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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 $2^\circ\ \mathrm{min}^{-1}$ 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:

$$\mathrm{OTR} = \frac{\text{volume } \mathrm{O_2}}{\text{area} \times \text{day} \times \text{pressure}} \qquad \mathrm{OP} = \mathrm{OTR} \times \text{film thickness} \tag{1}$$

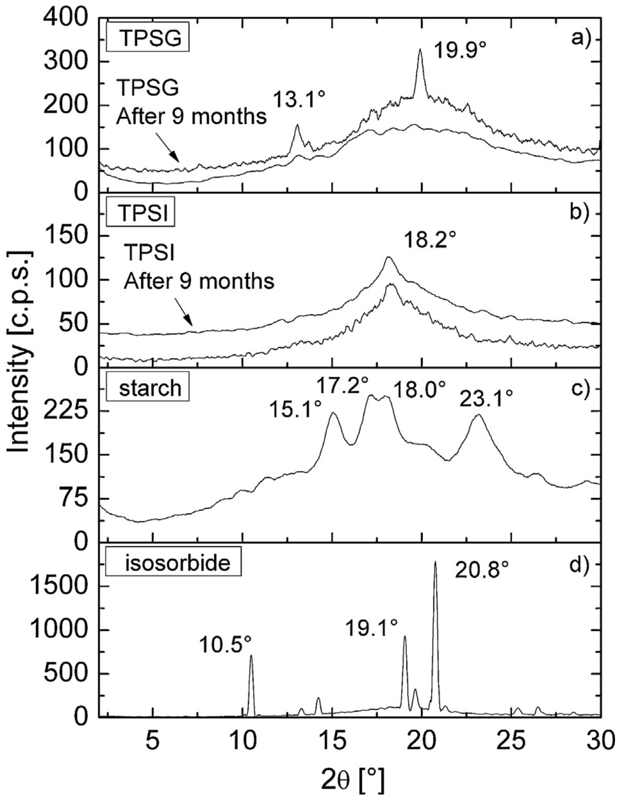

Fig. 1. XRD diffraction spectrum of: (a) TPSG immediately after extrusion and TPSG after 9 months, (b) TPSI immediately after extrusion and TPSI after 9 months, (c) maize starch, and (d) isosorbide.

3. Results and discussion

3.1. TPSI morphological analyses – XRD

In Fig. 1c the XRD spectrum of maize starch as received was reported, it has four main peaks: 15.1, 17.2, 18.0 and 23.1°, probably due to the presence of both A and B crystalline type (Van Soest et al., 1996). The isosorbide spectrum (Fig. 1d) also shows a series of diffraction peaks (main at 10.5, 19.1 and 20.8°), that confirm the high crystallinity of such plasticizer. In Fig. 1a the XRD spectra of glycerol-plasticized starch (TPSG) were compared at different times. Immediately after processing TPSG practically do not contain any residual crystallinity. After 9 months TPSG shows formation of a single helical amylose crystal structure, from the position of the diffraction peaks (13.1° and 19.9°) it can be identified as Vh-type (Van Soest et al., 1996). In Fig. 1b were reported spectra of isosorbide-plasticized starch, no traces of isosorbide crystallinity are present. The native starch crystalline structure is lost also in this case but TPSI shows a crystalline structure with a peak at 18.2° soon after extrusion. It can be identified as Eh-type (Van Soest et al., 1996) usually it is formed when the starch is processed with shear stresses higher than shear stresses necessary for the formation of Vh-type. Eh formation is typical of an high degree of disruption of the starch granules (Van Soest et al., 1996) thus isosorbide shows great plasticizing properties even at low processing temperature. The spectrum at 9 months is perfectly overlapping the first one, a proof of material stability, conversely to what occurs with glycerol and other plasticizers (García, Martino, & Zaritzky, 2000).

