Effects of plasticizers on the properties of oat starch films

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ARTICLE INFO

ABSTRACT

Oat starch films were prepared by casting using glycerol, sorbitol, glycerol–sorbitol mixture, urea and sucrose as plasticizers. The effects of these plasticizers on the microstructure, moisture sorption, water vapor permeability (WVP) and mechanical properties were investigated using films stored under a range of relative humidities. The plasticizer type did not affect significantly ($p \leq 0.05$) the equilibrium moisture content of films, except at 90% relative humidity (RH). Films without plasticizer adsorbed less water and showed higher WVP than plasticized ones, indicating the antiplasticizing effect observed in this work. In general, a decrease in stress at break and Young's modulus and an increase in strain at break were observed when RH increased in all film formulations. Films without plasticizer showed higher stress at break values than the plasticized ones and presented stable strain at break under a range of RH. Sucrose films were the most fragile at low RH while glycerol films were the most hygroscopic.

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1. Introduction

The environmental impact of the excessive amount of disposables consumed in contemporary society has been leading us to serious demands for biodegradable plastic materials made from renewable sources. The use of biopolymers, such as starch, instead of plastic polymers, for the production of such disposables can be an interesting solution; once the biopolymer can be much cheaper, quite abundant, biodegradable and even edible [1].

Starch consists primarily of branched and linear chains of glucose molecules, amylopectin and amylose, respectively. Amylose is a linear molecule with a few branches, while amylopectin is a highly branched molecule. Prevalence of amylose in starches yields a stronger film. The presence of branched structures of amylopectin generally leads to modifications of the mechanical properties of the film like for instance, the decrease of stress at break [2].

In the last years, several studies have been performed to analyze the properties of starch films produced from different botanical sources, such as corn [3], wheat [4], cassava [5,6], yam [7,8] and potato [9,10].

The addition of plasticizers to starch films helps to decrease its inherent brittleness by reducing intermolecular forces, increasing the mobility of polymer chains, decreasing the glass transition temperature of these materials and improving their flexibility. The plasticizers must be compatible with the film-forming polymers. Hydrophilic compounds, such as polyols (glycerol and sorbitol) are commonly used in starch films [11,12], but some sugars, amino acids and fatty acids [3,10,13] could also be employed.

The use of starch as raw material for films is somewhat limited, once the mechanical and barrier properties of such films dependent greatly on moisture [14]. It is observed that the films become brittle in dry atmosphere and lose strength and barrier properties in high humidity. Moisture sensitivity needs to be reduced if starch is to become an alternative to conventional plastics in industrial applications [10].

The presence of a hydrophobic component on starch matrix can improve water vapor sorption properties significantly. Some researchers have analyzed the effect of lipidic components on starch films to overcome moisture sensitivity [10,12] however they reported that separation of phases occurred in films were high amounts of lipids were added. Oat starch configures an interesting alternative for starch films because it contains about 1 to 3% of lipids in its native composition, a high value when compared with other common starches, additionally the lipid fraction in oat starch is complexed with amylose, which would prevent phase separation [15,16].

Therefore, the purpose of the present work is to analyze the effects of different plasticizers on microstructure, moisture sorption, water vapor permeability (WVP) and mechanical properties of oat starch films stored under a range of relative humidities.

2. Experiment

2.1. Materials

Oat starch was extracted according to Lim et al. [17] from oat flour provided by SL Cereais e Alimentos-Mauá da Serra, PR, Brazil. Ash,

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moisture and protein contents were determined according to the standard AACC methods. To determine the ash content, AACC method 08-01 was used and the samples were incinerated overnight in a muffle furnace at 600 °C [18]. Moisture content was determined using the 44-15A AACC method [19], the samples were dried in an oven at 105 °C until constant weight. Protein content was determined using the micro-Kjeldahl method, the 46-13 AACC method [20]. Lipids were determined according to Vasanthan and Hoover [21]. All of reagents used in the analyses were analytical grade.

2.2. Film preparation

Oat starch films were prepared by casting with different plasticizers: glycerol (20 g/100 g starch), sorbitol (25 g/100 g starch), 1:1 mixture of glycerol and sorbitol (23 g/100 g starch), urea (16 g/100 g starch) and sucrose (55.5 g/100 g starch). According to determined preliminary studies, the amount of plasticizer employed was the least possible to produce films without fissures and cracks. Table 1 shows the plasticizers selected for the study as well as their properties; the variation in molecular size and shape determined by the different chemical composition of each polymer provides opportunity to explore a variety of effects on the properties of the films.

