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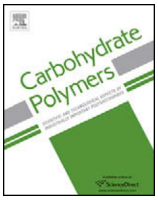

Isosorbide, a green plasticizer for thermoplastic starch that does not retrogradate

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ABSTRACT

Isosorbide is a non-toxic biodegradable diol derived from bio-based feedstock. It can be used for preparing thermoplastic starch through a semi-industrial process of extrusion. Isosorbide allows some technological advantages with respect to classical plasticizers: namely, direct mixing with starch, energy savings for the low processing temperature required and lower water uptake. Indeed, maize starch was directly mixed with the solid plasticizer and direct fed in the main hopper of a co-rotating twin screw extruder. Starch plasticization was assessed by X-ray diffraction (XRD) and dynamic-mechanical analysis (DMTA). Oxygen permeability, water uptake and mechanical properties were measured at different relative humidity (R.H.) values. These three properties turned out to be highly depending on the R.H. No retrogradation and changing of the material properties were occurred from XRD and DMTA after 9 months.

1. Introduction

Starch-based thermoplastic materials are relatively cheap: indeed, they are manufactured using an annually renewable source as raw materials such as corn, maize or potatoes. Starch is a multi-hydroxyl polymer that has so vast intermolecular and intramolecular hydrogen bonds that does not act as real thermoplastic (Liu, Zhong, Chang, Li, & Wu, 2010; Zobel, 1988). Despite that, in the presence of plasticizers, high temperatures and under shear stresses it promptly softens and could be used as a common thermo-plastic material (Liu et al., 2010; Van Soest, Hulleman, de Wit, & Vliegenthart, 1996). Natural starch is usually about 15–45% crystalline (Zobel, 1988) but during processing plasticizers are able to destroy this crystallinity. In most of the literature, polyols (such as glycerol, glycol, sorbitol and sugars (Barret, Kaletunc, Rosenburg, & Breslauer, 1995; Fishman, Coffin, Konstance, & Onwulata, 2000; Qiao, Tang, & Sun, 2011; Roz, Carvalho, Gandini, & Curvelo, 2006; Shi et al., 2007; Yu, Gao, & Lin, 1996; Wang, Shogren, & Carriere, 2000) were usually used as plasticizers for starch. Polyols-plasticized TPS have still drawbacks to be overcomes such as strong water sensitivities, poor mechanical properties and significant variation with times. The last phenomenon is usually known as retrogradation: re-crystallization of starch always associated with a progressive embrittlement (Avérous, 2004; Lourdin, Colonna, Brownsey, Noel, & Ring, 2002; Schmitt et al., 2015; Smits, Hulleman, Van Soest, Feil, & Vliegenthart, 1999; Van Soest & Knooren, 1997).

In order to eliminate weakness and improve TPS properties, plenty of studies have been carried out especially on nanocomposites (Müller, Laurindo, & Yamashita, 2012; Xie, Pollet, Halley, & Avérous, 2013) and on bio-composites with cellulose or lignin fibers (Chen, Lawton, Thompson, & Liu, 2012; Müller, Renner, Móczó, Fekete, & Pukánszky, 2014). In some cases fillers were able to both increase the mechanical properties and reduce the water sensitivity (Averous & Boquillon, 2004). Other researchers focused their attention to TPS with retrogradation resistance and good mechanical properties obtained by using plasticizers containing amide groups (such as formamide and acetamide) (Dai, Chang, Yu, Geng, & Ma, 2010; Ma & Yu, 2004a, 2004b; Ma, Yu, & Feng, 2004); however, in this case, the main drawback is the high toxicity of these reactants. For all these intrinsic problems, biodegradable polyesters are usually associated with TPS (Ayana, Suin, & Khatua, 2014; Bocchini, Battegazzore, & Frache, 2010; Li, Luo, Lin, & Zhou, 2013; Mahieu, Terrié, Agoulon, Leblanc, & Youssef, 2013; Schwach, Six, & Avérous,

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2008), but, in this case, the advantage of low cost is partially lost.

Other disadvantages are slowing down the possible industrial exploitation of TPS: as an example, some technological problems may occur during extruder feeding. Indeed, the use of a powder or a liquid as plasticizer can be a limiting factor. Innovative plasticizers can help to overcome some of these limits due to the material and/or process conditions.

Nowadays, bio-refining processes have produced a number of compounds that have structural features not available through petroleum refining. One of the most promising structures is isosorbide (1,4;3,6-dianhydro-D-glucitol) composed of a fused bicyclic ring with a chiral diol. Isosorbide is commercially produced through a number of different methods, including the enzymatic hydrolysis of starch and the catalytic dehydration of sorbitol (Rose & Palkovits, 2012). Recent works on isosorbide-based polymers have included the development of thermoplastic polyesters (Jasinska & Koning, 2010; Noordover et al., 2006; Noordover, Duchateau, van Benthem, Ming, & Koning, 2007; Okada, Okada, & Aoi, 1995), polyurethane resins (Cognet Georjon, Mechin, & Pascault, 1996; Noordover et al., 2006), and epoxy thermosetting resins (Feng, East, Hammond, Zhang, & Jaffe, 2011). However, to the best knowledge of the Authors, no work has been done in regards to the develop isosorbide as plasticizer for starch. Thus, this paper was focused on the possibility to obtain isosorbide-based TPS (TPSI) and on investigation of properties for a possible use in the packaging field. A special attention was addressed to the processing simplification with respect to common plasticizer and their stability in time. For this reason, TPS with glycerol as plasticizer (TPSG) was prepared as reference, as well. In doing so, the temperature profiles for the processing of TPSI and TPSG were compared, verifying a possible energy saving.

