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

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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 polyphosphonates 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

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 Nature Works LLC. This type of PLA has D isomer content of 4.3%. The molecular weight (Mw) of PLA was 245600 g/mol with poly dispersity 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 phenylphosphoricdiamide (PO AA)

The synthesis route 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 (PDCIP, 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%; ¹H NMR (DMSO d₆): δ (ppm), 7.4–7.0 (Ar–H, 5H); 5.9–5.7 (=CH, 2H); 5.2–5.0 (=CH₂, 4H); 3.5–3.4 (–CH₂–, 4H); ¹³C NMR (DMSO d₆): δ (ppm), 151.6, 137.4, 129.2, 123.6, 120.5, 114.5, 43.1; ³¹P NMR (DMSO d₆): 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, Bra bender). 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 mm³. 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 mm³ and 130 × 13 × 1.6 mm³ 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:

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

ΔH_m[∞] represented the melting enthalpy of 100% crystallized PLA and

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

the value is 93 J/g [42]; x represented the weight fraction of PLA.

2.2.2.2. Thermal decomposition behaviors. The thermal weight loss curves obtained from the thermal gravimetric analysis (TGA) which was performed on TGA Q50 instrument (TA Instruments Company). The sample amounts were in range of 8–10 mg and the heating procedure was: 10 °C/min heating from room temperature to 600 °C. Each sample was tested at twice. In order to study thermal degradation kinetics of PLA and PLA/PO AA composites, multiple heating rates (β) (5, 10, 20 30, 40 °C/min) were done for TGA analysis.

The gas phase products were collected and characterized by thermogravimetry coupled with Fourier transform infrared spectroscopy (TGA–FTIR) analysis, which carried out with TGA (TA, Q50), interfaced with Nicolet iS50 FTIR spectrometer. The heating procedure for TGA was: 10 °C/min from room temperature to 600 °C under nitrogen atmosphere. Then the decomposition products went through stainless steel line into the gas cell under nitrogen carrier gas for FTIR detection. The transfer line and the gas cell kept at 300 and 250 °C to prevent gas condensation. FTIR spectra recorded in a range of 4000–500 cm^{-1} with a 4 cm^{-1} resolution and averaging 16 scans. The sampling interval was 15.58 s. Samples masses ranging from 12 mg were used.

2.2.3. Viscoelastic properties of PLA and PLA/PO AA composites

A rotational rheometer (AR2000EX, TA Instrument, and USA) was used to investigate the linear viscoelastic properties of molten PLA and PLA/PO AA composites. The test mold was 25 mm parallel plate geometry. Dynamic oscillatory shear measurements were carried out with a gap about 1000 μm in a frequency range of 0.01–100 Hz at 160 °C under air atmosphere. Before doing dynamic oscillatory shear measurements, 1) isothermal strain sweep test was done from 0.1 to 100% at fixed frequency in order to determine the linear viscoelastic domain. Finally, 2% of strain was selected in the dynamic oscillatory shear measurement; 2) there was no degradation occurred before 200 °C under air atmosphere from the TGA test results of PLA and PLA/PO AA composites under air atmosphere.

2.2.4. Tensile properties of PLA and PLA/PO AA composites

Tensile test was performed on universal electromechanical testing machine (INSTRON 3384, MA, and USA) according to standard ASTM D638 at room temperature. The crosshead speed was set to 3 mm/min. The injected dog bone samples were annealed through heating for 30 min at 70 °C. At least 5 samples were tested for each polymer matrix. And the average values were reported.

3. Results and discussion

3.1. Flammability

In this section, UL 94 and LOI tests were employed to evaluate impacts of PO AA on ignition of PLA matrix under limited fire

conditions. Table 1 listed the LOI indexes and UL 94 ratings of PLA and PLA/PO AA composites.

Under the two small scale fire conditions, PO AA exhibits excellent positive effects. First of all, the oxygen sensitivity of PLA reduced owing to the adding of PO AA. PLA reference had low LOI of 20.5(± 0.2)%. However, LOI of 2 wt% PO AA containing PLA arrived to 26.3(± 0.2)%. Moreover, the addition of PO AA enhanced the extinguished ability of PLA. Only 0.5 wt% loading of PO AA made PLA pass V 2 rating (3.2 mm) in UL 94 test. When the dosage arrived to 1 wt%, V 0 rating was obtained. For the thinner samples (1.6 mm), 2 wt% PO AA was enough to qualify PLA for V 0 rating. As a consequence, PO AA showed high flame retardant efficiency on PLA matrix.