3.2. TPSI thermal properties

Thermal properties of the prepared TPSI single components and final materials were characterized by thermogravimetry in both nitrogen and air. Fig. 2 reports the weight loss as a function of the temperature (TG curve) (a and c) and the derivative curves (dTG) (b and d) in nitrogen and air, respectively. In Table S2 the data of the degradation rate peak ($T_{\max}$) and the residue percentage at 800 °C were summarized.

In nitrogen isosorbide rapidly lost weight by a single step, probably due to evaporation, at about 200 °C, and leaves no residue at 800 °C. Starch undergoes an initial decrease of weight due to the water evaporation, but, despite this, remains stable till the temperature of about 250 °C. Thus it degrades in a single step with a maximum degradation peak at 309 °C. The weight residue at 800 °C is 12.0% due to the partial carbonization of starch. The TPSI has a single degradation peak at 304 °C (temperature slightly lower than starch alone) and the final residue of 6.4% which is comparable with the amount of starch introduced. There is no sharp degradation peak due to isosorbide part, indeed its degradation is a continuous little weight loss in the range 180–300 °C. A comparison made with the calculated degradation curve obtained by the partial contribute of singular element (Fig. 2), demonstrates that TPSI is more stable to thermal degradation than neat isosorbide and starch alone, and

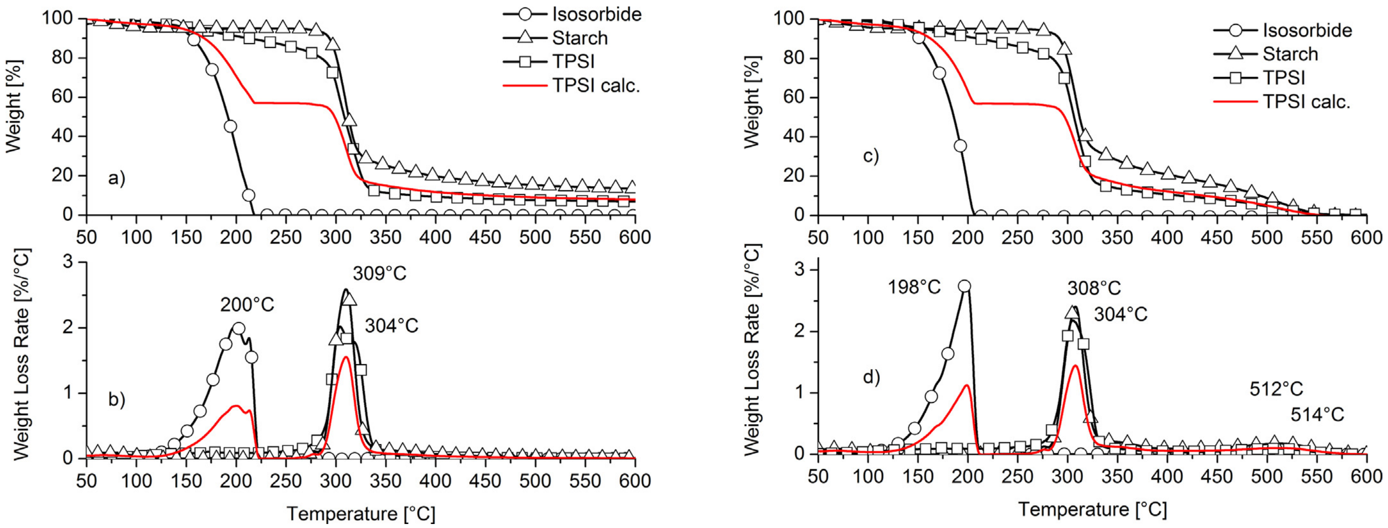

Fig. 2. TG and dTG in nitrogen (a and b) and air (c and d) of plasticized starch (TPSI) compared with curve calculated from mathematical superimposition of starch and isosorbide in the right proportions.