Filmogenic solutions were prepared on Brabender Viscograph (OHG, Duisburg, Germany); for each experiment, the solution (2.7 g starch/100 g solution) was heated from 30 to 80 °C at a constant heating rate of 3 °C/min and maintained at 80 °C for 10 min, with regular shaking (75 rpm). The volume of starch suspension poured into the plates was calculated to obtain a constant weight of dried matter for 100 μm films. The starch suspensions were dried at 60 °C in a ventilated oven model TE-394-3 (Tecnal, Piracicaba, SP, Brazil) to constant weight. The obtained translucent films could be easily removed from the plate and were equilibrated at different relative humidities (11, 57, 76 and 90%) for 72 h at 25 °C, before being tested.

2.3. Films characterization

2.3.1. Thickness measurement

The thickness of the films was determined by a manual micrometer (Mitutoyo, São Paulo, Brazil) and measures were taken at 10 random positions of the film. The mean standard deviation of these measures was 5% of the average thickness.

2.3.2. Scanning electron microscopy (SEM)

SEM analyses were performed with a JEOL JSM 6360 electron microscope (Japan). Film pieces were mounted on bronze stubs using a double-sided tape and then coated with a layer of gold (40–50 nm), allowing surface and cross-section visualization. To obtain the cross-section the samples were prepared by immersion into liquid nitrogen in order to avoid deformation during fracture. All samples were examined using an accelerating voltage of 10 kV.

2.3.3. Moisture sorption characteristics

2.3.3.1. Sorption isotherms. Film specimens (30×30 mm) were pre-dried for 20 days over anhydrous calcium chloride ($CaCl_2$) and then placed at 25±2 °C over saturated salt solutions in separated desiccators under desired relative humidity conditions (11, 32, 57, 76 and 90% RH) [23]. Each film specimen was weighted at regular intervals (minimum 1 h and maximum 6 h), and when two consecutive measures were equal, it was assumed that equilibrium moisture content was reached; what under the above conditions occurred after a period of 3 days. Equilibrium moisture content was calculated from the increase in mass of the dried sample after equilibration at a given RH. All tests were conducted in triplicate. GAB (Guggenheim–Anderson–de Boer) model was used to fit starch film sorption isotherm data, and monolayer values were calculated from the equations [24]. GAB isotherm model can be expressed as follows: $M = m_0CKa_w/(1-Ka_w)(1-Ka_w+CKa_w)$, where M is the equilibrium moisture content at a water activity (a_w), m_0 is the monolayer value (g water/g solids) and C and K are the GAB constants.

2.3.3.2. Moisture curve and rates. Film specimens (30 mm×30 mm) were pre-dried for 20 days over anhydrous calcium chloride ($CaCl_2$) and then were placed at 25±2 °C over saturated salt solutions in separated desiccators, under desired relative humidity conditions (11, 32, 57, 76 and 90% RH) [23]. Weights of film specimens were taken as a function of time and their moisture content was determined by oven drying at 105 °C. Moisture adsorption data were fitted to a mathematical model suggested by Peleg [25]: $M(t) = M_0 + (t/(k_1 + k_2t))$, where $M(t)$ is the moisture after time, M_0 is the initial moisture content and k_1 is the Peleg rate constant (h/(g water/g solids)) and k_2 is the Peleg capacity constant (g solids/g water). All tests were conducted in triplicate.

2.3.4. Water vapor permeability (WVP)

WVP tests were conducted using ASTM (1996) [26] method E96 with some modifications. Each film sample was sealed over a circular opening of 0.00181 m^2 in a permeation cell that was stored at 25 °C in a desiccator. To maintain a 75% RH gradient across the film, anhydrous calcium chloride (0% RH) was placed inside the cell and a sodium chloride saturated solution (75% RH) was placed in the desiccator. The RH inside the cell was always lower than the outside, and water vapor transport was determined from the weight gain of the permeation cell. After steady state conditions were reached (about 2 h), eight weight measurements were made over 24 h. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. The slope of each line was calculated by linear regression ($r^2 > 0.99$) and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (g/s) divided by the cell area (m^2). After the permeation tests, film thickness was measured and WVP (g Pa^{-1} s^{-1} m^{-1}) was calculated as WVP=[WVTR/$S(R_1-R_2)$]d, where S is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1, the RH in the desiccator, R_2, the RH in the permeation cell and d is the film thickness (m). Under these conditions, the driving force [$S(R_1-R_2)$] was 1753.55 Pa.

2.3.5. Mechanical properties

Oat starch films were equilibrated at different relative humidities (11, 57, 76 and 90%) for 48 h at 25 °C before being tested. The tensile properties were determined using a TA.TX2i Stable Micro Systems texture analyzer (Surrey—England) in accordance with ASTM D-882-91 method [27]. The samples were clamped between pneumatic grips so force (N) and deformation (mm) could be recorded using a extension rate of 50 mm min^{-1}, with initial distance between the grips equal 50 mm. The parameters determined were: stress at break (MPa), strain at break (%) and Young modulus (MPa). Five film specimens (100 mm×25 mm) of each formulation were used in the analysis.

