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# Comparative study of processing methods for starch/gelatin films

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ABSTRACT

In this work, the influence of processing methods on the properties of starch/gelatin films plasticized with glycerol and sorbitol is reported. Four different processing techniques: casting; pressing; pressing followed by blowing and extrusion followed by blowing were evaluated. Bioplastics prepared by casting were homogeneous and transparent with lower opacity and water vapor permeability (WVP) values when compared to films prepared by other techniques. Among the cast films studied, those with 3% lipophilic starch, in 1:1 proportions and plasticized with sorbitol, showed lower WVP values and higher tensile strength (TS). Films obtained by pressing and blowing showed little expansion during blow, had cracks in the surface, low TS and higher WVP. These films were the only samples to show crystallinity as determined by thermal analysis and X-ray diffraction. In conclusion, different processing techniques have significantly affected the properties of these films.



## 1. Introduction

Biopolymers are defined as polymers formed under natural conditions during the growth of cycles of all organisms. They are formed within cells by complex metabolic processes (Mitrus, Wojtowicz, & Moscicki, 2009). Starch has been considered one of the biopolymers with the greatest potential to produce biodegradable materials, especially disposable food containers, where the service time of use is relatively short (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998; Wang, Thompson, & Liu, 2012). Furthermore, starch is annually renewable, abundant and inexpensive (Davis & Song, 2006). It is present in semi-crystalline granules that varies in composition, size, shape and functionality when obtained from different botanical sources (Mali, Grossmann, García, Martino, & Zaritzky, 2006).

Starch based materials can be obtained by different processing techniques such as casting, injection or blow molding and so on (Teixeira et al., 2012), and different process can leave to different end material properties (Altskär et al., 2008). One of the unique characteristics of starch-based polymers is their thermal processing properties, which are much more complex than conventional polymers, since multiple chemical and physical reactions may occur during processing, such as water diffusion, granular expansion, gelatinization, decomposition, melting and crystallization (Liu, Xie, Yu, Chen, & Li, 2009). Among these phase transitions, gelatinization is particularly important because it is closely related to the others, and it is the basis of the conversion of starch to a thermoplastic. It has been shown that different starch gelatinization processes result in different material properties (Paes, Yakimets, & Mitchell, 2008).

Gelatin is an animal origin protein and is well-known for its good film forming properties. Gelatin is obtained by thermal denaturation or physicochemical degradation of collagen. Gelatin can be used together with starch as a reinforcement to the polymeric matrix (Fakhouri, Fontes, Innocentini-Mei, & Collares-Queiroz, 2009). Gelatin forms a three-dimensional network with zones of intermolecular microcrystalline junctions and the dehydration of

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this system may produce brittle films (Cao, Yang, & Fu, 2009). Also starch based materials are brittle, which justifies the use of polyols, such as glycerol, sorbitol and polyethylene glycol, to give them flexibility and elongation (Gontard, Guilbert, & Cuq, 1992). The choice of plasticizer added to the edible films must guarantee compatibility with the polymer and solvent used. Moreover, both starch and gelatin are produced in large scale in the domestic market.

The most used technique today for the production of bioplastics is casting; however, one of the problems with films produced by this technique is the limitation on the quantity produced. On the other hand, the structure–processing–property relationships in starch/gelatin films has not been reported in literature. Therefore, this study aims to evaluate the processability of starch/gelatin materials by different techniques, to observe the influence of different process on thermo mechanical, structural, and barrier properties of blends.

## 2. Materials and methods

### 2.1. Materials

Commercial lipophilic starch from maize with consisting of 25% amylose and 75% amylopectin were obtained from Corn Products® (Brazil). Gelatin type A and polypropylene extruded film were acquired from Leiner Davis Gelatin (Brazil) and Braskem (Brazil), respectively. Reagent grade glycerol and sorbitol were obtained from Synth (Brazil) and Getec (Brazil) respectively.

### 2.2. Preparation of bioplastics based on lipophilic corn starch and gelatin

#### 2.2.1. Casting technique

The films were obtained by dispersing 3 and 5 g of lipophilic corn starch in 100 ml of distilled water. After total dispersion, 10% of the plasticizer (sorbitol) was added in relation to the mass of the starch, and the suspensions were heated to 85 °C for 5 min, while stirring constantly. The concentration of the plasticizer added to the starch was previously determined through preliminary testing formulations (which were chose between 5% and 25%). The latter solution was prepared by hydrating 10 g of gelatin (GEL) in 100 ml of distilled water for 1 h. After this period, the solution was heated to 70 °C for 10 min. Subsequently, the plasticizer (sorbitol) was added, under magnetic stirring, until the homogenization of the sample at a concentration of 5% in relation to GEL amount. This agitation was carried out smoothly to avoid formation of bubbles in the sample and to keep the natural pH of the solution. The solution for preparing starch/gelatin films was added in proportions of 4:1, 1:1 and 1:4. Aliquots of 20 ml of a solution made to prepare films of starch and gelatin were then distributed in Plexiglas® plates with a diameter of 11.8 cm. The films were dried at room temperature (25 °C) for 24 h. After drying, the films were kept in desiccators with a relative humidity of 50 ± 2% for 48 h before characterization.

#### 2.2.2. Pressing technique

The pressed bioplastics were obtained, with same starch:GEL formulations (4:1, 1:1 and 1:4), following the steps: (i) grinding and partial hydration of the gelatin, followed by the incorporation of the starch and plasticizer (in the same concentration used for the casting films); (ii) homogenization of the mixtures with high shearing, using equipment from M. H. Equipment (MH 50, Sao Paulo, Brazil), with a speed of 1800 rpm (speed 1); and (iii) pressing of the homogenized mixtures at 90 °C using equipment from Carver (model Accustamp, Wabash, Indiana) for 5 min to obtain uniform flat sheets.