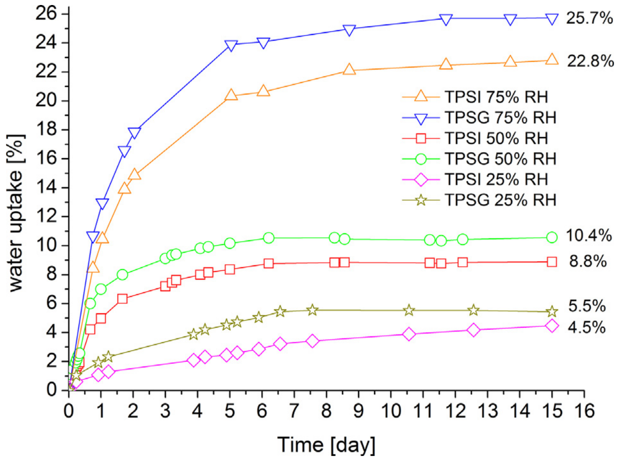

Fig. 3. Water uptake as a function of time of plasticized starches (TPSI and TPSG) at different R.H.

it is comparable with TPSG. Also this stabilization could be an indirect proof of starch/isosorbide strong interaction and thus of the occurred plasticization of TPSI.

As far as oxidizing atmosphere is concerned, Figs. 2c and 2d shows the thermogravimetric analysis of TPSI compared with neat starch, isosorbide and calculated curves. As occurs in nitrogen, isosorbide rapidly degrades by a single peak of degradation at 198 °C. Otherwise starch and TPSI initial weight loss is similar to thermal degradation in nitrogen but, after the first peak of degradation, the formed carbon char undergoes oxidation at 512 and 514 °C (for starch and TPSI, respectively), thus the final residues at 800 °C was negligible. Even in this case, as already reported for nitrogen, the peak due to the isosorbide degradation part is not recognizable in TPSI. In the end, TPSI also in air is more stable than the calculated curve obtained from the single component addition.

3.3. *TPSI water uptake*

The water absorption of TPS constitutes one of its shortcoming that limited possible applications, namely packaging materials. The presence of only two hydroxyl function in isosorbide is likely to contributed to reduce the water uptake compared to glycerol.

In Fig. 3 the water uptake at different R.H. of TPSG and TPSI was reported. On the contrary of what expected the time necessary to reach equilibrium decreases increasing the R.H. These results can be explained taking into account the decrease of T_g always associated with an increase of molecular mobility and thus diffusion coefficient (Biliaderis, 1999; Lourdin, Coignard, Bizot, and Colonna (1997)). All samples reached the equilibrium after approximately 7–9 days except for specimens conditioned at lower R.H. (namely 25%) that took longer time. Whereas, as expected, the water uptake is significantly affected by the R.H. and the plasticizer type. Indeed, the water uptake at equilibrium seems to increase exponentially with R.H. As expected, isosorbide has a lower equilibrium value at every R.H. tested.

3.4. *TPSI mechanical properties*

The addition of isosorbide to starch allows a good plasticization and does not exhibit any problem regarding thermal degradation before 200 °C, as well as any common plasticized starch. The mechanical properties of starch plasticized with isosorbide depend on water content thus related to the air relative humidity. Indeed, glass transition temperatures of TPS are known to be lowered by the plasticization of water (Avérous, 2004; Mathew & Dufresne, 2002; Van Soest & Knooren, 1997). To characterize such aspect, DMTA analysis on samples conditioned till equilibrium at 0, 25, 50 and 75% R.H. and 23 °C have been performed from −30 to 120 °C. The storage modulus and tan δ data obtained were reported in Fig. 4a and b, respectively. For comparison, a reference curve of TPS plasticized with glycerol and conditioned at 50% R.H. was reported in the two plots.