Mechanical properties by dynamic-mechanical thermal analysis (DMTA) and the oxygen permeability (OP) were performed at different relative humidity in order to quantify the water sensitivity and its influences. Moreover, a study water uptake versus time at different R.H. for TPSI and TPSG has been included.

2. Materials and methods

2.1. Materials

Maize starch CERESTAR RG 03408 and Isosorbide C PLUS 16804 (PubChem CID: 12597) were purchased from Cargill. Glycerol (PubChem CID: 753), used as reference plasticizer, was purchased from Sigma–Aldrich. All materials were used as received.

2.2. Thermoplastic starch processing

TPS based on isosorbide was prepared using a co-rotating twin screw extruder LEISTRITZ ZSE 18/40D ($\Phi = 18$ mm, L/D = 40). To minimize the amount of isosorbide used the starch had not been dried using the water naturally present inside as accessory plasticizer (estimated at about 6% by weight with Karl–Fischer titration). After preliminary tests the optimum ratio of the plasticizer was set at 40 wt.%. The starch was pre-mixed manually with plasticizer, then directly put by a gravimetric feeder in the main hopper placed at the beginning of the screw. During the extrusion process, a temperature profile from 90 to 130 °C was maintained in the eight barrel block (T1–T8 in Table S1) and the resulting extruded melt temperature, measured with a pyrometer, was around 125 °C. The screw speed was fixed at 125 rpm and the extrusion output at 1 kg/h. The screw configuration with the temperature profile from the feeding zone to the die is detailed reported in Table S1. After the extrusion, the material was air cooled and then cut in pellets.

With the same extrusion machine and profile, TPS with glycerol as plasticizer to use as reference was obtained. In this case, the optimized temperatures were set from 115 to 150 °C and the plasticizer amount at 30 wt.%. As it is simple to establish, the higher temperature profile for TPSG processing imply a general higher consumption of energy. On the other hand there is a saving of plasticizer, indeed only 30 wt.% is able to transform starch into a thermoplastic material. These two aspects should be taken into account for a possible industrial exploitation.

The samples for DMTA and OP tests (60 mm × 60 mm × 1 mm and 100 mm × 100 mm × 0.2 mm specimens, respectively) were prepared by compression molding with 5 MPa at 140 °C for 2 min.

2.3. Analyses

X-ray diffraction (XRD) analyses were performed with Thermo ARL diffractometer X-tra 48 on compression molded specimens using Cu Kα X-ray source ($\lambda = 1.540562$ Å), step-size 0.02° at 2° min^{-1} scanning rate.

Thermogravimetric analyses (TGA) were performed with TGA Q500 TA Instruments from 50 to 800 °C at 10 °C/min with nitrogen or air flow of 60 ml/min for inert and oxidative atmosphere, respectively.

Dynamic-mechanical thermal experiments (DMTA) were performed using a DMA TA Q800 with tensile film clamp. The analyses were performed on 30 mm × 6 mm × 1 mm samples cut with a razor blade from the compression molding specimen. The temperature range was set from −30 °C to 120 °C, the heating rate at 3 °C/min and the frequency at 1 Hz. The tests were performed in strain-controlled mode with 0.05% of deformation amplitude and 0.05 N of preload force. All the samples were conditioned before the test at 23 °C and different R.H., in a climate-controlled chamber Binder BFK240 till equilibrium was reached. All tests were made according to the ISO 6721 standard.

In addition, isothermal tensile tests at 30 °C after conditioning at the same R.H. were performed by using the same instrument and clamp setting, and the strain rate at 1%/min till the specimen was broken. Three samples were used for each R.H. condition and the average values and corresponding standard deviation were calculated. These tests provided the Young's modulus values (E), elongation-at-break (ε) and maximum tensile strength (σ) of the bio-based materials.

Water content at different R.H. was calculated with progressive weight control of compression molded samples (30 mm × 30 mm × 1 mm) until constant weight was reached. These results were expressed as percentage of weight increase from the initial dry condition.

Oxygen permeability (OP) was measured by using a Multiperm ExtraSolution instrument. The experimental conditions were set at 23 °C under variable relative humidity conditions (from 5 to 90% ±1), with an initial conditioning time of 6 h. The area of film tested was controlled with adhesive aluminum masks having 2 cm^2 openings. The end of the test was established when the collected data reached an oxygen transmission rate (OTR) accuracy of 0.5%. OTR value was automatically given by instrument on the basis of atmospheric pressure depending on weather conditions. OP was calculated following the Eq. (1), after measuring film thickness by a micrometer device:

$$\begin{aligned} \mathrm{OTR} &= \frac{\text{volume } O_2}{\text{area} \times \text{day} \times \text{pressure}} \\ \mathrm{OP} &= \mathrm{OTR} \times \text{film thickness} \end{aligned} \qquad (1)$$