#### 2.2.3. Pressing followed by blow technique

Pressed sheets of bioplastics, as described in Section 2.2.2, were then pelletized and used to feed the bench blow extruder from AX Plásticos (Model Lab-14, São Paulo, Brazil) with three heating zones to obtain the films. The temperature profile was as follows: 90 °C (Zone 1), 100 °C (Zone 2) and 110 °C (Zone 3), with a screw speed of 25 rpm in a continuous process.

#### 2.2.4. Extrusion followed by blow technique

The films were obtained using a BGM extruder (model EL-25, Sao Paulo, Brazil) located in the Department of Science and Food Technology at the State University of Londrina and consisted of the following components: a screw with a diameter of 25 mm, 4 heating zones, an internal air system to blow the balloons and an external ring of air for samples cooling. The balloons obtained had a diameter in the range of 150–300 mm, which were rolled by two drive coils.

The formulations were prepared in the following sequence: (i) production of pellets by extrusion of the starch and plasticizer; (ii) a second extrusion of these pellets, in the presence of gelatin; and (iii) a third extrusion to complete homogenization of the components. During the pellet production, the temperature in the extruder nozzle did not exceed 95 °C, thus avoiding the formation of bubbles due to the expansion of the gases released. The formulation used for comparative study the process technique was Starch/Gelatin 4:1.

Before obtaining the blown films of bioplastics by feeding the extruder with pellets of the pressed starch and gelatin, tests were carried out at various temperatures (100–160 °C) and screw speeds (19–40 rpm).

Then, the chosen temperatures to be used in the four heating zones were (from feed zone to nozzle): 110, 100, 100 and 95 °C; the screw speed was 25 rpm. The resulting pellets were extruded to produce blown films (extrusion followed by blowing), engaging a specific matrix with the extruder.

### 2.3. Methods of analysis for the bioplastics

#### 2.3.1. Visual aspect

Visual and tactile analyses were performed in order to choose the best films for analysis. Such selection was made by taking only the homogeneous (with uniform color and without insoluble particles of gelatin) and flexible (easy handling, with no significant cracks or brittle areas) films. Films which presented cracks, holes or non uniform color were discarded.

#### 2.3.2. Film thickness

The thickness of the films was determined using a micrometer (Model MDC-25M, Mitutoyo, MFG, Japan) and determined by the average of 10 random measures in different parts of the same sample. These measures were obtained after conditioning the films for 48 h at 25 °C and 50% relative humidity until equilibrium.

#### 2.3.3. Water solubility

The water solubility defines the tolerance to water and is determined by the chemical structure of the materials (Martelli, Rocha Placido Moore, & Laurindo, 2006). To determine the water solubility, three film samples were dried at 105 °C for 24 h in an air circulation oven (TECNAL TE 394/2, Piracicaba, Brazil) and then the percentage of initial solids content of each specimen was measured (Lee, Shim, & Lee, 2004). The film solubility (%) in water was defined as the ratio of water-soluble solids to initial solids content, after 24 h immersed in water. Three film samples of 2 cm diameter were cut and weighed. The specimens were immersed in an Erlenmeyer containing 50 mL of distilled water and were sealed with parafilm; the Erlenmeyer flasks were placed in a thermostatic bath with mild

stirring. The piece of each film was removed and dried at 105 °C for 24 h and then the solids content were measured. The final result for the dissolving of the film in water was the average of three measurements.

*2.3.4. Opacity*

The opacity of the film was determined using a HUNTERLAB colorimeter (Colorquest II, Faifax, USA). The determinations were performed in triplicate after the calibration of the colorimeter with a standard white background and a standard black background (Fakhoury et al., 2012). The opacity was determined by the following equation:

$$O_p = \frac{O_{pN}}{O_{pB}} \times 100,$$

where the terms are defined as follows:

$O_p$ = opacity of the film (%);
$O_{pN}$ = opacity of the film overlaid with a black background;
$O_{pB}$ = opacity of the film overlaid with a white background.

*2.3.5. Barrier properties*

The water vapor permeability (WVP) was determined by a modified standard ASTM E-96 (1980) method (Materials, 1980). The film was sealed with paraffin in a permeation cell made of aluminum and containing calcium chloride. The seal ensured that all moisture permeation occurred only through the film. The permeation cells were conditioned in desiccators kept at 25 °C and 75% relative humidity (Martelli et al., 2006). The water vapor transferred through the film was determined by the gain in mass of calcium chloride, measured every 24 h. The effect of air space between the region below the film and the surface of the calcium chloride in the test-cells, as described by Gennadios et al. (1994), was not considered when calculating the rate of water vapor transmission. All tests were performed in triplicate.

*2.3.6. Mechanical properties*

The tensile strength and the percentage of elongation to break were determined using a TA-XT2 Texture Analyzer (SMS, Surrey, UK), with an initial grip separation of 50 mm and a test speed of 1 mm/s. The film specimens, 25 mm wide and 100 mm long, were cut with metal scissors. The maximum tensile strength and elongation were determined at the point of rupture. The tensile strength was calculated by dividing the maximum force by the sectional area of the film (width × thickness). The percentage of strain at break was calculated by dividing the values of the final elongation by the initial grips' separation (50 mm) and multiplying the result by 100.

*2.3.7. Film morphology*

The morphology of the film surfaces were observed using a scanning electron microscope (SEM) from LEO, Model 440i (LEO Electron Microscopy Ltd., Uckfield, England), operated at 10 kV. Before the tests, the samples were covered with a thin layer of gold for thermal and electrical conduction.