The TPSI sample at 0% R.H. is very brittle and fragile at room temperature and these behaviors are evidenced by the high modulus and glass transition temperature (T_g), estimated from the maximum of tan δ, around 100 °C with a shoulder at 78 °C (Table 1). Unfortunately, because of the high fragility, it was not possible to perform the analysis at low temperatures. Conversely, when water is present, specimens are less brittle and the storage moduli are extremely reduced. Increasing the R.H. an evident tan δ peak appears at 36 °C for 25% R.H., it progressively shifts to lower temperatures once a higher amount of water is introduced (11 and −15 °C for 50 and 75% R.H., respectively). Probably the shoulder present at 78 °C in the dry sample shifts to lower temperatures due to the simultaneous presence of water that act as a further plasticizer. The presence of two tan δ maxima probably refers to two different phases. Similar phase separated structure with other polyols was also observed (Mathew & Dufresne, 2002). Usually an amorphous phase richer in plasticizer has a lower T_g that decrease with

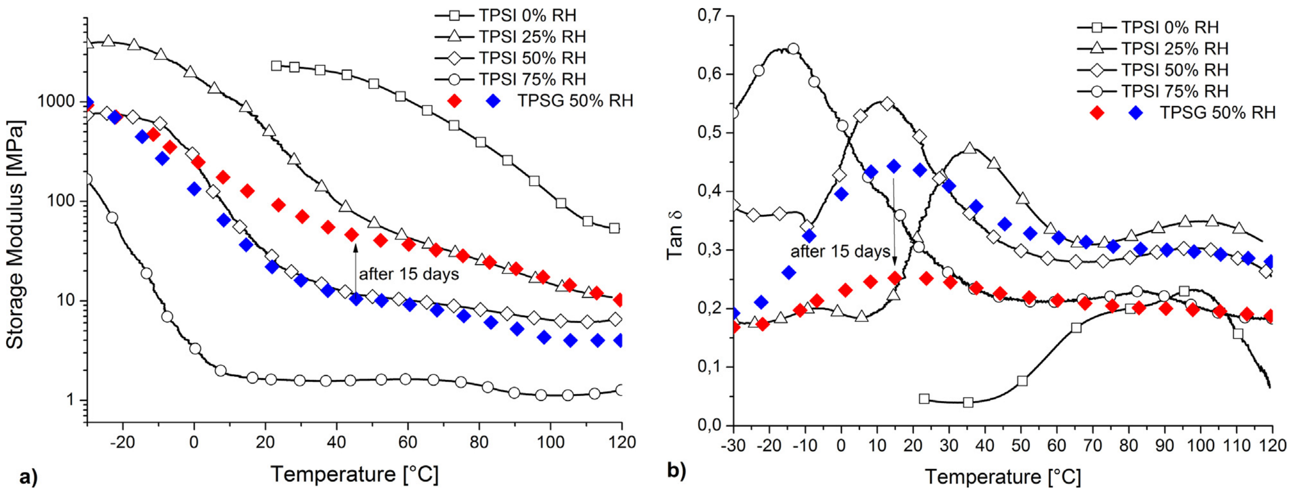

Fig. 4. TPSI storage modulus (E') (a) and tan δ (b) as function of temperature at different R.H. and reference TPSG at 50 R.H.

Table 1
DMTA data of TPSI and TPSG.

DMTA	TPSI				TPSG	TPSG 15 days
R.H. [%] ±1.5	0	25	50	75	50	50
E' at 30 °C [MPa]	2200 ± 150	210 ± 20	18 ± 2	1.6 ± 0.5	15 ± 2	71 ± 2
Max tan δ [°C]	78/99 ±2	36/100±2	11/97±2	−15/84±2	14/93±2	20 ±2

Table 2
Stress–strain and water uptake equilibrium data of TPSI.