Table 1
Plasticizers selected for study and their properties

Plasticizer	Formula	Chain shape	Molecular weight (g/mol)	Hydroxyls number	Concentration g/100 g starch	Concentration mol/100 g starch
Glycerol	$C_3H_8O_3$	Straight	92	3	20.0	0.217
Sorbitol	$C_6H_{14}O_6$	Straight	182	6	25.0	0.137
Glycerol:Sorbitol 1:1	–	Straight	–	–	23.0	0.125:0.063
Urea	$CO(NH_2)_2$	Straight	60	0	16.0	0.267
Sucrose	$C_{12}H_{22}O_{11}$	Ring	342	8	55.5	0.162

Adapted from Sothornvit and Krochta [22].

2.3.6. Statistical analysis

Statistica software (Oklahoma, USA, 1996) version 5.1 was used for all statistical analysis. Means, standard deviation and Tukey test for means comparison were applied. The significance level used was 0.05.

3. Results and discussion

3.1. Chemical composition of oat starch

The chemical composition of oat starch was: moisture (10.71%± 0.01%), ash (0.32±0.01%), protein (0.41±0.01%) and lipids (1.36± 0.02%). The lipid content in oat starch was higher when compared with other botanical sources, which agrees with data reported by other authors studying starches from corn (0.29%) [28], yam (0.27%) and cassava (0.28%) [29]. According to Wang and White [30], most of the lipids are present inside native starch granules in the cavity of amylose helix, which represents an advantage for film production, because it prevents phase separation.

3.2. Scanning electron microscopy (SEM)

SEM observations did not show any differences among samples containing different kinds of plasticizers. Plasticized films presented smooth surfaces without pores, and with compact structure (Fig. 1a, c, d and e), although films plasticized with sorbitol (1b), displayed some small pores on their surface. The unplasticized sample (Fig. 1f) showed a less compact structure, with large pores. The homogeneity of the matrix in films is a good indicator of their structural integrity, for this reason, it can be expected that the plasticized films will show better mechanical properties than the unplasticized ones [7,12].

3.3. Moisture sorption characteristics

3.3.1. Sorption isotherms

The moisture sorption isotherms of oat starch films are displayed in Fig. 2 while GAB model parameters are shown in Table 1. In general, the moisture sorption isotherms exhibited a sigmoid shape and were influenced by the plasticizer type. At 11% RH all film formulations presented low equilibrium moisture contents (<0.66 g water/g solids) and when RH increased, moisture content also increased in all film formulations. At 57% RH, urea films showed the lowest equilibrium moisture, while at 90% RH, unplasticized films and glycerol films adsorbed less and more water respectively (Fig. 2). The presence of lipids probably overcomes the effect of the plasticizers on oat starch films explaining why the plasticizer type did not affect the equilibrium moisture content of oat starch films as much as expected. According to Petersson and Stading [10], the presence of a hydrophobic component on starch matrix can improve the moisture sorption characteristics significantly.

Urea films presented the lowest monolayer value (0.033 g water/g solids) (Table 2). According to Ma and Yu [31] this could be explained by the fact that the interaction between starch and urea is stronger than the interaction between starch and polyols such as glycerol and sorbitol. Hollo et al. [32] reported that starch–urea interaction could originate a complex with low hydrophilicity.

The highest monolayer value (0.057 g water/g solids) was observed when glycerol was incorporated (Table 2).This result agrees with reports by other authors, proposing that glycerol, as a small molecule with high water affinity, is a more effective plasticizer than other polyols, such as sorbitol [5,12,33,34].

Unplasticized films presented higher monolayer value (0.052) than sorbitol (0.049), urea (0.033) and sucrose (0.041) films (Table 2). Similar observation was reported by other authors working with wheat starch–sorbitol films [35] and with amylose and amylopectin glycerol films [36]. They reported that plasticizers, when employed in small concentrations (below 27%), can be strongly bound with starch,

exerting antiplasticizing effect Instead. Mali et al. [5] observed the same trend for sorbitol films stored at RH below 33%.

3.3.2. Moisture curve and rates

Moisture adsorption curves of oat starch films are shown in Fig. 3. Moisture adsorption was faster during the initial stages of the storage and slowed down with the time, until the moisture content of oat starch films reached a plateau, indicating that equilibrium with the storage RH was reached. Moisture equilibrium time was proportional to storage RH; films stored at 90% needed more time to reach the equilibrium (Fig. 3).

