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Film forming capacity of chemically modified corn starches

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Abstract

Native starch can be chemically modified to improve its functionality and to expand its uses. Modified starches were characterized and the rheological behavior of filmogenic suspensions was analyzed. The film forming capacity of different chemical modified corn starches was evaluated. Acetylated starch was selected by the characteristics of the resulted films; its optimum concentration was 5% w/w since their films exhibited the lowest water vapor permeability (WVP, 1.26×10^{-10} g/m s Pa). The effect of glycerol as plasticizer on film properties depend on its concentration, being 1.5% w/w those that allows to obtain the lowest WVP value (1.64×10^{-11} g/m s Pa), low film solubility in water and a more compact structure than those of unplasticized films. Mechanical behavior of plasticized acetylated starch films depends on glycerol concentration, being rigid and brittle the unplasticized ones, ductile those containing 1.5% w/w of glycerol and very flexible those with a higher plasticizer content.

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Keywords: Film forming capacity; Chemically modified corn starch films; Plasticizer; Water vapor permeability; Mechanical properties

1. Introduction

Biopolymer films have been regarded as potential replacements for synthetic films in food packaging applications in response to a strong marketing trend towards more environmentally friendly materials. Starch has received considerable attention because of its totally biodegradable nature and low cost (Arvanitoyannis, Kalichevsky, Blanshard, & Psomiadou, 1994; García, Martino, & Zaritzky, 2000; García, Pinotti, & Zaritzky, 2006; Liu, 2005; Lourdin, Bizot, & Colonna, 1997a, 1997b; van Soest & Essers, 1997). It is an appropriate matrix-forming material and is also the most commonly used agricultural commodity, relative inexpensive with regard to other biopolymers. The potential functional and nutritional properties of such edible films, in conjunction with their enhanced biodegradability compared to other polymer systems, could almost certainly guarantee increased consideration in the immediate future (Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997).

The overall performance of starch films and coatings is highly likely to be customizable, because of the availability of a wide variety of starches and their capacity for physical and/or chemical modifications (Ellis, Cochrane, & Dale, 1998; Liu, 2002). The hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based materials; in fact, their properties depend on the ambient humidity (Shogren, Fanta, & Doane, 1993). An alternative to reduce these drawbacks is the use of modified starches (Lafargue, Lourdin, & Doublier, 2007). Chemical derivatization has long been studied as a way to solve this problem and to produce low water sensitive materials (Fringant, Rinaudo, Foray, & Bardet, 1998).

Chemical modification involves the introduction of functional groups into the starch molecule using reactions of derivatization (etherification, esterification, cross-linking and grafting) or reactions of decomposition (acid or enzymatic hydrolysis and oxidation). This is a useful alternative that allows to modify the structure and consequently the properties of native starches. Several authors have reported

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the use of chemically modified starches to obtain films; mainly substituted as well as pregelatinized starches (Bonacucina et al., 2006; Fringant et al., 1998; Tarvainen, Sutinen, Peltonen, Tiihonen, & Paronen, 2002; Tarvainen et al., 2004). On the other hand, they were employed in the formulation of composite films by mixing with other biopolymers, such as gelatin (Arvanitoyannis, Nakayama, & Aiba, 1998) and κ -carrageenan (Lafargue et al., 2007) between others. In addition modified starches, particularly starch esters, have been used in the preparation of biodegradable laminate films (Fang et al., 2005).

Besides, as for synthetic polymers, composition, microstructure and functional properties of films based on biopolymers determine their possible applications. Controlling film formulation allows to tailor the mechanical and barrier properties of these materials improving the efficiency of packaged foods conservation.

Generally, plasticizers are defined by two purposes which are to aid processing and to modify the properties of the final product. In the case of starch-based films, plasticizer addition overcomes film brittleness and improves flexibility and extensibility. Oligosaccharides, polyols and lipids are different types of plasticizers chemically compatible with hydrocolloid-based films; being glycerol the most widely use (Arvanitoyannis et al., 1997,1998; Banker, 1996; Cuq, Gontard, Cuq, & Guilbert, 1997; Gennadios, Weller, Hanna, & Froning, 1996; Gontard, Guilbert, & Cuq, 1993; Park, Bunn, Weller, Vergano, & Testin, 1994; Sothornvit & Krochta, 2005).

