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Acetylated and native corn starch blend films produced by blown extrusion

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ABSTRACT

Thermoplastic starch (TPS) materials were developed from mixtures of native and acetylated corn starches with glycerol. To optimize the formulations an experimental design for multicomponent mixtures was used and the assayed formulations were determined by statistical software. Blends and pellets humidity content increased with glycerol concentration. Starch destructuration during the extrusion process was studied by thermal analysis. Films presented homogenous structure, rough surfaces and certain stickiness. They presented different properties, related mainly to the differential characteristics of native and acetylated starches and to hydrophilic character of glycerol. Their mechanical behavior indicated that they are a good option as a food packaging materials since TPS films resulted enough resistant to protect the product and flexible to resist moderate deformations. Besides, the use of acetylated starch in the formulations enhanced film resistance and reduced their WVP, despite of its low modification degree. The storage of the films under controlled conditions increased their stiffness, while their flexibility and WVP were reduced. Plasticizer migration towards the matrix surface was observed in stored films. Films resulted stable till $a_w = 0.7$ and due to their selective gaseous permeability they are useful to package products susceptible to oxidation or to control vegetable respiration and senescence.

1. Introduction

Packaging materials developed from natural products may provide an alternative to the problem of plastics disposing. Due to its total biodegradability, low cost and worldwide availability, there has been a large interest in the use of starch to develop biodegradable films and edible coatings, especially for food applications, (López et al., 2008, 2010a,b, 2011). In order to convert starch into films, casting technique is the most widely used procedure in research areas, (Cerqueira et al., 2012; Flores et al., 2010; García et al., 2009; López et al., 2008, 2010a,b, 2011). Even though this is a useful technique at laboratory scale, it must be taking into account that this method involves the gelatinization of an aqueous starch suspensions and its subsequent dehydration under controlled conditions, being considered as an energy-consuming procedure. Besides, industry requires high levels of biodegradable film production so the scale-up of the obtaining process employing preferably the existing processes for synthetic materials is indispensable, (Thunwall et al., 2008). In this context, extrusion method followed by blowing or thermo-compression molding are two viable alternatives due to their energy-efficient combined with their high productivity, (Flores et al., 2010; Pellissari et al., 2012; Thunwall et al., 2006).

Thermoplastic starch (TPS) is a relatively new concept and, actually, it is one of the main research hints for the biodegradable materials manufacturing, (Chen et al., 2012; Curvelo et al., 2001; Ma et al., 2008, 2009; Teixeira et al., 2007). Starch is not a real thermoplastic material, but when it is processed with plasticizers, under high temperature and mechanical forces, granules suffer destructuring and starch melts and flows, (Bastioli, 2001; De Graff et al., 2003; Herrera-Brandelero et al., 2011; Ma et al., 2008, 2009). TPS can easily be adapted to different processes employing standard equipments used for synthetic polymers, such as extrusion, blowing, injection and compression molding, (Avérous and Boquillon, 2004; Teixeira et al., 2007; Zhai et al., 2003). This possibility would enhance the commercial potential of biodegradable films since it is feasible working in a continuous system with ready control of process variables such as temperature, moisture, and size/shape. Nowadays, there are a wide variety of available products obtained by processed TPS from different native starches, like disposable bags, containers, vessels, forks, knifes and garbage bags, (Ma et al., 2009; Shamekin et al., 2002).

However, TPS films uses are limited due to their low water resistance and the mechanical properties dependence with the moisture ambient, (Avérous and Boquillon, 2004, Bastos et al., 2009; Ma et al., 2009; Zullo and Iannace, 2009). Thus, most of

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Table 1
Formulations based on native and acetylated corn starches and glycerol determined by the Statistica software 6.0 and humidity content (%) of the blends (before processing) and pellets.

Formulation[a]	Acetylated corn starch (AS) (% w/w)	Native corn starch (NS) (% w/w)	AS/NS ratio	Glycerol (% w/w)	Humidity content (% w/w)	
					Blend (before processing)	Pellets
1 (10:70:20)	10	70	0.14	20	17.77 ± 0.16	10.49 ± 0.32
2 (80:5:15)	80	5	16	15	15.00 ± 0.17	7.70 ± 0.25
3 (75:5:20)	75	5	15	20	17.81 ± 0.23	10.50 ± 0.36
4 (15:70:15)	15	70	0.21	15	15.10 ± 0.08	7.88 ± 0.23
5 (45:37.5:17.5)	45	37.5	1.2	17.5	16.51 ± 0.20	9.30 ± 0.06

[a] (% w/w AS:% w/w NS:% w/w glycerol).

the studies on film blowing have been conducted on blends of TPS with other biodegradable and non-biodegradable polymers where TPS is usually the minor component, (Zullo and Iannace, 2009). Different TPS were blended with synthetic polymers (Fishmann et al., 2000; Jana and Maiti, 1999; Otey et al., 1987) or with other biodegradable material, such as poly(vinyl alcohol), poly(caprolactone), polyester (Halley et al., 2001; Matzinos et al., 2002) or chitosan (Pellissari et al., 2012). Besides, the use of TPS modified with polyurethane microparticles has been assayed as an alternative to reduce film hydrophilicity, (Chen et al., 2012).

On the other hand, chemical starch modifications such as esterification, etherification or oxidation before thermo-plasticization process, reduce water sensibility and enhance mechanical behavior of the obtained TPS materials, (Gaspar et al., 2005). Likewise, Thunwall et al. (2008) reported that the use of oxidized and hydroxypropylated starches, as well as, high plasticizer content could increase the TPS melt tenacity (ability of the melt to deform without rupture), one of the potential limitations in their processing. Thus, the use of modified starches, especially the substituted ones, led to improve the structural stability of the thermoplastic materials in addition to their barrier and mechanical properties; however references about this subject are scarce and require a deep insight.

The aims of the present work were to obtain biodegradable films from native and acetylated corn starches, as well as, different mixtures of them, employing the extrusion and blowing technique. In addition, an experimental statistic design to study the formulation effect on film properties and performance was applied.

2. Materials and methods

2.1. Starch samples

Native (Amidex 3001) and acetylated (RD571) corn starches were supplied by Corn Products Brazil. Amidex 3001 contains 27% w/w amylose and 73% amylopectin, while RD571 presents an acetylation degree between 0.5% and 0.8%.

2.2. Experimental design

An experimental design for multicomponent mixtures was used. In this method, factors are the components proportions in the mixture and their levels are not independent between them since the following restriction should be verified: the components proportions addition should be 1. For mixtures of q components:

$$\sum_{i=1}^{q} x_i = x_1 + x_2 + \cdots + x_q = 1 \quad (1)$$

where x_i represents the proportion of each component in the mixture.

The advantage of this design is the possibility to evaluate the effects of the individual and combined variables through an experimentally delimited assay, (Srinivasa et al., 2007).

To study the formulation components effect on film properties, a design for mixtures with three components, with three replicated in the central point was employed. The dependent variables were the concentrations of native corn starch (NS), acetylated corn starch (AS) and glycerol (G). Maximum and minimum concentrations of each component in the mixtures were established to delimit the study zone and to make feasible this investigation. These limits were proposed based on preliminary tests being 5–70, 10–80 and 15–20% w/w for NS, AS and G, respectively. The assayed formulations are shown in Table 1, they were determined using the Statistica software version 6.0, (Statsoft, USA).

2.3. Extrusion process

Starches powders were mixed with glycerol, in the proportions described in Table 1, by hand to achieve plasticizer incorporation and homogeneous mixtures. Blends were conditioned for 12 h at ambient temperature before submitting them to the pelletization process.

Preliminary extrusion assays were performed to select the operating conditions, such as, temperature profiles and screw rotation speed. These parameters were adjusted so as to avoid starch degradation but allowing a complete starch plasticization, as well as, a good material flow through the extruder barrel. The assayed temperatures ranging between 120 and 130 °C for the three cannon areas. The best results were obtained with 120 °C in the three heating zones of the extruder, since employing values above this one the resulting extrudate was light brown and smelled slightly burnt.

TPS pellets were obtained using a pilot extruder BGM ELR-25 (Brazil) equipped with a single screw of 250 mm in diameter and a 10-HP motor. A matrix containing six orifices of 2 mm in diameter was employed.