	R.H. [%] ±1.5	25	50	75
Stress–strain analysis	E [MPa]	55 ± 3	3.2 ± 0.7	1.6 ± 0.2
	σ max [MPa]	1.13 ± 0.05	0.24 ± 0.03	0.10 ± 0.01
	ε at break [%]	28.0 ± 2.0	28.5 ± 2.0	23.2 ± 6.0
Water uptake	[%]	4.8 ± 0.5	8.5 ± 0.5	22.1 ± 0.5

the increase of R.H. while the higher tan δ maximum refers to the starch rich phase in which starch crystalline phase is included.

As it is possible to notice from Table 1, the storage modulus at 30 °C is around 210 MPa for 25% of R.H. This value is not normally suitable for applications where mechanical properties are required, but could be a good solution for other flexible applications. When humidity is raised to 50% R.H., the storage modulus falls down around one tenth of the previous value and to one hundredth at 75% of R.H. As comparison DMTA curve at 50% R.H. of TPS plasticized with glycerol was plotted in the same graph and the value of the storage modulus at room temperature is quite identical to TPSI. Moreover, DMTA performed after 9 months on TPSI in the same conditions gives no signs of the retrogradation and thus embrittlement typical of plasticized starch, while the TPSG has a change in the storage modulus after only 15 days, as evidenced in Fig. 4.

In addition, to have a complete correlation between the mechanical properties and the R.H., stress–strain curves have been performed after conditioning at different humidity conditions. These data were reported in Table 2 and one exemplificative stress–strain curve for each R.H. was plotted in Fig. 5. Unfortunately, for the extremely fragile behavior, was impossible to perform the test with dry specimens. In the other cases, a progressive decrease of E and σ max was evidenced when the water content was increased. As far as ε at break is concerned, and taking into consideration the experimental error, no particular differences were pointed out during the different tested conditions.

For a practical application the variation of the mechanical properties changing environmental conditions is very important and discriminating for the choice of a material. Mechanical properties were plotted as a function of the R.H. (Fig. S1). This graph related with the application environmental condition is useful to understand if the material could be mechanically suitable.

3.5. TPSI oxygen permeability

Protein and starch films are good oxygen barriers but highly depending from water content. The plasticizing and/or swelling effect of water on hydrophilic polymers results in an increased of permeability values. Variation of glass transition temperatures explains the effect of plasticizer on permeability properties. Water or other plasticizers increase the free volume in polymers, thereby increasing polymer chain mobility, hence permeability. In the literature some studies have been done in this field: Rico-Pena and Torres (Rico-Pena & Torres, 1990) examined the effect of R.H. on the OTR through methylcellulose–palmitic acid edible films. They found that no significant increase in OTR was observed between 0 and 57% R.H.; however, above 57% R.H., an exponential increase of OTR (that is linearly depending on OP) has been found. Another research by Hagenmaier and Shaw (1991) demonstrate an exponential increase in OP of shellac coatings with increasing R.H. and another one by Lieberman and Gilbert (1973) found that the increase from 63 to 93% of R.H. provokes a significant OP increase in collagen films.

In our case, from an overall consideration, no significant variations of oxygen permeability were found till 75% R.H., as reported in Fig. 6 and Table S3. However, over this R.H., an exponential increase was found. For this reason, an exponential function (Table S4) was used to fit the oxygen permeability data of plasticized starch films

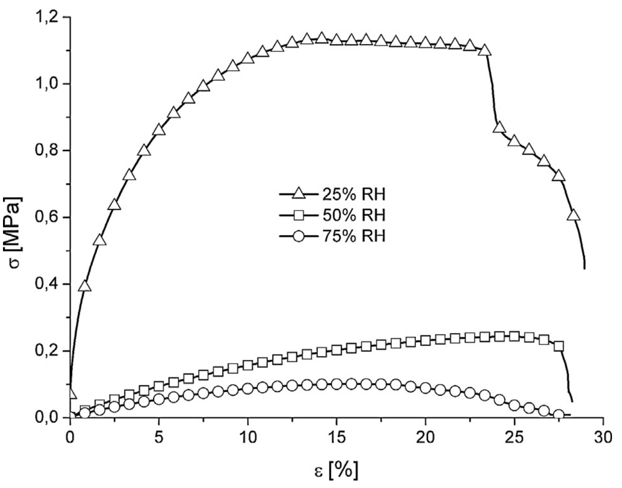

Fig. 5. TPSI stress–strain curves at different R.H.