3.2. Thermal properties

3.2.1. Melting and crystallization behaviors

Fig. 1 listed DSC thermograms of PLA and PLA/PO AA composites during 2nd heating cycle. In addition, the heating and cooling cycle of PO AA was also included in Fig. 1. The corresponding data of glass transition temperature (T_g), melting temperature (T_m) and cold crystallization temperature (T_{cc}) were summarized in Table 2. The melting enthalpy (ΔH_m) and cold crystallization enthalpy (ΔH_{cc}) in Table 2 were integrated from the DSC thermograms. The calculated χ_c were also showed in Table 2. Moreover, DSC thermogram of PO AA was also listed in Fig. 1. A remarkable crystallization behavior was showed for PO AA. T_m of PO AA was at 64.8 (± 0.5) °C and crystallization temperature (T_c) was 44.2 (± 0.6) °C. The corresponding ΔH_m and crystallization enthalpy (ΔH_c) of PO AA were 129.1(± 2.1) and 124.6(± 2.3) kJ/kg, respectively. The degree of crystallization of PO AA was followed the formula: $\chi = \frac{\Delta H_c}{\Delta H_m} \cdot 100\%$ in this work. The calculated degree of crystallization was up around to 96.5%.

From DSC thermograms of PLA and PLA/PO AA composites in Fig. 1, the addition of PO AA showed a decrease on T_g of PLA. PLA showed T_g at 57.1(± 0.6) °C, whereas when the loading of PO AA was 1 and 2 wt%, T_g of PLA/PO AA was 55.4(± 0.1) and 54.3(± 0.2) °C, respectively. Furthermore, both PLA and PLA/PO AA composites underwent cold crystallization as heating up. The peaks of cold crystallization of PLA shifted to low temperature after the addition of PO AA. From Table 2, the cold crystallization temperature (T_{cc}) decreased from 107.7(± 1.4) °C to 103.3(± 0.6) °C after

Fig. 1. DSC thermograms from second heating cycle of PLA and PLA/PO-AA composites.

Table 1
The results of LOI and UL 94 tests for PLA and PLA/PO-AA composites.

Sample	LOI (%)	UL 94	
		(3.2 mm)	(1.6 mm)
PLA	20.5 $\pm$ 0.2	NR	NR
PLA/PO-AA (0.5 wt%)	21.8 $\pm$ 0.2	V-2	NR
PLA/PO-AA (1 wt%)	24.5 $\pm$ 0.2	V-0	V-2
PLA/PO-AA (2 wt%)	26.3 $\pm$ 0.2	V-0	V-0

NR: no rating.

Table 2

Melting and crystallization data of PLA and PLA/PO-AA composites from DSC thermograms.

Samples	T _g (°C)	T _m (°C)		T _{cc} (°C)	ΔH _m (kJ/kg)	ΔH _{cc} (kJ/kg)	χ _c (%)
		1st	2nd				
PLA	57.1 ± 0.6	146.3 ± 2.0	153.3 ± 2.0	107.7 ± 1.4	26.9 ± 1.9	26.8 ± 2.1	0.1
PLA/PO-AA (0.5 wt%)	57.0 ± 0.8	146.2 ± 1.1	153.4 ± 0.7	105.4 ± 0.8	31.0 ± 2.2	26.7 ± 2.1	4.6
PLA/PO-AA (1 wt%)	55.4 ± 0.1	146.0 ± 0.5	153.3 ± 0.6	104.4 ± 0.5	29.0 ± 2.0	22.5 ± 2.6	7.0
PLA/PO-AA (2 wt%)	54.3 ± 0.2	145.9 ± 1.9	152.9 ± 1.8	103.3 ± 0.6	34.8 ± 2.0	27.3 ± 3.0	8.2

2 wt% of PO AA was added into PLA.