2.4. Differential scanning calorimetry

To demonstrate that operating conditions allowed obtaining thermoplastic starches from starch–glycerol assayed blends, thermal analysis by differential scanning calorimetry (DSC) were performed. The thermograms of the blends (before processing) and the pellets were obtained in a Perkin Elmer Pyris I equipment (USA). The samples were heated to 200 °C at a rate of 10 °C/min. To avoid the samples dehydration hermetic pans were used.

Humidity content of the blends before processing and the obtained pellets was determined by measuring the weight loss of the samples, upon drying in an oven at 105 °C until constant weight. Samples were analyzed at least in triplicate and results were expressed as percentage (%) of moisture content of samples.

2.5. Blowing process

The extruder described previously was feed by hand with TPS pellets (5 kg) to obtain starch films tubes of 15 cm in diameter approximately. The temperature along the screw was 120 ± 2 °C and the die temperature varied between 125 and 130 °C. The die

diameter was 25 mm and a cooler air ring of 300–350 mm in diameter was employed to film forming.

2.6. Film characterization

2.6.1. Morphology

TPS films were examined visually and by scanning electron microscopy (SEM) with a JEOL JSM 6360 electron microscope (Japan), as described in a previous work, (López et al., 2011).

2.6.2. Thickness

Film thickness was determined using a digital coating thickness gauge Check Line DCN-900 (New York, USA) for non-conductive materials on non-ferrous substrates. Ten measurements were randomly taken at different locations for each specimen and the mean value was reported.

2.6.3. Moisture content

It was determined by measuring the weight loss of films, upon drying in an oven at 105 °C until constant weight. Samples were analyzed at least in triplicate and results were expressed as percentage (%) of moisture content of samples.

2.6.4. Water vapor permeability

Tests were conducted at 20 °C using the ASTM E96 method with several modifications. Films were sealed in acrylic cells containing silica gel (0% RH) and they were placed in desiccators at 20 °C with NaCl saturated solution (75% RH). The tested cells were weighed periodically till steady state was reached. Water vapor permeability (WVP) was calculated using the following equation:

$$\mathrm{WVP} = \frac{\left(\frac{\Delta w}{\Delta t}\right) \times \delta}{A \times \Delta p} \tag{2}$$

where the term $\Delta w/\Delta t$ was calculated by linear regression from the weight gain data as a function of time (g/s), δ is the film thickness (m); A is the area of exposed film (1.81×10^{-3} m^2) and Δp is the differential water vapor partial pressure across the film (1753.55 Pa at 20 °C). Samples were analyzed at least in duplicate and the average is reported.

2.6.5. Gaseous permeabilities

Oxygen and carbon dioxide permeabilities were determined by the concentration increase method using a special permeability cell and gas chromatography to analyze the permeate gas concentration as was previously described, (García et al., 2009). The stainless steel cell has a cylindrical shape and this one is divided by the film tested in two compartments. The volume of each chamber is 29.45 cm^3 and the transfer area is 4.91 cm^2. The film was placed in the cell and this one was sealingly closed to prevent leakage. One compartment has two connections that allow the tested gas flow, maintaining the inside pressure at 1 atm. At regular time intervals, samples (500 μL) were extracted of the sample compartment using a gas syringe. The tested gas concentration was measured employing a Varian Star 3400cx chromatograph (USA) equipped with a thermal conductivity detector and a packed concentric column CTR I (USA). The column, injector and detector temperatures were 30, 120 and 120 °C, respectively and the carrier gas flow (He) was 60 mL/min. The retention times for O_2 and CO_2 were 8 and 5.5 min, respectively. The gas concentration was calculated from the areas corresponding to peaks using a calibration curve previously obtained. Measurements were performed at controlled temperature of 20 °C and they were performed at least on two film samples of each formulation and the average is reported.

2.6.6. Mechanical properties

Tensile tests were performed at 20 °C in a texturometer TA.XT2i – Stable Micro-Systems (England) using a tension grip system A/TG. Probes of 7 × 0.7 cm were used, analyzing at least 10 probes for each film formulation. The probes were cut parallel to the blowing flux direction; this remark is relevant since mechanical properties of films obtained by blowing technique could depend on the direction in which probes are cut (parallel or perpendicular to the blowing flux). It is attributed mainly to the polymeric chains alignment with the flux direction giving some anisotropy to the film samples. Tensile strength (TS, MPa) and elongation at break (E, %) were calculated according to the ASTM D882-00 (2001).

2.6.7. Dynamic-mechanical analysis

Temperatures and intensities of the relaxation phenomena in the films were determined by dynamic-mechanical analysis (DMA) in a Q800 (TA Instruments, New Castle, USA) with a liquid N_2 cooling system, using a clamp tension. Multi-frequency sweeps at fixed amplitude from −100 to 100 °C at 2 °C/min were carried out. The storage (E') and loss (E'') moduli and tan δ curves as a function of temperature were recorded and analyzed using the software Universal Analysis 2000. Assays were performed at least on four film specimens for each formulation studied.

2.6.8. Storage effect on film properties

Films were stored under controlled conditions at 20 °C and 65% RH during 360 days. The mechanical behavior and the water vapor permeability of the aged films were determined as was previously described. Besides, stored films were examined visually and by scanning electron microscopy (SEM) using the aforementioned equipment.

2.6.9. Sorption isotherms

A static gravimetric method was used to determine the sorption isotherms of the developed films. Pieces of films (20 × 20 mm) were conditioned placing them inside a desiccator with $CaCl_2$ during 3 weeks. Then, samples were placed in duplicate inside nine desiccators, each one containing oversaturated salt solutions of known equilibrium relative humidity at 20 °C. These environments provided an a_w range of 0.11–0.97, with the following salts used: LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, NaCl, KCl, $BaCl_2$ and K_2SO_4. Thymol was added to the high a_w solutions to prevent microbial growth. The desiccators were kept at 20 °C until equilibrium was attained. After that, moisture content of the equilibrated samples was determined by the previously described method. The experimental data obtained were adjusted employing GAB sorption equation and non-linear regression statistical analysis was performed using the software Systat 10.0 (SYSTAT, Inc., Evanston, IL, USA).

2.7. Data analysis

The obtained data for humidity content, mechanical properties, WVP and gaseous permeabilities were mathematical modeled using a polynomic model associated to the experimental design, (Khuri and Cornell, 1987). For mixtures with three components:

$$Y = k + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3 \tag{3}$$

where Y corresponds to the measured property, β coefficients are the estimated parameters for each model linear and cross term and X_1, X_2 and X_3 are the concentrations of each component in the mixture (1:AS, 2:NS and 3:G). Positive values of the binary and ternary components (β_{ij} and β_{ijk}) indicate a synergic effect; while negative ones represent antagonism. The mathematical modeling of the experimental results was performed with the

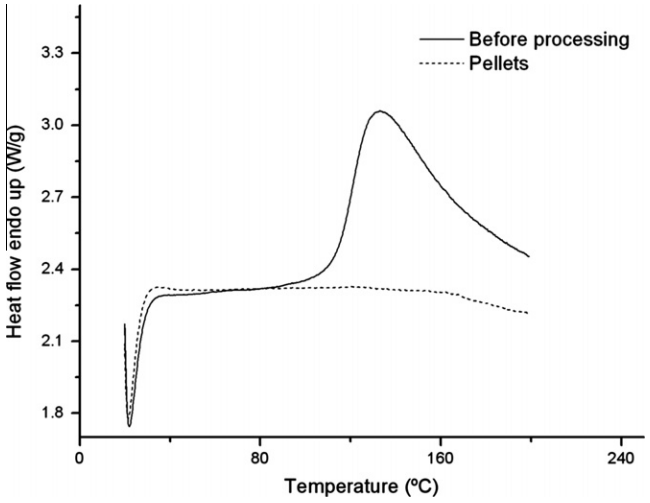


Fig. 1. DSC thermograms corresponding to formulation 1 blend (10% acetylated starch, 70% native starch and 20% glycerol) and the obtained pellets.

software Systat version 10.0 (SYSTAT, Inc., Evanston, IL, USA). Goodness of fit was evaluated by the use of the regression coefficient (r^2), mean relative deviation modulus (P) and standard error of the model (S). P and S were calculated according to the following equations, (Ayranci and Duman, 2005).

$$P = (100/N)\left(\sum |X_{pred} - X_{meas}|/X_{meas}\right) \quad (4)$$

$$S = \left[\sum (X_{meas} - X_{pred})/(N-p)\right]^{0.5} \quad (5)$$

where X_{meas} is the measured value of the evaluated property, X_{pred} is the corresponding predicted value calculated, N is the measurements number and p is the parameters number.

