Effects of production process and plasticizers on stability of films and sheets of oat starch

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ABSTRACT

The main disadvantage of biodegradable starch-based films is their hydrophilic character, which leads to low stability when these materials are submitted to different environmental conditions. The higher lipid content (1.36%) of oat starch compared to other traditional starches could impart more hydrophobic characteristics to its films, thereby increasing stability. The objective of this work was to investigate the behavior of oat starch films (produced by casting) and sheets (produced by extrusion), plasticized with urea, glycerol or sorbitol, and conditioned at 11, 57, 76 and 90% relative humidity (RH). In general, the increase of RH results in a decrease of stress and an increase of strain at break, independent of the type of plasticizer. The Tg of materials plasticized with polyols was similar. The extruded sheets were more permeable to water vapor than the casted films. Films containing urea presented a relative crystallinity (5.14%) four times lower when compared with the other films, but the same behavior was not observed for sheets. The lipid content of oat starch was not high enough to avoid altering of mechanical properties as a function of RH. When the two processes (*casting* and extrusion) applied for materials production were compared, similar trends were observed on the final effects.

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1. Introduction

The environmental impact caused by the excessive quantity of non-degradable waste materials discarded every day is a matter of great concern. This reality is stimulating a great R&D effort to develop new biodegradable packing materials that can be manufactured with the utilization of environmentally friendly raw materials [1].

Among the natural polymers, starch has been considered as one of the most promising candidates for future materials because of its attractive combination of price, abundance and thermoplastic behavior, in addition to biodegradability. Starch-based materials have poor mechanical properties, however, and particularly poor elongation (around 6%) at ambient conditions. Thus, the incorporation of a plasticizer is required to overcome the brittleness of these materials. Plasticizers reduce intermolecular forces and increase the mobility of polymer chains, decreasing the glass transition temperature (T_g) and improving flexibility [2].

The main disadvantage of biodegradable starch-based films is their hydrophilic character, which leads to low stability when these materials are submitted to different environmental conditions [3]. Thus, oat starch is an interesting alternative to starch films because it consists of about 1 to 3% lipids in its native composition, a high value when compared with other starches sources [4], which might contribute to the production of materials that could be stable and resistant to environmental changes.

The utilization of lipids to reduce the hydrophilic characteristics of starch films was studied by Petersson and Stading [5]. However, a phase separation occurred due to the *incompatibility* of the components. As in oat starch the lipids are naturally complexed to amylose, which would prevent phase separation, resulting in a reduction of the hydrophilic characteristics of the materials.

Biodegradable materials can be produced by casting, extrusion, thermomolding, injection, sheeting and blowing [1,6–8]. The ideal processing to make the production of plastics based on biopolymers feasible seems to be the utilization of the same extrusion technology that is used today in the production of plastics based on synthetic materials. Extrusion has the advantage of being a low cost, continuous and versatile production system [9].

Although casting has been extensively used in laboratory studies, because it not requires specific equipment and consumes less raw materials, there is a strong disadvantage concerning industrial scale-up. Thus, extrusion seems definitely to have advantages over casting, being a more attractive process to produce biofilms.

The aim of this work was to investigate the properties of biodegradable materials based on oat starch, combined with different plasticizers and produced both by casting and by extrusion.

2. Experimental section

2.1. Materials

The source of oat starch was regular whole oat flour, supplied by SL Alimentos Ltda (Brazil). Starch separation was done according to the alkaline pH low shear method, established by Lim et al. [10]. All reactants used in the analytical determinations were analytical grade.

2.2. Films and sheets production

2.2.1. Films

Films were produced by casting using glycerol (20% w/w starch or 0.217 mol/100 g starch), sorbitol (25% w/w starch or 0.137 mol/100 g starch) and urea (16% w/w starch or 0.267 mol/100 g starch) as plasticizers. As high quantities of hydrophilic plasticizers increase the permeability and water sorption of biofilms [11], all the plasticizers were tested in preliminary assays to determine the necessary minimum levels to be added in each filmogenic solution, aiming to produce flexible and crackless films.

Starch dispersions (2.7% w/v) were heated under agitation (75 rpm) in a Brabender Pt 100 Visco-Amylo-Graph at a rate of 3 °C/min up to 80 °C and kept at this temperature for 10 min. The filmogenic solutions were spread over an acrylic plate to obtain 100 μm thick films. Material was dried to a constant weight, at 60 °C, in a hot air circulation oven.