The melting curves of PLA and PLA/PO AA composites showed two melting peaks which was collected as two melting temperatures (T_m) in Table 2. 1st and 2nd T_ms were 146.3(±2.0) and 153.3(±2.0) °C, respectively. Two melting peaks were considered to be caused by two different types of crystals. From Table 2, the addition of PO AA did not change the two T_ms of PLA. However, the ratio between 1st and 2nd melting peak intensities of PLA and PLA/PO AA composites showed a clear change. From Fig. 1, 1st melting peak had almost same intensity with 2nd melting peak; whereas the 2nd melting peaks of PLA/PO AA composites were higher than 1st melting peaks obviously. χ_c of PLA calculated from ΔH_m and ΔH_{cc} increased along with the rising loading of PO AA. PLA showed 0.1% χ_c, which indicated that PLA almost had no crystallization during the cooling procedure. However, PLA/PO AA (2 wt%) showed 8.2% of χ_c.

The impacts of PO AA on crystallization behavior were considered to be caused by the combination effect of nucleation and plasticization [43] of PO AA on PLA. On one hand, the addition of organic phosphorus structure PO AA increased PLA chain mobility. Therefore, T_g of PLA/PO AA composites were decreased to low temperature. Moreover, the enhancement on chain mobility facilitated the formation of crystallization. Since that the cold crystallization of PLA/PO AA composites occurred at lower temperature than that of PLA. On the other hand, PO AA was able to be one kind of nuclear site for PLA due to its crystallization when the temperature of PLA/PO AA was cooling down. Furthermore, this effect occurred above T_g of PLA and below T_m of PO AA. This effect was considered to be the main reason for the reduced ratio of 1st melting peak intensity and the increase of χ_c of PLA/PO AA in comparison with PLA.

3.2.2. Thermal decomposition behaviors

Fig. 2 showed the thermal weight loss curves of PLA, PO AA and PLA/PO AA composites under nitrogen atmosphere (N₂) from TGA analysis. Fig. 2 showed TGA (A) and DTG (B) curves of PLA, PO AA and PLA/PO AA composites. The onset decomposing temperature

(Td_{5%}), the maximum decomposing rate temperature (T_{max}) and residue at 550 °C were collected from these curves in Table 3.

In Fig. 2, PLA reference underwent one stage decomposition under N₂. Since from 340.0(±1.4) °C, the decomposition started and went to the highest decomposing rate around 380.2(±0.9) °C. The small loadings of PO AA didn't influence the thermal decomposition properties of PLA in a remarkable way. However, some changes occurred during thermal decomposition. On one hand, Td_{5%} of PO AA was 176.3(±1.3) °C, indicated that PO AA decomposed at lower temperature than that of PLA reference. Therefore, the introduction of PO AA induced the decrease of Td_{5%} and T_{max} of PLA/PO AA composites in comparison with Td_{5%} and T_{max} of PLA, as shown in Table 3. This behavior induced the decreased Td_{5%} and T_{max} of PLA/PO AA composites which was showed in Table 3 in comparison with PLA. On the other hand, the charring ability of PLA reference was very low (0.7(±0.1)% at 550 °C). Based on the results in Table 3, it showed the char residues showed very slight increase after PO AA was added into PLA with small loadings at 550 °C.

3.2.2.1. Thermal decomposition kinetics. In this segment, the thermal decomposition kinetics of PLA and PLA/PO AA composites was studied by means of Coats Redfern (modified) method [44,45]. The fundamental equation to analyze the thermal decomposition kinetics was described as:

$$\frac{d\alpha}{dt} = A e^{\left(-\frac{E}{RT}\right)} f(\alpha) \quad (1)$$

Introducing heating rates equation: β = dT/dt into equation (1),

Table 3

TGA data of PLA and its composites.

Sample	Td _{5%} (°C)	T _{max} (°C)	Char residue (550 °C, %)
PLA	340.0 ± 1.4	380.2 ± 0.9	0.7 ± 0.1
PO-AA	176.3 ± 1.3	223.3 ± 1.3	10.5 ± 0.1
PLA/PO-AA (0.5 wt%)	337.5 ± 1.6	374.3 ± 1.5	1.0 ± 0.1
PLA/PO-AA (1 wt%)	337.4 ± 1.2	373.4 ± 2.1	1.3 ± 0.1
PLA/PO-AA (2 wt%)	324.3 ± 2.1	372.1 ± 1.8	1.6 ± 0.1

Fig. 2. (A) TGA and (B) DTG curves of PLA, PO-AA and PLA/PO-AA composites under N₂.

then a new equation was obtained as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(-\frac{E}{RT}\right)} f(\alpha) \quad (2)$$

Equation (2) was one typical expression to analyze thermal decomposition kinetics parameters on basis of a dynamic TGA process.