Besides, response surfaces were obtained for the modeled properties from the non-linear regression equations. In the three-dimensional graphics, Z axis corresponds to the dependent studied variable, X axis to the ratio between acetylated and native starch concentrations and Y axis to the glycerol concentration. Response surfaces were generated employing the software OriginPro version 7.0 (USA).

3. Results and discussion

3.1. Pelletization process

The pelletization included two basic steps, the first one corresponded to the starch plasticization process to acquire the "*spaghettis*", and the second step consisted in their cutting to obtain the corresponding pellets. On the other hand, the screw speed selected (40 rpm) generated an enough torque to destroy the starch crystalline structure and plasticize native and modified corn starch. Fig. 1 shows the DSC thermogram of the formulation 1 blend (before processing) and that of the corresponding obtained pellets. The thermogram of the blend presented a fusion peak indicating the presence of a crystalline phase associated mainly to amylopectin organization within the granule, while in the case of the pellets this fusion peak was absent. Thus, it was demonstrated that the selected operating conditions lead to obtain a thermoplastic material. On the other hand, single and double pelletization process was assayed, allowing the double processing obtaining more homogenous pellets (Fig. 2A).

The humidity content of the blends before they were submitted to the extrusion process and the values corresponded to the pellets are reported in Table 1. As it can be observed, due to the hydrophilic character of the plasticizer, with increasing glycerol concentration in the formulations increased the moisture content of the blends, as well as, the values corresponded to the pellets. The blends results were closer to those reported for Galicia-García et al. (2011) for mixtures based on native starch (corn, potato and waxy corn) and phosphorylated corn starch blended with bagasse fiber, plasticized with glycerol (22%). The blends processing in the extruder caused a sample dehydration decreasing the humidity content 45% on average. Avérous et al. (2001) also informed a decrease in the water content of blends of wheat starch and natural cellulose fibers, plasticized with glycerol, after being processed, but these decrease was around 5%.

3.2. Film obtaining

Pellets obtained from the different tested formulations showed adequate processability to form films by blown extrusion, supporting the tension exerted by rolling and the airflow pressure without showing tendency to tear. The blowing process conditions

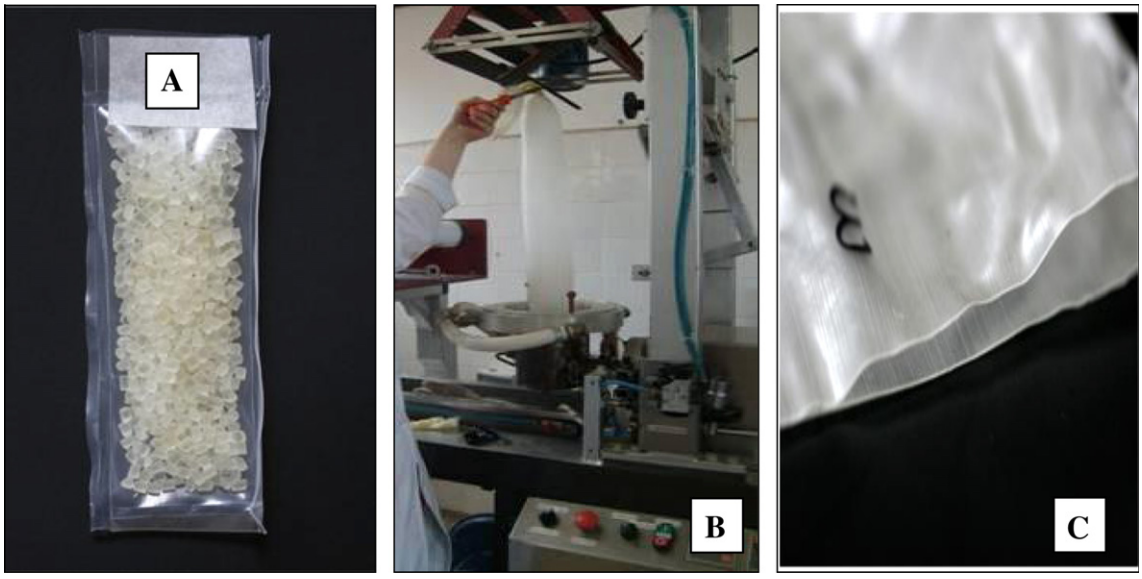


Fig. 2. (A) Thermoplastic starch pellets. (B) Starch films obtaining by blown extrusion. (C) Starch film obtained from formulation 3 (75% acetylated starch, 5% native starch and 25% glycerol).

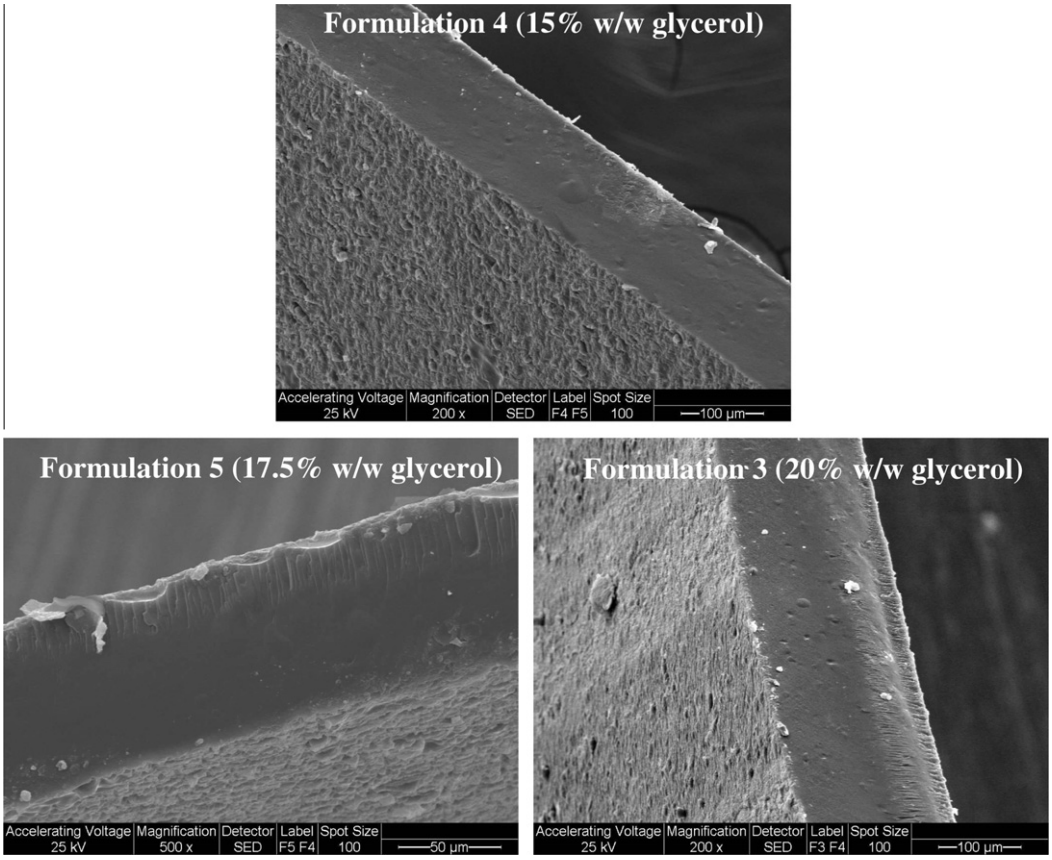


Fig. 3. Cross-section SEM micrographs of starch-based films obtained by blown extrusion.

employed led to develop homogeneous films without bubbles, regardless the TPS formulation (Fig. 2B and C). The rotation speed of the screw was 40 rpm, the temperature setting along this one was 120/120/120 ± 2 °C and the die temperature was also 120 ± 2 °C. Mościcki et al. (2011) stressed that it is not advisable to submit TPS materials at blown temperatures below 120 °C since some residual pellets could appeared on films surfaces.