*2.3.8. X-ray diffraction*

The XRD patterns were obtained using a Phillips X-ray diffractometer, Model X'pert (Almelo, Netherlands). Film samples with dimensions of 4.0 cm × 1.5 cm were cut and fixed in a circular clamp of the instrument. The analysis were carried out directly and the conditions were as follows: (i) voltage and current: 40 kV and 40 mA, respectively; (ii) scan range: 2$\theta$, from 5° to 30°; (iii) step: 0.1° and (iv) speed 1°/min, equipped with a secondary monochromator of graphite beam. The variation of the crystals' size was determined using the PC APD Diffraction Software. The samples were stored at 25 °C and 50% Relative Humidity (RH) and analyzed in triplicate. The relative crystalline was calculated by comparing the area under the crystalline peaks with the area of the amorphous halo under the peaks (Rindlav-Westling, Stading, & Gatenholm, 2002). In our case, the most distinct peaks, located at 21.8° and 24.1° (2$\theta$), were chosen to represent the crystalline peaks.

*2.3.9. Thermal properties*

Thermogravimetric analysis (TGA) were performed in a thermobalance TGA machine (SDT 2960, TA Instruments, USA-EUA), in an inert atmosphere of ultra-dry nitrogen gas, chromatographic grade, with a constant flow rate of 100 $cm^3$/min. The films were previously stored at 25 °C and 50% relative humidity. Aliquots of 20 mg of samples were subjected to temperatures ranging from 25 °C up to 600 °C, using a heating rate of 10 °C/min. The variation of the mass of the samples was monitored throughout the heating. The material used as a reference for these analyses was aluminum oxide ($Al_2O_3$), which had a mass that did not vary in the range studied.

Measurements of glass transition temperature and the variations of the fusion enthalpy of the films were performed by analysis of differential scanning calorimetry (DSC), using a calorimeter from TA Instruments (USA-EUA), Model TA 2010. The samples were prepared and pre-conditioned at 25 °C and 50% relative humidity. All measurements were performed in an inert atmosphere of ultra-dry nitrogen gas, chromatographic grade, with a constant flow rate of 50 $cm^3$/min. Tests were performed from 30 °C up to 140 °C, using a heating rate of 10 °C/min and atmospheric air as the material-reference.

*2.3.10. Statistical analysis*

The program Statistica® 5.5 (Stasoft, USA) was used to calculate the analysis of variance (ANOVA), and the Tukey test was used to determine the differences between the properties of the films in the 95% confidence range.

## 3. Results and discussion

Initially, tests were performed using casting technique for the selection of the plasticizer, the lipophilic starch and the gelatin concentrations to be used in other techniques, such as pressing, blow molding and extrusion. The chosen plasticizers, glycerol and sorbitol, are plasticizers known to strongly interact with starch at the molecular scale by forming hydrogen bonds with the starch (i.e., amylose) macromolecules (Li & Huneault, 2011).

Bioplastics produced by casting containing sorbitol and glycerol were visually transparent, homogeneous and bright, and easily removed from the drying molds. Films based on cassava starch, which were translucent and easily detached from the mold when dried were reported in literature (Jensen, 2007).

When increasing both the starch concentration from 3 to 5 g and the proportion of gelatin in the mix, there was an increase in the thickness of the bioplastics for both plasticizers studied (Table 2), there was also an increase in the WVP value (Table 1). Mali, Grossmann, Garcia, Martino, and Zaritzky (2004) also reported that the WVP increased as the concentration of yam starch in films increased (Mali et al., 2004). When comparing bioplastics prepared with glycerol and sorbitol in the same proportions, it can be observed that, those plasticized with sorbitol had lower WVP values than those made with glycerol. This can be due to the fact that glycerol molecule is smaller than sorbitol and then it possess more hydrophilic OH groups by a total plasticizer amount added. Consequently binding more water molecules in its structure. In most cases, for the films prepared with 3% starch in a 1:1 ratio, the value of the WVP decreased from 5.27 to 2.70 g mm/$m^2$ d kPa. The use of sorbitol to plasticize gelatin films, produces samples with better barrier and mechanical properties than those containing glycerol

**Table 1**
Mean values of water vapor permeability and of water solubility, in triplicate, of the films composed of lipophilic corn starch and gelatin, plasticized with glycerol or sorbitol, obtained by casting.

| Films[a] | Ratio | WVP (g mm/m$^2$ d kPa) | Water solubility (%) |
|---|---|---|---|
| AM LP (3 g/100 g) and GEL 10 g/100 g GLI | 4:1 | 3.63 ± 0.44 c | 25.44 ± 3.40 a |
| | 1:1 | 5.27 ± 0.47 abc | 24.80 ± 2.75 a |
| | 1:4 | 4.43 ± 0.01 abc | 25.17 ± 2.52 a |
| AM LP 5%/GEL 10% GLI | 4:1 | 4.19 ± 0.93 bc | 22.38 ± 1.45 a |
| | 1:1 | 5.42 ± 0.21 ab | 22.06 ± 0.73 a |
| | 1:4 | 6.11 ± 0.12 a | 23.45 ± 1.61 a |
| AM LP 3%/GEL 10% SOR | 4:1 | 3.02 ± 0.15 d | 26.13 ± 2.98 a |
| | 1:1 | 2.70 ± 0.23 d | 26.34 ± 2.52 a |
| | 1:4 | 5.23 ± 0.29 b | 26.01 ± 2.69 a |
| AM LP 5%/GEL 10% SOR | 4:1 | 2.98 ± 0.35 d | 29.99 ± 1.25 a |
| | 1:1 | 4.34 ± 0.06 c | 23.99 ± 2.22 a |
| | 1:4 | 5.98 ± 0.24 a | 26.62 ± 0.48a |

Tukey, mean values with the same letters (a–c) do not differ at $p \leq 0.05$. Tukey was carried out separately for films plasticized with glycerol and sorbitol.
[a] GEL = gelatin; AM LP = lipophilic corn starch; GLI = glycerol; SOR = glycerol.

(Andreuccetti, Carvalho, Galicia-Garcia, Martinez-Bustos, & Grosso, 2011; Thomazine, Carvalho, & Sobral, 2005).