The objectives of the present work were: (i) to characterize different modified corn starches, (ii) to evaluate the rheological behavior of the filmogenic suspensions, (iii) to develop by casting biodegradable films selecting the most suitable modified starch and its concentration, (iv) to evaluate the plasticizer requirements of films, optimizing its concentration and (v) to characterize the appearance, physicochemical and mechanical properties and water vapor permeability (WVP) of modified corn starch films.

2. Materials and methods

2.1. Starch samples

Native and chemically modified corn starches (acetylated, acetylated cross-linked, hydroxypropylated crosslinked and acid modified) were used in this study. They were provided by Misky (Arcor, Tucumán, Argentina). Native corn starch was used as control.

2.2. Starch characterization

2.2.1. Scanning electron microscopy

The morphology and size distribution of native and modified starches granules were studied by scanning electron microscopy (SEM). Assays were performed using a JEOL 35 CF electron microscope (Japan) equipped with a detector of secondary electrons, with a nominal resolution of 60 Å, an acceleration voltage of 15 KV and a magnification of $1000 \times$. The images were obtained with IDX, a software program designed to acquire images digitally (IDX), with a resolution of 1024×800 pixels. AnalySis Pro 3.0 software program was used for processing and analysis of the images.

2.2.2. Starch gelatinization

Thermal properties of starches were determined by differential scanning calorimetry. A Polymer Laboratories (Rheometric Scientific Surrey, UK) calorimeter with a PL-V5.41 software program and a heating program of 10 °C/min from 10 to 120 °C was used. Starch aqueous suspensions (20% w/w) were prepared. The samples were weighed in aluminum pans and were closed hermetically. An empty pan was used as reference. The thermograms (heat flow as a function of the heating temperature) were recorded. From these curves the following information was obtained: onset temperature (T_0) , peak temperature $(T_{\rm p})$ and the area under the peak (ΔH). $T_{\rm o}$ corresponds to the start of the birefringence loss of the granule; T_{p} is the temperature at which the birefringence is lost (gelatinization temperature) and ΔH is the energy necessary for the transition. T_{o} and T_{p} were determined in °C and ΔH in mJ/ mg of the dry sample. The dry weights of the samples were obtained in an oven of 105 °C until a constant weight was achieved.

 $T_{\rm o}$ determine the time-temperature conditions that assured the complete starch gelatinization, native and modified starch aqueous suspensions at 4%, 5% and 6% w/w were prepared. The gelatinization was carried out in a thermostatic bath Haake (Germany). The assayed temperatures were 80, 85 and 90 °C and the heating times varied between 5 and 30 min. Every 5 min samples were taken and analyzed in a microscope Leica DMLB (Heerbrugg – Germany) equipped with polarized light.

2.2.3. Amylose concentration

The method selected to determine the amylose concentration in starch granules is based on the assumption that the amylose fraction has affinity with iodine to form complexes, which can be quantified spectrophotometrically at 635 nm (Morrison & Laignelet, 1983). Absorbance measurements were performed in a Beckman DU650 (Palo Alto, CA, USA) spectrophotometer.

2.3. Filmogenic suspensions

2.3.1. Preparation

Starch concentrations tested were higher than 4% w/w since this one is the minimal concentration that allows to obtain a continuous film of sufficient thickness (Liu, 2005).

Filmogenic suspensions of the modified starches considered in this study at 4% w/w were prepared to select the most suitable modified starch for film developing.

To choose the best starch concentration, aqueous suspensions at 4%, 5% and 6% w/w of the selected modified starch were prepared.

Furthermore glycerol (J.T. Baker, México) was added as plasticizer to gelatinized modified starch suspensions, at a concentration of 0-5 g of plasticizer per 100 g of filmogenic suspension (0-5% w/w).