To improve the investigation about effects of different kinds of plasticizer on water sorption behavior, the moisture content data obtained at specific times were fitted to a Peleg model [25]. The Peleg parameters k_1 and k_2 are shown in Table 3. As k_1 is a constant related to mass transfer, the lower k_1, the higher the initial water adsorption rate; k_2 is a constant related to maximum water adsorption capacity and the lower the k_2, the higher the adsorption capacity [37].

Glycerol plasticized films stored at 11 and 32% RH had lower k_1 values (Table 3), indicating that these films adsorbed water at a higher initial rate. At RH values above 57%, unplasticized films adsorbed water faster (lower k_1 value) and when stored at 11 and 32% RH showed lower k_2 values (indicating lower water adsorption capacity), which was probably due to the antiplasticizing effect. As reported in literature [7,35,36,38], the antiplasticizing effect occurs at low RH when low concentrations of plasticizer are employed. The antiplasticizing effect can be observed in isotherms data already discussed.

Urea, sucrose and sorbitol films that presented the lowest monolayer values in isotherms data, showed lower adsorption rate and capacity than glycerol films in all RH conditions; with close k_1 and k_2 values that were alternated depending on the storage conditions (Table 3).

Comparing the polyols (glycerol and sorbitol), glycerol films had the lowest k_1 and k_2 values (Table 3), indicating that these films adsorbed water faster and in higher amounts during its storage. Films with mixtures of glycerol:sorbitol generally showed intermediate k_1 and k_2 values (Table 3). According to Sothornvit and Krochta [22], molecular differences between glycerol and sorbitol are probably responsible for the different sorption rate of films plasticized with them. Glycerol and sorbitol molecules are similar, both characterized by a straight chain, nevertheless, glycerol molecule is smaller (molecular weight equal 92) and carries three hydroxy groups while sorbitol molecule (molecular weight equal 182) carries six hydroxy groups. Although, theoretically, sorbitol should be more hydrophilic due to the presence of a higher number of hydroxy groups, in practice glycerol presented higher water affinity demonstrated by adsorption and desorption isotherms [39]. Since between the two polyols, sorbitol is the one that presents molecular structure more similar to the molecular structure of glucose units, it is plausible that sorbitol interacts better with polymeric starch chains. This would explain why, sorbitol-containing films presented higher intermolecular forces and showed a lower capacity to interact with water [12].

3.4. Water vapor permeability (PVA)

Table 4 shows WVP values of plasticized and unplasticized starch films. WVP of plasticized films were significantly lower ($p < 0.05$) than unplasticized ones. In general, the use of a plasticizer avoids cracking of films during handling and storage, increasing gas, water vapor and solute permeability of the films [6,7,11,12]. In this work, the opposite effect was observed, probably because of the antiplasticizing effect exerted by these plasticizers at the experimental conditions in which moisture sorption data were obtained.