The modified Coats Redfern method was employed to calculate the apparent activation energy (E_a) of thermal decomposition of PLA and PLA/PO AA composites. The final equation for this iso-conversional method was described as:

$$\ln\left(\frac{\beta}{T^2(1 - \frac{2E}{RT})}\right) = \ln\left(\frac{AR}{E \ln(1 - \alpha)}\right) - \frac{E}{RT} \quad (3)$$

In this method, the slope of the fitted curve which plotted by $\ln(\beta/T^2)$ against $1/T$ was $-E_a/R$. Through this relationship, the E_a values were calculated using slopes obtained from each plot for every degree of conversion (α) [44,45].

The fitted curves of $\ln(\beta/T^2)$ against $1/T$ for PLA and PLA/PO AA (1 wt%) were shown at each α in Fig. 3. The coefficients of determination (r^2) of the fitted curves and E_a calculated from these curves were collected with each α in Table 4. E_a and r^2 of PLA/PO AA (0.5 wt%) and PLA/PO AA (2 wt%) were also showed in Table 4. As a whole, E_a of PLA did not show remarkable change after the addition of PO AA no matter at low or high α . For example, E_a of PLA was 202 kJ/mol and E_a of PLA/PO AA composites ranged from 200 to 203 kJ/mol, showing very close values after the addition of PO AA when α was 0.2. The calculated E_a of PLA/PO AA (0.5, 1 or 2 wt%) showed a decreasing trend along with the increasing of α , which indicated that the thermal decomposing rate was getting higher along with the increasing of α . This result was in the similar way with that of PLA. Moreover, when $\alpha > 0.4$, E_a of PLA showed a slight decrease after the addition of PO AA: PLA $\geq$ PLA/PO AA (0.5 wt%) $>$ PLA/PO AA (1 wt%) $>$ PLA/PO AA (2 wt%).

3.2.2.2. The evolved gaseous products from TGA FTIR analysis. TGA FTIR coupling technique was applied to characterize the evolved gaseous products from TGA of PLA and PLA/PO AA (1 wt%). FTIR spectra of PLA and PLA/PO AA (1 wt%) at the temperature of maximum decomposition rate were showed in Fig. 4 (A). The addition of PO AA did not bring new peaks in FTIR spectra of PLA. The peaks on spectra of PLA in Fig. 4 (A) were assigned to the main evolved gaseous products during thermal decomposition. They were carbonyl compounds (lactide or cyclic oligomers, 1760 cm^{-1}), hydrocarbons (2980 cm^{-1}), CO (2190 cm^{-1}), CO₂ (2360 cm^{-1}) and

Table 4

Calculated E_a and r^2 of thermal decomposition of PLA and PLA/PO-AA composites at different α

α	PLA		PLA/PO-AA (0.5 wt%)		PLA/PO-AA (1 wt%)		PLA/PO-AA (2 wt%)	
	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2
0.2	202	0.9937	200	0.9951	200	0.9962	203	0.9979
0.3	198	0.9929	196	0.9954	196	0.9947	196	0.9970
0.4	195	0.9931	194	0.9957	193	0.9943	190	0.9962
0.5	191	0.9937	192	0.9960	190	0.9945	185	0.9955
0.6	188	0.9944	188	0.9964	187	0.9949	182	0.9948
0.7	187	0.9947	186	0.9968	184	0.9952	180	0.9942
0.8	184	0.9952	183	0.9971	181	0.9954	179	0.9937
0.9	181	0.9954	180	0.9969	179	0.9952	176	0.9933

water (3575 cm^{-1}) [46,47]. Fig. 4 (B–E) listed the absorbance intensity curves of carbonyl compounds (B), hydrocarbons (C), carbon monoxide (CO, D) and carbon dioxide (CO₂, E) vs temperature from TGA FTIR test.

