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Effect of hyperbranched poly(trimellitic glyceride) with different molecular weight on starch plasticization and compatibility with polyester

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ABSTRACT

Hyperbranched poly(trimellitic glyceride) (PTG) plasticizers for starch were prepared by using trimellitic anhydride and glycerol as raw materials in a simple one-step synthesis. The structure and branching degree of PTGs were confirmed by Fourier transformed infrared, gel permeation chromatography and ^{1}H nuclear magnetic resonance. The PTGs as plasticizers were composited with maize starch (S) *via* cooking and film formation. The structure and mechanical, thermal properties of the plasticized starch composites, and its adhesion to cotton and polyester yarns were studied in details. Results indicated that the PTG/S composites had better mechanical property and thermal stability, and lower moisture absorption than glycerol/starch (GLY/S) with the same content (w/w). With the increase in PTG molecular weight, elongation at break of PTG/S film decreased and tensile strength increased, and moisture absorption of PTGs/S reduced. In addition, PTGs/S had a better effect on adhesion to cotton and polyester yarns than GLY/S.

1. Introduction

Starch is a renewable, biodegradable, inexpensive material, and has been extensively used in food, textile, paper making, medicine and other industrial products (Burrell, 2003; Zdanowicz & Johansson, 2016). However, starch films without a plasticizer are brittle because of the intra- and inter-molecular hydrogen bonding of the starch molecules. Some small molecular hydrophilic substances, such as glycerol (Lourdin, Coignard, Bizot, & Colonna, 1997) and urea (Lin, Zeng, Hou, & Shi, 2008; Wang, Cheng, & Zhu, 2014), are used to plasticize starch in order to obtain thermoplastic starch (Guzmán & Murillo, 2015). Glycerol in plasticizing starch is apt to migrate and aggregate on the surface (Zdanowicz & Johansson, 2016). Amines have a good effect on starch plasticization and anti-retrogradation (Lagarón, López-Rubio, & Fabra, 2015; Schmitt et al., 2015), but amines are toxic (Zdanowicz & Johansson, 2016). In recent years, there are some investigations of ionic liquids as starch plasticizers. The use of ionic liquids leads to less hygroscopicity, more efficient plasticization and compatibility of starch blends (Bendaoud, & Chalamet, 2013; Leroy, Jacquet, Coativy, Reguerre, & Lourdin, 2012). Hydrophilic macromolecules in starch matrix are much more stable, but are ineffective in plasticizing starch. However, star-shaped polymer was testified to combine good plasticization and stability in the starch matrix by Nykänen (Nykänen et al., 2014). Analogously, Guzmán etc. (Guzmán & Murillo, 2015; Guzmán, Giraldo, & Murillo, 2017) found out that a hyperbranched polyester (HBPET) as a plasticizer could improve the mechanical properties of starch/polyethylene blends.

Because the HBPET has many superior properties (Seiler, Kohler, & Arlt, 2003; Zhang, Jia, & Chen, 2006; Zhang, Howell, Dumitrascu, Martin, & Smith, 2014; Zhang, Howell, & Smith, 2017) such as good liquidity, low viscosity, high solubility, good amorphism and activity, resulting from its highly branched structure and plenty of hydroxyl or carboxyl end groups, it has now been widely used in coating, polymer blending modification, biological materials and drug carrier technical fields (Jena, Mishra, & Raju, 2008; Zhang & Hu, 2008). An HBPET as a plasticizer has better compatibility with matrix (Sun, Liao, Zhang, & Du, 2011; Zhu, Li, Huang, Chen, & Li, 2013) and resistance to migration than a linear polyester and small molecules (Nykänen et al., 2014). For starch, the hydrophilic hydroxyl groups in the glucose residues can also be blocked by the end groups of HBPET, hence the humidity sensitivity of starch materials can be reduced (Mathew & Dufresne, 2002). From the above, HBPET may be an ideal candidate of starch plasticizers.

In the field of warp sizing technology, starch and water-soluble polyester sizes (Jin, Zhu, Yang, Miao, & Li, 2011; Jin, Zhu, & Yang, 2010) are commonly used for sizing cotton, spun polyester yarn and their blended yarns. In this study, we prepared a plasticizer of hyperbranched poly(trimellitic glyceride) (PTG) for starch based on the following considerations. Trimellitic anhydride and glycerol units of PTG

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may have affinity with polysaccharide and polyester respectively. It means that PTG could act as a plasticizer for starch or a compatibilizer for the blended size of starch/water-soluble polyester used in sizing cotton, spun polyester yarn and their blended yarn.

2. Experimental

2.1. Materials and chemicals

Normal maize starch was acquired from Xi'an Guowei Starch Co., Ltd. (Shanxi, P.R. China). The water content of the starch is 14% and amylose content is 25%. The viscosity-average molecular weight (M_v) of starch is 1.53×10^7 calculated by Mark-Houwink equation (Hu, Cheng, Lin, Zhao, & Zhu, 2016). Trimellitic anhydride and glycerol were purchased from Chengdu Kelong Chemical Reagent Factory (China). Distilled water was used in all experiments, and the chemicals employed in this study were of analytical grade.