WVP values of plasticized films ranged from 2.317 to 4.211×10^{-12} g $m^{-1} s^{-1} Pa^{-1}$ (Table 4) and among the plasticized films, sucrose showed the lowest value (Table 5). Sucrose molecules could form crystals that
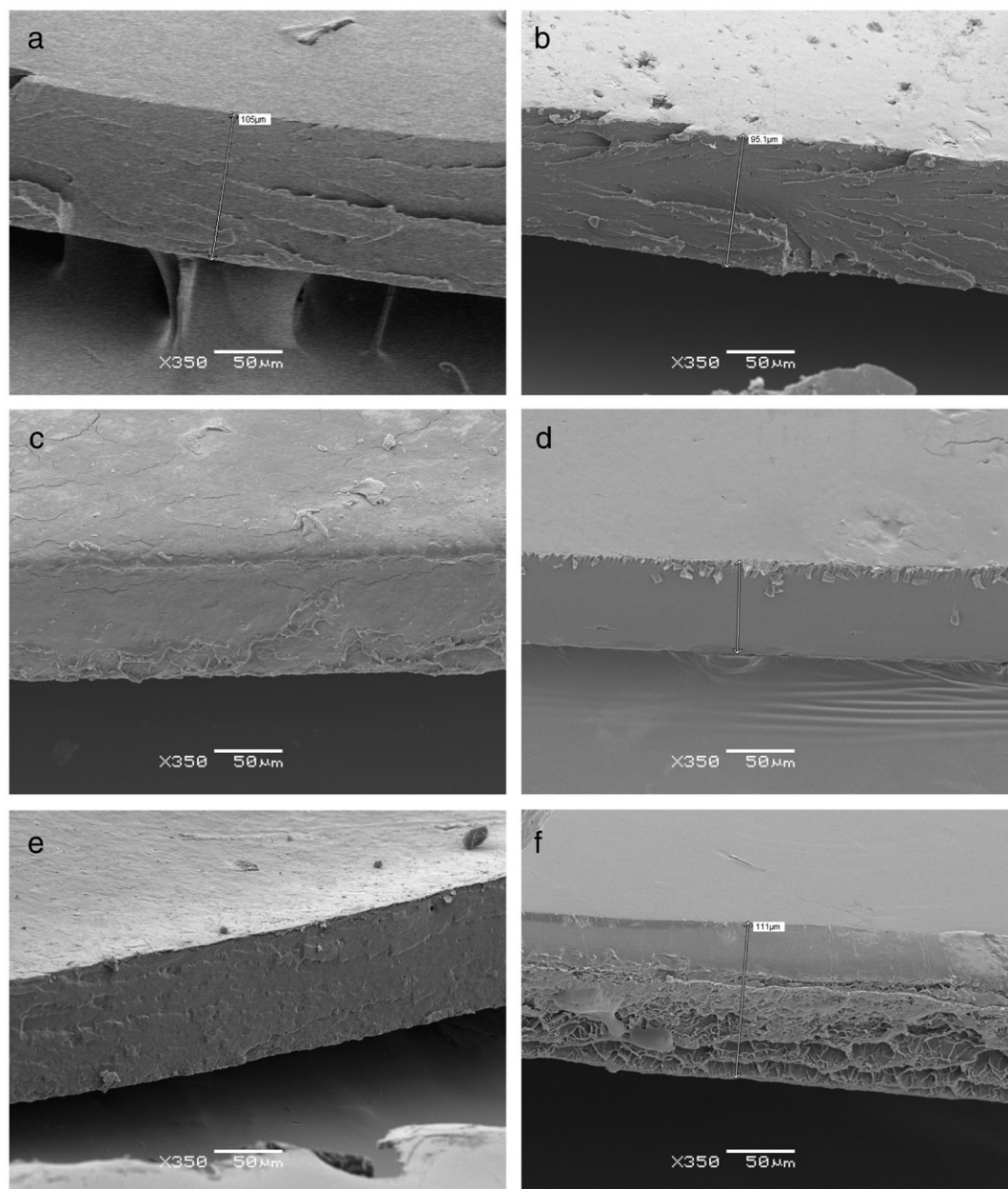
Fig. 1. SEM micrographs of cross-section of oat starch films plasticized with: (a) glycerol, (b) sorbitol, (c) urea, (d) sucrose, (e) glycerol:sorbitol 1:1 and (f) unplasticized films. Magnification: 50 μm between marks.

would affect the film-forming matrix, originating less permeable films [40]; this effect was also observed in this work. Others authors reported that the crystalline zones act as effective barriers to water vapor permeation, therefore the permeability of starch films decreases when the degree of crystallinity increases [12].

Among the plasticized films, glycerol films showed the higher WVP value (Table 4) according to what was expected, once glycerol is an effective plasticizer with a high capacity to interact with water, facilitating its solubilization and permeation through the film [5,11,12].

Oat starch films had lower WVP values than synthetic polymers, such as cellophane (84×10^{-12} g m^{-1} s^{-1} Pa^{-1}) and higher than low-density polyethylene (LPDE) (0.36×10^{-12} g m^{-1} s^{-1} Pa^{-1}). However, the permeability of oat starch films was lower when compared with biodegradable films such as cassava starch plasticized with glycerol (400×10^{-12} g m^{-1} s^{-1} Pa^{-1}) [29] and queratin plasticized with glycerol (39×10^{-12} g m^{-1} s^{-1} Pa^{-1}) and sorbitol (516×10^{-12} g m^{-1} s^{-1} Pa^{-1}) [35]. The presence of lipids in higher contents in oat starch compared
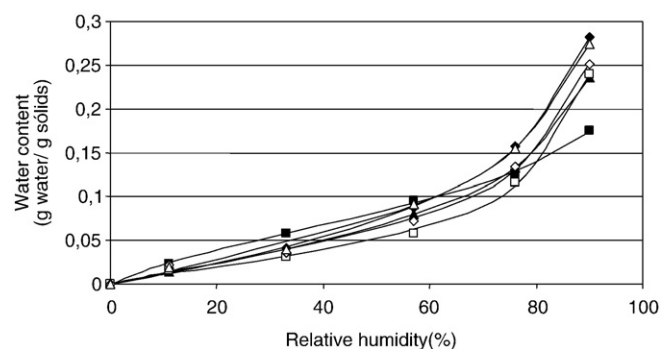

Fig. 2. Sorption isotherms of oat starches films at 25 °C with different plasticizers: unplasticized (■), glycerol (♦), sorbitol (▲), urea (□), sucrose (◊) and glycerol:sorbitol (△). The lines were derived from GAB model.