2.2.2. Sheets

Sheets were produced in two extrusion steps, plus a final sheeting step. The oat starch and plasticizer (20% glycerol, or 25% sorbitol, or 16% urea w/w starch) were mixed with water to 20% moisture (w/w). After 24 h at 4°C, the samples were extruded in a single screw extruder (Beutelspacher S.A., Mexico) assembled with the following characteristics: L/D 24.1, ø 9 mm barrel, 80 rpm screw rotation, four heating zones (50, 110, 110, 80 °C) and a circular hole (ø 1 mm) die. The obtained pellets were extruded a second time in a larger machine, with ø 30 mm barrel and a rectangular (200 mm wide × 1 mm thick) die, to produce extruded sheets. Extrusion temperatures of this step varied according to each plasticizer (Table 1). The thickness of the extruded sheets was reduced in a four rolls plastic sheeter to obtain the final sheets. When using glycerol as the plasticizer, final sheets were, on average, 684 μm thick. For sorbitol and urea, the average thicknesses were 1001 and 1216 μm, respectively. This difference in thickness is inherent to the way the components are structured in each polymeric matrix.

2.3. Film characterization

2.3.1. Thickness measurements

Thickness was measured with a manual micrometer (Mitutoyo, Brazil) with an accuracy of ± 1 μm. Measurement was performed at ten different points.

2.3.2. Mechanical properties

Tensile properties were determined in a Texture Analyser TA-TX2i (Surrey, England) using ASTM D882-91 standard method [12] for films and ASTM D638M-93 standard method [13] for sheets. The difference in methodology is related to the thickness of the materials. The parameters determined were stress at break (MPa) and strain at break (%). Prior

to analysis, materials were conditioned in 11, 57, 76 and 90% relative humidity (RH), at 25 °C, for 48 h. Tests were performed with the utilization of 25 samples for each condition.

2.3.3. Moisture

Moisture of films and sheets, conditioned at different RH (48 h), was determined according with the 925.10.AACC method [14].

2.3.4. Water vapor permeability (WVP)

WVP (g Pa^{-1} s^{-1} m^{-1}) was determined according to ASTM E96-95 method [15]. The samples, sealed with paraffin in permeation cells containing anhydrous calcium chloride, were put in desiccators with 75% RH, at 25 °C. Weighing was done at each hour, for 24 h. Data were recorded in a weight gain vs. time graph. The coefficient of the straight line, obtained by linear regression, was determined, and the water vapor transmission rate was calculated (WVT=$g/t \cdot A$), where, g/t is the coefficient of the straight line and A is the permeation area (m^2). WVP was calculated using the equation WVP=(WVT·x)/ΔP, where x is the average thickness of the material and ΔP is the difference of vapor pressure of the environment containing anhydrous calcium chloride (0% RH) and NaCl saturated solution (75% RH). Tests were conducted in quadruplicate.

2.3.5. Thermal properties

The films were analyzed in a TMDSC (Temperature Modulated Differential Scanning Calorimeter) Q100 (TA Instruments, USA) under an N_2 atmosphere. Samples (2.5 mg), conditioned for 7 days at 64% RH, were weighed and sealed in aluminum capsules. An empty capsule was used as a reference. Samples were analyzed between − 40 and 150 °C, at a heating rate of 3 °C/min. The amplitude of modulation was ± 0.5 °C, over 40 s. T_g was calculated as the inflection point of the baseline. The sheets were analyzed in a conventional DSC model 2010 (TA Instrument, USA) between 10 and 180 °C, at a temperature increase rate of 10 °C/min.

2.3.6. X-Ray diffraction

Assays were done in a model 2100 diffractometer (Rygaku, Netherlands), using copper Kα radiation (λ = 1543), 30 kV tension, and 16 mA current and analysis done between 2θ = 5° and 2θ = 50°. Prior to the analysis, the samples were conditioned for 7 days under 64% RH. Relative crystallinity (%) was calculated as the ratio of the integrated crystalline area (peak area, more intense) to the total area of the diffractogram, according to van Soest [16]. Crystalline fraction was calculated by the area above the smooth curve drawn on the basis of the main peaks. The program *Mathematica 5.2* was used for the calculation of the areas.

2.3.7. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra were recorded using a spectrophotometer Term Nicolet Nexus 470 FTIR (USA). The materials were dried in a desiccator with anhydrous calcium chloride for 20 days and crushed. The resulting powder was mixed with KBr and compressed to a high pressure for the formation of the tablets. The readings were made at 4000 to 500 cm^{-1}, with spectral resolution of 4 cm^{-1}.

2.4. Statistical analysis

The program STATISTICA 5.0 (Statsoft, Oklahoma) was used for the variance analysis (ANOVA). Significant differences ($p \le 0.05$) were achieved using the Tukey test.

3. Results and discussion

3.1. Visual aspect of materials

The extruded sheets showed a yellowish color, probably caused by the extrusion conditions, a point that will be discussed later in this

Table 1
Temperatures of the extruder zones for production of the sheets (second extrusion step)

Plasticizer	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)
Glycerol	70	125	125	125
Sorbitol	70	110	115	110
Urea	80	115	115	90

work, together with the infrared spectra results. The casted films were colorless.

