



A THEIC-based polyphosphate melamine intumescent flame retardant and its flame retardancy properties for polylactide



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ARTICLE INFO

Article history:

Received 7 May 2016

Received in revised form 21 October 2016

Accepted 27 October 2016

Available online 31 October 2016

Keywords:

Polylactide

Macromolecular intumescent flame retardant

THEIC

Thermal degradation

ABSTRACT

A macromolecular intumescent flame retardant tris(2-hydroxyethyl) isocyanurate polyphosphate melamine (TPM) was synthesized, its structure was confirmed by Fourier transform infrared spectroscopy (FTIR), ¹H and ³¹P nuclear magnetic resonances (NMR). The flame retardancy and combustion properties of PLA/TPM composites were evaluated by limiting oxygen index (LOI), UL-94, and cone calorimetry tests. It was found that PLA with 25 wt% APP/TPM (0.5:1) acquired LOI 36.5% and achieved UL-94 V-0 rating with no melt dripping. Cone calorimetry tests showed that pHRR and THR of PLA/TPM composites were dramatically reduced compared with that of pure PLA, the HRR curve suggested that TPM could accelerate char forming process. TGA demonstrated that TPM effectively improved thermal stability of PLA. The possible thermal degradation mechanism, structure and morphology of char layer were studied by FTIR, XPS and SEM.

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1. Introduction

With the growing awareness of environmental protection and the shortage of petroleum energy sources, biodegradable polymeric materials have drawn more and more attention [1–4]. Polylactide (PLA), a promising alternative to petroleum-based plastics, plays a predominant role due to its good biocompatibility and excellent mechanical properties [5]. PLA has been primarily used in packaging, medical apparatuses and textile sector. However, its high flammability and serious melt dripping limit its applications in electronic and electric fields [6]. It is of great significance to improve the flame retardancy of PLA.

Due to its advantages of little smoke, low toxicity, low corrosion and high charring capability, intumescent flame retardant (IFR) has been employed as a safe and environmental friendly additive to polymeric materials [7–11]. A typical IFR formulation is comprised of ammonium polyphosphate (APP), pentaerythritol (PER) and melamine (MEL) [12]. However, the conventional IFR system exhibits low flame retardant efficiency in PLA with melt dripping. For instance, Reti et al. [13] used an IFR system consisting of APP and charring agents including PER, lignin and starch to enhance flame retardancy of PLA. Results showed that APP/PER system could only

reach UL-94 V-2 rating with melt dripping even when the loading was as high as 40 wt%. Fontaine et al. [14] combined APP with MEL to improve flame retardancy of PLA. Although UL-94 V-0 rating could be obtained, melt dripping was unknown. Li et al. [15] reported that melt dripping of PLA during combustion could be significantly suppressed after the addition of organically modified montmorillonite (O-MMT) with traditional IFR. However, LOI value was relatively low. It is hard for traditional IFR system to achieve UL-94 V-0 rating without melt dripping and simultaneously obtain high LOI value at low content. Some studies on synthesizing new IFR for flame retarded PLA have been reported. For example, Zhan et al. [16] synthesized a novel flame retardant SPDPM, using pentaerythritol, phosphorus oxychloride and melamine as raw materials, because SPDPM combined char, acid and gas sources together, it presented high flame retardant efficiency for PLA, acquired LOI 38% and achieved UL-94 V-0 rating with 25 wt% loading. Ke et al. [17] employed a hyperbranched charring agent HCA in PLA, this HCA was prepared by cyanuric chloride, diisopropyl ethylamine and 4,4'-diaminodiphenyl, results showed that it exhibited excellent flame retardancy and anti-dripping capacity for PLA when combined with APP, LOI could reach 36.5% and UL-94 V-0 rating was reached with 30 wt% loading. However, triazine-based charring agents are synthesized from cyanuric chloride and need organic solvent, which can lead to safety anxieties. THEIC is a derivative of triazine compounds. It is nontoxic and there is no corrosive gas or toxic substance releasing in the reaction process. All these con-

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form to the environmental-friendly property of PLA. In our previous work, we found that the maximum LOI value of PLA/APP/THEIC composite could reach 44% when the loading was 30 wt% with APP/THEIC (5:1), but all ratios of APP to THEIC could only achieve UL-94 V-2 rating and the melt dripping was still serious. Yuan [18] used THEIC and terephthalic acid as raw materials to synthesize a novel charring agent tris(2-hydroxyethyl) isocyanurate terephthalic acid ester (TT4), which combined with APP (1:5) could acquire the LOI value of 40% and achieve UL-94 V-0 rating, but high dosage of 30 wt% was necessary. Because melt dripping is a particular problem in modifying the flame retardant performance of thermoplastics just like PLA, not only can melt dripping enlarge the burning surface area and increase fire intensity, but also it can result in fast fire spread. It has been suggested that melt viscosity has a strong impact on char formation and small molecular flame retardants such as MEL and PER can decrease the viscosity of polymer melt [15]. Synthesizing macromolecular flame retardant is a potential way to heighten anti-dripping capacity by increasing the viscosity of polymer melt.

