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Effect of N,N′-diallyl-phenylphosphoricdiamide on ease of ignition, thermal decomposition behavior and mechanical properties of poly (lactic acid)

Xiaomin Zhao [a], Sergio de Juan [a], Francisco Reyes Guerrero [a], Zhi Li [a], Javier Llorca [a, b], De-Yi Wang [a, *]

[a] IMDEA Materials Institute, C/Eric Kandel, 2, 28906 Getafe, Madrid, Spain
[b] Department of Materials Science, Polytechnic University of Madrid, 28040, Madrid, Spain

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ABSTRACT

In this study, a novel poly (lactic acid) (PLA) composite with low flammability based on N,N′-diallyl-phenylphosphoricdiamide (PO-AA) and PLA was developed via traditional melt compounding. PO-AA exhibited high efficiency on reducing the ease of ignition of PLA without scarifying the mechanical and thermal properties of PLA. Only 1 wt% of PO-AA containing PLA composite passed V-0 rating with 3.2 mm (thickness of the specimen), while 2 wt% of PO-AA addition made PLA passed V-0 rating with thickness of 1.6 mm. The improvement also performed on increased limiting oxygen index (LOI) of PLA composites. The melting and crystallization behavior of PLA and PLA/PO-AA composites were studied by differential scanning calorimetry (DSC). Meanwhile, thermal stability and thermal decomposition kinetics were studied by means of thermogravimetric analysis (TGA). Furthermore, the evolved gaseous products of PLA and PLA/PO-AA (1 wt%) were characterized by TGA coupled with Fourier transform infrared spectroscopy (TGA–FTIR) test. Finally, the impact of PO-AA on viscoelastic and tensile properties was investigated by dynamic oscillatory shear measurement and tensile test.

1. Introduction

Nowadays, bio-based polymers are great promising as renewable and biodegradable properties on account of eco-friendly and human healthy views [1–4]. As one kind of well-known bio-based polymer, poly (lactic acid) (PLA) is attracted more and more attention in recent twenty years [5–11]. Traditionally, PLA is applied in food packaging fields in industrial. However, new applications have been developed, such as transportation, textile and electronics & electrical appliances [3,12]. In these application fields, flammability of polymer matrix is one of significant concerns in these fields. Therefore, improving flame retardancy of PLA has been a challenge to be solved [8,10,11,13–20].

The methods to reduce the flammability of PLA have been summarized by Serge Bourbigot in 2010 [11]. In recent years, many researchers focused on blending different kinds of nano-inorganic flame retardants and phosphorus based flame retardants or the combination of these two kinds of flame retardants into PLA matrix and trying to improve the flame retardancy [13,21–41]. Grégory Stoclet et al. evaluated the flame retardancy of poly (lactic acid)/halloysite nanocomposites. 17% halloysite decreased the peak heating release rate (pHRR) by 40% [23]. Timothy C. Mauldin et al. incorporated isosorbide-based polyphosphonatesin into PLA matrix and found that UL 94 V-0 rating arrived when the loading increased to 15% [21]. Lei Song et al. reported the synergistic effect between intumescent flame retardant (IFR) (pentaerythritol phosphate and melamine phosphate) and polyhedral oligomeric silsesquioxanes (POSS) on PLA matrix. 25% of IFR only led PLA to V-1 rating while 20% of IFR plus 5% of POSS leaded to V-0 rating [13]. However the improvement on flame retardancy was accompanied by the high loading of flame retardant and scarifying of thermal or mechanical properties in these researches. Researchers are attempting to improve the flame-retardant efficiency. For example, Ping Wei et al. applied expandable graphite intercalated with sulphuric acid (GR) into PLA matrix and found that 5% was enough to lead PLA pass V-0 rating [38]. Qian Yong et al. reported that only

* Corresponding author.
E-mail address: deyi.wang@imdea.org (D.-Y. Wang).

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0.5 wt% incorporation of mesoporous flame retardant (Al-SBA-15) made PLA matrix pass V-0 rating along with 30% of LOI value [27]. N, N′-diallyl-phenylphosphoricdiamide (PO-AA) synthesized in our previous work had been proved to be an useful flame retardant to epoxy resin due to its high char forming performance [29]. In detail, by TGA test 5 wt% addition of PO-AA increased the char residue for epoxy resin from 15.1% to 33.4% at 650 °C in Nitrogen atmosphere. Moreover, such epoxy composite formed bulkily intumescent char residue in the cone colorimeter test.

In this work, poly (lactic acid) (PLA)/PO-AA composite was developed via traditional melt compounding. The impact of PO-AA on ease of ignition, thermal decomposition behavior and mechanical properties of PLA were studied. Impacts of PO-AA on thermal properties, thermal decomposing kinetics and mechanism of PLA were evaluated by DSC, TGA and TGA–FTIR tests. Limiting oxygen index (LOI) and UL 94 tests were employed to study the impact on ignition of PLA. Moreover, the impact of PO-AA on viscoelastic and tensile properties were investigated by dynamic oscillatory shear measurement and tensile test.

2. Experimental section

2.1. Materials

Poly (lactic acid) (PLA, 2003D) was purchased from NatureWorks LLC. This type of PLA has D-isomer content of 4.3%. The molecular weight (Mw) of PLA was 245600 g/mol with polydispersity index of 1.45. N,N′-diallyl-phenylphosphoricdiamide (PO-AA) was synthesized following the steps of previous report [29].