Glycerol-plasticized films and sheets showed good handling properties and homogeneity, as they did not have cracks or bubbles. On the other hand, the materials extruded with urea and sorbitol presented surface bubbles. According to Bastioli et al. [17], to minimize the occurrence of bubbles, the extrusion processing of starch should be carried out under low moisture content (no more than 16%), and urea-plasticized materials should be extruded in semi-dry conditions, which did not occur in this work and could have possibly contributed to the great number of bubbles on the urea sheets.

3.2. Stress at break

Figs. 1 and 2 show the effect of RH and plasticizers on the stress at break of oat starch films and sheets, respectively. Independent of the type of plasticizer, an increase in the RH decreases the stress at break of these materials. This behavior is probably due to the hygroscopicity of both starch and the plasticizers, which gain water to achieve equilibrium with the environment (Table 2). A partial rupture of the interaction between the polymeric chains occurred, leading to the weakening of the structure of the material [18].

There was no reduction in the stress at break of the films with an increase of RH from 76 to 90% (Fig. 1), in contradiction to what was observed by Lawton [19] in zein films. This author reported that, under an RH over 80%, there is a strong weakening of the polymeric matrix due to the substitution of the polymer–polymer and polymer–plasticizer interactions by polymer–water and plasticizer–water interactions. In our study, oat lipid might have acted as a barrier to water vapor, resulting in less sorption (max. 21% moisture—Table 2) when compared with the 40% moisture adsorbed by zein films when exposed to 80% RH.

The resistance of films plasticized with glycerol, sorbitol and urea did not differ from each other, even though the molar concentration of urea (0.267 mol/100 g starch) was two times higher than that of sorbitol (0.137 mol/100 g starch).

Mali et al. [18] reported that films plasticized with glycerol showed lower stress at break than films plasticized with sorbitol; although sorbitol presents a superior number of hydroxyls to interact with water, glycerol presents more water affinity. However, Cuq et al. [20] reported that sorbitol and glycerol, under the same molar content, did not show differences in the mechanical properties of the protein films.

According to Chuy and Bell [21], urea-plasticized films should show more resistance and stability than films plasticized with polyols because urea presents a greater ability to form more stable hydrogen links with starch chains, due to the double amino group. This performance was not observed in our work.

Concerning to the sheets (Fig. 2), those plasticized with urea and sorbitol showed a stability in the stress at break values from 11 to 57% RH, with further decreases as the RH increased. On the other hand,
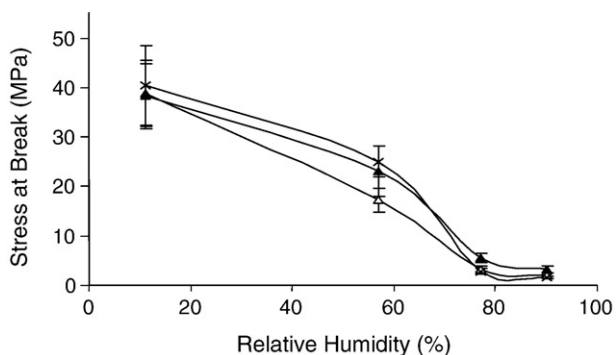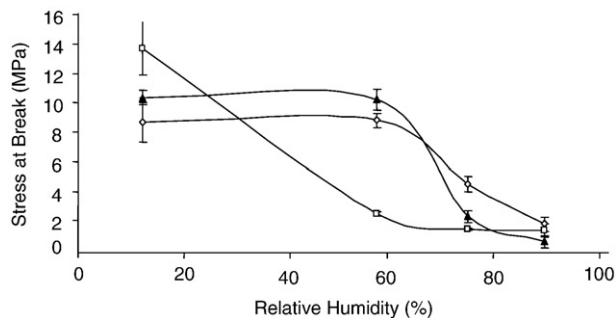

Fig. 2. Effect of relative humidity and plasticizer on the stress at break for oat starch sheets. □ glycerol; ◊ sorbitol; ▲ urea.

glycerol sheets have a rapid decrease in the stress at break with increasing RH until 76%, and then it remains constant at higher RH.

At 11% RH, the sorbitol and urea sheets showed the lowest stress at break values, while at 57 and 76% RH the inverse was observed, as a consequence of the weakening of the glycerol sheets. The superior water affinity of glycerol, stated by Mali et al. [18], could be the cause of this weakening. Also, according to Ma and Yu [22], the higher stability of the hydrogen interactions between starch and urea produces stronger sheets; they calculated the energy involved in these interactions (12.93 and 14.16 kcal/mol, between starch and glycerol and between starch and urea, respectively), indicating that urea formed stronger interactions.

At 90% RH, the plasticizing effect of water covered the effect of all plasticizers, thus producing materials with similar resistance (Fig. 2).

The films showed higher resistance values than the sheets. During extrusion, the starch chains exposed to high temperatures and shear can be degraded, which could justify the lowering of the resistance [23]. Although films and sheets showed different absolute values, the observed behavior of the plasticizers seems to be similar.

