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Flame-retarded biocomposites of poly(lactic acid), distiller's dried grains with solubles and resorcinol di(phenyl phosphate)

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ABSTRACT

The distiller's dried grains with solubles (DDGS) were treated by smashing and water washing processes. The treatment effects on DDGS were analyzed, and the results showed that the thermal stability and the hydrophobicity of DDGS were improved by the treatment processes. The flame retarded biocomposites of poly(lactic acid) (PLA) with DDGS and degradable polymeric flame retardant resorcinol di(phenyl phosphate) (RDP) were prepared. The prepared biocomposites had good mechanical properties and the tensile strength of the biocomposite containing 15 wt% RDP and 15 wt% DDGS reached approximately 53 MPa. Meanwhile, using the limited oxygen index (LOI) and the underwriters laboratory (UL-94) tests, for the biocomposite, the LOI value was approximately 27.5% and V-0 rating in UL-94 was attained. Furthermore, the peak heat release rate of this biocomposite was reduced to 275 kW/m^2 compared with 310 kW/m^2 for pure PLA. After burning of the biocomposites, compact and coherent charred layer was formed and the char residues were analyzed in detail.

1. Introduction

Due to environment and sustainability issues, the development of high-performance materials made from natural resources is increasing worldwide over the last few decades [1]. The materials called biocomposites, which are composed of agricultural residues and biodegradable polymers, have become very attractive materials in terms of their properties and biodegradability after their uses. They have become engineering materials with a very wide range of properties [2,3]. Poly(lactic acid) (PLA) is one of the best-known biodegradable aliphatic polyesters obtained from renewable sources, such as corn starch, potato starch and sugar beets. PLA exhibits excellent mechanical properties similar to traditional polymers such as polystyrene (PS), biodegradability and good compatibility, which makes it widely used in biomedical, packaging and textile industries [4,5]. Moreover, the applications and developments of the PLA-based biocomposites as engineering materials in electronics and automobile industries are gaining more and more attention [6].

Distiller's dried grains with solubles (DDGS) is the nonfermentable cereal coproduct of the corn brewing process and is increasing dramatically in the world, especially in China and the United States [7–9]. More than 20 million tons of stillage are generated from the production of Chinese liquor every year in China, of which DDGS is the main component. DDGS is a multiple-component biopolymer containing protein (26.8–33.7%, dry weight basis), carbohydrates (39.2–61.9%, including fibers), oils (3.5–12.8%), and ash (2.0–9.8%) [10]. Because there are limits to its intake by livestock based on nutritional requirements and the environmental pollution of its disposal, it is crucial to develop alternate uses for DDGS to avoid market saturation of this coproduct. DDGS, with the advantages of low cost, low density, biodegradability and renewable source, has recently been used as the bio-based filler in polymer composite materials. The addition of DDGS in PLA can reduce the cost of the biocomposites and improve the performances such as mechanical and thermal degradation properties of the composites [11,12].

PLA and DDGS based biocomposites are attractive for the manufacture of electrical/electronic devices or automotive parts. Unfortunately, because of the flammability of PLA and DDGS, the biocomposites based on them cannot be recommended for applications in these parts where advanced flame retarded properties are required [13,14]. To the best of our knowledge, very few studies have been made on the flame retarded biocomposites based on PLA and DDGS up to now although some reports about the flame retardancy of PLA composites have been revealed. However, most of the flame retarded PLA composites sometimes trigger problems such as cost and loss of mechanical properties, aspects that need to be considered when targeting a potential application [15,16]. In

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this study, the biocomposites of PLA, DDGS and resorcinol di(phenyl phosphate) (RDP) were prepared. The flame retardant RDP is a polymeric biodegradable compound with good thermal stability as shown in Scheme 1. RDP has the phenyl groups that can be considered as nonpolar moieties and phosphate groups that can be considered as polar moieties. It is reported that phosphate groups can act as the strong hydrogen bond acceptors. Therefore, RDP can be used as a compatibilizer to improve the compatibility of PLA with fillers. This procedure is simple and effective [17,18]. The mechanical properties, thermal degradation, flame retardancy of the biocomposites of PLA, DDGS and RDP are discussed. The DDGS treated by smashing and water washing is characterized and the flame retarded mechanism is also revealed in detail.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA 290, injection molding grade) was purchased in the form of pellets from Zhejiang Haizheng Biological Materials Co. Ltd (Zhejiang, China). Resorcinol di(phenyl phosphate) (RDP) was supplied by Zhejiang Wansheng New Material Co. Ltd (Zhejiang, China). The samples of distiller's grains with solubles (DDGS) were obtained from Yanghe Distillery Co. Ltd (Jiangsu, China).

2.2. Treatment of DDGS

Oven-dried DDGS samples were smashed in a small pulverizer and sieved down to 60 meshes. The powdery DDGS was then washed with deionized water in a beaker with stirring for about 30 min. The washed DDGS was finally dried in vacuum oven at 60 °C overnight.