From Fig. 4 (A), the peaks of PLA/PO AA (1 wt%) appeared at the same position as compared with PLA, indicated that the addition of PO AA did not change the main products from thermal decomposition of PLA. However, the absorbance intensity curves in Fig. 4 (B–E) showed significant difference on the release of evolved gaseous products during thermal decomposition of PLA after the addition of PO AA. First of all, the absorbance of carbonyl compounds reduced dramatically in Fig. 4 (B) when 1 wt% of PO AA was added into PLA. Meanwhile, the absorbance of hydrocarbons and CO₂ was also reduced in Fig. 4 (D and E). In contrast, CO did not show remarkable reduction on the absorbance between two samples in Fig. 4 (C). The absorbance intensity was related with concentration of corresponding chemical compounds. The reductions of absorbance in Fig. 4 (B, D, and E) indicated that the addition of PO AA depressed the release of carbonyl compounds, hydrocarbons and CO₂.

3.2.3. Thermal decomposition mechanism

Thermal decomposition of PLA which was reported by many groups predominantly [47,48] consists of random main chain scission and unzipping depolymerization reactions. The random decomposition reaction involves hydrolysis, oxidative degradation, cis elimination, and intramolecular and intermolecular transesterification [48]. In this work, random (inter and intra molecular) transesterification and cis elimination, described in Fig. 5, were assumed to be the main elementary reactions in the thermal decomposition of PLA at high temperature under nitrogen condition. R1 represented the (intra and inter) transesterification

Fig. 3. The plot curves of $\ln(\beta/T^2)$ against $1/T$ of PLA and PLA/PO-AA (1 wt%) at different α .

Fig. 4. (A) FTIR spectra of PLA and PLA/PO-AA (1 wt%) at T_{max2} ; absorbance vs temperature curves of Carbonyl compounds (B), CO (C), Hydrocarbons (D) and CO_2 (E).

reactions which produced lactide or cyclic oligomers. R2 represented the transesterification reactions which produced gaseous compounds with low boiling temperature, such as carbon dioxide (e), acetaldehyde (b) and carbon monoxide (a). R3 represented the cis elimination reaction which produced carboxylic acid compounds (f).

Based on the results of thermal decomposition kinetics shown in 3.2.2, the addition of PO AA did not change the main thermal decomposition path of PLA. However, it might impact the elementary reactions [47,48]. On one hand, phosphorus containing acids formed during the thermal decomposition of PO AA positively catalyzed most random transesterification (R1 and some R2 reactions) in PLA matrix. Under such catalyzed reactions, at the earlier thermal decomposition behavior, PLA/PO AA produced more oligomers than that of PLA. On the other hand, phosphorus containing acids showed negative effect on cis elimination reaction (R3) in PLA matrix. Some transesterification reactions which produced carboxylic acid compounds (c) also suffered negative effect. As a result, the depression of cis elimination and some transesterification reactions reduced the production of c, d and f during the early thermal decomposition. This inference was favor of the reduction of absorbance of carbonyl compounds showed in Fig. 4

(B). Moreover, the absorbance of CO_2 and hydrocarbons which were from further decomposition of carbonyl compounds was also showed reduction in Fig. 4 (D and E). The unchanged absorbance of CO meant that the acid compounds did not change greatly R2 transesterification reaction showed in Fig. 5. Overall, the impact of PO AA on thermal decomposition of PLA was drawn in Fig. 6.

In addition, the above inferences showed that the addition of PO AA depressed the production of flammable gaseous compounds during the thermal decomposition of PLA. Meanwhile, the oligomers with low molecular weight produced by catalyzed R1 reactions would be mainly generated at early ignition. Both of these reasons allowed PLA/PO AA composites showed low flammability under the small fire ignition condition, such as LOI and UL 94 tests.

3.3. Viscoelastic properties

Dynamic oscillatory shear measurement is an effective method to study the viscoelastic properties of polymeric materials, which reflects the relationship between structure and property for polymeric materials. Fig. 7 listed the storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) vs angular frequency curves of PLA, PLA/PO AA (1 wt%) and PLA/PO AA (2 wt%) systems. G' vs G'' curve

Random transesterification

Fig. 5. The main thermal decompose path of PLA.

Fig. 6. The impact of PO-AA on thermal decomposition of PLA.

in Fig. 7 described the viscoelastic properties of all systems in intuitive way. In this work, isothermal TGA test for PLA and PLA/PO AA composites was done at 160 °C within 5 min. The results indicated that PLA and PLA/PO AA composites were thermal stable during the dynamic oscillatory shear test.

