



Preparation and characterization of acetylated maltodextrin and its blend with poly(butylene adipate-co-terephthalate)



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ABSTRACT

Acetylated maltodextrins (AMDs) were synthesized. It was found that maltodextrin (MD) was easily acetylated to form AMDs with high degree of substitution (DS). The DS of the prepared AMDs was much higher than that of acetylated corn starches (ACSs) obtained under the same reaction conditions. The differential scanning calorimetry (DSC) measurements clearly highlighted that AMD underwent a glass transition at about 109 °C. Moreover, AMD possessed higher thermal stability than MD. The AMD with DS 2.13 (AMD2.13) was melt-blended with poly(butylene adipate-co-terephthalate) (PBAT) to fabricate novel PBAT/AMD polymer blends. Rheological measurements indicated that AMD2.13 had a plasticizing effect on PBAT. Moreover, scanning electron microscopy (SEM) measurements indicated good interfacial adhesion between PBAT and AMD2.13. The onset temperature of non-isothermal melt crystallization of PBAT increased from 81.95 to 92.19 °C due to the favorable heterogeneous nucleation effect. Mechanical tests showed that the yield strength of the PBAT/AMD blends was enhanced.

1. Introduction

In recent years, there has been increasing interest in the use of biodegradable and renewable materials as an alternative to conventional petroleum plastics for reducing persistent plastic waste and alleviating the energy crisis. Carbohydrates are the most abundant renewable resource on our planet. Starch, the principal carbohydrate reserve in a large variety of green plants, such as corn, wheat, rice, potato, tapioca, and others (Jantanasakulwong et al., 2016; Tan et al., 2016; Klaochanpong, Puttanlek, Rungsardthong, Pancha-arnon, & Uttapap, 2015), is a semicrystalline polymer composed of amylose and amylopectin. The unique physical and chemical characteristics and nutritional quality of starch set it apart from all other carbohydrates. Starch is completely biodegradable, inexpensive, and available in large quantities and its applications range from traditional food, paper, and textile industries to packaging and drug delivery. Two main forms of starch are employed in the polymer field. In some cases, starch granules have been directly used as inexpensive and renewable organic fillers for petroleum-based or biodegradable polymers (Nabar, Raquez, Dubois, & Narayan, 2005). However, the use of raw corn starch as a component for polymer compounding is rather challenging, owing to its large particle size (~20 μm), inherent hydrophilicity, and lack of interfacial interactions with most of polymers. Therefore, the most common form

of starch employed in biopolymer technology is thermoplastic starch (TPS). Native starch is not thermoplastic, due to strong hydrogen bond interactions that restrict the movement of its molecular chains. The most common approach to obtain TPS involves the use of small molecular plasticizers. Many studies have focused on this task, and the commonly employed plasticizers are water, glycerol, urea, sorbitol, and citric acid. Thermoplastic melt can be obtained from conventional extruders (or similar equipment) used for processing thermoplastics by disrupting the original structure of starch accomplished with simultaneous heating and shearing (Ceseracciu, Heredia-Guerrero, Dante, Athanassiou, & Bayer, 2015). Many studies have reported the preparation of TPS blends using other biodegradable hydrophobic polymers (Stagner, Alves, & Narayan, 2012; Li et al., 2016). In particular, some of the most common approaches involve associating TPS with polycaprolactone or poly(lactic acid) (Li & Favis, 2010; Muller et al., 2016). Unfortunately, the use of TPS in commodity plastics is limited by its moisture sensitivity and thermal instability (Shogren, Fanta, & Doane, 1993). Moreover, the plasticizers tend to promote starch retrogradation in TPS, which would accelerate their migration. Finally, the mechanical properties of TPS deteriorate with time. In order to avoid these adverse effects, it is necessary to develop new routes to prepare TPS without plasticizers. Therefore, chemical modification appears as the only suitable way to obtain intrinsic TPS by altering the molecular

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structure of starch.