The WVP values found for films of lipophilic starch and gelatin plasticized with glycerol ranged from 6.11 to 3.63 g mm/m$^2$ d kPa. These values were lower than those reported by Gontard and Guilbert (1996) for biofilms made of starch derivatives and cellulose acetate phthalate (29.3 g mm/m$^2$ d kPa), and for biofilms of pectin (8.2 g mm/m$^2$ d kPa), also obtained by casting, in the same study on the WVP of different materials (Nathalie Gontard & Guilbert, 1996). The water solubility of the bioplastics developed in this work did not present a significant difference between both plasticizers studied (Table 1).

The addition of gelatin caused an increase in the tensile strength of the bioplastics, as noted in Table 2. Regarding the elongation, significant differences were observed only in bioplastics containing glycerol as a plasticizer (Table 2); in this case, the elongation of bioplastics increased about 48% and 38% when gelatin was added into the mix for bioplastics containing 3% and 5% starch, respectively. The value of tensile strength (Table 2) found for the films composed of lipophilic corn starch and gelatin at a 1:4 ratio and plasticized with glycerol was 99.83 MPa; this value was higher than that found by Bertan (2003) for biofilms composed of wheat gluten and gelatin (69.94 MPa). On the other hand, the value of tensile strength of the bioplastics was similar to the biofilms of gelatin plasticized with triacetin, as found by Fakhouri et al. (2003), where the tensile strength was 99.68 MPa (Bertan, Tanada-Palmu, Siani, & Grosso, 2005). Films made from gelatin, with 3 or 5% starch (1:1) and plasticized with sorbitol, showed greater tensile strength than the other films (Table 2). Considering the homogeneity, the results obtained by casting and those films with a smaller WVP and higher tensile stress, we selected a formulation of bioplastics made of 3% lipophilic starch and gelatin (1:1), with sorbitol as the plasticizer. This proportion was utilized in the other techniques to prepare bioplastics, such as pressing (PRE), pressing followed by blowing (PRE/SP) and blowing extrusion (EX/SP).

Unlike the films obtained by casting at room pressure (Fig. 1a), the films pressed were visually whitish, despite the homogeneous aspect. The color of the bioplastic may be related to the degree of starch conversion. White color usually means certain degree of raw or partially converted starch granules. The white color can also be attributed to higher pressures, which caused a structural change in the starch and were responsible for its different color.

Before obtaining the blown films of bioplastics by feeding the extruder with pellets of the pressed starch and gelatin, tests were carried out at various temperatures (100–160 °C) and screw speeds (19–40 rpm). The films obtained at high temperatures were extremely brittle and yellowish (Fig. 1c). However, when lower temperatures were employed in the process (95 °C), a more uniform 5 cm wide whitish film was obtained (Fig. 1d), and this was probably due to the alignment of the chains and subsequent crystallization. Thus, the films obtained at higher temperatures were not considered.

The extruded and blown films (EX/SP) were yellowish and slightly transparent, with an approximate width of 13 cm (Fig. 1e–f); however, despite the material being blown, it suffered

**Table 2**
Mean values for the mechanical properties and thickness of bioplastic films composed of lipophilic corn starch and gelatin, obtained by casting and plasticized with glycerol or sorbitol.

| Films[a] | Ratio | Thickness (mm) | Tensile strength (MPa) | Elongation (%) |
|---|---|---|---|---|
| AM LP 3%/GEL 10% GLI | 4:1 | 0.0390 | 59.77 ± 7.80 b | 2.94 ± 0.21c |
| | 1:1 | 0.0424 | 77.18 ± 1.51 ab | 3.78 ± 0.37 bc |
| | 1:4 | 0.0540 | 99.83 ± 10.71 a | 5.07 ± 0.36 a |
| AM LP 5%/GEL 10% GLI | 4:1 | 0.0574 | 77.61 ± 7.53 ab | 3.20 ± 0.24 c |
| | 1:1 | 0.0742 | 96.83 ± 6.60ab | 4.21 ± 0.82 ab |
| | 1:4 | 0.0814 | 89.57 ± 8.91 ab | 5.14 ± 0.35 a |
| AM LP 3%/GEL 10% SOR | 4:1 | 0.0325 | 51.55 ± 7.09 c | 5.58 ± 1.34a |
| | 1:1 | 0.0434 | 106.09 ± 10.01 ab | 6.89 ± 0.42 a |
| | 1:4 | 0.0640 | 99.01 ± 9.85 b | 5.08 ± 1.36 a |
| AM LP 5%/GEL 10% SOR | 4:1 | 0.0523 | 66.92 ± 6.19 c | 5.31 ± 1.60 a |
| | 1:1 | 0.0655 | 117.02 ± 12.7a | 6.30 ± 1.09 a |
| | 1:4 | 0.0742 | 103.04 ± 6.12 ab | 6.08 ± 1.59 a |

Tukey mean values with the same letters (a–c) do not differ at $p \leq 0.05$. Tukey was carried out separately for films plasticized with glycerol and sorbitol.
[a] GEL = gelatin; AM LP = lipophilic corn starch; GLI = glycerol; SOR = sorbitol.