In Fig. 7 (A and B), storage and loss modulus decreased due to the addition of PO AA. The lessened trend diminished at high frequency. From η^* curves, PLA and PLA/PO AA composites exhibited shear thinning behaviors under 160 °C. And the η^* showed the lessened trend as that of G' and G'' . From Fig. 7 (D), the relationship of G' and G'' was $G' < G''$, which indicated that PO AA did not change the viscoelastic property of PLA matrix. The viscosity was the main property under 160 °C. The plasticization of PO AA enhanced the PLA molecular chain movement under melt status, meant that the viscosity and modulus would lower down. This impact was also able to induce the decrease of η^* at low frequency.

Another reason for the decrease of η^* was that the addition of PO AA showed impact on decreasing molecular weight (Mw) of PLA by accumulating degrading of molecular chain during melting process. In this work, Mw of PLA and PLA/PO AA composites were detected after processing by means of gel permeation chromatography (GPC). The result showed that Mw of PLA samples was around 140,000 Da (PI was 1.44), whereas Mw of PLA/PO AA composites was around 130,000 Da (PI was 1.57). It seemed that PO AA did not show great influence on decreasing Mw of PLA during melting process.

3.4. Tensile properties

The samples for the tensile properties were heated at 70 °C to eliminating the heat history. The tensile strength and Young's modulus were collected in Fig. 8 (A and B). Tensile strength of PLA reference was 66 MPa. Tensile strengths of PLA/PO AA (1 wt%) and PLA/PO AA (2 wt%) were 66 and 64 MPa, respectively. The variations of tensile strength of PLA/PO AA (1 and 2 wt%) were 1% and 3% in comparison with PLA, respectively. Meanwhile, Young's modulus increased from 2128 to 2264 MPa after 2 wt% of PO AA was added in to PLA. The variation was 6% in comparison with PLA, which indicated that the addition of PO AA slightly increased Young's modulus of PLA.

As a whole, tensile strength and Young's modulus of PLA did not show significant change after the addition of PO AA. In order to explain this phenomenon, both effects of the crystalline and plasticization caused by the PO AA on the tensile properties of PLA were considered in this study. First of all, χ_c of tested samples were detected by means of DSC after heat treatment in this work. χ_c of PLA was 5.5%, while PLA/PO AA (1 and 2 wt%) showed χ_c as 8.3% and 8.4% respectively. Usually, the high χ_c was positive for the improvement of the tensile properties of PLA. On the contrary, plasticization effect caused by the addition of PO AA would induce to decrease the tensile properties of PLA. Thus, these two effects on PLA were considered to be counterbalanced, resulting that the tensile properties were not changed in remarkable way.

Fig. 7. Rheology curves of PLA and PLA/PO-AA composites: (A) G' vs angular frequency; (B) G'' vs angular frequency; (C) $\ln(\eta^*)$ vs angular frequency; (D) G' vs G'' .

Fig. 8. Tensile strength (A) and Young's modulus (B) of PLA and PLA/PO-AA composites after heated.

4. Conclusion

In this work, a novel poly (lactic acid) (PLA) composite with low flammability based on N,N' diallyl phenylphosphoricdiamide (PO AA) and PLA had been developed via traditional melt compounding. It found that only 1 wt% of PO AA containing PLA composites passed V 0 rating with 3.2 mm (thickness of the specimen), while 2 wt% of PO AA made PLA pass V 0 rating with thickness of 1.6 mm. LOI value of PLA composites were increased by the incorporation of PO AA. Tg of PLA/PO AA composites decreased from 57 °C to 54 °C compared with that of PLA. Meanwhile, the cold crystallization of PLA/PO AA composites occurred at lower temperature than that of PLA. Moreover, the addition of PO AA did not reduce the thermal stability of PLA and apparent activation energy (E_a) based on the study of thermal decomposition kinetics. However, the addition of

PO AA depressed the production of flammable gaseous compounds during thermal decomposition of PLA, but increased the amount of oligomers with low molecular weight by catalyzed R1 reactions. It allowed PLA/PO AA composites showed low flammability under the small fire ignition condition, such as LOI and UL 94 tests. In addition, the addition of PO AA did not show significant impact on the tensile strength and Young's modulus of PLA.

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