In this paper, a macromolecular intumescent flame retardant tris(2-hydroxyethyl) isocyanurate polyphosphate melamine (TPM) was synthesized using tris(2-hydroxyethyl) isocyanurate (THEIC), polyphosphoric acid (PPA) and melamine as raw materials, which integrated char, acid and gas sources. All these materials are non-toxic and there is no corrosive and toxic substance in decomposed products, which conforms to the environmental friendly property of PLA. The structure of TPM was characterized by FTIR, ^1H NMR and ^{31}P NMR. Its flame retardancy properties were investigated through LOI, UL-94 tests and cone calorimetry, its thermal degradation behavior was analyzed by TG and FTIR at different degradation temperatures. The structure and morphology of char layer were studied by FTIR, XPS and SEM.

2. Experimental

2.1. Materials

PLA (2002D) was supplied by Natureworks Company. APP (form II, $n > 1000$) was provided by Shandong Shi'an Chemical Co., Ltd. THEIC was obtained from Changzhou Lantian Chemical Co., Ltd. Melamine was purchased from Sinopharm Chemical Reagent Co., Ltd. Polyphosphoric acid (PPA) was offered by Shanghai Lingfeng Chemical Reagent Co., Ltd. All materials were used as received without further purification.

2.2. Synthesis of TPM

THEIC (104.50 g, 0.4 mol) was melted first at 160 °C in a flask equipped with a stirrer, a condenser and a thermometer. After THEIC was completely melted, 4-methylbenzenesulfonic acid (2.0 g) as catalyst and PPA (270.34 g, 0.8 mol) were successively added into the reaction system in 10 min, and reacted for 3 h with constant stirring. Then temperature was increased to 190 °C, melamine (100.90 g, 0.8 mol) was added into the mixture to react for another 0.5 h. Thereafter, the product was poured into a plate and cooled to room temperature. A light grey product was obtained, and it was shattered by a small pulverizer (Scheme 1).

2.3. Preparation of flame-retarded PLA composites

All samples were prepared using an internal mixer (SU 70-1, Suyan Technological Company, China) at 180 °C, the rotate speed was maintained at 20r/min. Pure PLA was first added into the internal mixer. After PLA was melted, APP and TPM were introduced into the matrix and mixed for 10 min until a visible good dispersion was achieved. Finally, all mixed composites were hot-pressed into

sheets with thickness of 3 mm at 180 °C for about 8 min to make specimens for flame retardancy property tests. The formula of all samples were listed in Table 2.

2.4. Measurements

2.4.1. Characterization

Fourier transform infrared (FTIR) spectra were obtained in standard wavenumber range of 4000–500 cm^{-1} by a Nicolet6700 spectrometer, where samples were prepared with KBr powders and compressed into slices in advance. ^1H and ^{31}P NMR spectra were recorded at 500 MHz on an AVANCE 500 spectrometer (Bruker Company, Switzerland), using D_2O as solvent and 85% H_3PO_4 as reference.

2.4.2. Flame retardancy tests

LOI tests were measured according to ASTM D2863-97 by using a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were $130 \times 6.5 \times 3 \text{ mm}^3$.

UL-94 vertical burning tests were performed on a CZF-3 instrument (Jiangning Analysis Instrument Company, China) with sample dimension of $130 \times 13 \times 3 \text{ mm}^3$, the classifications were defined according to the American National Standard UL-94.

2.4.3. Combustion properties

The combustion properties were evaluated using a Stanton Redcroft cone calorimeter according to ISO-5660 standard procedures with specimen dimension of $100 \times 100 \times 3 \text{ mm}^3$. All samples, wrapped in aluminum foil, were put in horizontal orientation with a heat flux of 50 kW/m^2 .

2.4.4. Thermogravimetric analysis

Thermal degradation behaviors of all testing materials were characterized by thermogravimetry (TG) using a TA instrument EXSTAR 6000 thermogravimetric analyzer. The specimens with the weight of about 5 mg were heated from room temperature to 800 °C at heating rate of 10 °C/min under air atmosphere.

2.4.5. Properties of char layer

Scanning electron microscopy (SEM) was employed to observe the morphologic features of the char layer using a JSM-6360LV scanning electron microscope with the accelerating voltage of 20 kV. The specimens were sputter-coated with gold prior to observation.

X-ray photoelectron spectroscopy (XPS) was performed by a VG ESCALAB MKII spectrometer, using Al K α excitation radiation ($h\nu = 1253.6 \text{ eV}$).

3. Results and discussion

3.1. Characterization of TPM

The FTIR spectra of THEIC and TPM are presented in Fig. 1, all the assignments of absorption bands are listed in Table 1.

For THEIC, the strong absorption peaks at 3512 cm^{-1} , 3367 cm^{-1} , and 3251 cm^{-1} are assigned to the stretching vibration of O–H. The absorption peaks at 2974 cm^{-1} , 2949 cm^{-1} , and 2885 cm^{-1} are attributed to stretching vibration of $-\text{CH}_2-$, the peak at 1470 cm^{-1} corresponds to the bending vibration of $-\text{CH}_2-$. Other functional groups such as C=O and C–N can be found at 1710 cm^{-1} and 1360 cm^{-1} respectively. All of these are in good agreement with typical functional groups in THEIC.

For TPM, besides several similar functional groups with THEIC, there are some new absorption peaks at 3407 cm^{-1} , 1544 cm^{-1} and 1415 cm^{-1} , belonging to the stretching vibrations of $-\text{NH}_2$, $-\text{NH}_3^+$ and C=N in triazine ring [17], which denotes the presence

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