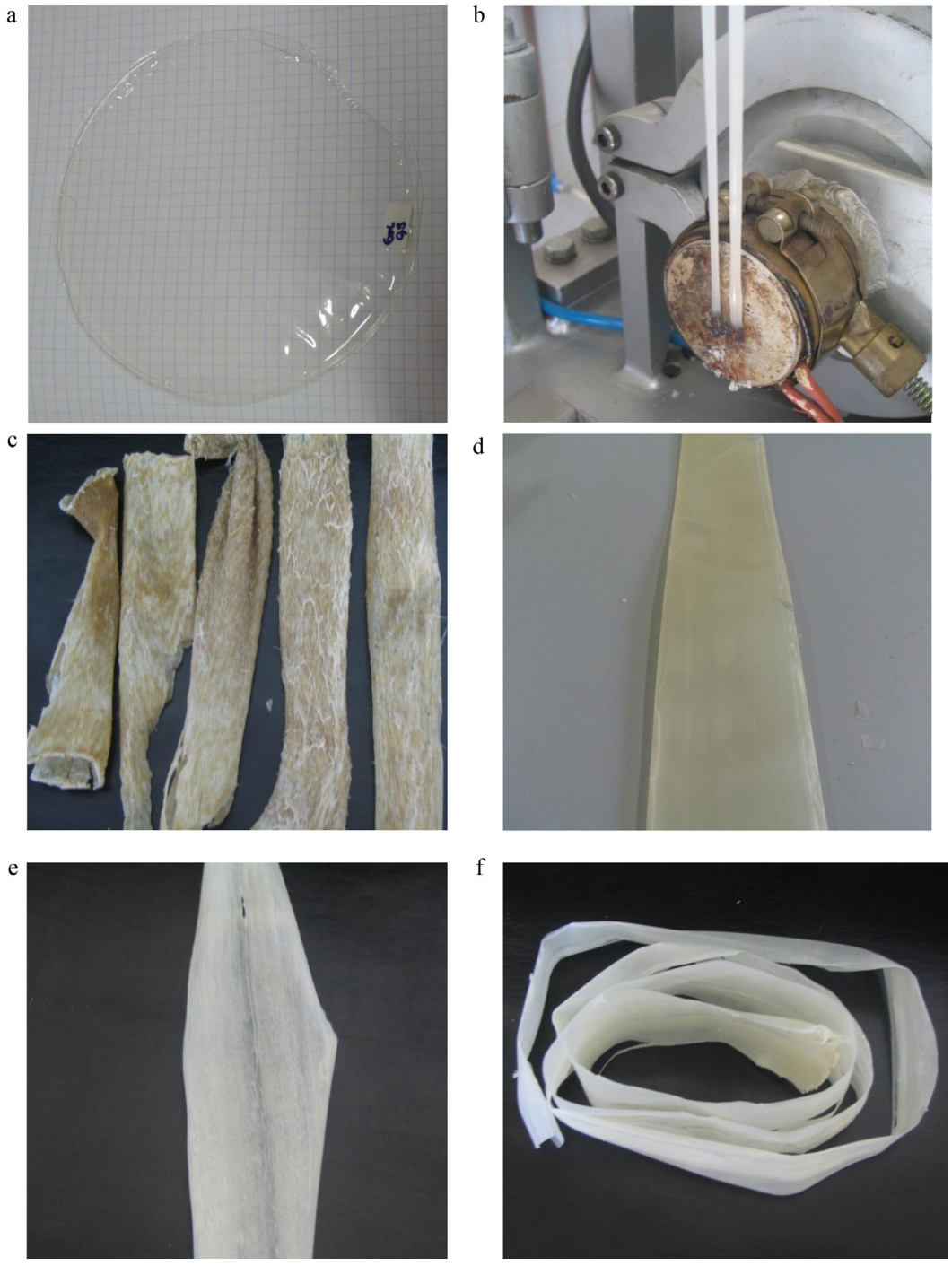


**Fig. 1.** Starch/gelatin films: (a) casting film, (b) samples from extruder before pelletization, (c) blow films obtained with high temperature, (d) blow films obtained with low temperature and (e–f) extruded and blown films.

little expansion and presented poor flexibility, making it difficult to complete its characterization by the methodology described in this work. Extruded bioplastics were also prepared with 1:4 and 4:1 proportions of starch and gelatin, and we observed that the higher the proportion of gelatin in the mix, the more rigid the material obtained. This fact can be explained by the characteristics of gelatin, which is a structural protein that confers a higher resistance when added to bioplastics (Cao, Fu, & He, 2007). However, if added in high amounts, gelatin may increase the fragility of the material due to its own stiffness (Cao et al., 2007).

Among the methods studied to obtain bioplastics, the casting technique (the same concentration of starch, gelatin and plasticizer in the mixture) yielded samples with lower density and lower values of WVP (Fig. 2a–b) than other methods. The value of WVP increased to 3.72 and 5.77 g mm/m$^2$ d kPa for bioplastics obtained by casting and pressing (Fig. 2b), respectively, but the highest values of WVP were obtained for the blown films (10.56 g mm/m$^2$ d kPa). The value of WVP is influenced by the thickness, that is, the lower the value, the lower the WVP. Moreover, the WVP of pressing/blowing films is higher because of cracks in the surface of

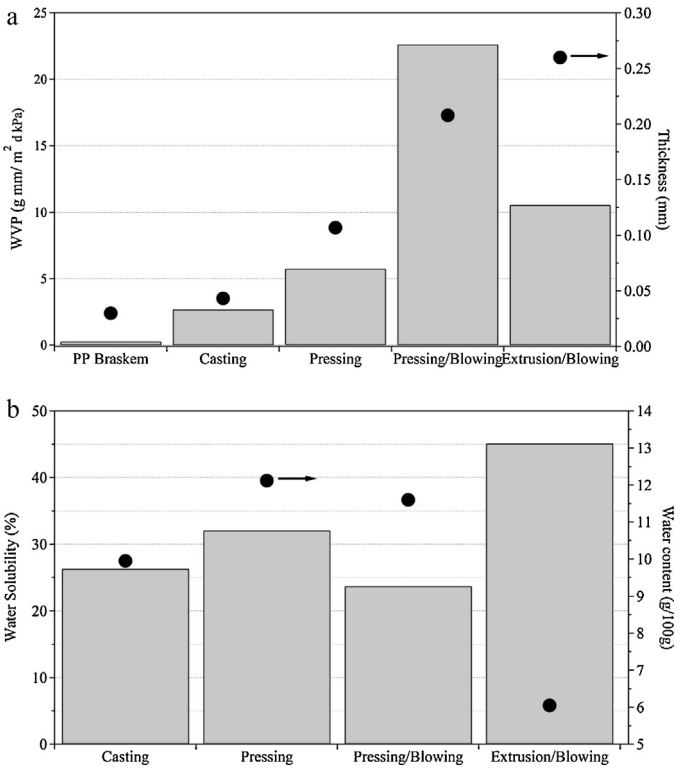


**Fig. 2.** Values of WVP, thickness (a) and (b) water solubility and water content of lipophilic corn starch and gelatin obtained by different techniques in comparison to the polypropylene (PP) film.