2.2. Synthesis of poly (trimellitic glyceride)

Trimellitic anhydride (TMA) and glycerol (GLY) with 1:3 molar feed ratios were added to a reaction container. Then the mixture was heated to 130 °C under stirring and nitrogen was used to prevent the oxidation of the sample. After TMA was completely melted, 0.15 wt% *p*-toluenesulfonic acid based on the total quality was added into the system and the temperature was raised to 150 °C. A vacuum was applied to the container to remove the water byproduct of the reaction. The vacuum pressure was kept at 0.090 ± 0.005 MPa for 1.5, 2, 2.5 h, respectively. The resultants were named as PTG-1, PTG-2 and PTG-3, correspondingly.

2.3. The structure characterization of PTGs

Fourier transformed infrared (FT-IR) measurements were performed with a FTS3000 FTIR Spectrum Scanner (Hercules, USA). The samples were dissolved in N, N-dimethyl formamide. Then two drops of solution were dripped on the KBr pellet and dried. Each spectrum was collected from an average of 16 scans from 650 to 4000 cm^{-1} with a resolution of 2 cm^{-1}.

^{1}H nuclear magnetic resonance (^{1}H NMR) data of samples were measured with Bruker AM-500 superconducting nuclear magnetic resonance spectrometer (Germany). The working frequency is 600 MHZ and internal standard is tetramethylsilane (TMS). The PTG was dissolved in deuterated dimethyl sulfoxide (d6-DMSO). NMR tube diameter is 5 mm. Degree of branching (DB) was defined by Hawker (Hawker, Lee, & Frechet, 1991) as follows:

$$DB = \frac{D + T}{D + T + L} \times 100\% \tag{1}$$

where D, T and L represent numbers of dendritic units, terminal units and linear units, respectively.

To measure the molecular weight of PTGs, gel permeation chromatography (GPC) experiment was performed by using a HLC-8320 GPC (Waters, USA) and a TSK gel Super AWM-H (6.0 cm × 150 mm i.d.) column connected to a differential refractometer. The flow rate of the mobile phase DMF was 0.6 mL/min at 40 °C. Polymethyl methacrylate (PMMA) standard samples were used for calibration.

2.4. Preparation of starch films

The native starch (S) was dispersed in distilled water, 4% w/w, and GLY or PTGs was added at varied contents of 5, 10, 15, 20, 25 and 30%, w/w based on the starch, respectively. Each PTG was neutralized with dilute alkali lye before used as plasticizer. The mixed starch dispersion was stirred at 150 rpm, 95 °C for 30 min and then was poured on a glass dish and dried at a constant relative humidity (RH) of 68% at 20 °C for 3 days. The films were peeled off and reconditioned in a desiccator at 68% RH (maintained by saturated $CuCl_2$ aqueous solution), 20 °C for 3 days before measurements. According to different plasticizers added, the films were named GLY/S, PTG-1/S, PTG-2/S and PTG-3/S, respectively.

2.5. Mechanical properties testing

The sample film was cut into strips in size of 10 × 100 mm. The average thickness of films was measured by a thickness gauge, between 100 μm and 120 μm from 5 points on a single strip, and the error was less than 5 μm. The tensile properties were studied using YG061-1500 electronic strength tester (Laizhou, China). The tensile strength (TS) and elongation at break (E%) were recorded during extension at 100 mm/min. Each of the taken data was the average value of ten repeated testing.

2.6. X-ray diffraction (XRD)

XRD patterns of starch samples were recorded by Philips X' Pert Pro MPD system (Netherlands) in a scanning 2θ range from 5° to 40° and a step length of 0.03°. Crystallinity of starch film was calculated by use of the software Jade 6.0. The procedure of the calculation consists of measuring integrated intensities of the crystalline peaks and the diffuse background which was assumed to be the reflection of disordered potion (Utrilla-coello et al., 2014).

2.7. Moisture absorption

Moisture absorption (MA) was measured according to Mathew and Dufresne (Mathew & Dufresne, 2002). The specimens were cut in rectangular pieces about 2 cm × 2 cm. The samples were first dried at 55 °C for 48 h, then weighted to get the dry weight, and then conditioned for 15 days at different RH (11, 33, 44, 68, and 80%) and 20 °C to evaluate moisture absorption. The final weight was got to calculate the MA value, as follows:

$$\text{MA}(\%) = \frac{M_1 - M_0}{M_0} \times 100 \tag{2}$$

where M_0 is the dry weight of the sample and M_1 is the weight after 15 days.

2.8. Thermal gravimetric analysis (TGA)

Thermal properties of plasticizers and sample films were measured with a TGA/DSC2 type thermal analyzer (Mettler Toledo, USA). Samples with weight 5–10 mg were heated from room temperature to 600 °C at a heating rate of 10 °C/min.

2.9. Adhesion to cotton and polyester yarns

The size paste 2500 mL with mass fraction of 1% of the size agent and plasticizer 15% w/w based on the starch was heated to 95 °C for 30 min for standby application. Cotton yarn or polyester yarn was enwound on the periphery of a tailor-made metal frame. The frame with yarns was immersed in the cooked paste at 95 °C for 5 min, and then was taken out and hung to dry in the air. The dried yarns were placed in a desiccator for balance 24 h, in which the environment humidity RH 68% was conditioned over a saturated solution of $CuCl_2$. After that, the breaking force of the sized yarns was tested using YG061 Tensile Testing Equipment, with a clamping distance of 100 mm and stretching speed of 100 mm/min. For each data point, twenty samples were tested. Then the average value with its standard deviation was calculated and taken as the adhesion strength of the size on the fiber.

The strength value of the yarns before sizing was close to zero, so the average breaking strength was regarded as the sizing adhesion to