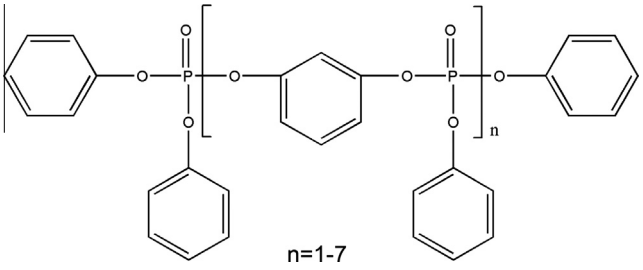
2.3. Preparation of the biocomposites of PLA, DDGS and RDP

DDGS was compounded with PLA and RDP in a RM-200A torque rheometer (Hapro Electric Technology Co. Ltd. Harbin, China) with three heating zones of 175, 175 and 175 °C, respectively. The obtained mixture was injection molded into appropriate specimens for tests by a SZ-15 micro injection molding machine (Ruiming Plastics Machinery Co. Ltd. Wuhan, China) at 185 °C. The formulations under investigation were listed in Table 1.

2.4. Measurement and characterization

Fourier-transform infrared spectra from 400 to 4000 cm^{-1} were obtained using KBr discs on a FTIR-8400S (Shimadzu, Japan) with a resolution of 4 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) was obtained using a PHI5300 spectrometer (ELMER, USA) with Al Kα as the excitation radiation.



Scheme 1. The chemical formula of RDP.

Table 1
The formulations and the results of UL-94 and LOI tests for the biocomposites.

Samples	Composition (wt%)			LOI (%)	E_{FR}[a]	UL-94	
	PLA	RDP	DDGS			Dripping	Rating
P0	100	0	0	20.0	—	Serious	NR[b]
PDDG1	70	0	30	18.5	—	No	NR[b]
PDDG2	70	5	25	21.0	0.500	No	V-0
PDDG3	70	10	20	24.0	0.550	No	V-0
PDDG4	70	15	15	27.5	0.600	Slight	V-0
PDDG5	70	20	10	29.0	0.525	Slight	V-0
PDDG6	70	25	5	31.5	0.520	Medium	V-0

[a] $E_{FR} = \Delta LOI/w(RDP) = [LOI(PDDGx) - LOI(PDDG1)]/w(RDP)$.
[b] NR – not rated.

X-ray diffraction (XRD) measurements were performed on a D8 ADVANCE diffractometer (Bruker, Germany) using Cu Kα generator (λ = 0.15418 nm) at 40 kV with a step size of 0.02°.

The contact angles were measured by a contact angle tester of SL200B goniometer (Kino, USA). The samples were compressed into tablets and investigated by the sessile drop method with water as the solvent.

Thermogravimetric analysis (TGA) was carried out from ambient temperature to 700 °C or 600 °C on a DGT-60 thermo-analyzer instrument (Shimadzu, Japan) in nitrogen flow (20 mL/min) at a heating rate of 20 °C/min. The samples used in this measurement were kept within 3–5 mg in ceramic crucibles.

The mechanical properties of the biocomposites were measured with the dumbbell-shaped test specimens molded. The samples with dimension of 10 mm × 3 mm × 3 mm in accordance with ASTM D638 on a CMT tensile tester (Sans, China). The measurements were performed with a rate of 10 mm/min at room temperature.

Limiting oxygen index (LOI) tests were conducted on an HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China) with the sample dimension of 100 mm × 6.5 mm × 3 mm according to ASTM D2863-97. UL 94 burning tests were performed on the samples of 130 mm × 13 mm × 3 mm in size with CFZ-3 instrument (Jiangning Analysis Instrument Co., China) according to ASTM D3801-96. The flammability for the flame retarded biocomposites was characterized by cone calorimetry (Fire Testing Technology, UK) according to ISO 5660. The samples with dimension of 100 mm × 100 mm × 1 mm were irradiated horizontally at a heat flux of 35 kW/m^2.

The char residues of the biocomposites were obtained from the burned samples. The char residues were analyzed using Hitachi S-4800 scanning electron microscopy (SEM) coupled with Noran SystemSix energy dispersive spectrometer (EDS) (USA) and InVia laser Raman spectrometer (Renishaw, UK) from 500 to 3000 cm^{-1}at room temperature.

3. Results and discussion

3.1. Treatment of DDGS

DDGS without treatment has low thermal stability and contains some water-soluble compounds, which limits its application as the filler for the polymer biocomposites. According to Bootsma et al. [19] and Kim et al. [20], water washing of DDGS could remove residual mono- and oligo-saccharides organic acids such as succinic acid and lactic acid, and fermentation by-products like glycerol and butanediol. The digital photographs of original and treated DDGS by smash and water washing are displayed in Fig. 1. Furthermore, Fig. 2 shows the SEM images of original and treated DDGS. In Fig. 2(a), most of the particles are approximately 25 μm without specific shapes. As shown in Fig. 2(b), after treatment, some