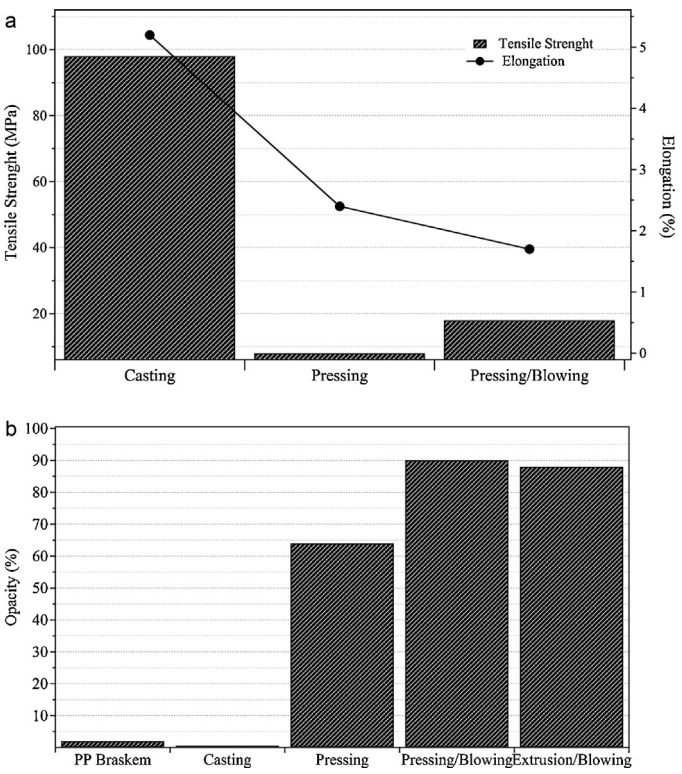


**Fig. 3.** Tensile stress (RM), elongation (EL) (a) and opacity (b) of lipophilic corn starch and gelatin obtained by different techniques.

samples, which can be observed in Fig. 4. While the surface of casting films were homogeneous without cracks.

A linear increase in WVP as a function of thickness was detected by Sobral (1999) in edible gelatin biofilms. The values obtained for the biofilms studied were higher than those observed for films of high-density polyethylene (0.02 g mm/m$^2$ d kPa), according to data from Smith (1986), and they were also higher than those observed for polypropylene films (0.33 g mm/m$^2$ d kPa), conditioned and analyzed under the same conditions (Smith, 1986).

Films obtained by extrusion followed by blowing presented higher values of solubility in water (Fig. 2c) than the films obtained by other techniques, probably because of their lower degree of hydration, a result of the three cycles inside the extruder mixture. Films prepared by the casting technique showed higher tensile strength and elongation and lower values of opacity than those produced by other methods (Fig. 3a–b). A higher value of tensile strength for bioplastics produced by casting in comparison to the extruded biofilms was also reported in literature, for biofilms produced with gelatin and plasticized with glycerol (Park, Scott Whiteside, & Cho, 2008). Bioplastics pressed, blown and extruded were processed at a higher temperature than those obtained by casting, which may have caused a denaturation of the proteins and, as a result, the proteins lost the ability to act as a structural reinforcement. In addition, there was an increase in free volume and in WVP, and there was a decrease in tensile strength of these bioplastics. The films obtained by casting presented lower opacity, which was very close to that found for synthetic polypropylene films.

Films based on PRE, PRE/SP and EX/SP showed much higher opacity (Fig. 3b), which can be explained considering two hypotheses: increased crystallinity of these bioplastics and/or structural changes in the materials that compose them. The highest values of WVP and the low tensile strength of these bioplastics, which were prepared by pressing and blowing, can also be explained based on the results of the SEM and thermal analysis.

The micrographs obtained for the films produced by casting show a homogeneous surface without cracks, suggesting a cohesive matrix (Fig. 4a). There was no phase separation, as also noted by Jensen (2007), who used SEM analysis of a homogeneous surface obtained with films based on cassava starch plus 2% emulsifier. The micrographs of bioplastics from the pressing technique show that their surfaces were irregular and had cracks (Fig. 4b), which can cause a certain fragility to the material, reflecting on their mechanical and barrier properties. As seen in Fig. 4c, the micrographs of bioplastics pressed and blown (PRE/SP) showed a rough surface, which may have compromised its tensile strength. One can also note the presence of cracks, which may interfere with the results of the WVP of these films. Sakanaka (2007) also noted an irregular surface, which indicated the direction in which the film of cassava starch and polybutylene succinate co-adipate (PBSA) was processed (Sakanaka, 2007).

Images obtained by SEM (Fig. 4d) for extruded and blown bioplastics show that, although the film presented some roughness, it was homogeneous and without starch granules, suggesting a cohesive matrix. The presence of starch granules can bring roughness and reduce the mechanical properties of films (Lim, Jane, Rajagopalan, & Seib, 1992; Thiré, Simão, & Andrade, 2003). In Fig. 4d, one can visualize the direction of extrusion in the bioplastics, similar to the pressed and blown films. The same observation was reported by Sakanaka (2007), who commented that it was possible to identify the direction of extrusion in the bioplastics he studied (Fig. 4d). Costa (2008) obtained micrographs of different concentrations of thermoplastic starch and PBTA (polybutylene adipate-co-terephthalate) for films obtained by extrusion. According to that study, the surface of the pure, thermoplastic starch film was more homogeneous than those of the blended films, although it was slightly damaged by the electron beam due to its fragility (Costa, 2008).