2.1.1. Synthesis of N, N′-diallyl-P-phenylphosphonicdiamide (PO-AA)

The synthesis rout of flame retardant PO-AA was shown in Scheme 1. Allylamine (AA) (0.21 mol) dissolved in diethyl ether (100 ml) together with TEA (0.2 mol) at 0–5 °C in three-neck flask. Then, the solution of phenyl dichlorophosphate (PDClP, 0.1 mol) in diethyl ether (100 ml) was added drop-wise into the flask. The temperature of reaction flask kept for 2 h at 0–5 °C and then the reaction continued at room temperature for 5 h. Finally, the generated triethylamine hydrochloride was filtrated off. The raw product PO-AA was separated from the filter liquor after reduced pressure distillation. The product PO-AA was obtained after washing the raw product by water for three times. PO-AA: m.p. 64.8 (±0.5) °C; white solid; yield, 95%; ^{1}H NMR (DMSO-d_6): δ (ppm), 7.4–7.0 (Ar–H, 5H); 5.9–5.7 (=CH, 2H); 5.2–5.0 (=CH_2, 4H); 3.5–3.4 (–CH_2–, 4H); ^{13}C NMR (DMSO-d_6): δ (ppm), 151.6, 137.4, 129.2, 123.6, 120.5, 114.5, 43.1; ^{31}P NMR (DMSO-d_6): δ (ppm), 16.3.

2.1.2. Preparation of PLA/PO-AA composites

The preparation of PLA/PO-AA composites followed traditional thermal plastic process by means of twin-screw extrusion and injection. Before the processing step, PLA and PO-AA was dried at 70 °C in vacuum oven for 12 h. Then PLA and PO-AA was mixed by co-rotating twin-screw extruder machine (KETSE 20/40 EC, Brabender). The screw speed was 50 rpm and the temperature profile was set as: 160 °C, 165 °C, 165 °C, 170 °C, 165 °C. After the extrusion process, the mixtures were injected to different dimensions of samples for tests referred in this work (Injection Molding Machine, Arburg 320 °C). The temperature profile was: 170 °C (zone 1), 175 °C (zone 2), 180 °C (zone 3), 185 °C (nozzle). Pure PLA samples were obtained by the same procedure. However, the extruding temperature profile was set as 170 °C, 175 °C, 180 °C, 185 °C, 180 °C. After the extrusion process, the mixtures were injected to different dimensions of samples for tests (see the details in 2.2.1 and 2.2.4) referred in this work (Injection Molding Machine, Arburg 320C).

2.2. Characterization

2.2.1. Flammability of PLA and PLA/PO-AA composites

Two typically small scale fire testing methods were used to study the effect of PO-AA on the flammability of PLA. Limiting oxygen index (LOI) was measured with precision of ±0.2% on oxygen index meter (FTT, UK) according to ASTM D2863-00. The size of specimen was 130 × 6.5 × 3 mm^3. Six sample bars were tested for each sample in this work. Vertical burning tests were carried on UL 94 Horizontal/Vertical Flame Chamber (FTT, UK) with two sheet dimensions of 130 × 13 × 3.2 mm^3 and 130 × 13 × 1.6 mm^3 according to ASTM D3801.

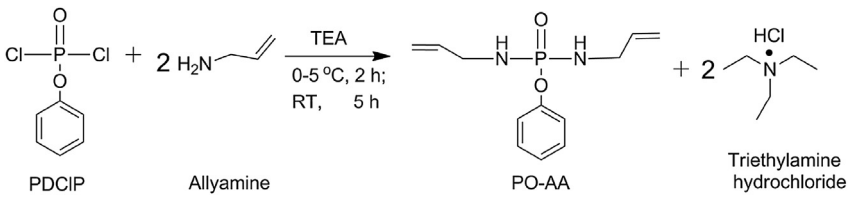
2.2.2. Thermal properties of PLA and PLA/PO-AA composites

In this segment, the investigation of thermal properties focused on two aspects: melting and crystallization behaviors, thermal decomposition behaviors (thermal weight loss, thermal decomposition kinetics and gas phase products).

2.2.2.1. Melting and crystallization behaviors. DSC measurements were employed to characterize the melting and crystallization behaviors. The tests were performed on DSC Q200 instrument (TA Instruments, USA) under nitrogen atmosphere. The sample weight for each composition was 5 (±0.5) mg. For flame retardant PO-AA, the test procedure was: 1st, 10 °C/min from 0 °C to 80 °C; 2nd, 10 °C/min from 80 °C to 0 °C and 3rd, 10 °C/min from 0 °C to 80 °C. For PLA and PLA/PO-AA composites, the test procedure was followed by following method: 1st, 10 °C/min from 20 °C to 200, then 10 °C/min from 200 °C to 0 °C; 2nd, 10 °C/min from 0 °C to 200 °C. Each sample was tested at least two times with the same procedure. However, the final results showed a high experimental reproducibility. Therefore, only one curve was used to do the following calculation. The 1st heating cycle was to eliminate the thermal history during processing. The data collection in this work was from the 2nd heating cycle. The degree of crystallization (χ_c) was calculated as following formulas:

$$\chi = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^{\infty} \cdot x} \cdot 100\%$$

ΔH_m^{∞} represented the melting enthalpy of 100% crystallized PLA and



Scheme 1. The synthesis rout of flame retardant PO-AA.

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