It is well-known that water is considered a natural plasticizer for starch matrixes and can be regarded as a process aid since the melt viscosity is lowered with increasing water content. However, in this study, no extra water was incorporated to the formulations since this one restricts the upper processing temperature because steam generation in the material leads to bubbles and foaming which is not desirable in film blowing, (Thunwall et al., 2008).

The obtained materials presented certain stickiness which disallowed that TPS films could be winding when they emerged from the die; this problem might be overcome maintaining the bubble blown till it reaches ambient temperature. Flores et al. (2010) and Thunwall et al. (2008) also informed the same inconvenient respect to the grassy appearance of films obtained by extrusion and blowing of cassava and potato starches, respectively. These authors stressed that the starch humidity susceptibility and the plasticizer migration to the material surface caused blown bubble failures, as well as, problems related with the film stickiness. According to Thunwall et al. (2008), an alternative to get over this problem could be to dry the pellets prior to film blowing. On the other hand, Buehler et al. (1994) proposed the use of other plasticizers, such as sorbitol and urea, as a complement or replacement of glycerol.

Film thickness varied between 76 and 129 µm. The films obtained by extrusion and blowing method did not result homogeneous respect to their thickness since this property depends on the insufflated gas flux during blowing step and it was very difficult to control.

3.3. Films morphology

Fig. 3 shows the surfaces and microstructures of starch films correspond to formulations 3, 4 and 5 which contained 20, 15 and 17.5% w/w glycerol, respectively. All starch formulations allowed to obtain films which surfaces presented certain roughness and their structures resulted homogeneous and compact. The similar microstructure of the developed films could be attributed to the chemical compatibility between native and acetylated starches due to the low acetylation degree of the modified starch employed (0.5–0.8%). Herrera-Brandelero et al. (2011) stressed that when two polymers are mixed by extrusion, it is relevant that a good dispersion and distribution of the particles occurs, forming a single polymeric phase and avoiding clusters formation from the entangled polymer chains. In Fig. 3 there is no evidence of clusters presence, indicating that an adequate dispersion occurred when blends of native and acetylated corn starches were processed.

Besides, even though the TPS formulations contained different glycerol concentrations, this variation did not affect the appearance and homogeneity of the films structures.

3.4. Response surface methodology (RSM)

Table 2 shows the results of the film properties obtained from the starch mixtures proposed by the experimental design (Table 1). On the other hand, Table 3 shows the best adjusted models to the film properties as well as the obtained goodness of fit. Ayranci and Duman (2005) stressed that an excellent fit is obtained when P values are lower than 5, the regression coefficient approaches to 1

Table 2
Properties of films based on native and acetylated corn starches plasticized with glycerol, obtained by extrusion and blowing technique.

Formulation[A]	AS/NS[B]	Thickness (μm)	Moisture content (% w/w)	Mechanical properties		WVP × 10^{10} (g/s m Pa)	Gas permeability		
				Tensile strength (MPa)	Elongation at break (%)		$CO_2 \times 10^9$ (cm^3/m s Pa)	$O_2 \times 10^{10}$ (cm^3/m s Pa)	Selective coefficient P_{CO2}/P_{O2}
1 (10:70:20)	0.14	80.53 ± 8.43^a	10.99 ± 0.33^a	27.09 ± 2.75^a	4.73 ± 0.13^a	1.41 ± 0.30^a	5.04 ± 0.35^a	4.13 ± 0.11^a	12.20
2 (80:5:15)	16	75.97 ± 13.68^a	9.05 ± 0.43^b	16.25 ± 0.42^b	2.59 ± 0.49^b	0.88 ± 0.05^b	2.66 ± 0.18^b	2.08 ± 0.08^b	12.78
3 (75:5:20)	15	122.93 ± 11.51^b	10.69 ± 0.78^a	10.31 ± 0.09^c	20.14 ± 1.56^c	1.31 ± 0.25^a	4.13 ± 0.14^c	3.31 ± 0.08^c	12.47
4 (15:70:15)	0.21	129.42 ± 14.18^b	9.26 ± 0.54^b	23.99 ± 2.95^a	6.14 ± 0.19^d	1.20 ± 0.20^a	3.85 ± 0.04^d	2.98 ± 0.08^d	12.93
5 (45:37.5:17.5)	1.2	122.10 ± 14.00^b	8.71 ± 0.20^b	17.54 ± 1.92^b	3.92 ± 0.25^e	1.36 ± 0.17^a	4.62 ± 0.12^a	3.65 ± 0.22^e	12.65

Reported values correspond to the mean ± standard deviation. Values within each column followed by different letters indicate significant differences ($p < 0.05$).
[A] (% w/w acetylated starch – % w/w native starch – % w/w glycerol).
[B] Acetylated to native starch ratio.

and the standard error associated to the model is low. Thus, considering these criteria, in all cases the proposed model provided a satisfactory fitting to the experimental data (Table 3).

Analyzing the β coefficients values, presented in Table 3, it was observed that the major effects on film properties corresponded to the individual independent variables (native starch, acetylated starch and glycerol concentrations). Besides, the double interactions influence were less important since the corresponding coefficients (β_{12}, β_{13} and β_{23}) presented lower magnitude than individual ones (β_1, β_2 and β_3). Finally, the effects of the triple interaction (β_{123}) were very low and even zero in the case of gaseous permabilities.

3.5. Films moisture content

Films moisture content varied between 8.71% and 10.99% (Table 2). The obtained values resulted lower than those reported by Flores et al. (2010) for cassava starch films plasticized with 18% of glycerol. Films moisture contents were similar to those reported for the extruded pellets (Table 1), which indicate that during the blowing process did not occur a significant additional dehydration of the material. Analyzing the model parameters presented in Table 3, the coefficients of the individual variables (β_1, β_2 and β_3) resulted positive, thus, an increase in any of the three concentrations would led to an increase in film moisture content. However, the most relevant coefficients were those corresponding to native starch (β_2) and glycerol (β_3) concentrations while acetylated starch one (β_1) had lower effect on this property. The formulation with the highest glycerol concentration (20% w/w) showed the highest moisture content due to the plasticizer hydrophilic character. The response surface obtained for this property also shows the described tendency (Fig. 4).

3.6. Films mechanical properties

Fig. 5A shows the surface response for maximum tensile strength and evidences that the more important effects corresponded to both starches concentrations, being the strongest films those with low acetylated/native ratio, regardless the glycerol concentration (Table 2). With regard to the proposed fitting model, the parameters corresponding to both starches (β_1 and β_2) exerted a significantly higher ($p < 0.05$) effect than glycerol concentration (β_3) on tensile strength (Table 3). Acetylated starch incorporation, in spite of its lower substitution degree, reinforced film matrix increasing the maximum tensile strength of the developed materials ($\beta_1 > 0$). A similar trend was observed in a previous work for starch based films prepared by casting method, (López et al., 2008). Thus, the obtained values of tensile strength for the developed films were higher than those reported by Zullo and Iannace (2009) for blown films from different starch sources.

With respect to elongation at break, the observed behavior was opposite to those described for the maximum tensile strength. The more important effects corresponded to both starches concentrations, β_1 and β_2 coefficients presented similar magnitude between them but they were opposite ($\beta_1 < 0$ and $\beta_2 > 0$). With regard to glycerol, the observed effect was low but positive; film flexibility was improved increasing glycerol concentration in the formulations, (Table 2). This trend was clearly evidenced by comparing the flexibility of the films corresponding to the formulations 2 and 3 since their ratio AS/NS were similar (16 and 15, respectively, Table 2). The films obtained from the formulation 3 with 20% glycerol presented flexibility 700% higher than those obtained from formulation 2 (15% plasticizer). However, for formulations with low AS/NS ratios (formulations 1 and 4, Table 1) this tendency was not observed; the films with the highest glycerol concentration resulted less flexible. The response surface shows that the most flexible films were those obtained with the formulation 3, which contained the highest glycerol and acetylated/native ratio, (Fig. 5B, Table 2).

