Journal of Cleaner Production 124 (2016) 114–119

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Phytic acid as a bio-based phosphorus flame retardant for poly(lactic acid) nonwoven fabric

Xian-Wei Cheng, Jin-Ping Guan, Ren-Cheng Tang*, Kai-Qiang Liu

National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, 199 Renai Road, Suzhou, 215123, China

ARTICLE INFO

Article history:
Received 19 September 2015
Received in revised form
12 February 2016
Accepted 23 February 2016
Available online 7 March 2016

Keywords:
Poly(lactic acid)
Phytic acid
Flame retardancy
Flame retardant
Phosphorus

ABSTRACT

Bio-based phytic acid as a nontoxic naturally occurring compound has a promising prospect in the field of the flame retardant modification of polymers because of its high phosphorus content. Bio-based and bio-degradable poly(lactic acid) has aroused considerable interest and its use is growing, but its flame retardancy needs to be improved when it is used as a flame retardant material. In this work, phytic acid was used to improve the flame retardancy of poly(lactic acid) nonwoven fabric by a pad-dry-cure technique, and the effect of phytic acid dosage on the flammability as well as the flame retardant mechanism of the treated fabric was discussed. The limiting oxygen index and vertical burning tests revealed that the treated fabric exhibited good flame retardancy. The microscale combustion calorimetry analysis showed that the treated fabric had significantly decreased heat release rate, total heat release and heat release capacity compared with the untreated fabric. The char residue formation of the treated fabric during thermal degradation, and the high phosphorus content of the burned fabric residue suggested that a significant condensed-phase mechanism contributed to the flame retardancy of the treated fabric. The flame retardant system in the present study is applicable to the poly(lactic acid) fabrics without the durability requirement. The use of phytic acid provides an opportunity for producing the flame retardant poly(lactic acid) materials using a sustainable and cleaner flame retardant agent.

1. Introduction

As one of the biodegradable polymers, poly(lactic acid) (PLA) has attracted more and more attention. PLA is environmentally friendly because it can be wholly derived from renewable sources such as sugar and corn starch (Auras et al., 2004; Hussain et al., 2015). PLA can be used in the production of fibers, extruded films and injection-molded products which have a wide range of applications in commodity plastics, packing materials, biomaterials and textile fibers (Auras et al., 2004; Hussain et al., 2015). But the flammability and dripping combustion of PLA have a great limitation for its application and development in many important fields (Fox et al., 2013; Wang et al., 2011). Parmar et al. tested various flame retardant (FR) properties of PLA woven fabrics, and found that PLA fiber was not suitable for upholstery, apparel, and work wear due to its poor FR properties (Parmar et al., 2014). Up to present, many works have been carried out on the flame retardancy of PLA composites, but few studies have been done on the fire retardancy of PLA fabric. The additive-type flame retardants such as phosphorus-containing additives, silicon-containing additives and inorganic additives have been applied to improve the flame retardancy of PLA composites (Hapuarachchi and Peijs, 2010; Mauldin et al., 2014; Qian et al., 2013; Wang et al., 2011). Recently, the intumescent FR system is regarded as an efficient method to improve the flame retardancy of PLA composites (Bourbigot and Fontaine, 2010). Avinc et al. have employed a cyclic phosphonate ester compound to improve the flame retardancy of PLA knitted fabric (Avinc et al., 2012). In our work, the great capability of a cyclic phosphonate ester for enhancing the flame retardancy of PLA nonwoven fabric has been found (Cheng et al., 2015).

Considering the cons of the existing flame retardants, the USA and EU directives concerning the “chemistry” of flame retardants are becoming increasingly rigid and severe, some of the currently used products will be limited or even banned (Alongi et al., 2013; Ravichandran et al., 2011). There is an immediate need for non-toxic and effective flame retardants produced preferably through sustainable routes or obtained from nature directly (Mauldin et al., 2014).

* Corresponding author. Tel.: +86 512 6716 4993; fax: +86 512 6724 6786.
E-mail address: tangrencheng@suda.edu.cn (R.-C. Tang).

http://dx.doi.org/10.1016/j.jclepro.2016.02.113
0959-6526/

Phytic acid (PA) or inositol hexakisphosphate acid (Fig. 1) is regarded as "green" molecule because it is the major storage form of phosphorus in plant tissues such as beans, cereal grains and oil seeds (Fox and Eberl, 2002; Zhou and Erdman, 1995). As a biocompatible, environmentally friendly, nontoxic and easily obtained organic acid, PA has been widely applied in antioxidant, anticancer agent, biosensor, cation exchange resin, nanomaterial and other fields because of its special inositol hexaphosphate structure (Fox and Eberl, 2002; Wang et al., 2014; Zhou and Erdman, 1995). PA contains 28 wt% phosphorus based upon molecular weight, and it has great potential application in the FR modification of polymers. Recently, PA as a nontoxic naturally occurring phosphorus-containing compound has provoked people's interest in the FR finishing of textiles. Zhou et al. used PA as a doping acid to greatly improve the flame retardancy of polyaniline-deposited paper composite (Zhou et al., 2015). To reduce the flammability of cotton fabric, Laufer et al. and Wang et al. used PA/chitosan and PA/nitrogen-modified silane hybrid respectively via layer-by-layer assembly to fabricate thin films on the fabric (Laufer et al., 2012; Wang et al., 2015).

