



Terminal group effects of phosphazene-triazine bi-group flame retardant additives in flame retardant polylactic acid composites



Yajun Chen ^{a, b, *}, Wei Wang ^{a, b}, Yong Qiu ^c, Linshan Li ^{a, b}, Lijun Qian ^{a, b, **}, Fei Xin ^{a, b}

^a School of Materials Science and Mechanical Engineering, Beijing Technology and Business University, Beijing 100048, PR China

^b Beijing Key Laboratory of Quality Evaluation Technology for Hygiene and Safety of Plastics, Beijing 100048, PR China

^c School of Materials, Beijing Institute of Technology, Beijing 100081, PR China

ARTICLE INFO

Article history:

Received 3 February 2017

Received in revised form

14 April 2017

Accepted 30 April 2017

Available online 2 May 2017

Keywords:

Flame retardant
Polylactic acid
Synergistic effect
Phosphazene
Triazine

ABSTRACT

Three phosphazene-triazine bi-group flame retardant additives (A1, A2, A3) with different terminal groups were synthesized from hexachlorocyclotriphosphazene (HCCP), cyanuric chloride and amine compounds (ethylenediamine, aniline, or *p*-phenylenediamine). Then they were applied with ammonium polyphosphate (APP) to prepare flame-retardant polylactic acid (PLA), separately. The molecule structures and thermal stabilities of these three flame retardant additives were characterized by Fourier transformed infrared spectrometry (FTIR), ¹H and ¹³C Solid-State NMR spectrometer and thermogravimetric analysis (TGA). The flame-retardant properties and mechanism of the flame-retardant PLA composites were investigated by the limited oxygen index (LOI) test, vertical burning test, cone calorimeter test (CCT), scanning electron microscopy (SEM), and thermogravimetric analyzer coupled to a Fourier-transform infrared spectrometer (TGA-FTIR). Results showed that the combination of phosphazene-triazine bi-group flame retardant additive with amino-terminated groups (A1 or A3) and APP brought better flame retardant properties to PLA resin than that of A2 without amino-terminated groups. PLA/A1/APP system got the best flame retardant properties, which exhibited the highest LOI value of 34.3% and preferably achieved UL-94 V-0 rating without dripping. Meanwhile, it not only obtained the lowest *pk*-HRR, THR, and TSR, but also reserved the largest amount of residual char, compared with other flame-retardant PLA composites. Such a significant improvement in flame retardancy was attributed to the PO₂[·] radical quenching effect and inert gas dilution effect in gas phase, as well as barrier and protective effect and charring effect in condense phase. Besides, the poor performance on flame retardancy of PLA/A2/APP system was due to the lack of barrier and protective effect and charring effect in condense phase. All these revealed that the adjustment on terminal groups of flame-retardant additives not only affects their flame-retardant work mode, but also helps to explore the more efficient flame-retardant structures or systems.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Over the past decade, with the urgent environmental pollution and shortage of petroleum energy source, biodegradable polymeric material has attracted more and more attention. Polylactic acid

(PLA) is one of the best-known biodegradable aliphatic polyesters that can be produced by renewable sources (mainly starch and sugar). PLA has been used in various applications due to its excellent mechanical properties. Nowadays the high molecular weight PLA has broadened its applications in electronic and electrical devices, mechanical and automotive parts industries [1–5]. Unfortunately, PLA has very poor flame retardancy especially the serious dripping during burning, which severely restricts its potential application. Therefore, the flame retardant modification of PLA has been an urgent task.

In recent years, intumescent flame retardant (IFR) additives have received extensive attention on the flame retardation application of PLA due to their advantages of low smoke and low toxicity

* Corresponding author. School of Materials Science and Mechanical Engineering, Beijing Technology and Business University, No.11, Fucheng Road, Haidian District, Beijing 100048, PR China.

** Corresponding author. School of Materials Science and Mechanical Engineering, Beijing Technology and Business University, No.11, Fucheng Road, Haidian District, Beijing 100048, PR China.

E-mail addresses: chenyajun@th.btbu.edu.cn (Y. Chen), qianlj@th.btbu.edu.cn (L. Qian).

[6]. A typical case of intumescent system is the combination of ammonium polyphosphate (APP) and pentaerythritol (PER) where APP plays the role of both acid source and blowing agent (evolution of ammonia during the degradation of APP) while PER is the charring agent [7,8]. However, from the perspective of sustainable development, some researchers have developed lots of substitute for PER, such as lignin, starch, and β -cyclodextrin (CD) which all produced from renewable resources [9–11]. The basic idea was to make an intumescent flame retardant PLA with the highest percentage of bio-based ingredients. Results showed that at 20 wt% loading of APP/CD/melamine, the PLA composite exhibited a LOI value of 34.2%, and passed UL-94 V-0 rating. Moreover, some other researchers have designed various environmental friendly hyper-branched molecules and combined them with APP to improve the flame-retardant performance of PLA resin [12–17].

In our previous work, a phosphazene-triazine bi-group flame retardant additives named heax-[N,N',N''-tris-(2-amino-ethyl)-[1,3,5]triazine-2,4,6-triamine]cyclotriphosphazene (HTTCP) was synthesized and utilized to prepare flame retardant PLA composites combined with APP [18]. The LOI value of the PLA composite was 41.3% and it passed UL-94 V-0 rating when the ratio of HTTCP to APP was 1:1 (25 wt% total amount), which indicated that HTTCP enhanced the flame retardant property of PLA remarkably. Therefore, in this article, three phosphazene-triazine bi-group molecules with the same main chain structures as HTTCP but different terminal groups were designed, synthesized and characterized. The flammability and flame-retardant mechanism of phosphazene-triazine bi-group flame retardant additives in PLA matrix were investigated. The effect of the adjustment on terminal groups of flame-retardant additives was explored.