2.3.2. Rheological characterization

The assays were performed in a Rheo Stress 600 ThermoHaake (Haake, Germany) rheometer using a plate-plate system PP35 at controlled temperature (25 °C). Rotational mode was used to investigate flux behavior of the native and modified starches suspensions, plotting shear stress (τ) vs. shear rate $(\dot{\gamma})$ The resulting curves were mathematically modelled as: Newtonian ($\tau = \eta \dot{\gamma}$) or Ostwald de Waele $(\tau = k\dot{\gamma}^n)$ fluids. η is the viscosity of the newtonian fluid; k is the consistency coefficient and *n* is the flow behavior index. For non-newtonian systems apparent viscosity was calculated at 500 s^{-1} ; and to evaluate the time dependence the corresponding thixotropic or antithixotropic indexes were determined. Thixotropic and rheopectic (antithixotropic) materials exhibit, respectively, decreasing and increasing shear stress (and apparent viscosity) over time at a fixed rate of shear (Steffe, 1996). These indexes were calculated as the area between the flux curves, taking positive values for thixotropic systems and negative for antithixotropic ones.

2.4. Film preparation

All the films were obtained by casting, approximately 20 g of filmogenic suspensions previously described were poured onto Petri dishes. The suspensions were dried (50 °C) in a ventilated oven to constant weight. Films were stored at 20 °C and a relative humidity (RH) of 65% in a controlled temperature and humidity room.

Thickness of the films 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 and used in the calculations of the mechanical properties and WVP.

2.5. Characterization of chemically modified starch films

2.5.1. Water vapor permeability

Water vapor permeability tests were conducted using ASTM method E96 with several modifications as described in a previous work (García et al., 2006). Each film sample was sealed over a circular opening of 0.00181 m^2 in a permeation cell that was stored at 20 °C in a dessicator. The driving force, expressed as water vapor partial pressure, was 1753.55 Pa. To maintain this driving force corresponding to a 75% relative humidity (RH) gradient across the film, anhydrous calcium chloride

(0% RH) was placed inside and a sodium chloride saturated solution (75% RH) was used in the dessicator. After steady state conditions were reached (about 2 h), eight weight measurements were made over 10 h. Samples were analyzed at least in duplicate.

2.5.2. Moisture content

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

2.5.3. Film solubility in water

Pieces of film of 2×3 cm were cut from each film and were stored in a dessicator with silica gel during 7 days. Samples were weighed to the nearest 0.0001 g and placed into test beakers with 80 ml deionizated water. The samples were maintained under constant agitation at 200 rpm for 1 h at room temperature (approximately 25 °C) or at boiling temperature. After soaking the remained pieces of film were collected by filtration and dried again in an oven at 60 °C to constant weight. The percentage of total soluble matter (% solubility) was calculated as follows:

% Solubility =
$$\begin{bmatrix} (\text{Initial dry weight} - \text{Final dry weight}) \\ \hline \text{Initial dry weight} \end{bmatrix} \times 100$$
(1)

Samples were analyzed at least in duplicate.

2.5.4. Film opacity

Film opacity was determined using a procedure described by Gontard, Guilbert, and Cuq (1992). Film sample was cut into a rectangle and placed on the internal side of a spectrophotometer cell. The absorbance spectrum (400–700 nm) was recorded for each sample using a Beckman DU650 (Palo Alto, CA, USA) spectrophotometer. Film opacity was defined as the area under the recorded curve determined by an integration procedure. The opacity was expressed as absorbance units per nanometers (AU \times nm).

2.5.5. Film appearance

Homogeneity and appearance of the films were examined by visual observation and by SEM with a JEOL JSM 6360 electron microscope (Japan). For cross-section observations films were cryofractured by immersion of the sample in liquid nitrogen. Film pieces were mounted on bronze stubs using a double-sided tape and coated with a layer of gold (40–50 nm), allowing surface and cross-section visualization. Besides, SEM observations of the cross-sections also allowed to evaluate film thickness. All samples were examined using an accelerating voltage of 10 kV.

2.5.6. Mechanical properties

Tensile tests were performed in a texturometer TA.XT2i – Stable Micro Systems (England) using a tension grip system A/TG. Probes of 7×0.7 cm were used; at least four probes were used for each film formulation.