Table 2
GAB model[a] for oat starch films with different plasticizers

Plasticizer	GAB parameters			
	m_0	C	k	R^2
Without	0.052	5.82	0.711	0.99
Glycerol	0.057	2.72	0.904	0.99
Sorbitol	0.049	3.11	0.893	0.99
Urea	0.033	4.21	0.964	0.99
Sucrose	0.041	4.75	0.938	0.99
Glycerol:sorbitol	0.054	2.74	0.892	0.99

[a] $M = m_0 C K a_w / (1 - K a_w)(1 - K a_w + C K a_w)$, where M is the equilibrium moisture content at a water activity (a_w), m_0 is the monolayer value (g water/g solids), and C and K are the constants.

with other starches could probably explain these lower permeability values, since the lipids seem to exert a water vapor barrier effect.

3.5. Mechanical properties

3.5.1. Stress at break

As shown in Table 5, a decrease in stress at break was evidenced when RH increased in all formulations. Films stored under higher RH presented higher equilibrium moisture content (Fig. 2), which resulted on a plasticizing effect acting as a mobility enhancer. The low molecular weight of water molecules leads to a large increase in molecular mobility of amorphous and partially crystalline polymers due to an increased free volume, resulting in a weak starch matrix. Similar trend was observed by other authors [3,5,8,29,41].

Unplasticized films showed significantly higher stress at break values than all plasticized films in all RH conditions (Tukey test, $p \leq 0.05$) (Table 5). This behavior could be related to the structural modifications of starch network when plasticizer was incorporated. The matrix of the film becomes less dense, facilitating movements of polymer chains under stress, therefore decreasing the film resistance [5].

At 11% RH, sucrose films showed significantly lower values for stress at break than other plasticized films. According to Sothornvit and Krochta [22], the bulky rings of α-D-glucose and β-D-fructose that form sucrose molecules, restrict the effective interaction between sucrose and polymer chains, as opposite to what occurs with molecules formed by straight chains, such as glycerol, sorbitol and urea, in which the interaction with polymer chains has less stereo restriction. Another factor to be considered could be the crystallization process of sucrose chains; in low water contents, sucrose molecules can be associated forming crystals that would affect the film-forming matrix [40]. When RH increased from 57 to 90%, stress at break of all plasticized films did not vary significantly (Tukey test, $p \leq 0.05$) (Table 5).

In this work, glycerol and sorbitol films did not differ significantly (Tukey test, $p \leq 0.05$) in concerns to stress at break values (Table 5). These results were not in accordance with other authors [5,12,22,29,42] who reported that glycerol films had lower stress at break values than sorbitol, because glycerol presented a more efficient plasticizing effect. In this work the difference between glycerol (20 g/100 g starch) and sorbitol (25 g/100 g starch) contents employed in film formulations could explain the results, since the amount of glycerol used was not sufficient to overcome sorbitol plasticizing effect on stress at break of oat starch films.

According to Chuy and Bell [43], urea presents a much higher ability to form hydrogen bonds with starch chains than glycerol and sorbitol, producing more resistant films. In this work, the mentioned results were not confirmed and the three plasticizers produced similar effect on stress at break of starch films (Table 5).

Films produced in this work and stored at 57% RH showed stress at break between 17 and 44 MPa. These results are comparable with the

ones obtained when using conventional materials, such as high-density polyethylene (7–16 MPa) and low-density polyethylene (26 MPa) [44].

3.5.2. Strain at break

Strain at break of unplasticized films was not affected by different RH conditions (Table 5), the result was thirty times lower than the one obtained from plasticized films when stored at 90% RH.

From 11 to 57% RH all plasticized and unplasticized films did not differ significantly (Tukey test, $p \leq 0.05$) in its strain at break, with values below 10% of elongation (Table 5). At 76% RH, these values largely increased for plasticized films, reaching to 137%. At 90% RH, strain values practically stabilized (Table 5), probably due to the stability of oat starch films to water adsorption under the mentioned RH condition (Fig. 2).

