Polymer Degradation and Stability 98 (2013) 1389–1396

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

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

Effect of a phosphorus-containing oligomer on flame-retardant, rheological and mechanical properties of poly (lactic acid)

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ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form
6 March 2013
Accepted 25 March 2013
Available online 17 April 2013

Keywords:
Poly (lactic acid)
Phosphorus
Flame retardant
Rheological property
Mechanical property

ABSTRACT

A new flame retardant poly (1, 2-propanediol 2-carboxyethyl phenyl phosphinate) (PCPP) was synthesized with 2-carboxyethyl phenylphosphinic acid (CEPPA) and 1, 2-propanediol (PD). The structure of PCPP has been studied by FTIR and ^{13}C NMR spectra. A series of poly (lactic acid) (PLA) blends were prepared by direct melt compounding with PCPP as flame retardant and plasticizer. And it was proved to be an effective flame retardant for the PLA as evidenced by increasing limiting oxygen index (LOI) value, which increasing from 19.7 for pristine PLA to 28.2 for the PLA with 10 wt% PCPP. Additionally, the introduction of PCPP also amended the rheological and mechanical properties of the PLA. When the content of PCPP in the composites was up to 15 wt%, the flame retardant and the mechanical properties were improved simultaneously.

1. Introduction

Poly (lactic acid) (PLA) as a biodegradable polymer has received considerable attention for its abundant renewable source, biodegradability, excellent mechanical and thermal properties [1–3]. At present, PLA has been utilized in many applications including medical applications, packaging materials and product of fibers. Moreover, PLA is expected for technical applications (electronic and electrical devices, mechanical and automotive parts, etc) as composites [4–9]. However, the highly flammability of PLA restricted its further application. Thus, the modification for flame retardant property of PLA is still an important and urgent task.

Up to now, many investigations have been done to improve the flame retardant property of PLA. And most of them are focusing on the efficiency of intumescent flame retardant formulations which contains acid source mainly consisting of acids, ammonium salts and phosphates; carbonization agents being commonly hydroxyl-containing compounds such as pentaerythritol (PER), lignin and starch; blowing agents containing various compounds which can produce gases during heating [10–12]. Reti et al. optimized a good flame retardant system with 60 wt% of PLA, 12 wt% of ammonium polyphosphate and 28 wt% of starch to reach an LOI value of 32 [13]. Chen et al. synthesized hyperbranched polyamine charring agent as an effective char-forming agent for PLA and the LOI value of 36.5 was obtained [14]. As well, some other additive-type flame retardants were used to improve the flame retardant of PLA such as phosphorus-containing, silicon-containing, and inorganic additives [15–19]. Among those additive flame retardants, the phosphorus-containing flame retardants have been attested to have good performance in many polymer matrixes [20,21]. However, in the most case, the addition of flame retardants always brings worse mechanical and processing properties of PLA. Thereby, it is urgent to find a way to improve the flame retardant and processing properties of PLA simultaneously. As far as we know, the processing and mechanical properties of PLA may be enhanced by blending it with a plasticizer or with a second compound such as lactide, oligomeric lactic acid and low molecular weight esters like scitrates [22]. At the same time, some reactive fire retardant has already been used to improve the flame retardant property of polymer. For example, 2-carboxyethyl phenylphosphinic acid (CEPPA), which contains carboxylic and phosphoric acid functionalities, has been used as a kind of reactive fire retardant for PET and proved it was effective [23].

Therefore, an attempt was made to amend the flammability and processing properties of PLA simultaneously via introducing polyester which contain phosphorus into PLA matrix. The phosphorus-containing polyester (PCPP, the structure is shown in Scheme 1)

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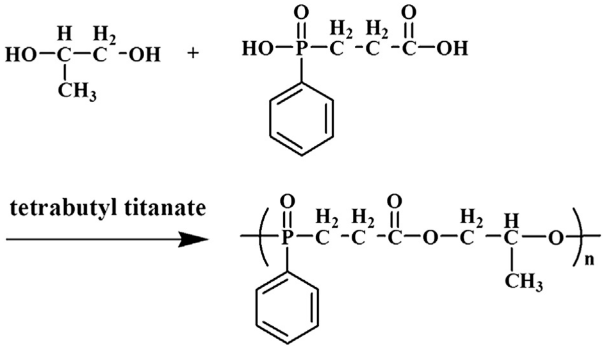
http://dx.doi.org/10.1016/j.polymdegradstab.2013.03.025



Scheme 1. The synthesis of PCPP.

was synthesized with 2-carboxyethyl phenylphosphinic acid (CEPPA) and 1, 2-propanediol (PD). And a series of PLA blends were prepared via direct melt blending and LOI, UL-94, thermal gravimetric analysis and mechanical tests were used to analyze flame retardant and processing properties of the blends.

2. Experimental part

2.1. Materials

Poly (lactic acid) resin (4032D) from Natureworks produced by Cargill Dow LLC with a weight–average molecular weight of 207 KDa and polydispersity of 1.73 (GPC analysis) was used in this study. The CEPPA was supplied by Shandong Flame Retardant Science and Technology Co. (Shandong, China). PD was offered by Changchun Dacheng Industrial Group CO. LTD. (Jilin, China). Tetrabutyl titanate was purchased from Alfa Aesar, A Johnson Matthey Company (Tianjin, China). All of these materials were used as received.