3.3. Strain at break

The effects of RH and plasticizers in the strain at break of the oat starch films and sheets are shown in Figs. 3 and 4, respectively. Generally, RH affected the elongation capacity of the materials. The higher the RH, the higher the strain at break.

Between 11 and 57% RH, the films showed no significant alteration in the strain at break; the values obtained were lower than 10%. Under 76% RH, the values increased in an important way, reaching 130%. Between 76 and 90% RH, the strain at break values tended to stabilize; this effect can be attributed to the lipid contained in oat starch, causing less water sorption under high RH condition.

The increase in the strain at break under higher RH is in concordance with Forssell et al. [3] and can be explained by the hygroscopicity of the starch and plasticizers (Table 2). Adsorbed water

Fig. 1. Effect of relative humidity and plasticizer on the stress at break of oat starch films. Δ glycerol; ▲ sorbitol; × urea.

Table 2
Moisture content of films and sheets stored for 48 h at different RH

	Relative humidity (%)			
	11	57	75	90
Films				
Glycerol	2.03[a,A]	8.28[a,B]	16.43[a,C]	19.63[a,C]
Sorbitol	1.05[a,A]	7.64[a,B]	13.64[a,C]	16.52[a,C]
Urea	1.94[a,A]	8.80[a,B]	14.37[a,C]	19.48[a,C]
Sheets				
Glycerol	1.00[a,A]	8.86[a,B]	13.87[a,C]	20.44[a,C]
Sorbitol	0.20[a,A]	3.12[b,B]	8.14[a,C]	17.41[a,C]
Urea	0.41[a,A]	4.32[b,B]	10.12[a,C]	18.21[a,C]

Means at same column with different minuscule letters are significantly different (Tukey test, $p \leq 0.05$) and means at same line with different capital letters are significantly different (Tukey test, $p \leq 0.05$) (analysis were done separately for films and sheets).

allows better mobility of the chains, resulting in an increase of the space between them, thus increasing the elongation [18].

For RH lower than 57%, the urea films showed less strain at break than the polyol films (this difference is not perceptible in the Fig. 3). With an increase of RH, no differences were observed between polyols and urea films. According to Ma et al. [24], about 0.25 g of urea is linked to 1 g of starch, and the surplus urea acts as a solid (high melting point), with low internal flexibility, which weakens the films, leading to an adverse effect concerning strain at break. With the increase of water comes the complete dilution of urea.

Between 11 and 57% RH, there were no variations in the strain at break observed for the sheets plasticized with sorbitol and urea (Fig. 4), which also had a lower value when compared to sheets containing glycerol.

Under 90% RH, the sheets with sorbitol and those with urea continued to show similar strain at break values, but, under this RH, they became more deformable than the materials plasticized with glycerol. Under this high water level condition, thickness was probably the most important factor in the variation. Higher thickness resulted in more deformable materials (the values for sheets containing glycerol, sorbitol and urea had 684, 1001 and 1216 μm thicknesses, respectively).

The comparison between the processes showed lower elongation for sheets under all RH conditions, independent of the type of plasticizer used. Thickness and the fragmentation of the polymeric structure during extrusion can be responsible for this result.

3.4. Water vapor permeability (WVP)

The WVP of the oat starch films and sheets are presented in Table 3. Between the films, those produced with glycerol and those produced with urea were the most permeable. Glycerol easily penetrates into the film structure and, due to the presence of one hydroxyl on each carbon, produces a very hydrophilic film, resulting in a higher WVP [11]. Sorbitol showed lower WVP, which, in this case, places it as the most efficient plasticizer concerning this property.

Considering the sheets, the materials plasticized with urea showed the highest values, and this could be related to its lack of structural integrity (presence of bubbles). The glycerol sheets were more permeable than sorbitol ones; a similar behavior was observed with glycerol and sorbitol films.

The differences in the plasticizer concentrations (molar basis) of the oat starch films, (sorbitol, 0.137 mol/100 g starch; glycerol, 0.217 mol/100 g starch; and urea, 0.267 mol/100 g starch) could also explain the different WVP values. According to Sobral et al. [25], the higher the level of the plasticizer is, the less dense the starch network and, consequently, the more permeable the film.