The effects of different plasticizers were evident at RH > 76% (Table 4), sucrose films had higher values of strain at break (137%) than all other films and there was no significant variation on the results obtained from the other films. Certainly, under these RH conditions, the moisture
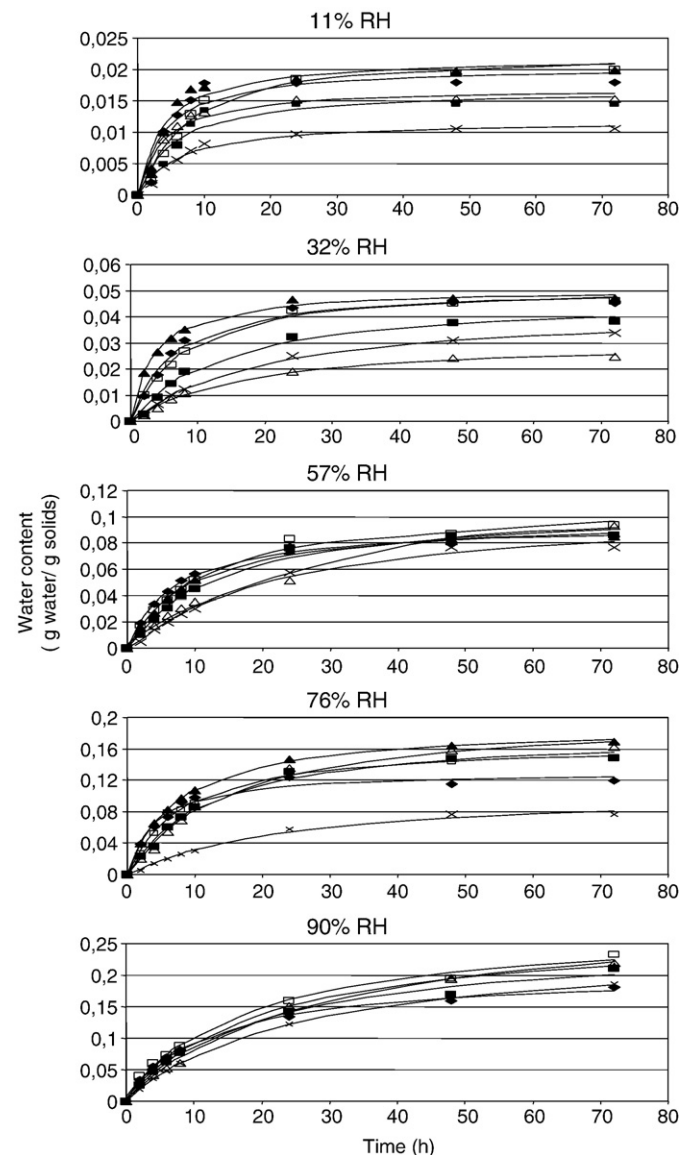

Fig. 3. Moisture sorption curves of oat starch films at various RH: unplasticized (♦), glycerol (▲), sorbitol (×), urea (□), sucrose (△) and glycerol:sorbitol (■). Lines are derived from Peleg's model [21]. Coefficient of variation of analysis was 10%.

Table 3
Constant values (k_1 and k_2) and coefficient of determination (R^2) for sorption curve equations (Peleg model)[a] of oat starch films at different RH conditions

	Plasticizer type					
	Without	Glycerol	Sorbitol	Urea	Sucrose	Glycerol:sorbitol
11% RH						
k_1	168.99	158.80	472.05	290.95	203.05	288.31
k_2	43.61	43.69	81.13	43.89	56.34	56.92
R^2	0.95	0.97	0.99	0.98	0.98	0.96
32% RH						
k_1	113.69	69.11	417.39	145.72	477.29	242.41
k_2	18.94	19.68	22.74	19.71	31.46	20.56
R^2	0.99	0.99	0.99	0.99	0.99	0.99
57% RH						
k_1	70.59	91.82	200.22	99.89	260.29	114.87
k_2	10.51	9.98	9.17	8.89	7.73	9.10
R^2	0.99	0.99	0.99	0.99	0.99	0.99
76% RH						
k_1	30.23	40.24	45.42	45.33	66.93	60.05
k_2	7,48	5.26	5.85	6.32	4.80	5.41
R^2	0.99	0.99	0.99	0.99	0.99	0.99
90% RH						
k_1	60.25	74.30	99.94	67.71	92.25	77.96
k_2	4.96	3.70	4.02	3.66	3.29	3,94
R^2	0.99	0.99	0.99	0.99	0.99	0.99

[a] $M(t) = M_0 + (t/k_1 + k_2 t)$, k_1 in h/(g water/g solids) and k_2 in g of solid/g water.