3.7. Films water vapor permeability (WVP)

The WVP values of the developed TPS films varied between 0.88 and 1.41 × 10^{-10} g/s m Pa (Table 2). These results were lower than those reported by Flores et al. (2010) for TPS films of cassava (3.72–6.40 × 10^{-10} g/s m Pa) obtained under similar operating conditions.

Native starch and glycerol concentrations exerted a positive effect on this property, being the plasticizer one the most important ($\beta_2 < \beta_3$) due to its hydrophilic character, (Table 3). Cerqueira et al. (2012) stressed that the action of this plasticizer on hydrocolloids films, especially on chitosan ones, increased the free volume and chain movements reducing the rigidity and increasing the molecular mobility of the films, allowing higher water vapor transport through their structure. On the other hand, the coefficient of the acetylated starch concentration (β_1) resulted lower than β_2 and β_3 (Table 3). The incorporation of acetylated starch to film formulations decrease their WVP due to the hydrophobic character of the substituent, (López et al., 2008, 2010a,b, 2011), however the low acetylation degree of the used modified starch could explain the obtained results.

The response surface represents the results of the model and indicates that the films with the lowest WVP were those with low glycerol concentration and high acetylated/native ratio (Fig. 6A).

3.8. Films gaseous permeabilities

Developed films presented the same behavior for both gaseous permeabilities (O_2 and CO_2). The response surfaces corresponding to the permeability to both gases show that films obtained from

Table 3
Best-fit equations and regression coefficients (r^2), mean relative deviation modulus (P) and standard error of the model (S) for experimental data of some properties of the films based on native and acetylated corn starches plasticized with glycerol obtained by extrusion and blowing technique.

Dependent variable	Best-fit equation	r^2	P	S
Moisture content	$Y = -0.204 + 0.107 * A + 0.264 * N + 0.216 * G - 0.017 * A * N - 0.001 * A * G - 0.009 * N * G + 0.001 * A * N * G$	0.998	3.94	2.47
Tensile strength	$Y = -0.073 + 0.149 * A + 0.640 * N + 0.029 * G + 0.060 * A * N - 0.001 * A * G + 0.053 * N * G - 0.003 * A * N * G$	0.988	1.12	2.49
Elongation at break	$Y = -0.608 - 0.586 * A + 0.617 * N + 0.206 * G - 0.022 * A * N + 0.041 * A * G - 0.030 * N * G + 0.001 * A * N * G$	0.988	0.50	0.29
WVP	$Y = (0.200 + 0.085 * A + 0.224 * N + 0.287 * G - 0.017 * A * N - 0.008 * A * G - 0.015 * N * G + 0.001 * A * N * G) \times 10^{-10}$	0.967	6.06	0.47
CO_2 permeability	$Y = (0.097 - 0.055 * A - 0.089 * N + 0.112 * G + 0.007 * A * N + 0.004 * A * G + 0.006 * N * G) \times 10^{-9}$	0.999	4.32	1.31
O_2 permeability	$Y = (0.085 - 0.049 * A - 0.093 * N + 0.107 * G + 0.006 * A * N + 0.003 * A * G + 0.006 * N * G) \times 10^{-10}$	0.999	2.10	0.67

A: % w/w acetylated starch; N: % w/w native starch; G: % w/w glycerol.

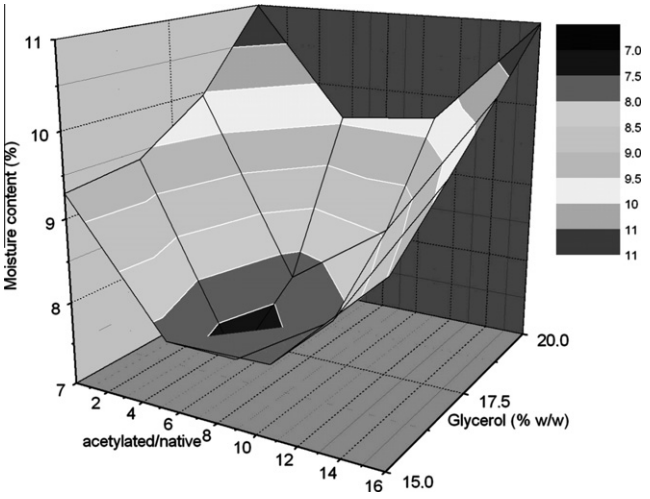


Fig. 4. Response surfaces corresponding to moisture content of starch-based films obtained by blown extrusion.

formulations with the highest glycerol concentration and the lowest acetylated/native ratio presented the highest gaseous permeability values (Fig. 6B and C).

The corresponding coefficients for native and acetylated starch (β_1 and β_2) resulted negative, so an increase in starch concentration, regardless of its type, led to films with a lower permeability (Table 3). In contrast, glycerol concentration influence was positive ($\beta_3 > 0$) and more important than acetylated and native starches ones (Table 3). These results indicate that an increase in glycerol content, even though enhanced films mechanical properties, the obtained material presented higher gaseous permeabilities. A similar trend on films based on TPS was also informed by several authors, (Rhim, 2004; Stepto, 2006).

Besides, the developed starch films obtained from extrusion and blowing method were selective with respect to gaseous permeabilities. The CO_2 permeability values were significantly ($p < 0.05$) higher than those corresponding to O_2 permeability; the selective coefficients are presented in Table 2. The development of biodegradable films with selective gaseous permeabilities could be very promising for controlling respiratory exchange and improving the conservation of fresh or minimally processed vegetables or foods susceptible to oxidation, (García et al., 2009).

3.9. Films thermo-mechanical analysis

Materials based on starch and glycerol are partially miscible systems and they present two phases: one rich in glycerol and the other in starch, (Da Roz et al., 2006; López et al., 2011; Teixeira et al., 2007). In this study, the dynamic-mechanical assays were performed in a temperature range that only led to analyze the viscoelastic behavior of the glycerol rich phase of these materials. Fig. 7A shows the curves corresponding to storage (E') and loss

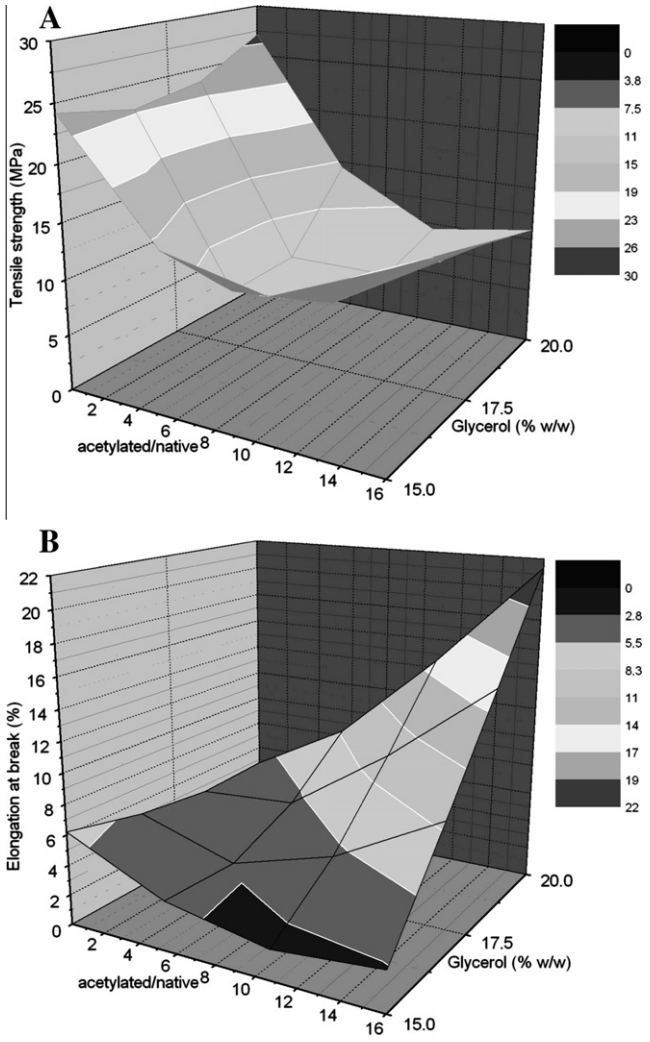


Fig. 5. Response surfaces corresponding to mechanical properties of starch-based films obtained by blown extrusion: (A) maximum tensile strength and (B) elongation at break.