The presence of 1.36% lipids in oat starch seemed to affect the WVP of the materials. The permeability was lower than that of cassava starch
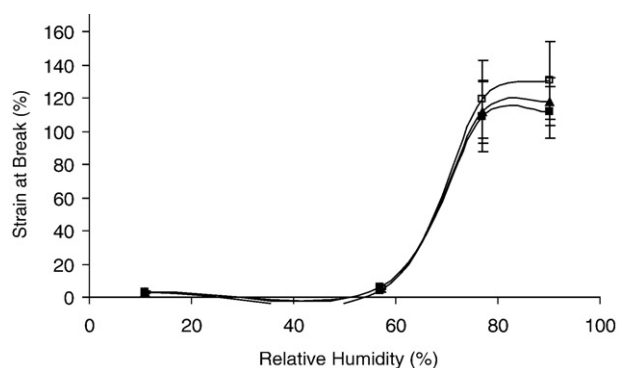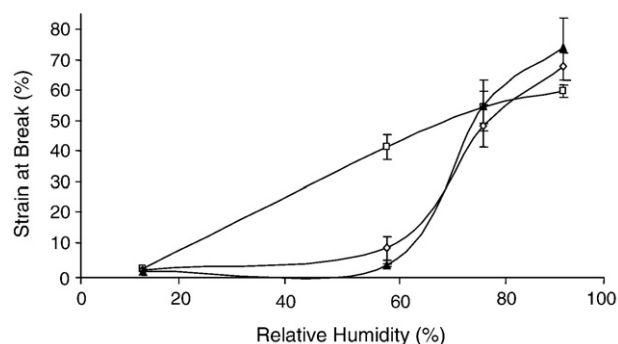
Fig. 4. Effect of relative humidity and plasticizer on the strain at break for oat starch sheets. □ glycerol; ◊ sorbitol; ▲ urea.

films plasticized with 20% of glycerol (2400×10^{-12} g m^{-1} s^{-1} Pa^{-1} [26]), queratine films plasticized with 30% of glycerol (39×10^{-12} g m^{-1} s^{-1} Pa^{-1} [11]) or gelatin films plasticized with 25% of glycerol (139×10^{-12} g m^{-1} s^{-1} Pa^{-1} [27]).

Synthetic plastic films, such as LDPE, show lower WVP (0.36×10^{-12} g m^{-1} s^{-1} Pa^{-1} [28]) than oat starch ones; in comparison to sorbitol films, this value was about nine times lower.

In general, sheets were more permeable than films (Table 3). Lai and Padua [29] related that the oriented microstructure, consisting of intimately packed structures that are shown in the films produced by casting, can be responsible for the lower water sorption of those materials, resulting in lower WVP.

3.5. Thermal properties

Table 4 shows the T_g values for the oat starch films. No transition was observed in the sheet thermograms (data not shown), which is due the lower sensitivity of the equipment used on the assays.

Although it was expected that films plasticized with urea presented the highest T_g due to the strong interactions between the amino group and starch [30], the opposite was observed.

One of the main problems related to biomaterials is their fragility, which is caused by high T_g values and which affect their properties: (1) materials stored over T_g show higher flexibility than when stored in glassy state, and (2) the permeation of gases and water vapor molecules through the material is also higher over T_g [31].

The optimal situation is that biomaterials have T_g close to the storage temperature, to avoid changes that could lead to aging (crystallization), at the same time that the eventual losses in mechanical properties are minimized. Oat starch films plasticized with urea reached this best condition at 64% RH.

3.6. Crystallinity

Although oat starch normally presents an A-type crystallinity, which is characteristic of cereals [32], the materials obtained showed a pattern of V_H ($2\theta = 19.7°$ and $12.9°$) type crystallinity (Figs. 5 and 6). This indicates that the crystals of native starch were fully melted, and the processing was responsible for the formation of new crystals.

Fig. 3. Effect of relative humidity and plasticizer on the strain at break for oat starch films. ■ glycerol; ▲ sorbitol; □ urea.

Table 3
WVP[a] of oat starch films and sheets

WVP $\times 10^{-12}$		
Plasticizer	Film	Sheet
Glycerol	4.211[a]	22.499[a]
Sorbitol	3.117[b]	16.891[b]
Urea	3.828[a, c]	31.909[c]

[a] Water vapor permeability (g Pa^{-1} s^{-1} m^{-1}); Means at same column with different letters are significantly different (Tukey test, $p \leq 0.05$).

Table 4
Glass transition temperature (T_g) of oat starch films

Films	T_g (°C)
Glycerol	50.50[a]±8.51
Sorbitol	59.58[a]±5.01
Urea	36.18[b]±7.32

Means at same column with different letters are significantly different (Tukey test, $p \le 0.05$).

The type of crystallinity found in oat starch films (Fig. 5) was not concurring with what was reported by Krogars et al. [33]. According to these authors, starch dried from diluted solutions presents type B crystalline structures. This discordance can be related to the level of lipids in oat starch, as the formation of type V crystalline structures depends on the presence of lipids.

In the case of sheets (Fig. 6), the crystallinity pattern found is compatible with that reported by Forssell et al. [3]. According to these authors, the extrusion process results in the formation of structure V_H and its variants (V_A and E_H). Furthermore, van Soest et al. [34] stated that, at processing temperatures below 180 °C, one observes the formation of structure V_H, while, at processing temperatures above 180 °C, one observes the formation of structure E_H.

The comparison of the plasticizers (Table 5) shows that the urea films had lower relative crystallinity than the polyol films. According to Ma et al. [30], the capacity of urea to form more stable bonds avoid the interaction and the crystallization of the starch molecules.