Table 5
Mechanical properties of oat starch films

RH condition	Plasticizer type					
	Without	Glycerol	Sorbitol	Urea	Sucrose	Glycerol:sorbitol
Stress at break (MPa)						
11% RH	49 Aa (4)	39 Ba (4)	38 Ba (4)	40 Ba (3)	14 Ca (2)	37 Ba (4)
57% RH	44 Aa (6)	17 Bb (2)	23 Bb (5)	25 Bb (2.4)	15 Ba (3)	20 Bb (4)
76% RH	30 Ab (3)	3 Cc (0.6)	6 Bc (0.9)	3 Cc (0.5)	3 Cb (0.6)	3 Cc (0.6)
90% RH	17 Ac (2)	2 Cc (0.2)	3 Bd (0.5)	2 Cc (0.2)	2 Cb (0.2)	3 Bc (0.4)
Strain at break (%)						
11% RH	3 Aa (0.1)	3 Ac (0.2)	3 Ac (0.5)	3 Ab (0.5)	1 Cc (0.1)	2 Bc (0.3)
57% RH	3 Ca (0.5)	6 Bb (0.5)	6 Bb (0.9)	4 Cb (0.7)	3 Cb (0.4)	10 Ab (0.1)
76% RH	3 Ba (0.4)	100 Aa (20)	111 Aa (18)	119 Aa (23)	137 Aa (27)	107 Aa (20)
90% RH	4 Ba (0.6)	111 Aa (15)	117 Aa (14)	130 Aa (23)	130 Aa (15)	116 Aa (17)
Young's modulus (MPa)						
11% RH	1451 Aa (198)	1338 Aa (17)	1366 Aa (243)	1556 Aa (172)	678 Ba (85)	1218 Aa (232)
57% RH	1283 Aa (105)	692 Bb (67)	682 Bb (83)	785 Bb (137)	574 Ba (102)	628 Bb (118)
76% RH	1161 Aa (207)	27 Cc (4)	47 Bc (4)	15 Cc (3)	21 CDb (4)	43 Bc (8)
90% RH	543 Ab (48)	6 Dd (1)	15 Bd (2)	1 Fd (0.2)	4 Ec (0.4)	10 Cd (2)

Means at same line with different capital letters are significantly different (Tukey test, $p \leq 0.05$); means at same column with different small letters are significantly different (Tukey test, $p \leq 0.05$). Numbers in parentheses are the standard deviation of each analysis.

content was ideal to inhibit sucrose crystallization and enhance the plasticizer effect, increasing molecular mobility of starch chain, and promoting the interaction between starch and sucrose chains.

Strain at break values of oat starch films plasticized with glycerol: sorbitol mixture (9%) were much lower than the values obtained from synthetic films, such as high-density polyethylene (300%) and low-density polyethylene (600%) [44]. Results from films plasticized with sucrose were also lower (137%) but still comparable to the ones obtained from synthetic films.

3.5.3. Young's modulus
Young's modulus or elastic modulus is the fundamental measure of the film stiffness, which increases when Young's modulus increases. In general, increasing RH resulted in films with lower Young's modulus and then more flexible (Table 5).

Young's modulus of unplasticized films was not affected by different RH conditions, although under 90% RH a lower value was observed (Table 5). These results were in agreement with stress at break values. These unplasticized films were more rigid than the plasticized ones; below 76% RH Young's modulus values were 24–77 times higher, and below 90% RH 36–543 times higher than the values obtained from the plasticized ones, which do not differ among them under these conditions. The increment of the flexibility in the presence of a plasticizer in hydrophilic films has been reported previously [5,45].

Table 4
Water vapor permeability of oat starch films

Plasticizer type	WVP×10^{-12} (g m^{-1} s^{-1} Pa^{-1})[a]	Coefficient of variation (%)
Without	10.015a	0.01
Glycerol	4.211b	3.04
Sorbitol	3.117d	3.83
Urea	3.828b,c	1.80
Sucrose	2.317e	4.56
Glycerol:sorbitol	3.697c	6.36

[a] Means at same column with different letters are significantly different (Tukey test, $p \leq 0.05$).

This behavior could be related to structural modifications of the starch network when plasticizer was incorporated, causing the film matrix to become less dense and facilitating the movements of the polymer chain under stress, consequently improving the flexibility.

At 11% RH, Young's modulus was not affected by different plasticizers, with values ranging from 1218 to 1556 MPa, except for sucrose films that showed lower values (678gMPa) (Table 5). The sucrose effect can be explained, as already discussed in this work, through sucrose molecule structure, which makes more difficult an efficient interaction with polymeric chains compared to straight chains of other plasticizers [22].

4. Conclusions

The presence of lipids in higher contents on oat starch compared to other starches could act as a water vapor barrier, resulting in a smaller variation of the equilibrium moisture contents in all film formulations under varied relative humidities and, thus, the plasticizer type would not affect significantly the properties of oat starch films. WVP of plasticized films were lower than those of unplasticized ones, this result was an indication of antiplasticizing effect observed in this work. In general, a decrease in stress at break and Young's modulus and an increase in strain at break were evidenced when RH increased. Sucrose films were more fragile than others under low RH conditions, but under RH of 76 and 90% sucrose films showed resistance comparable to the resistance of other plasticized films. Urea did not have the expected reinforcing effect over the starch matrix; it was observed that urea plasticized films and polyol films had similar mechanical properties.

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