Tough and flame-retardant poly(lactic acid) composites prepared via reactive blending with biobased ammonium phytate and *in situ* formed crosslinked polyurethane

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ABSTRACT

Simultaneously endowing poly(lactic acid) (PLA) with flame retardancy and toughness still is a challenge. In this study, a novel biobased phosphorus-nitrogen containing flame retardant (PA-HDA), synthesized from phytic acid and 1,6-hexanediamine, is employed into a toughened PLA (TPLA) composite, which is achieved by *in situ* formed crosslinked polyurethane (CPU). The comprehensive properties of PLA composites such as thermal stability, thermal transition behaviors, mechanical properties and flame retardancy have been well investigated. Only with 5 wt% PA-HDA loading, TPLA can pass UL-94 V-0 rating while its limiting oxygen index (LOI) value is as high as 26%. Besides, the flame retardant TPLA still keeps good tensile and impact toughness, *i.e.* its elongation at break and notched impact strength are enhanced to 207.3% and $5.0 \, kJ/m^2$, which are 26.6 and 2.8 times of those of neat PLA, respectively. Surprisingly, it is found that PA-HDA can rise the crystallinity of PLA. But the glass transition temperatures and the initial decomposition temperatures of flame-retardant TPLA are decreased compared to those of pure PLA. By adjusting the PA-HDA loading, we can achieve the balance between the flame retardancy and good mechanical properties of PLA.

1. Introduction

PLA is regarded as one of the most promising biobased polymers [1,2]. Due to the excellent biocompatibility, easy processibility, and high melting temperature, PLA has been widely used as packaging materials, biomedical devices, fibers and daily supplies [3–5]. Nowadays, PLA is expected to apply in many new fields such as electronic appliances, automotive and rail transit materials [6,7]. However, its elongation at break is less than 10% and its notched izod impact strength is as low as $2 \, kJ/m^2$, which restrict its wide application [8]. Besides, the inherent flammability of PLA has to be resolved when it is used in the industrial fields mentioned above [9].

Lots of work have successfully improved the flame retardancy [9–14] or the toughness of PLA [15–18], separately. Unfortunately, seldom researches focus on improving the mechanical properties, especially the notched izod impact strength, and the flame retardancy of PLA simultaneously [19,20]. Our group has added ammonium polyphosphate (APP)/poly(ethylene glycol) (PEG) into PLA to improve the brittleness and flame retardancy of PLA. The obtained PLA composites can pass UL-94 V-0 rating, while its elongation at break is 10 times higher than that of neat PLA [10].

To further improve the flame retardancy and mechanical properties of PLA, as well as maintain the biomass content of PLA composites, in this work, a biobased flame retardant derived from phytic acid and hexane-1,6-diamine has been synthesized and used in TPLA, which is toughened by blending with *in situ* formed crosslinked polyurethane (CPU) according to our previous report [21]. Phytic acid, with high phosphorus content of 28.2%, is a natural plant compound, found in most cereal grains, legumes, nuts, oilseeds, tubers, and organic soils [22]. Hexane-1,6-diamine (HDA) also can be obtained from biobased 5-hydroxymethylfurfural. It is reported by Rennovia Inc. [23,24] that the production cost of HDA by this way is 20–25% below that of conventional petroleum-based one. It is expected that this biobased flame retardant with high phosphorus and nitrogen content can enhance the flame retardancy of toughened PLA with a low loading. The effect of this novel biobased flame retardant on the mechanical properties, flame retardancy, thermal stability and crystallization of toughened PLA is investigated in detail.

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2. Experimental section

2.1. Materials

4, 4'-Diphenylmethane diisocyanate (MDI, 98%) and phytic acid solution (PA, 70% in H₂O) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). PEG-20000, hexane-1,6-diamine (HDA, AR grade) and glycerol (AR grade) were obtained from Kelong Chemical Industrial Reagent Co., Ltd. (Chengdu, China). PLA (4032D) was purchased from NatureWorks LLC. All the reagents were used without any further purification.

2.2. Synthesis of 1, 6-hexanediammonium phytate (PA-HDA)

HDA (340 mmol) was dissolved in deionized water (40 mL) in a three-neck flask equipped with a condenser pipe. PA (38 mmol, diluted in 80 mL water) was added dropwise into the flask at room temperature with stirring. After the drop was finished, the solution was heated up to 80 °C and maintained at this temperature for 4 h. Then the mixture was cooled to room temperature and washed with 50 mL ethanol for 3 times after water was removed by rotary evaporator. The product PA-HDA with light gray was filtrated off and dried until constant weight. Yield: 86.5%. ¹H NMR (D₂O): δ (ppm), 2.81 (α-CH₂, 2H, s); 1.52 (β-CH₂, 2H, s); 1.26 (γ-CH₂, 2H, s). ¹³C NMR (D₂O): δ (ppm), 39.0 (α-C, s); 26.4 (β-C, s); 24.9 (γ-C, s); ¹³P NMR (D₂O): δ (ppm), 4.49-3.31 (2P, m); 2.61-2.10 (4P, m). FTIR spectra: KBr, 2933, 2855 cm⁻¹ (-CH₂-); 1641 cm⁻¹ (-CH-); 1555 cm⁻¹ (-NH₄⁺). ICP-AES: actual P content: 12.86 wt%, theoretical P content: 13.69 wt%. The chemical structure, NMR and FT-IR spectra of PA-HDA are shown in Scheme S1 and Figs. S1-S2, respectively.