(E'') moduli and $\tan\delta = (E''/E')$ as a function of temperature for films developed from formulation 1 (10:70:20). Assays were performed at different frequencies and this behavior was representative for all tested formulations. It can be observed that $\tan\delta$ and E'' curves presented a maximum peak while E' curve shows an abrupt fall. Temperature at which these observed changes occurred corresponded to the relaxation temperature associated to the glass transition (T_g) of the glycerol-rich phase. Besides, the inflexion point of the E' curve as well as the maximum peaks of the E'' and $\tan\delta$ curves shifted to higher temperatures with the frequency. This assay frequency dependence of the T_g was also described by several authors, (López et al., 2011; Zhang and Han, 2006).

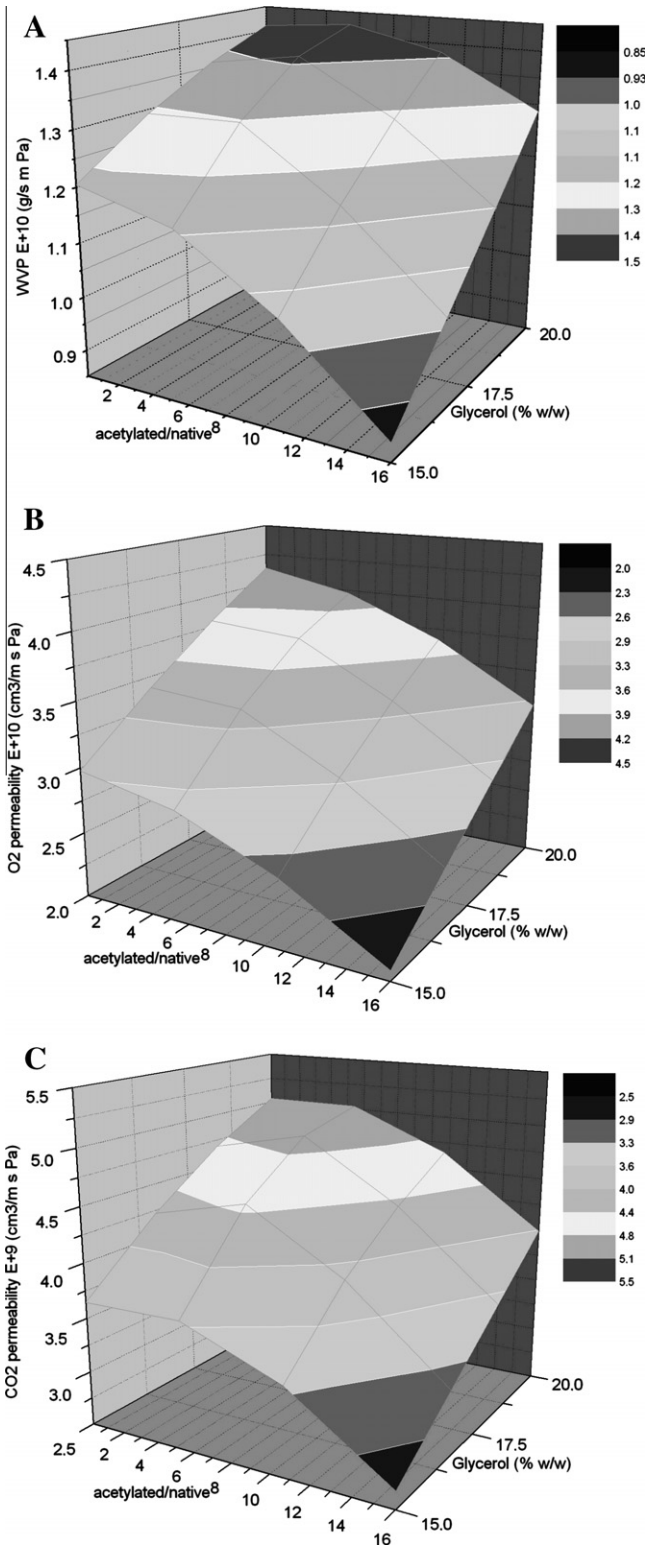


Fig. 6. Response surfaces corresponding to barrier properties of starch-based films obtained by blown extrusion: (A) water vapor permeability (WVP), (B) O_2 permeability and (C) CO_2 permeability.

The relaxation temperatures associated to the T_g for the developed films, evaluated through the E', E'' and $\tan\delta$ curves, obtained from dynamic-mechanical assays performed at 5 Hz frequency are presented in Table 4. The significantly ($p < 0.05$) lowest values were obtained for films plasticized with the highest glycerol content (20% w/w; formulations 1 and 3), while the films with 15% w/w glycerol (formulation 2 and 4) presented the significantly ($p < 0.05$) highest values. Intermediate values were obtained for films developed from formulation 5 which contains 17.5% w/w plasticizer. The observed tendency was in agreement with the widely well-known effect of glycerol on T_g. There were no significantly differences ($p > 0.05$) between the T_g values of the films with the same plasticizer concentration but different proportions between the studied starches, (Table 4). Again, it could be attributed to the structural similarity between native and acetylated starches, due to the low acetylation degree of the modified starch employed.

Fig. 7B reinforces the results observed in Table 4 showing the effect of glycerol on $\tan\delta$ curves and the T_g values for starch films obtained by blown extrusion. Variations in the starches proportions did not modified the T_g values.

3.10. Storage effect on film properties

In the present work, films obtained from TPS were storage for 360 days under controlled conditions and their mechanical behavior and water vapor barrier properties were evaluated.

The mechanical patterns for TPS films obtained from the blend 3 at initial time and after controlled storage are shown in Fig. 8; a similar trend was observed for all tested formulations. During storage, film matrixes increased their crystallinity degree and the crystalline domains formed act as physical cross-links and reinforce the material (Viguié et al., 2007), increasing tensile strength and decreasing their flexibility. This is a typical behavior described earlier by van Soest and Knooren (1997) and Forssell et al. (1999) who stressed that upon aging, starchy materials usually become stronger and stiffer but less flexible due to the crystalline fraction increased. According to the literature, the changes in elongation are clearly related to the changes in starch structure and B-type crystallinity, (Van Soest and Knooren, 1997). On the other hand, Teixeira et al. (2007) reported that after aging for 90 days, no structural changes were observed in TPS containing glycerol or glycerol and sugar.

Besides, the reduction of elongation at break (from 20.12% to 12.02%) was in agreement with the glycerol phase separation observed in stored films due to its leakage to the film surface. This fact was evidenced in the cross-sections SEM micrographs of films obtained from formulation 3 after the controlled storage where the presence of numerous channels perpendicular to film surface indicates plasticizer migration (Fig. 8). Likewise, this trend was more evident in formulations 1 and 3 containing the higher glycerol concentration (20%w/w) since migration and diffusion rates depend on plasticizer concentration (Wypych, 2004). Similarly, Kuutti et al. (1998) reported the plasticizer leakage in thermoplastic oat and barley starch based films. On the other hand, Krogars et al. (2003) stressed that the use of a combination of sorbitol and glycerol prevented the plasticizer migration towards the matrix surface in high amylose maize starch films.

Storage also affected film barrier properties, as is shown in Fig. 8 for films obtained from the blend 3. During aging, WVP decreased due to crystallinity increase, since water transport takes place through the amorphous zone, being this a well known behavior for synthetic and biodegradable materials, (Famá et al., 2007; García et al., 2009).

Thus, in general, during storage tensile strength increased around 45% while elongation at break decreased 40%, and WVP 15%. The changes observed in the films mechanical behavior was related to the plasticizer mobilization.