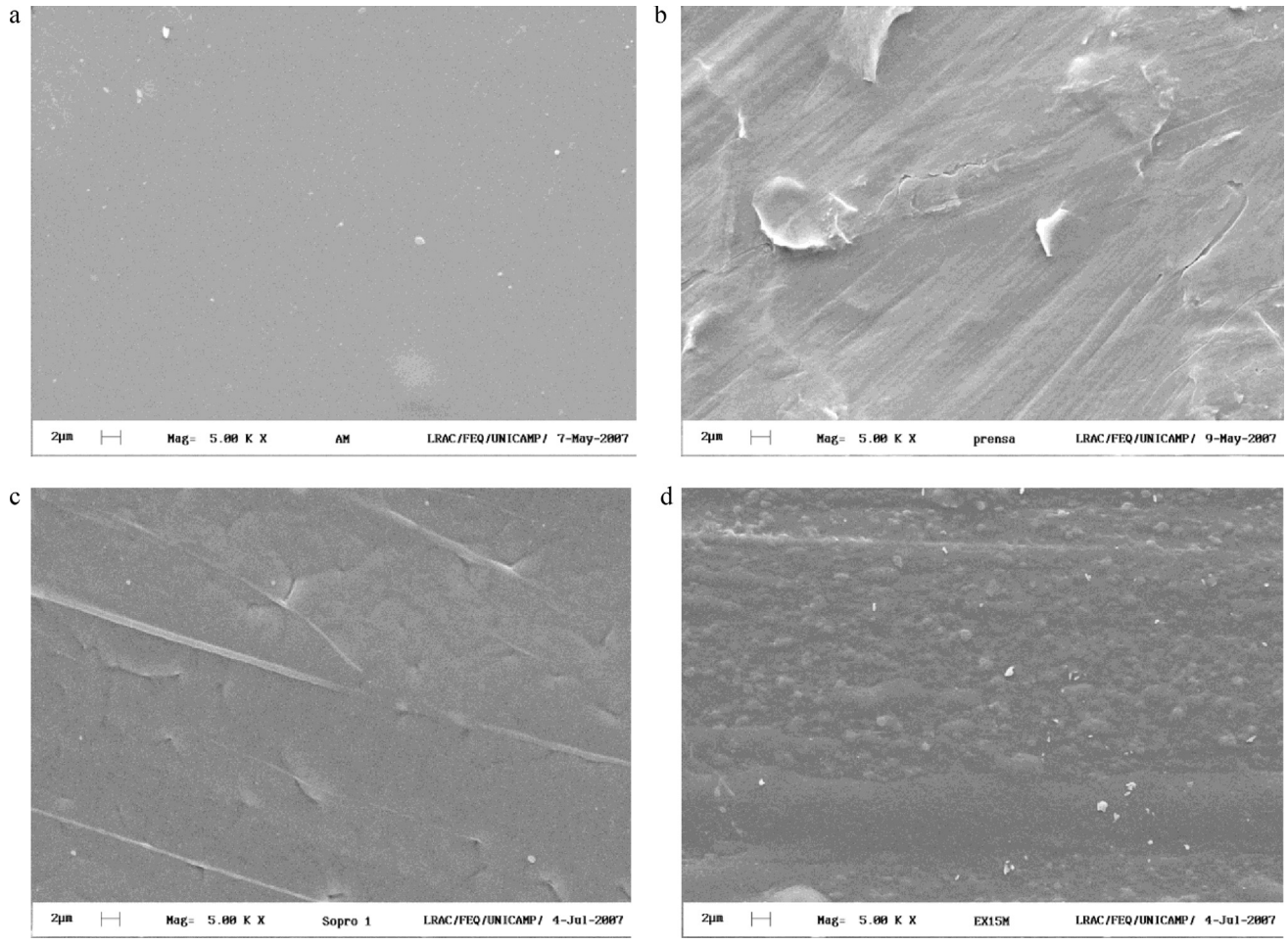


**Fig. 4.** Scanning electron microscopy of starch and gelatin obtained by different techniques (magnification of 5000×): (a) casting, (b) pressed, (c) pressed and blown and (d) extruded and blown.

The thermograms in Fig. 5a show the behavior of the thermal degradation of the bioplastics obtained by casting, pressing, and pressing and blowing. All three films showed a small loss of mass in the region of 100 °C, probably caused by the loss of water molecules. Another observation was that the films obtained by casting and pressing techniques had similar curves, which illustrate a marked degradation in the range of 250 °C to 450 °C. Alternatively, the blown film presented a different decay curve, with two distinct regions of degradation, one in the range of 250 °C to 350 °C, and the other in the range of 350 °C to 450 °C.

The results of DSC analysis (Fig. 5b) for the bioplastics obtained by casting, pressing, and pressing and blowing agree with the results observed from the TGA; the results of the DSC for the films prepared by the first two techniques were similar to each other but different from those prepared by pressing and blowing. In the bioplastic obtained by casting, there were two intense endothermic transitions between 58 to 68 °C and 80 to 95 °C; similarly, in PRE bioplastic, two similar transitions were observed but were less intense. The first transition was slightly shifted to lower values in the range 50 to 62 °C, whereas the second remained the same for the bioplastic obtained by casting (80 to 95 °C). Endothermic transitions not specified in these temperature ranges were observed by Sobral and Habitante (2001) in a study using gelatin obtained from pig skin, where the authors worked with several storage conditions. However, the values of the DSC transitions, which most closely resembled those found in this study, were those where packaging was subjected to a relative humidity of 53% (Sobral & Habitante, 2001).

