying. The TGA results indicated that the incorporation of IFR promoted PP matrix decomposition and charring at a relative low temperature, and then enhanced the char yield and thermal stability for IFR-PP composites at high temperature. The cone calorimeter tests revealed that the introduction of IFR greatly decreased the combustion parameters, such as heat release rate (HRR), smoke production rate (SPR) and so on. After water resistance test, the combustion parameter for IFR-PP was slightly increased. The scanning electron microscopy (SEM) tests indicated the introduction of IFR benefited to the formation of a sufficient, intumescent and homogeneous char layer on the materials surface during burning, which effectively prevented the underlying materials from further degradation and combustion. The structure and morphology of char layer for IFR-PP remained very well after water treated, consequently the water-treated IFR-PP presented excellent flame retardancy.

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1. Introduction

Polypropylene (PP) is one of the most widely used in automobiles, electronic, buildings, chemical corrosion resistance and so on due to its outstanding mechanical properties, ease-processing, low density and good chemical resistance. However, PP is flammable

and its limiting oxygen index (LOI) value is only 17.5%, and the flammability of PP restricts its application in some aspects at which required high flame retardancy [1–4]. Therefore, it is imperative to improve the flame retardancy for PP matrix. Intumescent flame retardant (IFR) system are thought of as environment-friendly flame retardant because they generate less toxic and corrosive substances during combustion, meanwhile, there are other advantages for IFR, such as high efficiency, anti dripping and so on [5–10]. The most outstanding ternary IFR system is the mixture of ammonium polyphosphate (APP), pentaerythritol (PER) and

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melamine (MEL). However, the traditional IFR system mainly composed of small molecular compounds, such as PER, which are moisture sensitive and easily attacked by water and exuded out of the mixture, leading to a severe deterioration of the flame retardancy.

Recently, a lot of work has been done on development and application of different kinds of carbonization agents [11]. Triazine derivatives as charring agent in IFR system have been attracted great attention owing to the stable triazine rings, little water solubility and char formation easily during combustion [12]. Moreover, these agents have superior charring and foaming effect because they contain abundant nitrogen and possess a structure of tertiary nitrogen [13,14]. In recent years, triazine macromolecule derivatives used as charring agent in IFR system has been extensively investigated [15–29]. Feng et al. [25] synthesized a novel triazine charring agent CNCO-HA and mixed with APP to prepare IFR system, and the 1.6 mm samples passed UL-94 V-0 rating when the additive amount of IFR was 25 wt % with the mass ratio of APP to CNCO-HA was 4:1. Meanwhile, there are abundant hydrophilic hydroxyethyl groups, which led to the hydrophilic property of CNCO-HA and the formed IFR, and the existence of the hydrophilic groups is harmful for increasing the water resistance of IFR-PP composites. Wen et al. [19] synthesized a novel triazine charring agent defined as HCFA, which possessed high thermal stability, excellent char forming capability and good water resistance, and the IFR-PP composites with the thickness of 1.6 mm both passed UL-94 V-0 rating before water treated and after water soaking in hot water for 168 h when the loading amount was 30 wt % with the mass ratio of APP to HCFA ranged from 3:1 to 1:1. However, when the mass fraction of APP to HCFA increased to 4:1, the LOI value for water treated IFR-PP composites decreased from 29.5 to 22.0% and its UL-94 rating is degraded from V-0 to V-1 rating due to the increasing of APP with superhydrophilic property. In our previously reported work [26], *N*-ethyl triazine-piperazine copolymer (ETPC) with hydrophobic property was synthesized and ETPC mixed with APP and silica to prepare IFR system, and the samples with the thickness of 1.6 mm both passed UL-94 V-0 rating before water treated and after water soaking and drying when the additive amount of IFR was 24 wt %, and the mass loss percentage of the samples with 3.2 mm and 1.6 mm were 0.26% and 1.08%, respectively. The fact indicated this IFR system presented excellent flame retardant efficiency and water resistance for IFR-PP composites. With the rapid development of electrical and electronic industry, the flame retardant polymeric materials is required excellent comprehensive performance, such as ultra thin, good mechanical property, excellent water resistance and so on. Consequently, it is imperative to further improve the flame retardant efficiency and water resistant property for flame retardant polymeric materials.