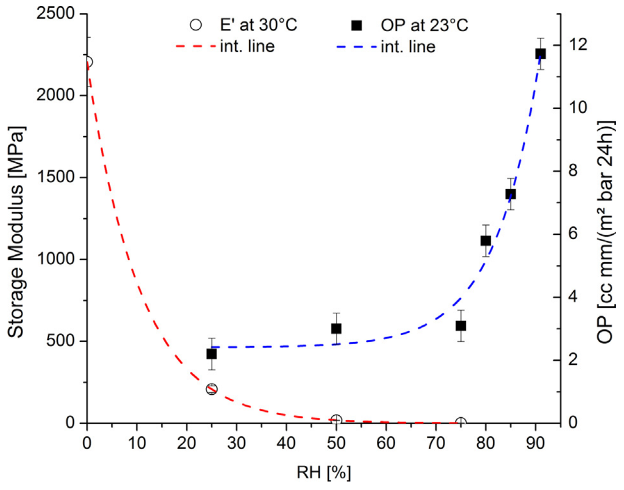

Fig. 6. Storage modulus and OP as a function of R.H. and their exponential fitting lines.

at increasing relative humidity conditions and reported as dotted curve in Fig. 6. These data are critical for modeling the behavior of packaging films for food products, having different water activities and/or stored under different relative humidity conditions. As already mentioned, one of the others key factors for the applications are mechanical properties. Therefore, a combined analysis where storage modulus is correlated with oxygen permeability values was reported in Fig. 6. Also for the storage modulus, the best exponential curve was plotted as dotted curve. The parameters for the fitting curve used were reported in Table S4.

The use of this starch-based films for the control of oxidation and/or respiration in food systems could be a promising area of research because the permeability is quite constant in the range 25–75% R.H. For what concern the mechanical properties under this range, these are very poor, but, at room temperature, the material is not brittle and very flexible. A possible application could be a flexible packaging that could also be edible. Outside 25–75% R.H. window, the material is unlikely utilizable for the excessive rigidity and fragility on one hand, or weakness on the other.

4. Conclusions

In the present study, isosorbide is used as innovative plasticizer for starch. Its effectiveness was assessed by XRD and DMTA analyses. This new bio-based material has been prepared by a semi-industrial extrusion process easily scalable for an industrial exploitation. Starch and plasticizer can be easily mixed manually before the extrusion process. The temperature profile necessary for the processing is about 20 °C lower than that employed for the classic glycerol plasticization, allowing energy savings. The obtained TPS is easily processable and film production from compression molding was proven. The collected data by thermogravimetry have shown that the plasticized starch is stable up to 200 °C in nitrogen as well as oxygen atmosphere like a common starch plasticized with glycerol. The mechanical properties and oxygen permeability of starch plasticized with isosorbide are dependent from water content related to the air relative humidity.

A study of this relationship was presented with the introduction of exponential fitting curve to close follow the experimental data. Through this evaluation, TPSI can be taken into account as material for several applications in the packaging field in the 25–75% R.H. range. After appropriate analyses, the material could also be used as edible film, opening a wide range of uses.

However, from the scientific point of view, the most important characteristic of this plasticizer is the missing of retrogradation, fact that normally occurs with glycerol and other plasticizer agents. Furthermore, in presence of a small quantity of moisture, TPSI is not brittle such as starch plasticized with other polyols (e.g. sorbitol). Thus, isosorbide is a plasticizer that forms a flexible and stable TPS with very few drawbacks.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.11.030.

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