The curves of force (N) as a function of deformation (mm) were automatically recorded by the Texture Expert Exceed software. Maximum breaking force (N), breaking factor (maximum breaking force divided by film thickness, N/ μ m), deformation at break (extension at the moment of rupture, mm), percent elongation at break (deformation divided by initial probe length and multiplying by 100, %) and elastic modulus (slope of force–deformation curve, N/mm) were obtained from force vs. deformation curves according to the ASTM D882-91 (1996) method. Tensile strength (MPa) was calculated by dividing maximum force by film cross-section (thickness × width).

2.6. Statistical analysis

All experiments were performed at least in duplicates, with individually prepared and casted films as replicated experimental units as described previously in each determination. Systat-software (SYSTAT, Inc., Evanston, IL, USA) version 10.0 was used for multifactor analysis of variance. Differences in the properties of the films were determined by Fisher's least significant difference (LSD) mean discrimination test, using p < 0.05 as level of significance.

3. Results and discussion

3.1. Chemically modified starch characterization

3.1.1. Morphological properties of modified starch granules

Scanning electron micrographs and size distribution histograms of the native and chemically modified granules starches are shown in Fig. 1. All samples showed a Gaussian granule size distribution. Chemical modifications did not cause any change in the general shape and appearance of the surface of starch granules. Modified corn starch granules were typically irregular shaped with wrinkled surface and similar to the native corn starch granules.

3.1.2. Starch gelatinization

Onset temperature $(T_{\rm o})$, peak temperature $(T_{\rm p})$ and enthalpies (ΔH) of the tested native and modified starches are shown in Table 1. The statistical analysis showed that chemical modifications altered significantly these values (p < 0.05).

Microscope polarized light observations showed that filmogenic suspensions of all starches were totally gelatinized when they were heated at 90 °C during 20 min, regardless the starch concentration.

3.1.3. Amylose concentration

Amylose concentration is relevant for the film forming capacity of the starch. When the starch granules are heated in water, they start to swell, rupture and collapse, releasing



Fig. 1. Histograms of granular diameters and micrographs of the different starches: (A) native starch; (B) acetylated starch; (C) acetylated cross-linked starch; (D) hydroxypropylated cross-linked starch; (E) acid modified starch.

amylose and amylopectin. Branched amylopectin chains, in solution, had little tendency to interact, and consequently, amylopectin gels and films are weak, cohesive and flexible. Linear chains of amylose had a high tendency to interact by hydrogen bonds, and consequently, amylose gels and films are stiffer and stronger than those of amylopectin. The values of amylose concentrations in starch granules are shown in Table 1.

3.2. Rheological characterization of filmogenic suspensions

Fig. 2a shows the flow curves of the filmogenic suspensions at 4% w/w. Acid modified starch suspension showed a Newtonian behavior with a viscosity of 11.95 ± 0.16 mPa s. However, native, substituted and cross-linked starches exhibited a pseudoplastic behavior which could be fitted by Ostwald de Waele model. The thixotropic and antithixotropic indexes, the consistency coefficients and the apparent viscosities at 500 s⁻¹ are presented in Table 2.

Table 1						
Onset temperature (T)	peak temperature (T)	enthalpies (ΛH) and	amplose concentration	of native and	chemically modified	l corn starche

Corn starch	<i>T</i> _o [°C]	$T_{\rm p} [^{\circ}{ m C}]$	ΔH [mJ/mg, dry basis]	Amylose [% w/w]
NS	67.95 ± 0.56	72.16 ± 0.14	11.45 ± 3.37	23.86 ± 0.66
AS	61.88 ± 0.47	65.60 ± 1.56	1.14 ± 0.21	14.27 ± 1.43
ACS	63.60 ± 1.22	68.64 ± 0.87	5.98 ± 2.23	11.67 ± 0.95
HCS	61.47 ± 0.66	67.23 ± 0.83	7.71 ± 1.61	19.28 ± 0.23
AMS	67.19 ± 0.03	73.69 ± 0.93	36.72 ± 1.65	22.61 ± 0.19

NS, native starch; AS, acetylated starch; ACS, acetylated cross-linked starch; HCS, hydroxypropylated cross-linked starch; AMS, acid modified starch.