3.11. Films sorption isotherms

Fig. 9 shows the sorption isotherms of the developed materials, which presented the typical sigmoidal form of starchy products and according to BET classification, correspond to Type II. All

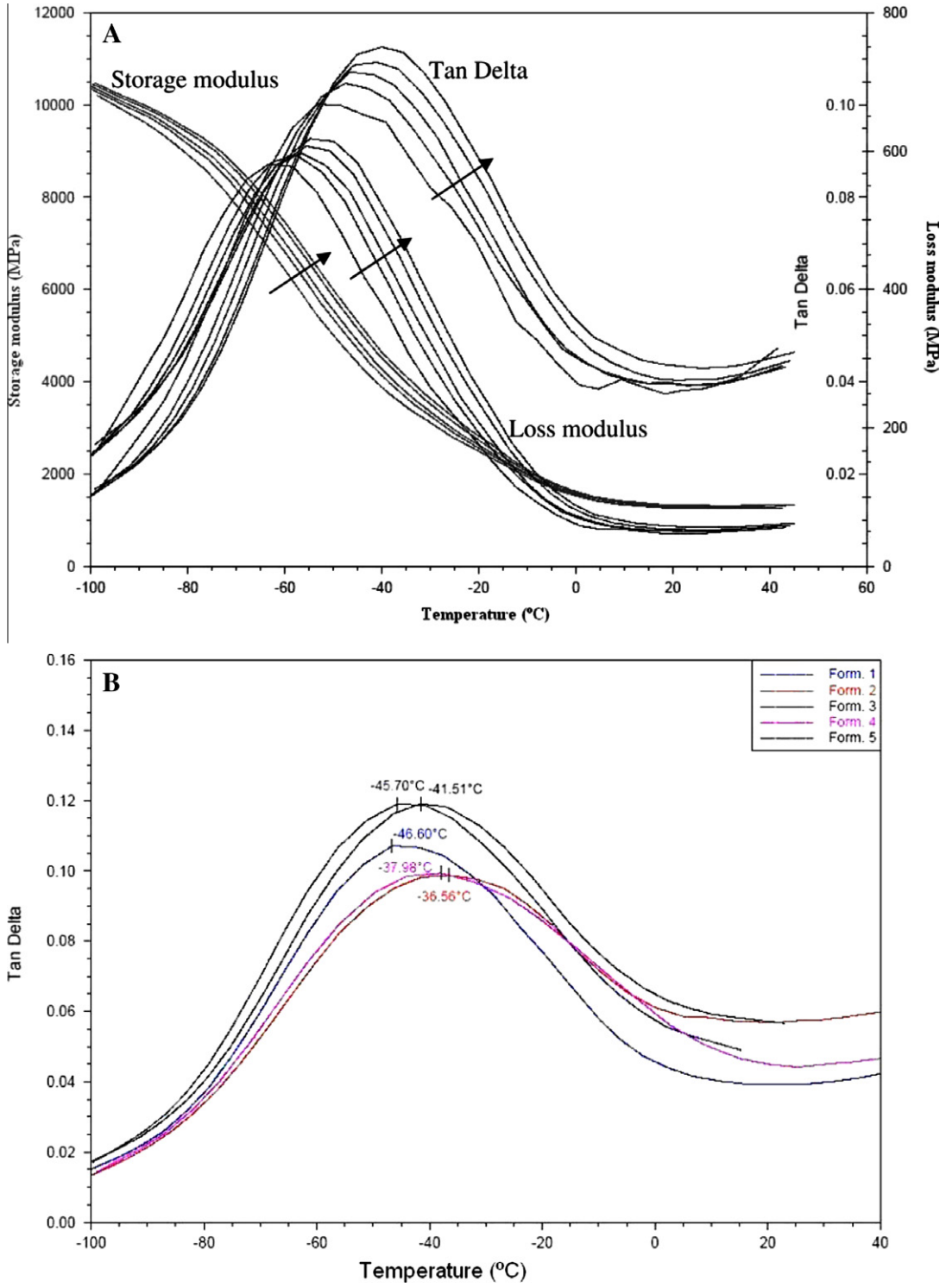


Fig. 7. (A) Storage (E') and loss (E'') moduli and loss factor ($\tan\delta = E''/E'$) as a function of heating temperature of starch-based films obtained by blown extrusion. The arrows indicate the frequency increase from 1 to 15 Hz. (B) Isochronal evolution of loss factor as a function of heating temperature. The indicated temperatures correspond to the maximum of the $\tan\delta$ curves.

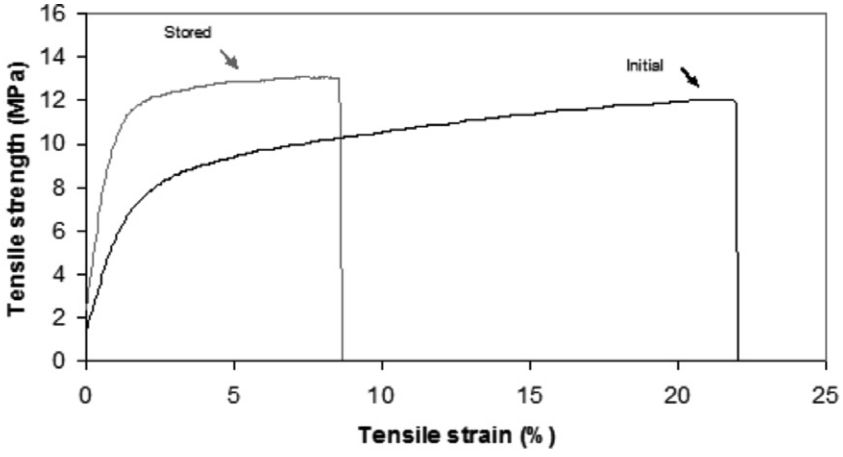
developed films were stable up to $a_w \approx 0.7$; this is a relevant characteristic if the materials will be used for packaging design. Humidity sensitive behavior and water mobility of materials based on TPS had been evaluated through sorption and diffusion studies during controlled storage by several authors, (Avérous and Boquillon, 2004; Herrera-Brandelero et al., 2011; Mali et al., 2005).

The obtained data were adjusted employing the GAB (Guggenheim–Anderson-de Boer) equation, which can be applied in the practical interest a_w interval of food area. The fitting parameters and the corresponding correlation coefficients for all assayed formulations are presented in Table 5. GAB equation described satisfactorily the sorption behavior of the starch films since de correlation coefficients (r^2) resulted higher than 0.990 and P and S exhibited low values. The obtained X_m values were higher while those of K were lower than those reported for Herrera-Brandelero et al. (2011) for cassava TPS films with 30% of glycerol (0.090 and

Table 4
Relaxation temperature associated to glass transition of the glycerol rich phase of films based on native and acetylated corn starches plasticized with glycerol, obtained by extrusion and blowing technique.

Formulation [b]	Relaxation temperature associated to glass transition of the glycerol rich phase (°C)[a]		
	Inflexion of the storage modulus curve (E')	Maximum of the loss modulus curve (E'')	Maximum of the tan δ curve
1 (10:70:20)	−56.48 ± 0.33[c]	−56.45 ± 0.24	−46.15 ± 0.64
2 (80:5:15)	−52.99 ± 0.45	−50.27 ± 0.28	−36.38 ± 0.95
3 (75:5:20)	−56.16 ± 0.41	−56.22 ± 0.31	−46.20 ± 0.32
4 (15:70:15)	−53.33 ± 0.39	−50.17 ± 0.23	−37.27 ± 0.92
5 (45:37.5:17.5)	−54.22 ± 0.40	−53.30 ± 0.21	−40.53 ± 0.38

[a] Reported data corresponds to curves obtained at 5 Hz frequency.
[b] (% w/w acetylated starch – % w/w native starch – % w/w glycerol).
[c] Reported values correspond to the mean ± standard deviation.



