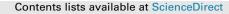
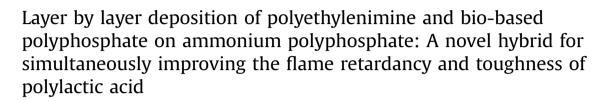
Polymer 108 (2017) 361-371



Polymer

journal homepage: www.elsevier.com/locate/polymer



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ARTICLE INFO

Article history: Received 27 September 2016 Received in revised form 24 November 2016 Accepted 3 December 2016 Available online 5 December 2016

Keywords: Bio-based polyphosphate Synthesis Layer by layer deposition Flame retardant Toughness Polylactic acid

ABSTRACT

In this study, a facile approach to fabricate a novel bio-based hybrid (BBH) with core/shell structure is presented by taking advantage of plant-derived resources. The BBH developed herein comprises of an inorganic core of ammonium polyphosphate (APP), covered with an organic shell that is constructed via layer-by-layer assembly of a novel bio-based polyelectrolyte (BPE) and polyethylenimine (PEI). BBH can simultaneously enhance the flame retardancy and toughness of polylactic acid (PLA) with very high efficiency. The flame retardant PLA composite can pass UL94 V0 rating at the BBH loading content of 10 wt%. The efficient flame retardant performance is due to its effectiveness in both gas and condensed phases. More importantly, the flame retardant PLA composite containing 10 wt% BBH exhibits ductile fracture with an elongation at break of 27.3%, which is much higher than that of neat PLA (8%). The enhanced toughness. This work provides important hints for devising highly efficient multifunctional flame retardant and broadening the application field of renewable resources.

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1. Introduction

As a bio-degradable thermoplastic, polylactic acid (PLA) derived from starches and sugars is stimulating unprecedented scientific and technological interest [1,2]. The past decade has witnessed an extensive expansion of its application in textiles, fibers, transparent packaging materials, electronic instruments and biomedical devices areas due to sustainable development issues [3]. However, PLA, similar to its petroleum-derived counterparts, is highly flammable and must be flame retarded for further applications.

Seeking effective strategies to flame retard PLA is of considerable significance and various methods have been developed in the past decade, such as blending PLA with flame retardant additives (FRs) and chemically modifying PLA with flame retardant element [4–7]. The former approach is more preferred on the basis of cost, and feasibility to massive production, which comprises of PLA blending with nano-inorganic, phosphorus-containing, and intumescent flame retardants. As for nano-inorganic fillers, metal oxides [8], nanoclays [9], and carbon-based nanomaterials [10] have been extensively studied to fabricate the flame retardant PLA composites. And the resulting composites exhibit excellent performance in terms of depressing the peak of heat release rate in cone tests. However, the composites show poor performance in UL-94 test and limiting oxygen index (LOI). With regards to the phosphorus-containing FRs, normally, a high loading level of the additives (i.e., at times >20 wt% of FRs) is required to achieve ideal flame retardant grade for PLA [11]. Recently, some highly efficient flame retardants for PLA have been developed. For example, Wang et al. applied N, N'-Diallyl-P-phenylphosphonicdiamide into PLA and found that only 1 wt% dosage of such additives was enough to lead PLA to pass UL94 V-0 rating [12]. We also synthesized a







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diphenoic acid based polyphosphonate (BPPT). Only 4 wt% incorporation of BPPT made a PLA matrix pass UL94 V-0 rating along with 33.7% of the LOI value [13]. Though highly efficient flame retardant PLA was realized in the above mentioned approaches, the resulting flame retardant PLA composites normally become more brittle than the virgin matrix.

Apart from being highly flammable, PLA is a comparatively brittle and rigid polymer material with low deformation at break and its application in various end-use areas are impeded [14]. Although, some highly efficient flame retardants have been developed, the deterioration on toughness of the resulting PLA composites is inevitable and in most cases the flame retardant additives seriously impair the toughness of PLA matrix. Hence, developing efficient flame retardant additive and simultaneously toughening PLA is of great significance but a tough work.

On the basis of the discussions mentioned above, herein, a novel bio-based polyelectrolyte (BPE) was designed and synthesized in two steps using diphenolic acid (DPA) as raw material, which is a plant-derived compound widely used for synthesis of polyesters [15] and polycarbonates [16,17] etc. The as-synthesized BPE exhibits a good char forming ability and has good compatibility with the PLA matrix. Besides, the BPE contains abundant pendant carboxyl group, which is a polyanion in water. The negatively charged BPE and positively charged polyethylenimine (PEI) were consecutively deposited on ammonium polyphosphate, which is a widely used flame retardant additive on its own or as an acid source in intumescent system [18] through electrostatic interactions via LbL method. The polycation PEI can serve as both the polycation and the blowing agent source in an intumescent system [19,20]. The as tailored organic-inorganic hybrid flame retardant would on one side bring enhanced flame retardant efficiency owing to the tunable formulation of individual component through adjusting the layer numbers and on the other side serve as a shell to improve the compatibility between the flame retardant and the matrix resin. The influence of the BBH on the flame retardancy and mechanical properties of PLA was studied.