Fig. 2. Rheological behavior of the different filmogenic suspensions. (a) 4% w/w filmogenic suspensions of: acetylated starch (AS), acetylated cross-linked starch (ACS), hydroxypropylated cross-linked starch (HCS), acid modified starch (AMS) and native starch (NS). (b) Filmogenic suspensions of 4%, 5% and 6% w/w AS. (c) Filmogenic suspensions of 5% w/w AS without glycerol and with glycerol at a concentration of 1.5 g/ 100 g of filmogenic suspension.

3.3. Selection of the type and concentration of modified starch to form films

The film forming capacity of the filmogenic suspensions and the characteristics of the resulted films were tested for the different modified starches. All filmogenic suspensions from chemically modified starches tested were able to form films. From all the tested chemically modified starches, the acetylated starch showed the best characteristics to form films since they were more transparent and easily removed from the cast plate. The film forming capacity of starches is related to their amylose concentration as well as the architecture of the macromolecular components, mainly the size of the amylose and amylopectin chains (Mali, Karam, Pereira Ramos, & Grossmann, 2004). Thus, even though acetylated starch exhibited low amylose content it would probably have amylose chains of high degree of polymerization.

Then, once the type of chemically modified starch was selected, the optimum starch concentrations are determined evaluating both, rheological behavior of the filmogenic suspension and WVP of acetylated starch films.

The flow curves of filmogenic suspensions at different acetylated starch concentration were shown in Fig. 2b. All of them presented a pseudoplastic behavior, regardless the starch concentration. However, both thixotropic index and apparent viscosity at 500 s^{-1} increased with starch concentrations (Table 2).

Filmogenic suspensions of the acetylated starch using concentrations ranging between 4% and 6% w/w formed films with good appearance. Since, WVP is a critical property in films developed from hydrophilic materials it was used to select the optimum acetylated starch concentration. Considering that 5% w/w starch concentration allowed to get the lowest WVP value $(1.26 \times 10^{-10} \text{ g/s m Pa})$ it was selected as the optimum concentration (Fig. 3a).

3.4. Plasticizer requirement evaluation and characterization of acetylated starch films

The acetylated starch films without plasticizer addition presented rigid and fragile structure, thus, the addition of glycerol as plasticizer was analyzed. To evaluate the effect of glycerol addition, filmogenic suspensions of 5% w/w acetylated starch and different glycerol concentrations (0 - 5 g glycerol/100 g of filmogenic suspension) were prepared.

The rheological behavior of these suspensions was evaluated showing all of them a pseudoplastic behavior. The plasticizer addition decreased the apparent viscosity and both the thixotropic and consistency indexes of the filmogenic suspensions while the flow behavior index increased

Table 2	
Rheological characterization of corn starch (native and chemically modified) suspension	ns

Suspension starch	Index (Pa/s)		Consistency coefficient (k) [Pa s ⁻ⁿ]	Flow behavior index (<i>n</i>)	Aparent viscosity [mPa s]	
	Tixotropic	Antithixotropic				
AS (4% w/w)	526.60		2.86 ± 0.53	0.510 ± 0.022	125.78 ± 0.04	
AS (5% w/w)	2019.57		2.91 ± 0.46	0.466 ± 0.042	198.67	
AS (6% w/w)	6175.5		7.77 ± 1.91	0.443 ± 0.019	214.20	
AS $(5\% \text{ w/w}) + \text{G} (1.5\% \text{ w/w})$	81.9		2.81 ± 0.41	0.50 ± 0.01	126.40 ± 10.92	
ACS (4% w/w)	819.20		2.12 ± 0.15	0.490 ± 0.003	87.99 ± 4.56	
HCS (4% w/w)		-1084.83	2.50 ± 0.66	0.490 ± 0.042	104.87 ± 2.57	
NS (4% w/w)	335.93		1.24 ± 0.09	0.510 ± 0.005	59.96 ± 2.44	

NS, native starch; AS, acetylated starch; ACS, acetylated cross-linked starch; HCS, hydroxypropylated cross-linked starch; AMS, acid modified starch; G, glycerol.