There were no differences between glycerol and sorbitol films, although the values for sorbitol were slightly superior to those for glycerol. Polyols sheets showed lower relative crystallinity.

Glycerol and sorbitol sheets showed an intensity of crystallinity similar to one of the films containing the same plasticizers, which contradicts the results obtained by van Soest et al. [34]. According to the authors, different kinds of processing result in significant changes in X-ray diffraction patterns, affecting the number of the peaks and also their intensity. Funke et al. [23] reported that the fragmentation of the chains, resulting from the extrusion process, leads to the reduction of molar mass, which facilitates the gathering of the chains (crystallization).

However, urea films and sheets were significantly different in their relative crystallinity values (Table 5). While in films the capacity of urea to form more stable bonds probably avoided the interaction and the crystallization of the starch molecules (as reported before by Ma et al. [30]), the more drastic conditions in extrusion process probably resulted in the fragmentation of the chains, what lead to a greater crystallinity.

Crystallinity influences the mechanical behavior of thermoplastic materials based on starch. Crystals strengthen the polymeric chains of starch by cross-linking, causing an increase in the stress and a decrease in elongation capacity [34].

Although the conditions were different for mechanical properties and X-ray diffractometry analyses, it is possible to establish a correlation between these properties with caution.
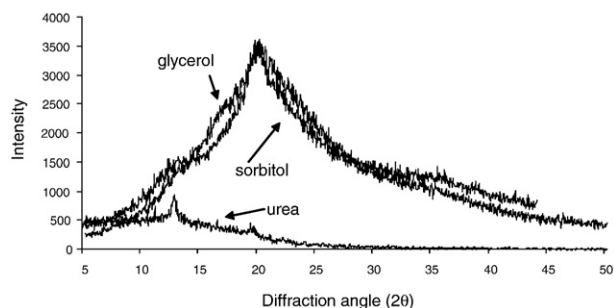

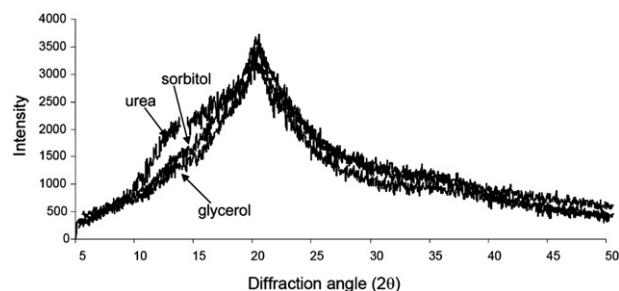**Fig. 5.** X-ray diffractograms of oat starch films.

Fig. 6. X-ray diffractograms of oat starch sheets.

Under 57% RH (near the 64% RH used in X-ray analysis), we did not observe a difference in the resistance of the films containing glycerol and sorbitol (Fig. 1), and the relative crystallinity values were similar (Table 5). With the sheets, we verified that more crystalline materials showed higher stresses at break at 57% RH (Fig. 2), which is in agreement with the theory that crystallinity reinforces the polymeric chains.

However, crystallinity was not well correlated with the elongation of films. Those containing polyols, although they had higher crystallinity, were more deformable at 57% RH (Fig. 3), while the inverse was observed for urea films. For sheets, the higher the crystallinity was, the lower the elongation (Fig. 4).

3.7. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra of films and sheets are shown in Fig. 7. The different plasticizers did not cause great variations in the spectra, probably due to the fact that the main components of the materials (amylose and amylopectin in starch) and functional groups in the plasticizers were similar. According to Silverstein and Webster [35], the spectra were characterized by the presence of six important absorption bands: OH in hydrogen bond between 3300 and 3600 cm^{-1}; axial deformation (2922 cm^{-1}) and angular deformation (1457 cm^{-1}) of CH_2 and CH_3 groups, O–C stretching of anhydroglucose ring at 1029–1162 cm^{-1}, OH in hydrogen bonds near to 574 cm^{-1} and C–O stretching at approximately 1157 cm^{-1}.

All the materials showed a band near 1636 cm^{-1} (Fig. 7) that was associated with the water sorbed by hygroscopic materials [22]. In urea sheets, this band was disguised by N–H stretching, which is located in the same region.

An absorption band at 1654 cm^{-1} was observed for the films, and an absorption band at 1615 cm^{-1} was observed to the sheets, attributed to N–H deformation. There was also an axial deformation of N–H between 3794 and 3077 cm^{-1}, but, in this case, because of superposition with the great OH band, the N–H vibration was not efficiently marked. According to Ma and Yu [22], the fact that urea was present but the OH band was not altered indicates that only a small part of the starch reacted with the plasticizer, which can justify the lack superiority of this film over the films containing polyols.

