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An effective multi-hydroxy-containing ammonium phosphate towards flame-retarding poly(lactic acid): Flame retardance, thermal and pyrolysis behaviors

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ABSTRACT

To retard the flammability of poly(lactic acid) (PLA), a multi-hydroxy-containing ammonium phosphate (DPPT) derived from 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (DOP) and trihydroxymethyl amino-methane (TRIS) through a one-pot reaction was introduced. By comparison with PLA, the limiting oxygen index (LOI) of PLA modified with 2.5% DPPT increased from 19.5% to 32.7%, and UL-94 vertical rating was improved from no rating to UL-94 V-0 rating. Besides, the results of cone calorimetric tests (CC) showed that DPPT could suppress the heat release of PLA during combustion to some extent. Although the thermal behaviors of PLA were affected by DPPT, DPPT could promote the degree of crystallinity of PLA. According to the relevant results as well as the analyses of thermogravimetric analysis coupled with fourier transform infrared spectroscopy (TG-FTIR) and pyrolysis-gas chromatograph/mass spectrometer (py-GC/MS), the flame retardant mechanism of DPPT was also disclosed that it could decompose to generate the incombustible compounds such as water and ammonia, and simultaneously release phosphorus-containing free radicals; Besides, the removal of non-flammable dripping could also bring away heat and cut off the heat-transfer to the matrix.

1. Introduction

In recent years, poly(lactic acid) (PLA) has received much attention in the application of packaging, agricultural film, biomedical, and pharmaceutical fields due to its renewable resource, biodegradation, biocompatibility, mechanical property, thermoplastic processibility, et al. [1–3]. However, extending the applicability of PLA to the transportation and electronics sectors poses significant challenges, since PLA is easily flammable like most thermoplastics, which always accompanies with heavy dripping during combustion. Therefore, the improvement of flame retardance is of great significance for the application of PLA [4–6].

The common and effective strategies on flame-retardant PLA are blending PLA with flame retardants (FRs) and chemically modifying PLA with flame-retardant elements such as phosphorus. Nowadays, the frequently-reported ways to enhance fire resistance of polymers are physically blended with flame retardants including nano fillers [7–11] such as MMT [12,13], graphene oxide [14,15], and carbon nanotube [16–18] etc, phosphorus-containing compounds [19–24], and

intumescent flame retardants [25–31]. Nevertheless, nano fillers show weak effect on improving the flammability of PLA in terms of UL-94 rating and LOI value. Consequently, the main route to obtain flame-retardant PLA is the employment of phosphorus-containing compounds and intumescent flame retardants. For instance, Liu et al. combined ammonium polyphosphate (APP) and a novel phosphorus-containing flame retardant (PFRS) to flame retard PLA, and intumescent flame retardant including 3.8 wt% PFRS and 11.2 wt% APP was employed to prepare PLA composite with good flame retardance [32]. Besides, Bourbigot reported the combination of melamine and APP allowed to obtain a low flammability of PLA [33]. Moreover, Song et al. developed a combined flame retardant (IFR) including 2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane-4-methanol (PEPA), trisilanolisbutyl-POSS (TPOSS) and melamine phosphate (MP), and introduced it into PLA. The result showed that the modified PLA passed UL-94 V-0 rating with 25 wt% IFR and owned a LOI value of 36% [34]. However, high loading of these abovementioned additives were required to achieve a satisfying level of flame retardance, which might decrease other properties of the PLA blends to some extent. Therefore, it is necessary to develop a highly

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efficient flame retardant. As seen, except for APP or MP, other ammonium phosphates are seldom reported to flame retard PLA. In this work, DOP and TRIS are adopted to synthesize multi-hydroxy-containing ammonium phosphate. It is well-known that DOP-based flame retardants are effective on flame retarding polymers; meanwhile, TRIS contains both amino group and multi-hydroxy group, and it can dehydrate to release water, and simultaneously produce inert nitrogen-containing gases during decomposition. Hence, it is reasonable that DPPT would have positive effect on PLA.

In this paper, multi-hydroxy-containing ammonium phosphate (DPPT) was synthesized through a one-pot reaction using DOP and TRIS, and then applied to prepare flame-retardant PLA. The chemical structure of DPPT was studied by Fourier transform infrared spectra (FTIR), nuclear magnetic resonance (NMR) and high resolution ionization mass spectrum (HRESI-MS). Besides, flame retardance of materials were evaluated through UL-94 vertical burning tests (UL-94 V), LOI and CC. The thermal behavior was studied by thermogravimetric analysis (TG) and differential scanning calorimeter (DSC). Finally, flame-retardant mechanism was also investigated.