Esterification is an established method for reducing the extent of intra- and intermolecular hydrogen bonds in starch and improving starch hydrophilicity (Adak & Banerjee, 2016; Fringant, Rinaudo, Foray, & Bardet, 1998; Hazarika & Sit, 2016; Gilfillan & Doherty, 2016). This method can increase the thermoplasticity of starch without requiring small molecule plasticizers (Lopez, Garcia, & Zaritzk, 2008; Chang, Jian, Zheng, Yu, & Ma, 2010; Brandelero, Yamashita, & Grossmann, 2010). Acetylated starch has been extensively studied over the last decades. The solubility in acetone and chloroform and thermoplasticity can happen when the degree of substitution (DS) of acetylated starch up to 2–3 (Elomaa et al., 2004; Chi et al., 2008). The acetylation reaction is hindered by the high molecular weight, strong hydrogen bond interactions, and crystal structure of starch. The preparation of highly acetylated starch usually involves pretreatment and harsh conditions (Singh, Nath, & Guha, 2011) to destroy the granular starch structure. High conversion efficiencies were obtained when starch was pretreated with dimethyl sulfoxide (DMSO) or hot water. However, the high cost, difficult recovery, and toxicity of the pretreatment limited the commercial development of this approach.

Maltodextrin (MD) is obtained through enzymatic or acid hydrolysis of starch with dextrose equivalent (DE) value lower than 20 (Pycia, Juszczak, Galkowska, Witczak, & Jaworska, 2016; Lacerda et al., 2016). DE is an indicator of the degree of depolymerization of starch. MDs with lower average molecular weights exhibit higher DE values. MD-based films were proposed to improve the flexibility and reduce cracking (Selmin, Franceschini, Cupone, Minghetti, & Cilurzo, 2015). If we use MD as the raw material, the acetylation reaction can proceed more readily due to the low molecular weight and the loss of crystalline structure.

Poly(butylene adipate-co-terephthalate) (PBAT) is a biodegradable aromatic-aliphatic copolyester, which can be prepared by polycondensation of 1,4-butanediol with both adipic and terephthalic acids. PBAT is also a hydrophobic and semicrystalline copolyester. Its processing conditions and mechanical properties are similar to those of polyethylene (Raquez, Nabar, Narayan & Dubois, 2008a). What's more, PBAT can be fully degraded within a few weeks with the aid of naturally occurring enzymes. The glass transition ($-20\text{ }^{\circ}\text{C}$) and melting temperatures ($105\text{--}115\text{ }^{\circ}\text{C}$) of PBAT offer a good compromise between processing and service temperatures. PBAT has attracted considerable attention not only as a substitute of non-biodegradable polymers for commodity applications, but also for specific applications in commercial and agricultural areas, owing to its similar processing conditions and mechanical properties to low-density polyethylene (LDPE) (Wang, Wei, Zheng, & Xiao, 2015). However, despite the promising potential of PBAT for the production of environmentally friendly biodegradable polymers, its wide application has been hampered by intrinsic issues such as low heat distortion temperature and low yield strength. Its high price, in particular, significantly limits its use in disposable items. Polymer blending is an important way to obtain new materials that can meet different requirements and represents an important route to overcome the limitations of the individual polymers. Several studies have focused on PBAT/TPS composites. It was reported that maleic anhydride (MA) grafted onto TPS can improve the miscibility between PBAT and TPS with different MA content; however, the tensile strength and modulus of elasticity of maleated thermoplastic starch (MTPS)-g-PBAT blends did not change by increasing the MA content (Raquez, Nabar, Narayan, & Dubois, 2008b). In addition, some researchers used nanosized particles to enhance the strength of PBAT/TPS blends (Raquez, Nabar, Narayan, & Dubois, 2011; Seligra, Moura, Fama, Druzian, & Goyanes, 2016). Whereas the incorporation of the nanoparticles improved their tensile strength and modulus, these blends were not suitable for long-term applications due to the instability of TPS.