Condition	Mechanical properties		WVPx10^{10}
	Tensile strength (MPa)	Elongation at break (%)	(g/s m Pa)
Initial	10.31±0.09	20.14±1.56	1.31±0.25
Stored 360 days	14.94±1.97	12.02±1.33	1.11± 0.09

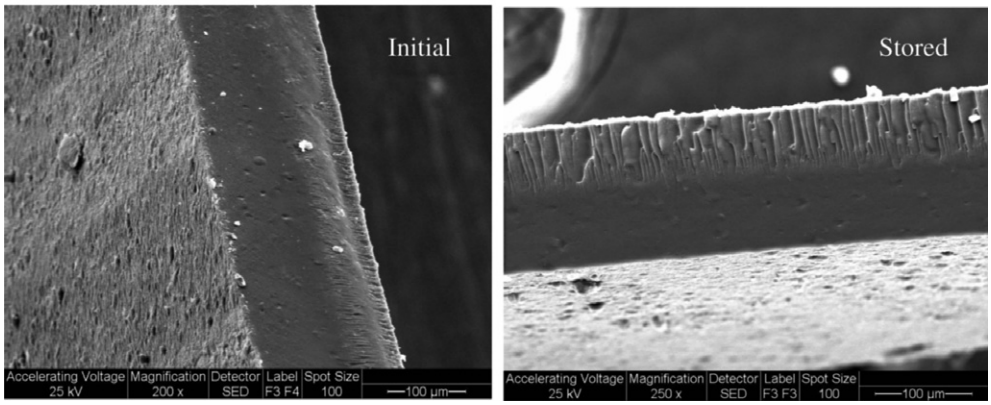


Fig. 8. Effect of storage on cross-section SEM micrographs, mechanical and water vapor barrier properties of films obtained from the formulation 3 (75% acetylated starch, 5% native starch and 20% glycerol). Films were stored under controlled conditions (20 °C and 65% RH) during 360 days.

0.97 for X_m and K, respectively). Besides the monolayer water content obtained was higher than those reported for cassava starch films obtained by compression molding (Perdomo et al., 2009) but within the range of those informed for potato starch based-films obtained by casting method (Talja et al., 2007). The glycerol concentration affected the monolayer water content (X_m) and the parameter K. In both cases, due to the hydrophilic character of the plasticizer, the highest values corresponded to the films obtained from starch formulations with 20% w/w of glycerol, while those with 15% w/w of plasticizer presented the lowest ones. Starch films plasticized with an intermediate glycerol concentration presented, as it was expected, intermediate values of these parameters. The proportion of native and acetylated starch did not affect the X_m and K values, this result could be attributed again to the low modification degree of the acetylated starch.

4. Conclusions

Biodegradable films of native and acetylated corn thermoplastic starches employing extrusion and blowing method were developed. The effect of film formulation was satisfactorily evaluated using an

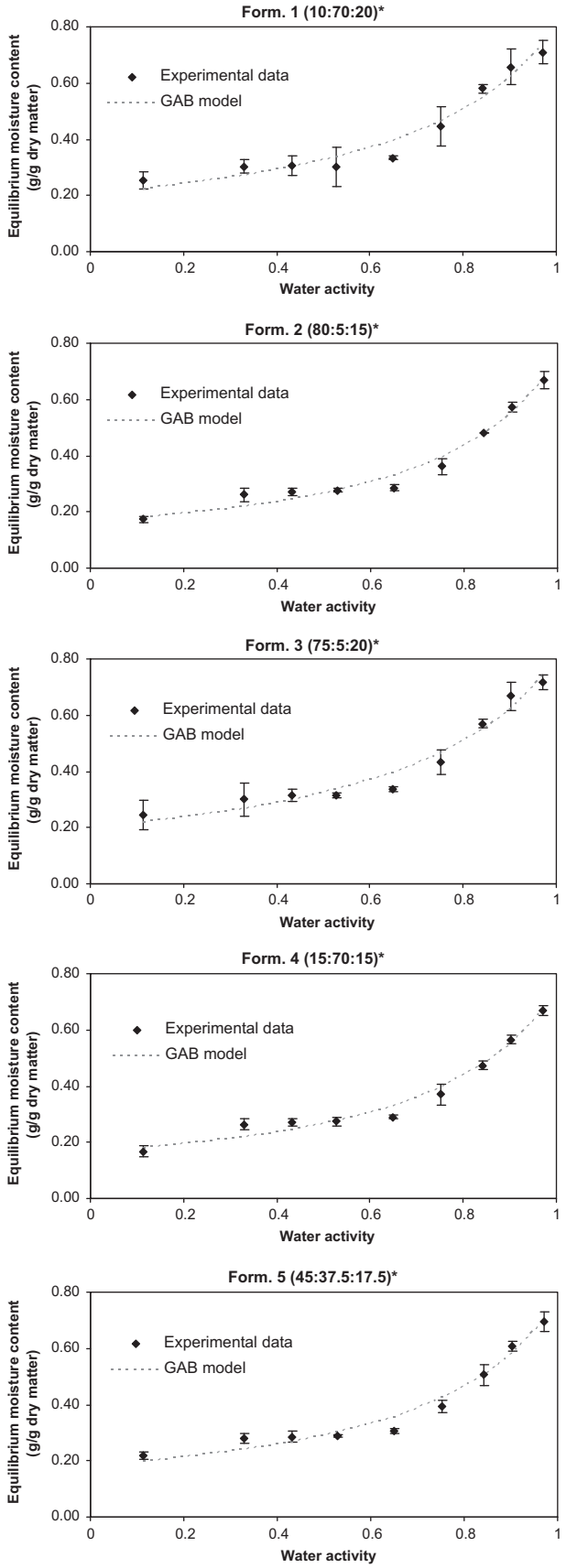


Fig. 9. Sorption isotherms of starch-based films obtained by blown extrusion.

experimental design for multicomponent mixtures. Films resulted sticky due to the humidity susceptibility of the starches used and the hydrophilic character of glycerol; in future researches this drawback could be overcome drying or conditioning the pellets before submit them to the blowing step. The humidity content of the blends before processing and the corresponding pellets increased with glycerol concentration due to its hydrophilic character. Besides, DSC analysis allows studying the starch destructuration in the blend produced during the extrusion process. The obtained films did not result uniform with respect to the thickness due to the difficulty of controlling processing variables. Visual observation and SEM micrographs showed that films, regardless their composition, presented homogenous structure and rough surfaces. The materials were characterized and the experimental data were satisfactorily modeled. Acetylated starch incorporation modified the mechanical behavior of the films since the substituent groups reinforced the polymeric matrix, despite of the low acetylation degree of the used derivative. Since acetyl groups are hydrophobic, increasing the concentration of this modified starch in the formulations it was possible to develop films with lower WVP. Likewise, films presented selective gaseous permeability, property very useful for food packages purposes. It was demonstrated that formulations with the highest assayed glycerol concentration (20% w/w) led to the most flexible films with highest moisture content and lowest barrier capacity to water vapor and gases. The relaxation temperature of the glycerol rich phase was shifted to lower values when plasticizer concentration increased. Film storage under controlled conditions (20 °C and 65% RH) during 360 days caused their tensile strength increase and the decrease of their flexibility and WVP. Likewise stored films also showed glycerol migration from the matrix to the film surface, contributing this plasticizer leakage to the increase of material stiffness. Finally, sorption isotherms indicated that films were stable up to $a_w \sim 0.7$ and when the glycerol concentration was higher the GAB parameters (X_m and K) increased.

Table 5
GAB parameters (X_m: monolayer equilibrium humidity content, g water/g dry solid; C and K: fitting parameters) for experimental data of sorption isotherms at 20 °C of films based on native and acetylated corn starches plasticized with glycerol, obtained by extrusion and blowing technique. Regression coefficients (r^2) mean relative deviation modulus (P) and standard error of the model (S).

Formulation[a]	Coefficients estimated values					
	X_m	C	K	r^2	P	S
1 (10:70:20)	0.204	3.1×10^{15}	0.745	0.990	0.10	0.07
2 (80:5:15)	0.162	4.4×10^{14}	0.783	0.995	3.28	0.05
3 (75:5:20)	0.202	9.9×10^{14}	0.749	0.992	3.79	0.11
4 (15:70:15)	0.162	3.0×10^{14}	0.782	0.995	3.17	0.05
5 (45:37.5:17.5)	0.178	5.3×10^{8}	0.768	0.995	3.59	0.05

[a] (% w/w acetylated starch:% w/w native starch:% w/w glycerol).

In conclusion, it was possible to obtain biodegradable films from thermoplastic native and acetylated corn starches and glycerol as plasticizer, employing the blowing technique. Future studies should continue optimizing film formulation as well as the processing conditions to improve humidity susceptibility and film properties for specific applications of the developed materials.

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