2. Experimental

2.1. Materials

Ingeo 3052D polylactic acid (PLA) was obtained from Nature-Works LLC. Diphenolic acid (DPA) was purchased from J&K Scientific Co., Ltd (China). Phenylphosphonic dichloride (PPDC) was purchased from Acros Organics. Formaldehyde aqueous solution (37 wt%), dimethylamine aqueous solution (33 wt%) and 732-type cation-exchange resin (crosslinked styrene and butadiene copolymer with pendant -SO₃H groups) were purchased from Sinopharm Group Chemical Reagent Co., Ltd (China). Prior to use, 5 g 732-type cation exchange resin was treated with 50 mL of 1 M NaOH and 1 M HCl, respectively, equilibrating for 12 h under constant agitation. The resulting 732 hydrogen-form cation exchange resin was washed with deionized water and then packed in a 10 cm length of glass column (5.0 mm i.d.) and furnished with glass wool at both ends to retain the resin inside. Ammonium polyphosphate (APP, P% = 31.0-32.0 wt%, degree of polymerization (DP) > 1000) was purchased from Hangzhou JLS Flame Retardants Chemical Co., Ltd (China). Polyetheylenimine (PEI) ($Mn = 10\ 000\ g/mol$) was purchased from Aladdin-reagent (China). All other materials were A. R. grade and used as received.

2.2. Synthesis of 2,2'-bimethylaminemethylene-4,4'-diphenolic acid (BADA)

The synthesis route of the monomer 2	ner 2,2'-
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bimethylaminemethylene-4,4'-diphenolic acid (BADA) is depicted in Scheme 1 (a). A 250 mL round-bottomed flask with a mechanical stirrer. a N₂ inlet and a reflux condenser device was equipped, into which DPA (14.3 g, 0.05 mol), ethanol (100 mL), aqueous solutions of dimethylamine (20.5 g, 33 wt%) and formaldehyde (16.2 g, 37 wt %) were added. The mixture was stirred at 25 °C under N₂ atmosphere for 24 h. Then the solvent of the resultant was removed by rotary evaporation at reduced pressure. The crude product was dissolved in deionized water (100 mL) and purified by 732 cation exchange resin, followed by the evaporation of the water by rotary evaporation at reduced pressure. The solid was dried in a vacuum furnace at 80 °C for 8 h to obtain white powder (yield: 18.0 g, 90 wt %);¹H NMR (500 MHz DMSO- d_6 , ppm): δ 6.88 (4H, Ar–H), 6.64 (2H, Ar-H), 3.48 (4H, -CH₂-N-), 2.25-2.14 (14H, -CH₃-N, -CH₂-COOH), 1.92 (2H, -CH₂-CH₂-COOH), 1.47 (3H, CH₃-C-). ¹³C NMR (126 MHz DMSO-d₆, ppm): δ 175.2, (154.5, 153.6), (139.3, 138.7), (127.6, 126.6), 126.8, 121.7, 114.6, 60.1, 59.1, 43.8, 36.6, 34.3, 27.3.

2.3. Synthesis of BPE

The BPE was prepared through the polycondensation between BADA and PPDC, as depicted in Scheme 1 (b). To a flame-dried 250 mL round-bottom flask equipped with a nitrogen inlet, reflux condenser device and mechanical stirrer, a mixture of acetonitrile (120 mL), triethylamine (5.1 g) and BADA (20 g, 0.05 mol) was added. The reactants were heated to 40 °C under continuous flow of N₂. Then PPDC (9.75 g, 0.05 mol) in acetonitrile (20 mL) was slowly added into the flask in one batch. The mixture was heated to 80 °C within 10 min and maintained for 5 h. The precipitated solid was collected by filtration and washed with ethyl acetate (200 mL) twice prior to being dried in a vacuum furnace at 60 °C for 8 h to obtain a yellow product (yield: 25.3 g, 85%). ¹H NMR (500 MHz, DMSO-*d*₆, ppm): δ 7.75–6.82 (m, Ar–H), 4.21 (dd, –CH₂–N), 2.67 (d, -CH3-N), 2.37 (m, -CH2-COOH), 2.11 (m, -CH2-CH2-COOH), 1.53 (m, CH₃-C-). ³¹P NMR (202 MHz DMSO- d_6 , ppm): δ 16.13, 13.47. Polymerization degree (5–6).

2.4. Fabrication of BBH

The process for fabricating the bio-based hybrid (BBH) via LbL assembly is presented in Scheme 2. 2.0 g APP powder was dispersed evenly in deionized water to form a suspension (5 wt %) by mechanical stirring. Then, 40 mL of the PEI aqueous solution (pH 9) was added into the APP suspension, and the adsorption process was allowed to proceed for 2 min with constant stirring of the mixture. Then, the particles were isolated by centrifugation. In a washing step, 60 mL of deionized water was added. The particles underwent two centrifuge/wash cycles before the addition of the next layer. For absorption on another layer, 40 mL of the BPE aqueous solution (pH 3) was added, followed by the same washing protocol. The procedure was repeated until two bilayers of PEI/BPE were constructed.

2.5. Preparation of PLA composites

PLA was dried under vacuum at 80 °C for 12 h prior to use, desired amounts of BBH and PLA were blended at 170 °C in ThermoHaake rheomixer (Polylab, Germany) at a rotor speed of 60 r/ min, and the mixing time was set as 8 min for all samples. For comparison, the specimens of neat PLA were prepared by the same procedure. The as-prepared PLA composites were denoted as xPLA/ yBBH, while x and y denotes their weight percentage in the composites. For instance, 85PLA/15BBH means that the sample contains 85 wt% PLA and 15 wt% BBH in the resultant composites. Download English Version:

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