In this study, MD was used as low-cost raw material for the preparation of acetylated maltodextrin (AMD) with high DS. PBAT was

then blended with AMD in order to obtain a new material with suitable mechanical properties and well-balanced cost-property relationships. To the best of our knowledge, this is the first report describing the synthesis of AMD from MD and development of advanced PBAT/AMD blends through melt blending. In addition, other properties of the blends were further investigated.

2. Experimental

2.1. Materials

Commercial maltodextrin (MD) was purchased from Shandong Xiwang food Co., Ltd. (China). The Dextrose Equivalent (DE) of MD was 6. Corn starch (CS) was obtained from Changchun Dacheng Corn Development Co. Ltd. (China). Glacial acetic acid was purchased from Beijing Chemical Factory. Acetic anhydride was obtained from Sinopharm Chemical Reagent Co. Ltd. Methanesulphonic acid (MSA) was purchased from Tianjin Guangfu Fine Chemical Research Institute. The biodegradable polymer, PBAT (Ecoflex FBX 1200), was purchased from Chemical Company BASF with a melt flow index of 3.3–6.6 g/10 min (at $190\text{ }^{\circ}\text{C}$, 2.16 Kg), density of $1.25\text{--}1.27\text{ g/cm}^3$, the molecular weight of $1.42 \times 10^5\text{ g/mol}$. All chemicals used in the study were of analytical grade.

2.2. Preparation of acetylated maltodextrin (AMD)

AMDs with variable DS were prepared according to a previously published method (Chi et al., 2008). The MD was first dried at $90\text{ }^{\circ}\text{C}$ for 24 h before reaction to get rid of moisture. 10 g MD was placed in a 250 ml three-neck round bottom glass flask with a mechanical stirrer and a reflux condenser. 21.62 g glacial acetic acid and 32.67 g acetic anhydride were added. The mixture was stirred at 200 rpm. After 15 min, 0.34 g of MSA was subsequently added to the reactor. The reaction was stirred for 3 h. The mixture was washed with excess distilled water and the solid was dried at $50\text{ }^{\circ}\text{C}$ for 12 h in vacuum oven. By changing the reaction temperature at 50, 60 and $70\text{ }^{\circ}\text{C}$, AMDs were obtained with three DS values. In addition, acetylated corn starch (ACS) was prepared by same procedure for comparison. The ACS with different DS was obtained by varying the reaction temperature at 50, 60 and $70\text{ }^{\circ}\text{C}$, respectively.

2.3. Preparation of PBAT/AMD2.13 blends

PBAT was dried at $80\text{ }^{\circ}\text{C}$ in a vacuum oven for 24 h. This PBAT/AMD blends were prepared by using PBAT and AMD with the DS 2.13. AMD and MD were also dried at $60\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$ for 24 h in a vacuum oven, respectively. PBAT/MD blends and PBAT/AMD blends were prepared by melt mixing with a Haake Rheomix 600 (Karlsruhe, Germany) with a rotating speed 60 rpm at $140\text{ }^{\circ}\text{C}$ for 6 min. The mixing compositions of the blends were 90/10, 70/30, and 50/50 Wt/Wt. The torque was recorded during the mixing. After mixing, all of the compounds were cut into small pieces. Then, all the samples were compression-molded into sheets with thicknesses of 1.0 mm at $140\text{ }^{\circ}\text{C}$, a hold pressure of 10 MPa and a hold time of 3 min, followed by quenching to room temperature. The samples were then sealed in plastic bags for various tests.

2.4. Characterization

2.4.1. Degree of substitution

The percent acetylation and DS were determined titrimetrically using the method of Luo & Zhou, (2012) with minor modifications. The obtained AMD (0.50 g) samples were weighted accurately and hydrolyzed with the sodium hydroxide solution (20 mL, 0.25 mol/L). The mixture was maintained under agitation at 200 rpm for 72 h. Excess NaOH was then back-titrated with 0.1 mol/L HCl using 3 to 5 drops of

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