FULL PAPER-SYNTHESIS AND CHARACTERIZATION OF FLAME RETARDENT THERMOSET POLT (LACTIC ACID) (PLA)

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ABSTRACT

As the raw material of poly (lactic acid) (PLA), lactic acid can be produced from renewable resources. Therefore, PLA has a wide development and applications. Compared to thermoplastic PLA, the thermoset one has a polymer net structure and better properties such as high strength, high modulus and good thermal stability. However, as the common shortcomings in all polymer materials, PLA is flammable, which limits its applications and development in many fields. The study aims to synthesize thermoset PLA with grafted 9,10-dihydro-9-oxa -phosphaphenanthrene-10-oxide (DOPO) onto PLA chains to realize its intrinsic flame retardancy, since PLA blended with flame retardant could deteriorate the performance of PLA. The optimal synthesis process was concluded, and the flame retardancy of the resin was investigated.

1 INTRODUCTION

With the continuous development of composite material design and manufacture technology, the dosage of the composite material in civil aircraft is also growing. According to a rough estimate that by 2025 there will be more than 8500 civilian aircrafts retiring in the world. The amount of aircraft will be scrapped, and abandoned composites using in aircrafts will also be a severe test to the environment. The methods to deal with traditional abandoned composites using in aircrafts are incineration and landfill, however these methods are harm to the environment.

For traditional resin matrix, unsaturated polyester and epoxy resin are usually used in business as thermosetting resin. These resin mostly come from the petroleum resources, as a result, they will lead to environmental pollution and resources shortage problem. The raw materials of bio-based thermoset resin are vegetable oil, such as soybean oil, flax seed oil and rapeseed oil[1]. They are renewable, abundant and relatively cheap. Therefore the development of future bio-based resin is good for reducing application of fossil resources, reducing costs and protecting the environment.

In terms of bio-based resin, polylactide or poly (lactic acid) (PLA) as a completely biodegradable and bio-based polymer, has special performance: recycle, biocompatibility, biodegradability[2]. At present, industrial PLA is thermoplastic polymer; however it has low heat resistance ability, and the mechanical properties which can't meet the high requirements in some fields. Compared with thermoplastic polymer material, thermosetting resin can form a mesh structure after curing due to intermolecular crosslinking, so their stiffness, hardness, heat resistance and dimension stability are relatively high[3]. Moreover, as the common shortcomings in all polymer materials, PLA is easy to

burn, which limits its applications and development in many fields. The study aims to synthesize thermoset PLA with grafted 9,10-dihydro-9-oxa -phosphaphenanthrene-10-oxide (DOPO) onto PLA chains to realize its intrinsic flame retardancy, since PLA blended with flame retardant could deteriorate the performance of PLA. The optimal synthesis process was concluded, and the flame retardancy of the resin was investigated.

2 EXPRIENMENTAL

2.1 Materials

The materials used were obtained from commercial supplier. L-lactic acid (85% $C_3H_8O_3$), pentaerythritol (98% $C_5H_{12}O_4$ PENTE), tin octoate ($C_{16}H_{30}O_4Sn$), methacrylic anhydride (94% $C_8H_{10}O_3$), hydroquinone ($C_6H_6O_2$), tert-Butyl peroxybenzoate ($C_{11}H_{14}O_3$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). DOPO, commercial grade, from the Huizhou Sunstar Technology Co. Ltd., China.

2.2 synthesis of flame retardant thermoset PLA

The synthesis of flame retardant thermoset PLA is divided into 4 steps:

(1) Synthesis of DOPO-itaconic acid (IA) (DI).

DOPO was dried to remove water at 100°C for 2 h before use, sine a certain amount of hydrated DOPO was usually found in the reagent. 21.6 g of dried DOPO was added in 69 g toluene in a 500 mL three-necked flask equipped with condenser. The flask was heated to 120°C and stirred with a mechanical stirrer. After the complete dissolution of DOPO, 13 g IA was added. Finally, the produced DI was dried under vacuum at 90°C for 5 h.

(2)Dehydration of lactic acid (LA).