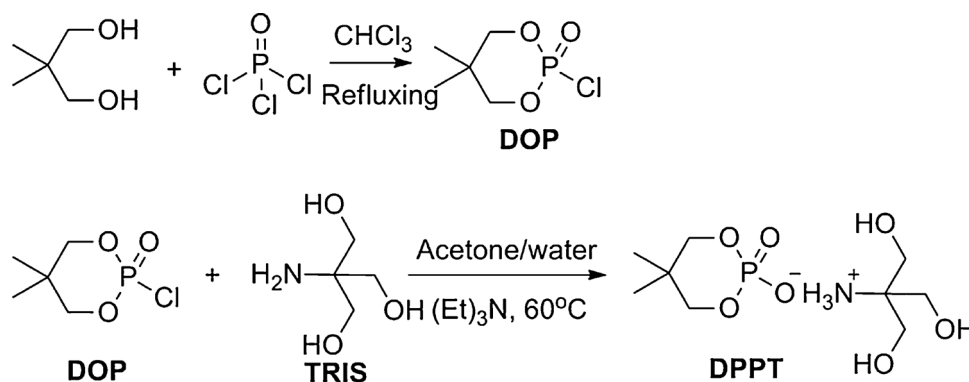
2. Materials and methods

2.1. Materials

PLA (4032D) was obtained from Nature Works (USA). Phosphorus oxychloride and neopentyl glycol were available from Shandong Xiya Chemical industries Co. Ltd. TRIS was provided from Shanghai Macklin Biochemical Co., Ltd. Trichloromethane, triethylamine (TEA), acetone and methanol were purchased from Tianjin Zhiyuan Chemical Reagent co., Ltd. (Tianjin, China), and were used without further purification.

2.2. Synthesis of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (DOP)

The detailed synthetic route of DOP is depicted as follows: 52 g neopentylglycol (0.5 mol) and 200 mL chloroform were added in a 500 mL three-necked round-bottom-flask equipped with a mechanical stirrer, a reflux condenser linked with a gas-absorption device, and a dropping funnel. The mixture was heated to 60 °C until the neopentyl glycol was dissolved. 47 mL phosphorus oxychloride (0.5 mol) was added slowly by dropwise to the reaction flask. After the addition, the reaction mixture was heated to reflux until no HCl gas could be detected. The solvent was evaporated under vacuum to obtain the crude product. Then the crude product was washed with distilled water several times, and dried at 70 °C overnight to get a white powder DOP (80 g, yield: 85.8%). FTIR (KBr, cm^{-1}): 2978, 2940, 2898 ($-\text{CH}_3$, $-\text{CH}_2-$), 1304 (P = O), 1052, 1005 (P-O-C), 549 (P-Cl).



Scheme 1. Synthetic route of DPPT.

2.3. Synthesis of DPPT

The synthetic route of DPPT is shown in Scheme 1, and the detailed route is shown as follows: Firstly, 27.7 g DOP (0.15 mol) was added to the 200 mL solution of acetone/water (volume ratio, 1:2) in a 500 mL three-neck round flask accompanied with agitation. Then the mixture of 18.2 g TRIS (0.15 mol) and 42 ml TEA dissolved in 200 mL solution of acetone/water was added dropwise into the flask, and the solution become transparent gradually. After the addition was completed, the solution was heated to 60 °C and kept for 8 h. Finally, the solution was post-treated through removing the solvent with a rotary evaporator, and the obtained crude product was washed successively by trichloromethane and cold methyl alcohol, and then dried in vacuum at 60 °C for 8 h to obtain a white product. (Yield: 31.2 g, 77.5%). FTIR (KBr, cm^{-1}): 3251 ($-\text{OH}$), 3200–2500 ($-\text{NH}_3^+$), 2941, 2851 ($-\text{CH}_3$, $-\text{CH}_2-$), 1210 (P = O); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm): δ 7.78 (s, 3H, $-\text{NH}_3^+$), 5.56 (s, 3H, O-H), 3.64 (d, $J = 12$ Hz, 4H, $-\text{CH}_2\text{O}-$), 3.46 (s, 6H, $-\text{CH}_2\text{OH}$), 0.88 (s, 6, $-\text{CH}_3$); $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$, ppm): 75.18, 61.58, 59.61, 32.21, 21.74; $^{31}\text{P NMR}$ (162 MHz, $\text{DMSO-}d_6$, ppm): -4.25 ; HRMS (ESI $^+$): calcd for $\text{C}_9\text{H}_{23}\text{NO}_7\text{P}$ $[\text{M} + \text{H}]^+$ 288.12, found 288.11.

2.4. Preparation of PLA/DPPT

PLA was dried in vacuum at 80 °C for 8 h prior to use. PLA and DPPT were added into a two-screw extruder (Haake rheometer, PolyLab QC, Germany). The temperatures corresponding to the heating sections of the extruder were set at 175, 180, 180, 180, 180, 175, and 175 °C, respectively. The rotation speed was set at 40 rpm. PLA blends with 1 wt %, 2.5 wt% and 5 wt% DPPT are coded as PLA1, PLA2 and PLA3, respectively. PLA without DPPT was also processed according to the aforementioned procedure as the control. Finally, these extrudates were cut into pellets, and then compression-molded in 10 MPa at 185 °C to obtain the testing samples.

2.5. Characterization

2.5.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded in the range of 4000–450 cm^{-1} using KBr pellets on a Thermo Nicolet 5700 FTIR instrument.

2.5.2. Nuclear magnetic resonance (NMR)

$^1\text{H NMR}$, $^{13}\text{C NMR}$ and $^{31}\text{P NMR}$ spectra were obtained with a Bruker AVANCE AV II-400 NMR instrument using $\text{DMSO-}d_6$ as the solvent and tetramethylsilane (TMS) as the internal standard.

2.5.3. High resolution ionization mass spectrum (HRESI-MS)

Mass spectrum was recorded on a Bruker compact Q-TOF apparatus.

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