In the present study, PA was applied to improve the FR properties of PLA nonwoven fabric using a pad-dry-cure technique. The combustion properties of the treated fabric were evaluated via limiting oxygen index (LOI) test, vertical burning test, and microscale combustion calorimetry (MCC). The stability and char formation ability of the treated fabric during thermal degradation were determined using thermogravimetric (TG) analysis. The surface morphologies of the treated fabrics and the burned fabric residues were observed via scanning electron microscopy (SEM). In addition, the phosphorus content of PLA surface before and after burning was evaluated by energy dispersive spectrum (EDS) analysis. Finally, the FR mechanism of the PA treated fabric was suggested.

2. Experimental

2.1. Materials

The PLA nonwoven fabric with a weight of 80 g/m^2 manufactured by melt-blown spinning technology was obtained from Shenzhen Shengdefu Fiber Products Co. Ltd., China. Phytic acid (PA) (70% aqueous solution) of analytical reagent grade was bought from Chengdu Ai Keda Chemical Technology Co. Ltd., China.

2.2. Fabric treatment

The PLA non-woven fabric was first immersed in the PA solution for 10 min, and then passed through a two-roll laboratory padder (Shanghai HuangJu Industry Co. Ltd., China) with the wet pick-up being approximately 120%. The padded fabric was dried in a mini-dryer (Shanghai HuangJu Industry Co. Ltd., China) at 80 °C for 5 min and then cured at 125 °C for 3 min. In this study, PLA-0, PLA-100 and PLA-250 represent the fabrics treated with 0, 100 and 250 g/L PA, respectively.

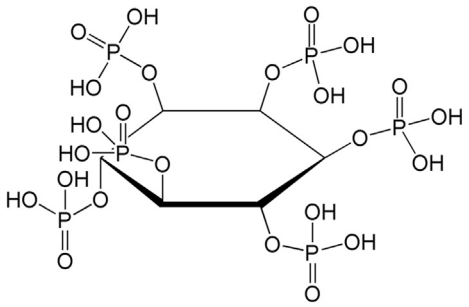

Fig. 1. Chemical structure of phytic acid.

2.3. Measurements

2.3.1. Determination of weight gain

The fabrics before and after treatment were dried in the oven at 60 °C for 30 min, and then weighed quickly. The weight gain of the treated fabric was calculated using the following formula:

$$\text{Weight gain}\ (\%) = 100 \times (W_1 - W_0)/W_0$$

where W_0 and W_1 represent the weight of the dry fabric before and after treatment, respectively.

2.3.2. LOI test

The LOI value of the fabric was measured according to ASTM Standard Method D2863 using the FTT0080 oxygen index apparatus (Fire Testing Technology Ltd., UK).

2.3.3. Vertical burning test

The vertical burning test was performed on the YG815B automatic vertical flammability cabinet (Ningbo Textile Instrument Factory, China) according to ASTM Standard Method D6413.

2.3.4. MCC test

The MCC test was carried out on the FTT0001 microscale combustion calorimetry (Fire Testing Technology Ltd., UK) according to ASTM Standard Method D7309. About 5 mg specimen was thermally decomposed in an oxygenated environment at a constant heating rate of 1 °C/s.

2.3.5. TG analysis

The Diamond TG/DTA SII thermal analyzer (Perkin–Elmer, USA) was used to record the TG curve in the temperature range of 30–600 °C at a heating rate of 10 °C/min with a continuous nitrogen flow rate of 20 mL/min. The sample weight for each measurement was 4–5 mg or so.

2.3.6. SEM observation

The PLA fabrics as well as the chars obtained in the LOI test experiments were first sputter-coated with a gold layer whose thickness was 10 nm or so, and then their surface morphologies were observed by the TM3030 tabletop scanning electron

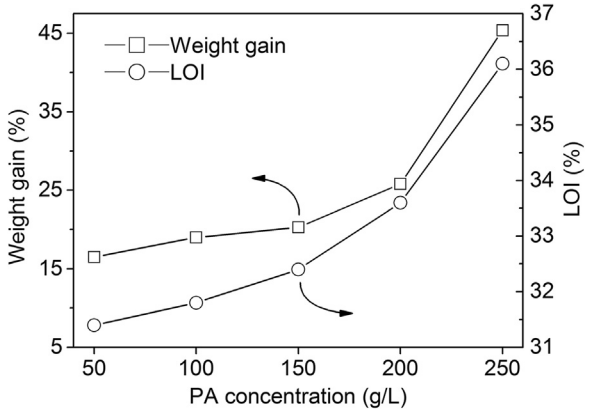

Fig. 2. Weight gain and LOI values of the PLA fabrics treated with PA solutions of various concentrations.