2.2. Synthesis of PCPP

Typically, the PCPP was synthesized in a reaction kettle, equipped with a mechanical stirrer, with a nitrogen inlet valve and a vacuum distillation outlet, which was fitted with a vacuum takeoff. To this reactor, 1070 g CEPPA (5 mol), 433.2 g PD (5.7 mol) and 4.51 g tetrabutyl titanate (as a catalyst) were introduced. In order to remove the moisture and residual air, the reactor was purged with nitrogen alternatively before heating the reactor. Then the reactor was heated to about 160 °C. Now the esterification reaction began. And during this stage, a nitrogen flow was necessary to purge into the reactor in order to remove the vapor, which was the produce of the esterification reaction during all the process. After 3 h, the temperature of the system was increased to 180 °C. And equate the reactor at this temperature for 1 h. Then a vacuum of 0.097 MPa was applied and maintained during the whole polycondensation process of 8 h. A melts with bright, light yellow color could be observed during the final stage of the reaction.

2.3. Preparation of PLA blends

PLA was dried in vacuum oven at 80 °C for 12 h. Then all samples were prepared by using a melt mixer (Rheomix 600p, Haake, Germany) at the temperature 180 °C with the roller speed 60 rpm for 10 min. Different additive contents of PCPP were added into PLA resin range from 5 wt% to 30 wt%. After mixing, all samples were hot-pressed under 5 MPa for 3 min at 190 °C followed by cold-press at room temperature to form the sheets for all tests.

2.4. Measurements

Fourier transform infrared (FTIR) spectra were obtained with a Bruker Vertex 70 FTIR spectrometer at a resolution of 4 cm^{-1}, where the samples were prepared as film on the KBr tablets. ^{13}C NMR spectra were recorded at 400 MH_Z on a Bruker 400 AVANCE spectromer, using d6-sulfoxide (d6-DMSO) as solvent. The Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was used to measure the molecular weight of the polyesters.

The morphology of the samples was observed by Scanning Electron Microscopy (SEM; XL30, Philips) at an accelerating voltage of 12 kv. All the samples were fractured after immersion in liquid nitrogen for about 5 min and etched by ethanol at room temperature for 100 min. All fracture surfaces were coated with gold before observation.

Dynamic mechanical analysis (DMA) was carried out with a DMA/SDTA 861e apparatus (Mettler-Toledo, Switzerland) in a tensile-compression mode. Test specimens were cut from the tensile samples (dimensions $W \times H \times L = 4 \times 1 \times 9$ in mm). The temperature ranged from 0 to 125 °C at a heating rate of 3 °C/min. The strain was set at 10 μm, with a frequency of 1 HZ. Tan δ and storage modulus (E') were noted as a function of temperature.

Thermogravimetric analysis (TGA; Perkin–Elmer TGA-7) was done in the range between room temperature and 700 °C at a heating rate of 10 °C/min in air atmosphere. The LOI test was conducted on a JF-3 Oxygen Index Flammability Gage (Jingning, China) with samples of dimensions 125 mm × 6.5 mm × 3.0 mm according to ISO4589-1984. The UL-94 vertical burning test was performed on the vertical burning test instrument according to the ASTM D3801 testing procedure. The samples were molded to a size of 125 mm × 12.5 mm × 3.0 mm. The actual P-loading of the samples was determined using oxygen flask combustion-inductively coupled plasma atomic emission spectroscopy (ICP-AES) method.

Rheological measurements were performed using a stress-controlled rotational rheometer (TA Series AR2000, TA Instrument, USA) at 180 °C with the parallel plates geometry (plate diameter 25 mm, gap 0.9 mm). Dynamic frequency sweep tests were executed in the frequency range of 0.05–100 rad/s. And the strain was equated at 1.25%. MCR300 software was used to acquire data.

Tensile test was carried out to determine the tensile strength, tensile modulus and strain at break using the Instron1121 testing machine (Canton, MA) at room temperature. The testing was carried out at a rate of 5 mm/min according to ASTMD638 on standard Type I dog-bone shaped samples with sample thickness of around 1.0 mm. At least five specimens were tested for each sample to get an average value.

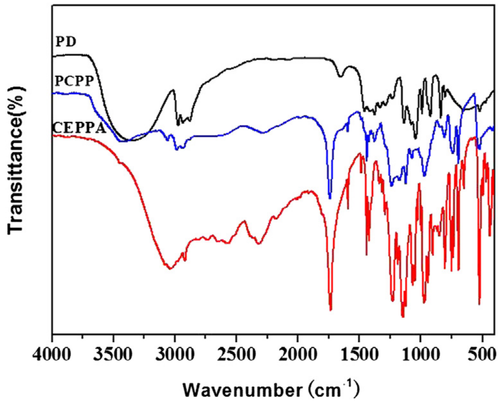


Fig. 1. FTIR spectrum of PD, CEPPA and PCPP.