2. Experimental

2.1. Materials

PLA resin (2003D) was supplied by Nature works Company. Cyanuric chloride was purchased from Hebei Chengxin Chemical, China. Hexachlorocyclotriphosphazene (HCCP) was provided by Zibo Lanyin Chemical Co. Ltd., China. APP ($n > 1000$) was offered by Polyrocks Chemical Co., Ltd. Ethylenediamine, aniline, *p*-phenylenediamine, dioxane, potassium carbonate (K_2CO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of phosphazene-triazine bi-group flame retardant additives

The synthetic routes of three phosphazene-triazine bi-group flame retardant additives (A1, A2, and A3) are shown in Scheme 1. In the process, ethylenediamine (4.32 g, 0.072 mol) was dissolved in dioxane (30 ml), K_2CO_3 (30 g, 0.216 mol) was added in a 500 ml flask equipped with a stirrer, a thermometer and constant pressure dropping funnel. Then HCCP (4.172 g, 0.012 mol) dissolved in dioxane (30 ml) was added at the rate of 0.09 g/min under ice bath and constant stirring. The intermediate I was obtained 3 h later. After that, cyanuric chloride (13.28 g, 0.072 mol) dissolved in dioxane (150 ml) was added at the rate of 0.19 g/min. After stirring for extra 2 h at 0 °C, the Intermediate II was obtained.

Afterwards, the reaction temperature was increased to 50 °C and ethylenediamine (4.32 g, 0.072 mol) was added within 30 min. After 3 h the mixture was heated to 90 °C–100 °C and another 4.32 g ethylenediamine was added at the same rate and reacted for 3 h. The mixture was then cooled down to room temperature, followed by filtration, washing the product with distilled water, drying it to a constant weight in vacuum oven at 110 °C, and 16 g white solid (A1) was obtained (80% yield).

In the same way, after the Intermediate II was obtained, 6.70 g (0.072 mol) aniline was added to the mixture within 30 min. Keep the temperature at 50 °C for 3 h. Then the reaction temperature was increased to 90 °C–100 °C and another 6.70 g aniline was added at the same rate. After 3 h, the mixture was cooled down to room temperature, followed by filtration, washing the product with distilled water, drying it to a constant weight in vacuum oven at 100 °C, and 20 g buff solid (A2) was obtained (81% yield).

Similarly, 7.78 g (0.072 mol) *p*-phenylenediamine was added to the mixture within 30 min at the rate of 0.2 g/min after the Intermediate II was prepared. After 3 h, the mixture was heated to 90 °C–100 °C and another 7.78 g *p*-phenylenediamine was added at the same rate and reacted for 3 h. Then the mixture was cooled down to room temperature, followed by filtration, washing the product with distilled water, drying it to a constant weight in vacuum oven at 100 °C, and 22.8 g brown solid (A3) was obtained (84.9% yield).

2.3. Preparation of flame retardant PLA composites

The flame-retardant PLA composites were prepared by melt blending method. Before mixing, flame retardants were dried at 100 °C and PLA resin was dried at 80 °C for 24 h. Then all composites were prepared on a torque rheometer at 190 °C with 50 rpm for 8 min. The samples were then transferred to a mold and preheated at 190 °C for 5 min, then pressed at 10 MPa, and cooled to room temperature to obtain the composite sheets for further tests. The formulations of prepared samples are listed in Table 1.

2.4. Characterization

The FTIR spectrum was detected on a Nicolet iN10MX type spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets. The 1H SSNMR and ^{13}C SSNMR data were obtained using a Bruker 400 MHz WB Solid-State NMR Spectrometer. The 1H NMR curves of flame retardants A2 and A3 were processed by the method of Gauss fitting.

Thermogravimetric analysis (TGA) was carried out on a TA instrument Q5000IR thermal gravimetric analyzer. The sample was placed in a zirconia crucible and heated with a rate of 20 °C/min from 50 to 800 °C with 4 mg weight under N_2 atmosphere. All the tests were repeated three times, and the typical TGA data were reproducible within $\pm 5\%$.

To detect volatile pyrolysis products, a Mettler-Toledo TGA/DSC-1 thermogravimetric analyzer was coupled to a Bruker Tensor 27 Fourier-transform infrared spectrometer (TGA-FTIR). Each sample was placed in an alumina crucible and heated from 50 to 700 °C at a heating rate of 20 °C/min under N_2 atmosphere. The thermogravimetric analyzer and FTIR spectrometer were connected by a quartz capillary at 230 °C.

The limiting oxygen index (LOI) values were performed on an FTT (Fire Testing Technology, UK) Dynisco LOI instrument according to ASTM D2863-97, with sheet dimensions $130.0 \times 6.5 \times 3.2$ mm³. The LOI measurement for each specimen was repeated three times, and their error values were $\pm 0.3\%$. The vertical burning test (UL-94) was performed on FTT0082 instrument according to ASTM D 3801 testing procedure with sheet dimensions of $125.0 \times 12.7 \times 3.2$ mm³. The fire behavior was characterized on a FTT cone calorimeter according to ISO5660 under an external heat flux of 50 kW/m². The dimension of samples was $100 \times 100 \times 3$ mm³. The measurement for each specimen was repeated three times, and the error values of the typical cone calorimeter data were reproducible within $\pm 10\%$.

The micromorphology images of the residues after cone calorimeter test were obtained using a FEI Quanta 250 FEG field

Download English Version:

<https://daneshyari.com/en/article/5200796>

Download Persian Version:

<https://daneshyari.com/article/5200796>

[Daneshyari.com](https://daneshyari.com)