For the bioplastics made via PRE/SP, the result of the DSC (Fig. 5b) differed from other methods; in this case, there was only one very intense endothermic transition around 59 °C. Apparently, this well-defined peak represents a fusion of semi-crystalline or crystalline structures. The results of X-ray diffraction (Fig. 6) confirm the hypothesis that PRE/SP bioplastics have crystalline regions, as opposed to the other obtained bioplastics. These crystalline regions were clearly observed by defined peaks in the region of $2\theta$, between 15° and 25° (specifically the peaks are centered at 21.8° and 24.1°). Rindlav-Westling et al. (2002) found peaks that indicated the presence of crystallinity in potato starch films, which were dried under different treatment conditions but in the same range of $2\theta$, between 15° and 25° (Rindlav-Westling et al., 2002). Peaks indicating crystallinity in diffractograms of native cassava starch, practically in the same range of $2\theta$, from 14.8° to 22.9° were reported in literature (Veiga-Santos, Suzuki, Nery, Cereda, & Scamparini, 2008). The relative crystalline of PRE/SP sample was calculated as 34.06% in relation to the amorphous phase, similar crystalline values were found by Rindlav-Westling et al. (2002) for starch films, which was attributed to the crystallization of amylose.

As shown by these results, the bioplastics made by PRE/SP showed the greatest opacity, which is a common characteristic of crystalline and semi-crystalline materials. This sample also showed the lowest water content (6.05 g/100 g) (Fig. 2d). The opacity is highly influence by the crystalline content of a sample, whereas more compact are the polymer chains, more difficult is for the light pass through and higher is the opacity of films (Matsuguma et al., 2009). They also had poor mechanical properties, demonstrating

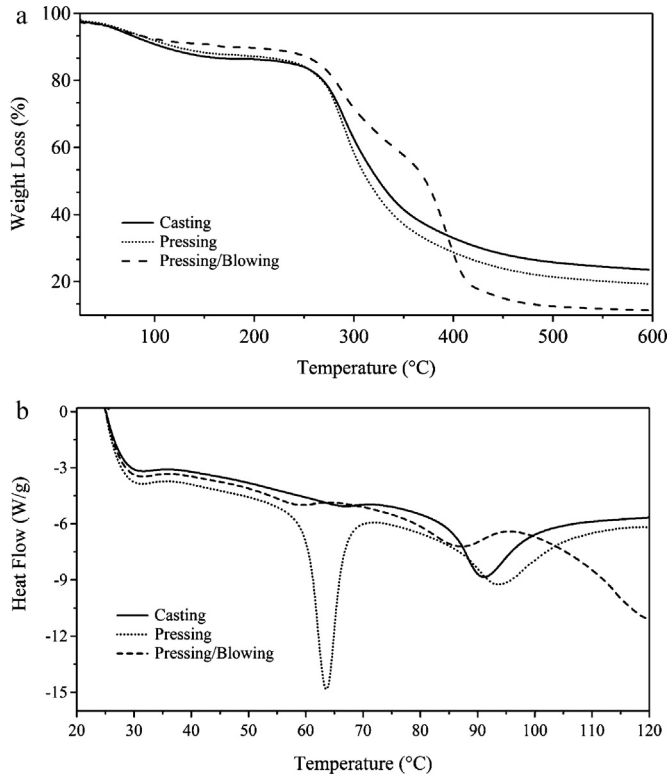


**Fig. 5.** Thermal analysis of starch/gelatin films plasticized with sorbitol and prepared by different techniques: (a) TGA and (b) DSC.

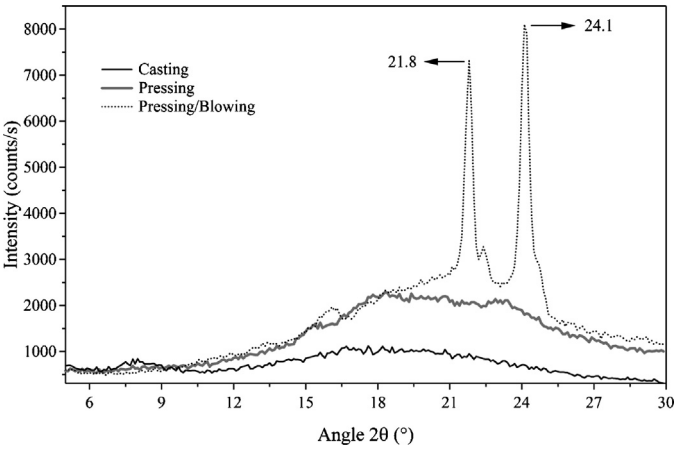


**Fig. 6.** X-ray diffraction of starch-based bioplastics prepared by different techniques.

the fragility of these blends. The distinct semi-crystalline behavior from blown samples could be justified by the nature of the process, where the chains are forced to line up, leading to a change in the molecular structure of the gelatin and/or starch due to the bi-orientation of the chains, resulting in higher crystallinity.

## 4. Conclusions

This paper demonstrates the importance of the composition and obtention process in the properties of starch based bioplastics. Among the films studied using the casting technique, those with 3% lipophilic starch, in 1:1 proportions and plasticized with sorbitol, showed lower values of PWV and higher tensile strength. Bioplastics prepared by casting showed lower thickness, opacity and PWV compared to the other films studied and had greater tensile strength. Those bioplastics obtained by pressing had lower values of tensile strength in relation to others and also had an irregular surface morphology with cracks. Films obtained by pressing and blowing showed little expansion during the blow, had cracks in the surface, low strength and higher water vapor permeability. In addition, pressing and blowing samples showed the highest density among the studied films and were the only ones to exhibit crystallinity by thermal analysis and X-ray diffraction. SEM showed that there was no phase separation between the starch, gelatin and plasticizer, illustrating some affinity between these components. DSC analysis showed the presence of a semi-crystalline structure for films obtained by pressing followed by blow extrusion. This result was confirmed by analysis of X-ray diffraction.

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