Fig. 3. (a) Effect of acetylated corn starch concentration on water vapor permeability (WVP) of films. (b) Effect of glycerol concentration (% w/w: g of glycerol/100 g of filmogenic suspension) on water vapor permeability (WVP) of films formulated with 5% w/w acetylated corn starch.

(Table 2). In Fig. 2c the effect of 1.5% w/w glycerol in acetylated starch filmogenic suspensions is shown.

With regard to film characterization, Fig. 3b shows the effect of glycerol concentration on the WVP of acetylated starch films. The obtained results could be related to the structural changes associated to glycerol addition evidenced by SEM.

Since unplasticized films were fragile and rigid, they showed cracks or pores (Fig. 4a and b) that could probably facilitate the transfer of the water vapor. Cross-sections of acetylated films without plasticizer showed smooth and homogeneous surfaces and multilaminar structures (Fig. 4b).

No pores or cracks were detected in films that included glycerol in their formulations. Plasticized film surfaces resulted more wrinkled than unplasticized ones, however their structures were more homogenous (Fig. 4c).

Plasticizers interfere with polymeric chain association decreasing the rigidity of the network, producing a less ordered film structure (Sothornvit & Krochta, 2005). When glycerol at a concentration of 1.5 g/100 g of filmogenic suspension is added, a more compact structure was obtained reducing the values of WVP. However, higher plasticizer concentrations produced a significant increase (p < 0.05) in the WVP due to the hydrophilic character of glycerol. Besides, acetylated starch films formulated with more than 2 g of glycerol/100 g of filmogenic suspension presented higher adhesiveness and more handling difficulties. This could be attributed to plasticizer migration which was evidenced by a greasy and cloudy appearance of film surfaces. A similar trend was observed in films formulated with different hydrocolloid matrixes and plasticizers (Sothornvit, Reid, & Krochta, 2002).

3.5. Moisture content, film solubility in water and film opacity

Table 3 summarizes the physicochemical characterization of acetylated starch films without glycerol and with glycerol addition (0-5% w/w).

After drying, unplasticized films exhibited the lowest equilibrium moisture contents while the highest value was observed when glycerol at a concentration of 5 g/100 g of filmogenic suspension was added, due to the hydrophilic properties of glycerol.

Film solubility increased as the temperature becomes higher. The plasticizer addition also increased the solubility due to the hydrophilicity character of glycerol.

Film opacity is a critical property if the film is used as a surface food coating. Transparent films are characterized by low values of the area below the absorption curve. The obtained values showed that films without glycerol addition were more transparent than plasticized ones. Besides, the opacity increased with plasticizer concentration becoming this tendency more noticeable in films formulated with glycerol concentration higher than 2.5% w/w. Table 3 indicates that opacity results are strongly related with glycerol migration during storage which could be visualized as a cloudy appearance of the films.



Fig. 4. SEM micrographs of (a) surface and (b) cross-section of acetylated corn starch films. (c) Cross-section of acetylated corn starch plasticized with 1.5% w/w of glycerol. Films were formulated with acetylated corn starch at 5% w/w. Magnification is indicated in the micrographs.

Table 3 physcochemical properties of corn starch (native and chemically modified) films

Film composition	Film solubility [%]		Moisture content	Film opacity [AU × nm]	
	At 25 °C	At 100 °C	[g water/100 g film]		
AS (5% w/w)	2.31 ± 0.09	14.76 ± 3.89	10.61 ± 0.50	45.42 ± 1.38	
AS + G (0.5% w/w)	5.81 ± 0.07	16.24 ± 1.97	11.84 ± 0.97	52.31 ± 5.60	
AS + G (1% w/w)	8.79 ± 3.44	18.36 ± 0.10	13.64 ± 0.44	55.69 ± 3.44	
AS + G (1.5% w/w)	13.73 ± 0.09	22.27 ± 0.43	14.19 ± 0.69	56.78 ± 0.90	
AS + G (2% w/w)	15.25 ± 4.91	25.89 ± 0.57	32.35 ± 1.12	60.26 ± 2.85	
AS + G (2.5% w/w)	18.96 ± 3.48	27.60 ± 0.99	34.26 ± 1.06	64.71 ± 4.68	
AS + G (3.25% w/w)	25.72 ± 4.46	28.02 ± 0.44	38.37 ± 1.40	72.29 ± 0.50	
AS + G (5% w/w)	27.26 ± 0.01	28.56 ± 2.72	57.28 ± 4.54	115.12 ± 2.45	