According to Silverstein and Webster [35], the formation of hydrogen bonds alters the strength constant of the groups involved, and thus, the frequency of deformations is altered. The axial deformation bands move to lower frequencies, usually with an increase of intensity and a

Table 5
Relative crystallinity of the oat starch films and sheets

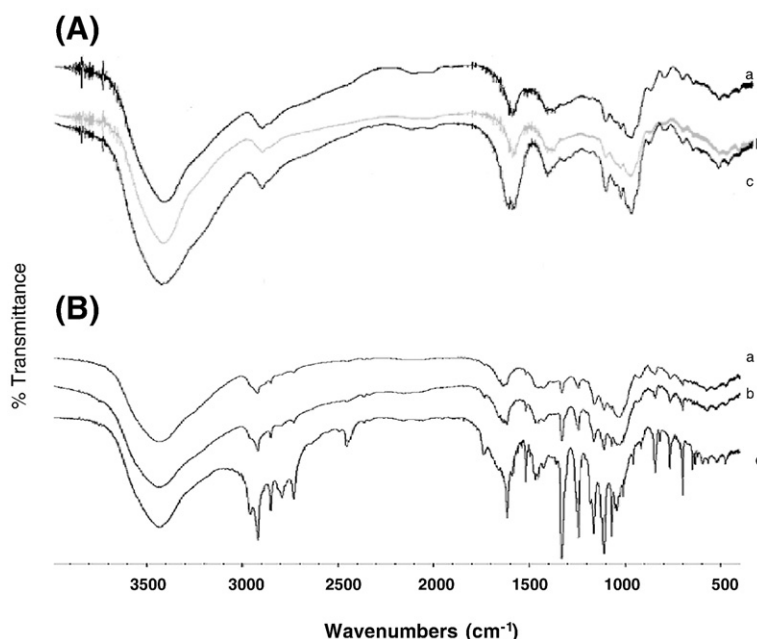| Plasticizer	Relative crystallinity (%)	
	Film	Sheet
Glycerol	22.6	22.9
Sorbitol	24.1	24.8
Urea	5.1	27.5

Fig. 7. Infrared spectra of the oat starch films (A) and sheets (B). (a) glycerol; (b) sorbitol (c) urea.

widening of the band. The angular deformation vibration usually moves to lower frequencies; however, the movement is lower than that observed in axial deformations. The movement to a lower band frequency of the C–O group band indicates the possibility of an occurrence of a more stable hydrogen bond between C–O and the plasticizer [30]. In oat starch films, the frequencies in this region were similar and cannot indicate the occurrence of more or less interaction.

Urea sheets presented 2958, 2792 and 2733 cm^{-1} (C–H deformation) bands more intense than those of polyols sheets, and this could be explained because the milled samples were not weighed to form the tablet in these analyses. According to Canevarolo [36], the intensity of an absorption band is proportional to the concentration of the component that originates the band.

Films and sheets showed similar regions; however, the sheets showed a higher number of bands, indicating that the extrusion process resulted in structural modifications (partial degradation) in the polymeric chain. Actually, van der Einder et al. [37] reported that extrusion results in the reduction of the molar mass of starch due to the combination of mechanical and thermal forces. Mercier et al. [38] reported that starches extruded in single screw extruders can have small sugar molecules, mainly due to the randomness of the breaking of the chain.

Several bands, for example, 1331 and 1243 cm^{-1} for the sheets containing sorbitol, and 2958, 2792, 2733, 2453, or between 1350 and 1000 cm^{-1} for the sheets containing urea, appeared during extrusion, but they were not seen in the films. According to Ma et al. [22], the reaction between starch and urea does not happen only by hydrogen bonds. During extrusion, part of the urea forms complex with the starch, resulting in free NH$_3$, which can explain the appearance of new bands in these sheets.

Another indication of the participation of extrusion in the degradation of starch is the appearance of a yellowish color in the sheets, as mentioned before. The stretching near 1738 cm^{-1} in sheets is attributed to the aliphatic aldehyde carbonyls. This result is in accordance with the yellowish color presented by these materials.

4. Conclusions

The lipid content of oat starch was not high enough to avoid variations in the mechanical properties caused by the change of RH. In general, a decrease in the stress at break and an increase in strain at break were evidenced when the RH was increased. However, the presence of the lipids provided films with a better barrier to water vapor when compared to other biofilms. The plasticizers did not influence the mechanical properties, even when sorbitol was added in a lower molar concentration. Urea did not act as expected (reinforcing starch matrix); urea-plasticized films had similar mechanical properties compared to polyols films. Different processes produced different crystallinity patterns. Nevertheless, films and sheets showed similar relative crystallinity, with an exception related to the urea films that showed lower values. A notable effect of the extrusion process was the partial fragmentation of the starch chains, which was confirmed by lower resistance and strain, higher permeability and a greater number of bands in the infrared spectra.