In this work, a novel triazine charring agent *N*-methyl triazine-ethylenediamine copolymer was designed and synthesized based on our previous works [23,26]. Its structure and properties were characterized by FTIR, ¹³C solid-state NMR, elemental analysis, TGA and water contact angle tests. The synthesized charring agent mixed with APP and silica to prepare IFR system, and the obtained IFR was incorporated into PP resin to prepare IFR-PP. The flame retardant properties, thermal degradation behavior, water resistance and combustion behavior of IFR-PP were characterized and disclosed.

2. Experimental

2.1. Materials

Cyanuric chloride (industrial) was purchased from Yingkou Sanzheng Organic Chemical Industry Company, China. Ethylenediamine (analytical), sodium hydroxide (analytical) and acetone

(analytical) were obtained from Tianda Chemical Reagent Factory (Tianjin, China). Methylamine (analytical) was supplied by Shanghai Aladdin Industrial Co., Ltd., China. Polypropylene (PP) resin (T30s, homopolymer, melt flow rate 3.5 g/10 min) and PP wax severed as processing lubricate were supplied by Daqing Huake Company, China. Ammonium polyphosphate (APP, GD-101, crystalline form II, $n > 1500$, average particle size: 15 μm) was obtained from Shian Chemical Industry Company (Shandong, China). Nano-SiO₂ (silica, 100 nm) was purchased from Shandong Zibo Chemical Company.

2.2. Preparation of *N*-methyl triazine-ethylenediamine copolymer

The synthetic route of the charring agent *N*-methyl triazine-ethylenediamine copolymer defined as MTEC is shown in Scheme 1. In a 3 L, four-necked flask equipped with mechanical stirrer, thermometer, pressure-equalizing dropping funnel and reflux condenser, 1 mol cyanuric chloride and 1 L acetone were added. 1 mol methylamine aqueous solution (mass fraction 40%, 77.5 g) and 1 mol NaOH were completely dissolved in water and then mixed homogeneously to prepare mixture solution, and the prepared solution was added dropwise to the flask under the reaction temperature was 0–5 °C. After the dropwise addition, the intermediate 2-methylamino-4, 6-dichloride-1, 3, 5-tiazine was obtained, and it need not to be isolated from the reaction system. Then a mixed aqueous solution containing 0.5 mol ethylenediamine (mass fraction 99%, 30.35 g) and 1 mol NaOH was added dropwise over 2 h to the reaction mixture, and the reaction temperature was maintained at 45–50 °C. The reaction mixture was maintained at that temperature for another 2 h with stirring after addition. Finally, a mixed aqueous solution of ethylenediamine (0.5 mol) and NaOH (1 mol) was added dropwise over 6 h to the reaction mixture, and the reaction mixture was gradually heated to reflux temperature, meanwhile the acetone was removed from the reaction system. The reaction mixture was maintained at reflux temperature over 10 h after addition and a great deal of white precipitate appeared in the reaction solution. Afterwards, the reaction mixture was cooled to temperature and then filtered, the obtained white solid particles was washed three times with water and dried at 105 °C in a drying oven for 2 h. Finally, 162.2 g white solid particles of MTEC were obtained with the yield of 93.7%.

2.3. Preparation of IFR and IFR-PP composites

PP, APP, MTEC and SiO₂ were dried in a vacuum oven at 80 °C overnight before use. The IFR composite was prepared by the mixing of 19 wt % MTEC, 76 wt % APP and 5 wt % SiO₂. All the samples were prepared by mixing PP (81–75 wt %), IFR (18–24 wt %), PP wax (0.7 wt %) and antioxidant 1010 (0.3 wt %) in a two-roll extruder (D: 20 mm, L/D: 32, model: SLJ-20 Nanjing Jieya Chemical Engineering Equipment Co., China) at a temperature profile of six heating zones (170, 180, 185, 190, 190 and 185 °C). The IFR-PP testing samples were molded by an injector (HTF86X1, Zhejiang Haitian, China) at a temperature profile of five heating zones (210, 220, 220, 220 and 210 °C).

2.4. Characterization methods

The Fourier transform infrared (FTIR) spectra were obtained with a spectrophotometer (PerkinElmer 400) in range from 400 to 4000 cm^{-1} . The elemental analysis was performed with a Carlo Erba 1110 elemental analyzer. The ¹³C solid-state NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 WB spectrometer.

The contact angles (CA) were measured with a drop-shape analysis system (POWERREACH JC2000A) at room temperature. The powder of MTEC, APP and SiO₂ were homogeneously mixed

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