2.3. Preparation of flame retardant TPLA/PA-HDA

PLA, PEG-20000, glycerol and PA-HDA were vacuum dried at 80 °C for 8 h before processing. After all reagents included MDI were added, the reactive melting blending was carried out in an internal torque rheometer (Kechuang XSS300, China) at 190 °C, 100 rpm for about 6 min until the torque became stable (Fig. S3). The weight ratio of PLA: PEG-20000: Gly: MDI was controlled as 80: 10: 2: 8, and the actual formed crosslinking CPU content was determined by gel fraction according to the literature [21]. The obtained gel fraction for TPLA is 14.3% (Table S1). The PA-HDA loading was changed from 2.5 wt% to 10 wt% based on the TPLA. The obtained samples are named as TPLA/PA-HDAₓ, in which x is the content of PA-HDA. All the test samples were prepared by injection molding (Haake MiniJet Pro, Thermo Scientific, Germany) operated with a cylinder temperature of 200 °C and a molding temperature of room temperature.

2.4. Characterization

The limiting oxygen index (LOI) of samples were measured by oxygen index meter (HC-2C, Jiang Ning Analysis Instrument Factory, China) with the dimension of 130 × 6.5 × 3.2 mm³ according to ASTM D2863-97. Vertical burning test was carried on UL-94 vertical flame chamber (CZF-3, Jiang Ning Analysis Instrument Factory, China) with the dimensions of 130 × 13 × 3.2 mm³ according to ASTM D3801. The thermogravimetric analysis (NETZSCH, Germany) was used to investigate the thermal stability of samples, heating from 40 to 700 °C at a heating rate of 20 °C/min in a nitrogen flow of 60 mL/min. The thermal transition behaviors of samples were measured by differential scanning calorimetry (DSC) [25]. All the samples were heated up to 190 °C to remove the thermal history, then cooled from 190 to -60 °C and heated up to 190 °C again at the rate of 10 °C/min in TA DSC Q200 (USA) under nitrogen atmosphere to collect DSC data. The Eq. (1) was used to determine the degree of crystallinity (χ_c).

$$\chi_c = \frac{\Delta H_m}{\omega_f \, \Delta H_m^0} \times 100\% \tag{1}$$

Where ΔH_m is the enthalpy of melting crystallization during the second heating; ΔH_m^0 is the enthalpy assuming 100% crystalline PLA homopolymers (93.7 J/g) [26], and ω_f is the weight fraction of PLA component in the composites. The tensile test were measured on an Instron Universal Testing Machine (Model 3366, Instron Engineering Corporation, USA) at a crosshead speed of 5 mm/min at room temperature. The dimension of the dumbbell-shaped tensile bars was 25 × 4 × 2 mm (length × width × thickness). The notched Izod impact test was performed on a Sansi ZBC-50 (Shenzhen, China) impact tester at room temperature with 2 mm depth and 45° angle. A minimum of five specimens were tested for each sample, and the averaged results were reported. Scanning electron microscopy (SEM; Phenom ProX, Netherlands) was used to observe the morphology of the fractured surfaces of specimens with an accelerating voltage of 10 kV.

3. Results and discussion

3.1. Flame retardancy of TPLA/PA-HDAx

PLA is a flammable polymer with a LOI of 19%. In addition, it will drip with flame and burn out during the vertical burning test. After 2.5 wt% PA-HDA is added into TPLA, its LOI raises up to 23%, but it still drips after ignition. Further increasing PA-HDA content to 5 wt% or above, although the specimens will drip in the vertical combustion test, it doesn't ignite the absorbent cotton and is extinguished in 2 s. According to the rules of UL-94, they reach V-0 rating. Besides, the LOI values of TPLA/PA-HDAx gradually increase with the rise of PA-HDA addition (Table 1). These results demonstrate that PA-HDA is an efficient flame retardant for PLA because of its high phosphorus and nitrogen contents. As we know, some phosphorus-containing flame retardants will produce PO· radical to block the combustion [27], and form phosphoric acid or polyphosphoric acid to catalyze char formation isolating the combustible gas [9]. Besides, the droplets take away the heat to prevent the continuous combustion of the samples. Although the

Table 1
Flame retardancy, thermal stability, and crystallinity of PLA, TPLA and TPLA/PA-HDAx.

Samples	$T_{5\%}$ [a] (°C)	T_{max} [b] (°C)	V_{max} [c] (%/°C)	CR[d] (Wt. %)	χ_c (%)	LOI (%)	Dripping	Cotton ignited	$t_1 + t_2$	UL-94
PLA	333.8	367.6	3.35	0	16.2	19	Y	Y	Burning out	NR
TPLA	305.4	350.7	2.22	2.99	35.0	18	Y	Y	Burning out	NR
TPLA/PA-HDA₂.₅	313.4	361.0	1.78	5.17	40.2	23	Y	Y	8 + Burning out	NR
TPLA/PA-HDA₅	305.7	360.5	1.06	6.46	48.6	26	Y	N	3 + 2	V-0
TPLA/PA-HDA₇.₅	304.6	359.6	1.77	6.53	50.0	29	Y	N	2 + 1	V-0
TPLA/PA-HDA₁₀	304.1	357.1	1.76	8.66	52.2	30	Y	N	1 + 1	V-0

[a] $T_{5\%}$ is defined as the temperature at which 5 wt% weight loss occurred.

[b] T_{max} is defined as the temperature at the maximum weight loss rate.

[c] V_{max} is defined as the maximum mass lost rate.

[d] CR is the char residue at 700 °C.