90 g L-lactic acid was added into a 500 ml four-necked flask. The flask was immersed in an oil bath with a set temperature of 90℃ and stirring. Keep vacuum environment to remove the water in the lactic acid for 2 h.

(3) Condensation reaction of flame retardant star-shaped PLA (4sPLA)

Dehydrated LA was heated to 120℃. 22 g DI and 9 g PENTA were added into dehydrated LA, and tin octoate was added slowly into the flask. Then the mixture was heated to 140 ℃ with a set stirring rate of 140 rpm. The nitrogen flow was directed into the reactor, and the set temperature was increased at a rate of 20 ℃ /h during 2 h to 180 ℃ , where the temperature was kept until finalizing the polymerization. The total polymerization time was 3 h.

(4)End-functionalization of the flame retardant 4s PLA

The 4sPLA was further functionalized with MAAH to yield methacrylated 4sPLA (M4sPLA). After condensation reaction described above, the oligomer was cooled to 110 ℃ and 0.2 wt% hydroquinone was added as a stabilizer. Then MAAH (triple molar weight of PENTE) was added dropwise into the reaction mixture. The reaction was carried out at 120 ℃ for 3 h under nitrogen atmosphere with mechanical stirring, and the resulting product was purified by distillation under reduced pressure at 140 ℃.

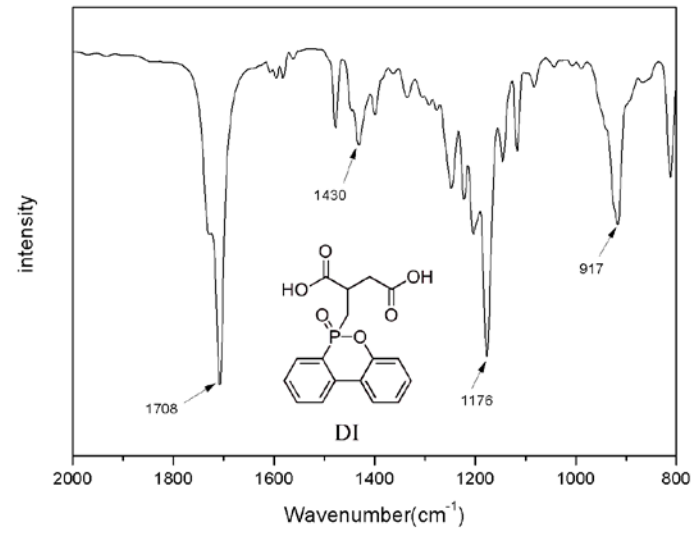
2.3 Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were measured with a NEXUS 470 spectrometer (Thermofisher, USA) using KBr pellets at a range of 400–4000 cm^{-1}. Limiting oxygen index (LOI) values were measured using an LOI instrument (HC-3 Analytical Instrument Factory, China) according to the standard GB2406-82 (China). The specimen dimension was 100×6.5×3 mm^3. DSC measurements were conducted using a DSC-Q100 thermal analysis system (TA Instruments) with a constant nitrogen flow of 50 ml min^{-1}.In order to characterize the curing behavior of the synthesized resin, a total amount of 1.0 wt% of TBPB was well blended into M4sPLA with acetone as solvent at room temperature to avoid premature curing reaction. A small part (10–15 mg) of the sample was transferred into a hermetic aluminium DSC pan. Dynamic curing at 0–220 ℃ was