AS, acetylated starch; G, glycerol.

3.6. Mechanical properties

The stress-strain curve of unplasticized acetylated starch films shows the typical pattern of brittle materials, since they exhibited high values of tensile strength at break, breaking force and elastic modulus and low values of strain at maximum breaking force that is, low elongation values (Fig. 5) (Mali, Grossmann, García, Martino, & Zaritzky, 2002; Mali, Sakanaka, Yamashita, & Grossmann, 2005; Sarantópoulos et al., 2002). Fig. 5a indicates that the mechanical behavior of plasticized acetylated starch films depends on glycerol concentration. Films containing 0.5% and 1% w/w glycerol exhibited lower tensile strength than unplasticized ones; however, their elongation did not increase significantly (p > 0.05) (Fig. 5b and c).

The tensile behavior of films with 1.5% w/w of glycerol could be associated to those of ductile polymers since ten-

sile strength decreased and elongation at break increased significantly (p < 0.05) compared with unplasticized films. Similar results were obtained by Bonacucina and coworkers (2006) working on pregelatinized starch acetates. Plasticizers interfere with polymeric chain association facilitating their slipping and thus enhancing film flexibility. Glycerol decreases the rigidity of the network, producing a less ordered film structure and increased the ability of polymer chains movement (Sothornvit & Krochta, 2005). Besides, Arvanitoyannis et al. (1997) reported that sorbitol and sucrose showed a similar plasticizing effect than glycerol, at low concentrations, on gelatin–soluble starch films.

Glycerol concentrations higher than 1.5% w/w modified drastically the mechanical behavior of films showing the stress–strain curves the typical pattern of very flexible materials (Fig. 5a). For these films, tensile strength values



Fig. 5. (a) Stress-strain curves; (b) tensile strength and (c) percent elongation at break of acetylated starch films without and with glycerol addition (0-5% w/w). Films were formulated with acetylated corn starch at 5% w/w.

decreased and elongation at break increased significantly (p < 0.01). Thus, the addition of plasticizer to acetylated starch films has a large effect on film mechanical properties, such as increasing film flexibility and resilience. However, as described previously, in films formulated with more than 2 g of glycerol/100 g of filmogenic suspension migration of plasticizer was observed during storage.

The non-linear decrease of tensile strength and the increase of elongation at break with plasticizer content were also reported by several authors for starch-based films (Chang, Cheah, & Seow, 2000; Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999; Lourdin et al., 1997a, 1997b; Myllarinen, Partanen, Seppala, & Forssell, 2002).

4. Conclusions

The film forming capacity of acetylated corn starch was demonstrated. The optimum concentration of this chemically modified starch was 5% w/w since it allowed to obtain the lowest water vapor permeability value $(1.26 \times 10^{-10} \text{ g/s m Pa})$.

The addition of plasticizer was necessary to improve film properties, specially the mechanical ones. The effect of glycerol on mechanical behavior of plasticized acetylated starch films depends on its concentration, being unplasticized ones rigid and brittle, ductile those containing 1.5% w/w of glycerol and very flexible those with a higher plasticizer content. However, concentrations higher than 2% w/w exhibited plasticizer migration which could be visualized by the greasy and cloudy appearance of the films as well as the opacity values obtained. Thus, 1.5 g of glycerol/100 g of filmogenic suspension was the selected plasticizer concentration which allowed to reduce 87% WVP and to increase 34% flexibility of acetylated corn starch films.

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