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References

[1] L. Avérous, C. Frigant, L. Moro, Starch/Stärke 53 (2001) 368.
[2] M.A. Garcia, M.N. Martino, N.E. Zaritzky, Journal of Food Science 65 (6) (2000) 941.
[3] P.M. Forssell, S.H.D. Hulleman, P.J. Myllarinen, G.K. Moates, R. Parker, Carbohydrate Polymers 39 (1999) 43.
[4] L.Z. Wang, P.J. White, Cereal Chemistry 71 (3) (1994) 263.
[5] M. Petersson, M. Stading, Food Hydrocolloids 19 (2005) 123.
[6] R.C.R. Souza, C.T. Andrade, Polímeros: Ciência e Tecnologia 10 (1) (2000) 24.
[7] J.A. Ratto, P.J. Stenhouse, M. Auerbach, J. Mitchell, R. Farrell, Polymer 40 (1999) 6777.
[8] A. Gennadios, C.L. Weller, R.F. Testin, Cereal Chemistry 40 (1993) 426.
[9] R. Sothornvit, C.W. Olsen, T.H. Mchugh, J.M. Krochta, Journal of Food Engineering 78 (2007) 855.
[10] W.J. Lim, Y.T. Liang, P.A. Seib, C.S. Rao, Cereal Chemistry 69 (3) (1992) 233.
[11] S.M. Martelli, G. Moore, S.S. Paes, C. Gandolfo, J.B. Laurindo, Lebensmittel-Wissenschaf und-Technology 39 (2006) 292.
[12] ASTM D882-91, Annual Book of ASTM, 1996, Philadelphia, USA.
[13] ASTM D638 M-93, Annual Book of ASTM, Philadelphia, USA, 1993.
[14] AACC, Methods of the AACC, (8ed.) American Association of Cereal Chemists, St. Paul, 1990.
[15] ASTM E96-95, Annual Book of ASTM, 1996, Philadelphia, USA.
[16] J.J.G. van Soest, S.H.D. Hullemann, D. de Vit, F.G. Vliegenthart, Carbohydrate Polymers, 29 (1996) 225.
[17] X. Bastioli, L. Roberto, T. Gianfranco, G. Italo, US 5,569,692, 1996.

[18] S. Mali, L.S. Sakanaka, F. Yamashita, M.V.E. Grossmann, Carbohydrate Polymers 60 (2005) 283.
[19] J.W. Lawton, Cereal Chemistry 81 (1) (2004) 1.
[20] B. Cuq, N. Gontard, J.L. Cuq, S. Guilbert, Journal Agricultural Food Chemistry 45 (3) (1997) 622.
[21] S. Chuy, L.N. Bell, Food Research International 39 (2006) 342.
[22] X. Ma, J. Yu, Carbohydrate Polymers 57 (2004) 197.
[23] U. Funke, W. Bergthaller, M.G. Lindhaure, Polymer Degradation and Stability 59 (1998) 293.
[24] X.F. Ma, J.G. Yu, Y.B. Ma, Carbohydrate Polymers 60 (2005) 111.
[25] P.J.A. Sobral, F.C. Menegalli, M.D. Hubinger, M.A. Roques, Food Hydrocolloids 15 (2001) 423.
[26] V.D. Alves, S. Mali, A. Beléia, M.V.E. Grossmann, Journal of Food Engineering 78 (2007) 941.
[27] I. Arvanitoyannis, A. Nakayama, S-I. Aiba, Carbohydrate Polymers 36 (1998) 105.
[28] O. Orliac, A. Rouilly, F. Silvestre, L. Rigal, Industrial Crops and Products 18 (2003) 91.
[29] H-M. Lai, G.W. Padua, Cereal Chemistry, 75 (2) (1998) 194.

[30] X.F. Ma, J.G. Yu, J.J. Wan, Carbohydrate Polymers 64 (2006) 267.
[31] T. Davanco, P.S.T. Palmu, C.R.F. Grosso, Ciência e Tecnologia de Alimentos 27 (2007) 408.
[32] M. Zhou, K. Robards, M. Glennie-Holmes, S. Helliwell, Cereal Chemistry 75 (3) (1998) 273.
[33] K. Krogars, J. Heinamaki, J. Karjalainen, J. Rantanen, P. Luukkonen, J. Yliruusi, European Journal of Pharmaceutics and Biopharmaceutics 56 (2003) 215.
[34] J.J.G. van Soest, S.H.D. Hullemann, F.G. Vliegenthart, Industrial Crops and Products 5 (1996) 11.
[35] R.M. Silverstein, F.X. Webser, Identificação Espectrométrica de Compostos Orgânicos, 6nd.Ltc, Rio de Janeiro, 2001.
[36] S.V. Canevarolo, Técnicas de Caracterização de Polímeros. Artliber, São Carlos, 2004.
[37] R.M. van der Einde, C. Akkermans, A.J. van der Goot, R.M. Boom, Carbohydrate Polymers 56 (2004) 415.
[38] C. Mercier, P. Linko, J.M. Harper, Extrusion Cooking, AACC, St Paul, 1989.