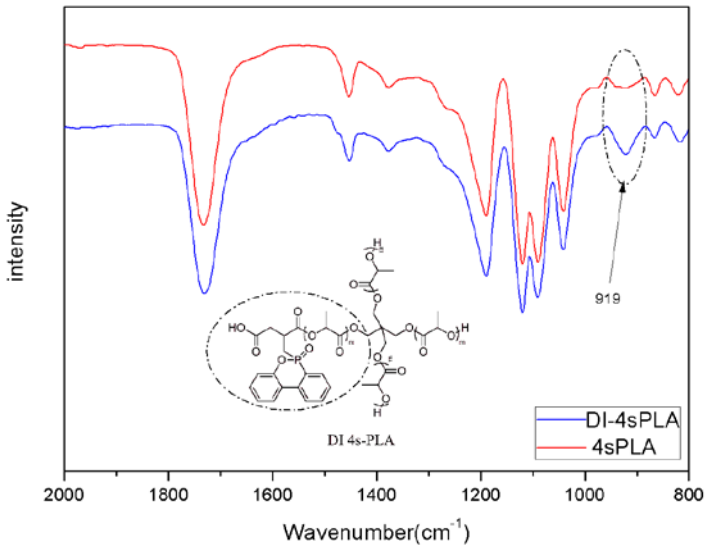
conducted at a heating rate of 10 ℃/min to determine the total reaction heat. T_g of the cured sample was determined in the second heating run during the dynamic measurement. The synthesized resins were analyzed by H-NMR. Samples were dissolved in $CDCl_3$ and analyzed on a Bruke DMX-500 NMR spectrometer.

3 RESULTS AND DISCUSSION

3.1 FTIR analysis



(a)



(b)

Figure.1. FTIR spectra of DI (a) and 4sPLA and DI-4sPLA (b).

Fig.1 shows the FTIR spectra of DI, 4sPLA and DI-4sPLA. From the spectrum of DI (Fig.1a), the absorption bands of DI at 1708 cm^{-1}, 1430 cm^{-1}, 1176 cm^{-1} and 919 cm^{-1} are ascribed to C=O, P-C, P=O and P-O-C respectively. After the condensation reaction of LA with PENTA and DI, DI-4sPLA can be found the absorption band at 919 cm^{-1} attributed to P-O-C compared with 4sPLA, which can reflect that DI have reacted with 4sPLA.

3.1 HNMR analysis

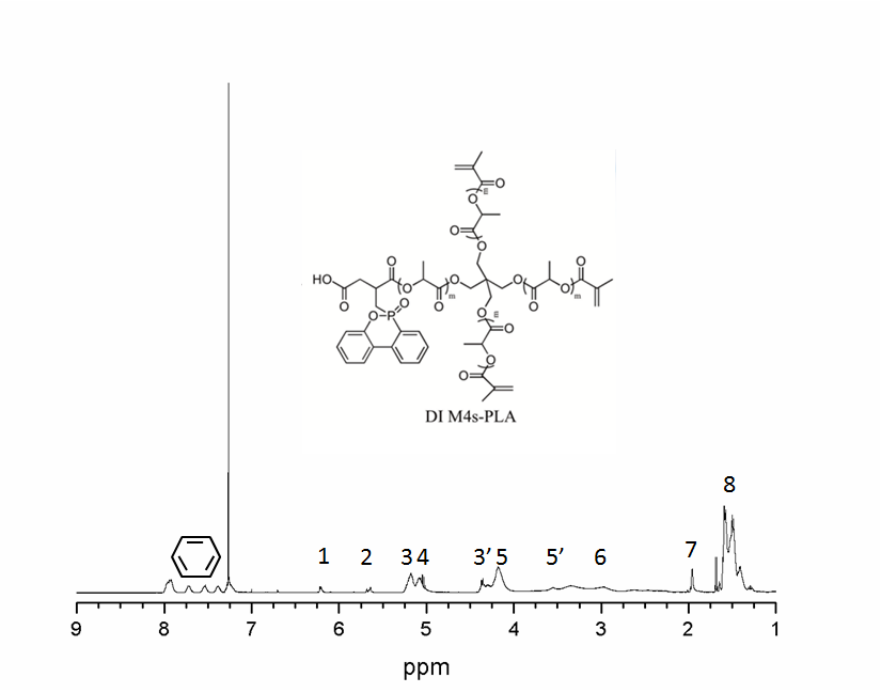


Figure.2. H-NMR spectra of DI M4sPLA

Fig.2 shows the H-NMR spectrum of DI-M4sPLA. At 7-8 ppm, it is the signal of benzene ring from DI. Number 1 and 2 at 6.2 and 5.6 ppm reflect MAA from MAAH. 4sPLA gives 6 signals, and they are at 5.2 ppm, 5 ppm, 4.7 ppm, 4.2 ppm, 3.5 ppm, 1.6 ppm and 1.5 ppm, respectively. Signal at 1.9 ppm is from CH_3 of methacrylate. Combined with FTIR spectra of DI-4sPLA, it can be further confirmed that DI M4sPLA had been synthesized successfully.

3.2 LOI measurement

Samples	**LOI(%)**
Thermoset PLA	19.8
Thermoset PLA-DI	23

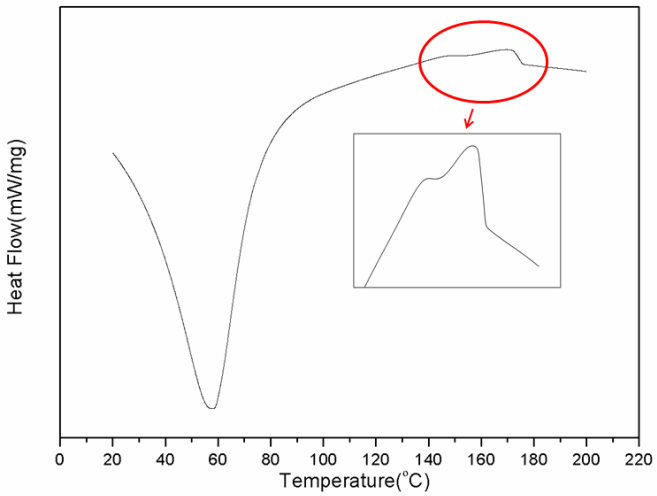
Table1 Results of LOI measurement

(a) (b)

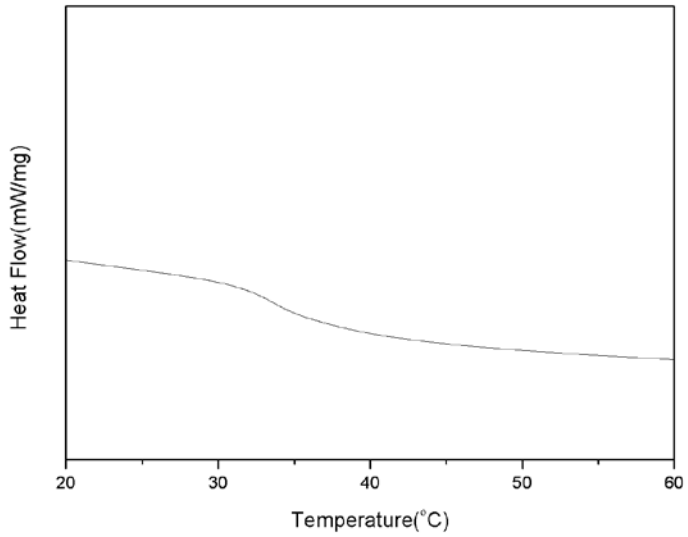
Figure.3. combustion conditions of cured M4sPLA without (a) and with (b) DI

The flammability of the PLA and PLA-DI resin were assessed using LOI measurement. The results are shown in Table 1. As is well known, PLA resins are highly flammable, and the LOI value of PLA resin is 19.8%. Enhanced flame retardancy appeared with DI loading. The LOI values increase to 23%. The results indicated that the flame retardancy of PLA resin was increased significantly with the addition of DI.

3.3 Curing behavior of M4sPLA



(a)



(b)

Figure.4. Dynamic scans of DI M4sPLA (a) First heating run (b) Second heating run

The curing reaction is shown in Fig.4. In the process of the first heating run, a strong endothermic peak and a weak exothermic peak can be observed. The endothermic peak is due to volatilizing of acetone while the exothermic peak is result from the curing reaction of M4sPLA.The exothermic peak id around 150 ℃. After the first heating run, the glass transition temperature (T_g) at around 34 ℃ is shown in Fig.3(b), which is an important parameter for polymer.

4 CONCLUSIONS

The flame retardant thermoset poly(lactic acid) (PLA) has been synthesized successfully and the flame retardant DOPO has been grafted on thermoset chain of poly (lactic acid) (PLA). The products have been confirmed by FTIR and HNMR. According to the result of LOI testing, the thermoset PLA with DI has better flame retardancy than that without DI.

ACKNOWLEDEMENTS

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